

Technische Universität München
Fakultät für Chemie

Homogeneous Industrial Catalysis: Hydrosilylation, Epoxidation, Transvinylation

Teresa Karina Meister

Vollständiger Abdruck der von der Fakultät für Chemie der Technischen Universität München zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften (Dr. rer. nat.)

genehmigten Dissertation.

Vorsitzender: Univ.-Prof. Dr. K. Köhler

Prüfer der Dissertation:

1. Univ.-Prof. Dr. F. E. Kühn

2. Prof. Dr. Dr. h.c. J. Mink

3. Hon.-Prof. Dr. R. W. Fischer

Prof. Dr. J.-M. Basset (nur schriftliche Beurteilung)

Die Dissertation wurde am 18.02.2016 bei der Technischen Universität München eingereicht und durch die Fakultät für Chemie am 14.03.2016 angenommen.

I am always ready to learn although I do not always like being taught.

Winston Churchill

Die vorliegende Arbeit wurde am Lehrstuhl für Anorganische Chemie im Fachgebiet Molekulare Katalyse der Technischen Universität München im Zeitraum von Oktober 2013 bis Februar 2016 angefertigt.

Ich bedanke mich herzlich bei meinem Doktorvater

Herrn Prof. Dr. Fritz E. Kühn

für die freundliche Aufnahme in seine Arbeitsgruppe, für die vielfältigen und spannenden Forschungs- und Arbeitsmöglichkeiten, weitreichende Freiheiten in der Bearbeitung meines Promotionsthemas, für die großartige Unterstützung und das entgegengebrachte Vertrauen in meine Arbeit – auch über die Forschung hinaus.

Besonderer Dank geht auch an

Herrn Prof. Dr. Dr. h.c. mult. Wolfgang A. Herrmann

für die Schaffung eines außergewöhnlichen Forschungsumfelds am Lehrstuhl für Anorganische Chemie., dessen herausragende Infrastruktur von langjährigem Engagement getragen wird.

Teile dieser Arbeit entstanden im Rahmen eines Kooperationsprojektes mit der Wacker Chemie AG im Institut für Siliciumchemie.

Danksagung

Die vorliegende Arbeit fasst die wissenschaftlichen Ergebnisse meiner Promotionszeit zusammen. Tatsächlich wären diese im Alleingang wohl nie entstanden, und so möchte ich mich an dieser Stelle bei zahlreichen Unterstützern und wichtigen Wegbegleitern bedanken.

Mein Dank für die finanzielle Unterstützung meines Studiums gebührt der **Studienstiftung des Deutschen Volkes e.V.**, dem **Max-Weber Programm**, der **Hans-Rudolf-Stiftung**, der **Wacker-Chemie AG** sowie der **Stiftung Stipendienfonds des Fonds der Chemischen Industrie e.V.**

Ich danke von Herzen meinem engagierten Betreuer, Berater und Wegbereiter dieser Dissertation **Dr. Peter Gigler** der **Wacker Chemie AG**, ohne den ich den Weg zu diesem Projekt wohl nie gefunden hätte. Zahlreiche aufschlussreiche Diskussionen haben mir nicht nur auf wissenschaftlicher Ebene auf die Sprünge geholfen und maßgeblich zum Erfolg dieser Doktorarbeit beigetragen. Auch **Dr. Jürgen Stohrer** stand mir, wann immer möglich, mit fachlichen Einblicken in die Thematik zur Seite und ermöglichte mir neue Perspektiven auf ein manchmal verfahrenes Thema.

Mein Dank geht außerdem an **Dr. Alex(ander) Pöthig**, der mich in die Geheimnisse der Röntgenstrukturanalyse eingeweiht hat und mir auch bei meiner eigenen Forschung immer mit Rat und Tat zur Seite stand, sowie an **Dr. Markus Drees**, der sich mir als blutiger Anfängerin in Sachen DFT angenommen und mir geduldig die Details der Computerchemie und verschiedenster Formalia zum Promotionsstudium erklärt hat.

Ich bedanke mich zudem bei **Dr. Gabriele Raudaschl-Sieber** für aufschlussreiche fachliche Gespräche sowie zahlreiche Tips und Hilfestellungen in Bezug auf (Festkörper-)NMR.

Maria und **Jürgen** haben mir geduldig und unter großem Zeitaufwand die Entwicklung eines NMR Setups für meine zahllosen Katalysen ermöglicht und mir bei vielen Messungen mit Rat und Tat zur Seite gestanden – an dieser Stelle ein herzliches Dankeschön für eure Hilfe! Die NMR Analytik an unserem Arbeitskreis ist wirklich hervorragend und lebt von eurem Engagement. **Anika** war meine unerschrockene Partnerin bei der Betreuung der Anorganischen Experimentalchemie und zeichnet für die Vorführung eines exzellenten Versuchsprogramms verantwortlich. Ihr gebührt nicht nur mein Dank, sondern auch der mehrerer Studentengenerationen.

Christian hat mir oft zu unmöglichen Uhrzeiten und mit Engelsgeduld bei kristallographischen Verwirrungen aller Art geholfen. Ein großes Dankeschön auch dafür!

Dem nunmehr vollständig demolierten **Labor 37106** danke ich für einen herausragenden Start in das Promotionsleben, meiner neuen Heimat **37409** für einen immer unterhaltsamen **Laborchanel** und die beste Labororganisation, in der ich je arbeiten durfte.

Mein Freund und Kollege in der Wacker Kooperation **Korbi** stand mir bereits von Beginn meiner Masterarbeit an immer mit Rat und Tat zur Seite. Der rege Austausch in Vorbereitung auf unsere Statusberichte hat meine Arbeit wesentlich vorangetrieben und wertvolle Anstöße geliefert, der sportliche Ansporn für die nötige Motivation für das Marathonprojekt neben dieser Doktorarbeit gesorgt.

Aus dem Arbeitskreis besonders hervorzuheben sind **Stefan, Jens** und **Mario**, die mir oft über den Horizont meines eigenen Projektes hinaus wertvolle Diskussionspartner waren und hoffentlich noch lange als gute Freunde erhalten bleiben.

Ich danke den Mädels **Lavinia, Mona, Rina, Andrea, Julia** und **Eva** für die beizeiten notwendige Ablenkung von den Laborfrustrationen, **Laufen für Anfänger** für den sportlichen Ausgleich frühmorgens

und in den Mittagspausen, sowie meiner lieben **Saskia** für ihren rigorosen Optimismus sowie das geduldige Korrekturlesen dieser Arbeit.

Manu war und ist meine tapfere Trainingspartnerin in der Marathonvorbereitung und wichtige Vertraute in allen möglichen und unmöglichen Lebenslagen. Der Ironman kommt bestimmt!

Aus aller Ferne trägt auch meine langjährige „Kindergarten-Freundin“ **Anaïs** einen großen Anteil an dieser Arbeit, indem sie in beruflichen wie privaten Dingen immer wieder für die richtige Perspektive sorgt.

Zudem bin ich meiner quasi-Tante **Debbie** nach wie vor sehr dankbar, dass sie mich an die TUM beordert und mich dabei so großzügig unterstützt hat. Es ist mein großes Glück, eine so tolle Mentorin zu haben.

Mein Dank gebührt zudem meiner **Familie**, besonders meiner kleinen Schwester **Camilla** und meinen **Großeltern**, die mich - wann immer nötig - auf den Boden der Tatsachen zurück holen und für die nötige Ablenkung von der Chemie sorgen.

Ich danke von Herzen meinen **Eltern Peter** und **Gaby**, die mir mein Studium ermöglicht haben und mich dabei nach Kräften unterstützen, die immer versuchen, auch die fachlichen Schwerpunkte meiner Arbeit zu begreifen, sich mit mir darüber lustig machen und tagelang geübt haben, „Hydrosilylierung“ zu sagen. Ihr seid großartig!

Und zu guter Letzt und doch vor allen Anderen: ich danke dir, lieber **Simon**, meinem Anker und meiner besseren Hälfte, für deine liebevolle Unterstützung, deine unerschütterliche Gelassenheit und die Raketenperspektive auf so manches Problem. Und natürlich für *die* Überraschung meiner Promotionszeit.

Zusammenfassung

Unser Alltag wird maßgeblich durch die Produkte industriell katalysierter Prozesse geprägt. Der Fortschritt des letzten Jahrhunderts hängt somit maßgeblich mit den Meilensteinen, die im Bereich der Katalyse und der Polymerwissenschaften erreicht wurden, zusammen. Vor diesem Hintergrund liegt der Schwerpunkt dieser Arbeit auf der Untersuchung verschiedener industriell relevanter katalytischer Prozesse, der Hydrosilylierung, Epoxidierung und Umvinylierung. Im Fokus steht dabei zum einen die mechanistische Untersuchung dieser Reaktionen, zum anderen werden neue Katalysatorstruktur motive und Komplexe vorgestellt.

Hydrosilylierung zählt zu den wichtigsten homogenkatalytisch geführten Verfahren unserer Zeit. Die Reaktion wird industriell vor allem mit Platinkatalysatoren realisiert, die seit etwa 50 Jahren bekannt sind. Trotz dieser langen Zeit der Anwendung hinkte das Verständnis der Reaktion in der Vergangenheit den enormen synthetischen Möglichkeiten hinterher. In dieser Arbeit wird eine fundamentale mechanistische Untersuchung der platinkatalysierten Hydrosilylierung vorgestellt, die seit dem ursprünglich vorgeschlagenen Modell im Jahr 1965 erstmals eine Weiterentwicklung des etablierten Katalysezyklus beinhaltet. Daneben werden neue Struktur motive von Pt(0) NHC Komplexen präsentiert. Die Analyse der bemerkenswerten katalytischen Leistungsfähigkeit dieser Verbindungen mit Hilfe von Methoden der Elektrochemie (Cyclovoltammetrie) und der Dichtefunktionaltheorie (DFT) erlaubt die Ableitung von Gesetzmäßigkeiten für die Vorhersage der Aktivität potentieller, strukturell verwandter Zielstrukturen. Zudem wird die erste mechanistische Untersuchung der iridiumkatalysierten Hydrosilylierung von Allylverbindungen vorgestellt, die in den letzten Jahren aufgrund der erhöhten Selektivität gegenüber der Platinkatalyse Anwendung findet. Die stöchiometrische Reaktion eines der bekanntesten Iridiumkatalysatoren, $[\{\text{IrCl}(\text{cod})\}_2]$, führt zu einem strukturechemischen Kuriosum, einem allylverbrückten Iridiumdimer, dessen strukturelle und analytische Besonderheiten ebenfalls berichtet werden.

Die katalytische Epoxidierung erlangt vor allem durch die Bereitstellung industriell relevanter Intermediate kommerzielle Bedeutung, allen voran Ethylen- und Propylenoxid. Daneben macht man sich die Zugänglichkeit hochfunktionalisierter Produkte über intermediär auftretende Epoxide in der pharmazeutischen Industrie zu Nutze. Vor diesem Hintergrund widmet sich ein Teil dieser Arbeit der Fortentwicklung etablierter Struktur motive von Molybdänkatalysatoren zur Olefinepoxidierung.

Die rutheniumkatalysierte Umvinylierung bietet einen einfachen synthetischen Zugang zu Vinylestern, die als Monomerbausteine zu vielfältigen Endproduktpolymeren umgesetzt werden können. In dieser Arbeit wird eine mechanistische Untersuchung dieses katalytischen Prozesses und ein wahrscheinliches Struktur motiv der aktiven Spezies vorgestellt. Mit diesem Themenkomplex eng verknüpft ist die Synthese und Charakterisierung einiger mehrkerniger Rutheniumcarbonylcarboxylate. Strukturell verwandte Molybdändimere sind von konzeptionellem Interesse für die Herstellung funktioneller Materialien zur Anwendung in der Molekularelektronik.

Abstract

Industrial catalysis shapes many aspects of modern life. Numerous advances of the past century are closely tied to milestones in the fields of catalysis and polymer science. In this context, this work focuses on the investigation of several industrially relevant, catalytic processes, namely hydrosilylation, epoxidation and transvinylation. In particular, the mechanistic aspects of these reactions as well as novel catalyst structural motifs and related complexes are examined.

Today, hydrosilylation ranks among the most important homogeneously catalyzed industrial processes. The reaction is executed using mainly platinum catalysts which were developed about half a century ago. Regardless of its well established application, the understanding of this reaction lags significantly behind the vast synthetic possibilities. This work presents a fundamental mechanistic study of platinum-catalyzed hydrosilylation, providing a further development of the catalytic cycle for the first time since the original model in 1965. In addition, new structural motifs of Pt(0) NHC complexes are reported. Their remarkable catalytic performance can be rationalized by means of electrochemistry (cyclic voltammetry) and density functional theory (DFT). The ensuing principles can be used for the prediction of catalytic activity of potential structurally analogous target structures. Furthermore, the first mechanistic investigation of iridium-catalyzed hydrosilylation of allyl compounds is presented in view of its increasing importance over the last years due to the significantly enhanced selectivity compared to platinum catalysts. The stoichiometric reaction of one of the most common iridium catalysts, $[\text{IrCl}(\text{cod})]_2$, yields a structurally intriguing allyl-bridged iridium dimer, which is also subject of this work.

The commercial relevance of catalytic epoxidation stems from the production of industrially relevant intermediates such as ethylene and propylene oxide. In addition, the accessibility of highly functionalized products via epoxide intermediates is harnessed by the pharmaceutical industry. Bearing this in mind, part of this work is dedicated to the further development of established structural motifs of molybdenum epoxidation catalysts.

Ruthenium-catalyzed epoxidation offers a facile synthetic access to vinyl esters, which are commonly used monomers for the production of a variety of end-use polymers. A mechanistic study of the principles governing this reaction in conjunction with the determination of the probable structural motif of the catalytically active species is presented in this work. The synthesis and characterization of several novel multinuclear ruthenium carbonyl carboxylates is closely related to this topic. Structurally related molybdenum dimers are of conceptual interest for the production of functional materials for molecular electronics, particularly molecular wires.

List of Abbreviations

aq.	aqueous
B3LYP	Becke, three parameter, Lee-Yang-Parr exchange-correlation functional
BP	British Petroleum, plc
cod	cycloocta-1,5-diene
Cp	η^5 -cyclopentadienyl
CV	cyclic voltammetry
DAniF	<i>N,N'</i> -di(<i>p</i> -anisyl)formamidinate
DArF	<i>N,N'</i> -diarylformamidinate
DFT	density functional theory
DMSO	dimethylsulfoxide
DPV	differential pulse voltammetry
dvtms	1,1,3,3-tetramethyl-1,3-divinylsiloxane
$\Delta E_{1/2}$	half-cell potential
equiv.	equivalents
ESI	electrospray ionization
Fc	ferrocene
Fc ⁺	ferrocenium
Fc-CO ₂ ⁻	ferrocene carboxylate
GC	gas chromatography
HOMO	highest occupied molecular orbital
IFP	Institut Français du Pétrole
IL	ionic liquid
IVCT	intervalence charge transfer
<i>i</i> PrOH	<i>iso</i> -propanol
IR	infrared
LLDPE	linear low-density polyethylene
LUMO	lowest unoccupied molecular orbital
Mes	mesityl
MO	molecular orbital
MS	mass spectrometry
NHC	<i>N</i> -heterocyclic carbene

NMR	nuclear magnetic resonance
oz	ounce (28.3 g)
Ph	phenyl
PO	propylene oxide
Py	pyridine
R-CO ₂ ⁻	carboxylate
RTIL	room temperature ionic liquid
SAc	thioacetate
^s Bu	<i>sec</i> -butyl
^t Bu	<i>tert</i> -butyl
TBHP	<i>tert</i> -butylhydroperoxide
THF	tetrahydrofuran
TOF	turnover frequency
Tol	toluene, <i>para</i> -tolyl
TON	turnover number
UV-Vis	ultraviolet-visible

Table of Contents

1	Introduction.....	12
1.1	Industrial Catalysis	2
1.2	Homogeneous Industrial Catalysis.....	4
1.3	Hydrosilylation	7
1.3.1	Platinum-catalyzed Hydrosilylation.....	8
1.3.2	Iridium-catalyzed Hydrosilylation.....	12
1.4	Epoxidation	14
1.5	Transvinylation	17
1.5.1	Mechanistic Considerations	18
1.5.2	Structural Motifs	19
1.6	Ligand Fine Tuning: Structural Motifs for Molecular Wires.....	20
2	Objective	24
3	Results – Paper Outlines.....	26
3.1	Molecular Catalysts for Bond Activation – Paving the Way for Alternative Resources	28
3.2	Platinum Catalysis Revisited – Unraveling Principles of Catalytic Olefin Hydrosilylation	29
3.3	Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts	31
3.4	Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds.....	33
3.5	Direct Synthesis and Bonding Properties of the First μ^2 - η^2 , η^2 -Allyl Bridged Diiridium Complex	35
3.6	Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis	37
3.7	Ruthenium-Catalyzed Transvinylation – New Insights.....	39
3.8	$[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCCH}_2\text{CH}_3)_4(\text{THF})_2]$ and $[\text{Ru}_3(\mu_3\text{-OH})(\text{CO})_6(\mu\text{-OOC}^t\text{Bu})_4(\text{OOC}^t\text{Bu})]$: Novel Multinuclear Ruthenium Carbonyl Carboxylates	41
3.9	Structure and Catalytic Activity of the Ruthenium(I) Sawhorse-Type Complex $[\text{Ru}_2\{\mu, \eta^2\text{-CF}_3(\text{CF}_2)_5\text{COO}\}_2(\text{DMSO})_2(\text{CO})_4]$	43
3.10	Synthesis and Electrochemical Properties of <i>cis</i> - and <i>trans</i> - $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DArF})_2]$ ($\text{O}_2\text{C-Fc}$ = Ferrocenecarboxylate, DArF = <i>N,N'</i> -Diarylformamidinate) .	44

3.11	Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C}-\text{Fc})_{4-n}]$ (DArF = <i>N,N'</i> -Diarylformamidinate; $\text{O}_2\text{C}-\text{Fc}$ = Ferrocenecarboxylate)	46
4	Conclusion and Outlook	47
5	Reprint Permissions	51
5.1	Molecular Catalysts for Bond Activation – Paving the Way for Alternative Resources	52
5.2	Platinum Catalysis Revisited – Unraveling Principles of Catalytic Olefin Hydrosilylation	56
5.3	Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts	57
5.4	Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds	62
5.5	Direct Synthesis and Bonding Properties of the First $\mu^2-\eta^2,\eta^2$ -Allyl Bridged Diiridium Complex	67
5.6	Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis	68
5.7	Ruthenium-Catalyzed Transvinylation – New Insights	73
5.8	$[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCCH}_2\text{CH}_3)_4(\text{THF})_2]$ and $[\text{Ru}_3(\mu_3\text{-OH})(\text{CO})_6(\mu\text{-OOC}^t\text{Bu})_4(\text{OOC}^t\text{Bu})]$: Novel Multinuclear Ruthenium Carbonyl Carboxylates	76
5.9	Structure and Catalytic Activity of the Ruthenium(I) Sawhorse-type Complex $[\text{Ru}_2\{\mu,\eta^2\text{-CF}_3(\text{CF}_2)_5\text{COO}\}_2(\text{DMSO})_2(\text{CO})_4]$	77
5.10	Synthesis and Electrochemical Properties of <i>cis</i> - and <i>trans</i> - $[\text{Mo}_2(\text{O}_2\text{C}-\text{Fc})_2(\text{DArF})_2]$ ($\text{O}_2\text{C}-\text{Fc}$ = Ferrocenecarboxylate, DArF = <i>N,N'</i> -Diarylformamidinate)	78
5.11	Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C}-\text{Fc})_{4-n}]$ (DArF = <i>N,N'</i> -Diarylformamidinate; $\text{O}_2\text{C}-\text{Fc}$ = Ferrocenecarboxylate)	79
5.12	Figures and Schemes	80
6	Bibliographic Data of Complete List of Publications	82
7	References	94
8	Complete List of Publications	104
9	Appendix	106

1 INTRODUCTION

1.1 Industrial Catalysis

The energy and chemical industries have thrived on the economic developments of the past century, fuelled by a surge in world population, soaring demand for products, major breakthroughs in the fields of catalysis and polymer sciences, and finally the transition from coal to oil and gas as feedstock.¹ In this context, catalysis can be considered the enabling science and technology for the sustainability challenge, being the most important technology in environmental protection, with applications including e.g. emission prevention with the paramount example of the catalytic converter in automobiles.² Traditional domains of industrial catalysis comprise the fine chemical industry as well as the production of fuels and chemical raw materials from fossil resources such as coal, oil and gas,³ with its commercial relevance increasing with the rising demand for new products and improvements in engineering technology.^{2,4-6} The rapid, innovative development and efficiency enhancement of refining technologies and industrial processes in the past can largely be attributed to advancements made in the field of catalysis, a term which originates from the Old Greek word for “activate” or “unleash”.⁷ It constitutes the most important value-added process in chemical industry with a 100-400% rate of value increase,⁸ accounting for a worldwide catalyst market of \$ 16.3 billion.^{3,9} Estimates indicate that 90% of chemical products are manufactured using catalytic processes,^{2,3,10} including many everyday amenities such as pharmaceuticals, construction materials, cosmetics, synthetic fibres and fluid containers.¹¹⁻¹³ In addition, the nutrition of a large proportion of the world’s population depends on the Haber-Bosch process for the production of fertilizers (Figure 1).¹⁴

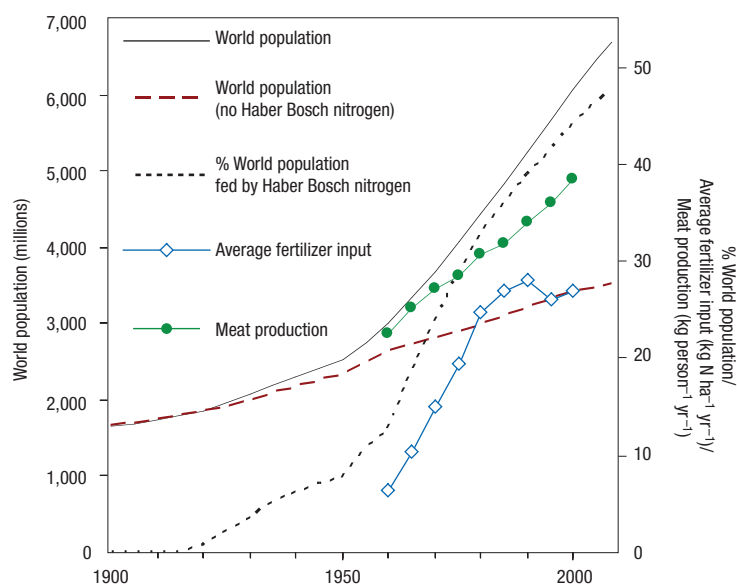


Figure 1. Trends in human population and nitrogen use throughout the twentieth century. Of the total world population (solid line), an estimate is made of the number of people that could be sustained without reactive nitrogen from the Haber-Bosch process.¹⁴ Reprinted with permission from *Nat. Geosci.* **2008**, *1*, 636-639. Copyright 2008 Nature Publishing Group.

The art of catalysis lies in the efficient and selective transformation of raw materials into useful base and fine chemicals with robust and highly active catalysts. A number of indispensable catalytic processes have been developed in the past century, shaping modern life.⁹ Apart from ammonia production (*vide supra*), important milestones include for instance methanol synthesis from syngas, catalytic cracking, the Fischer-Tropsch process, acetaldehyde production via ethylene oxidation (Wacker process) and the Shell higher olefin process (SHOP, Figure 2).³

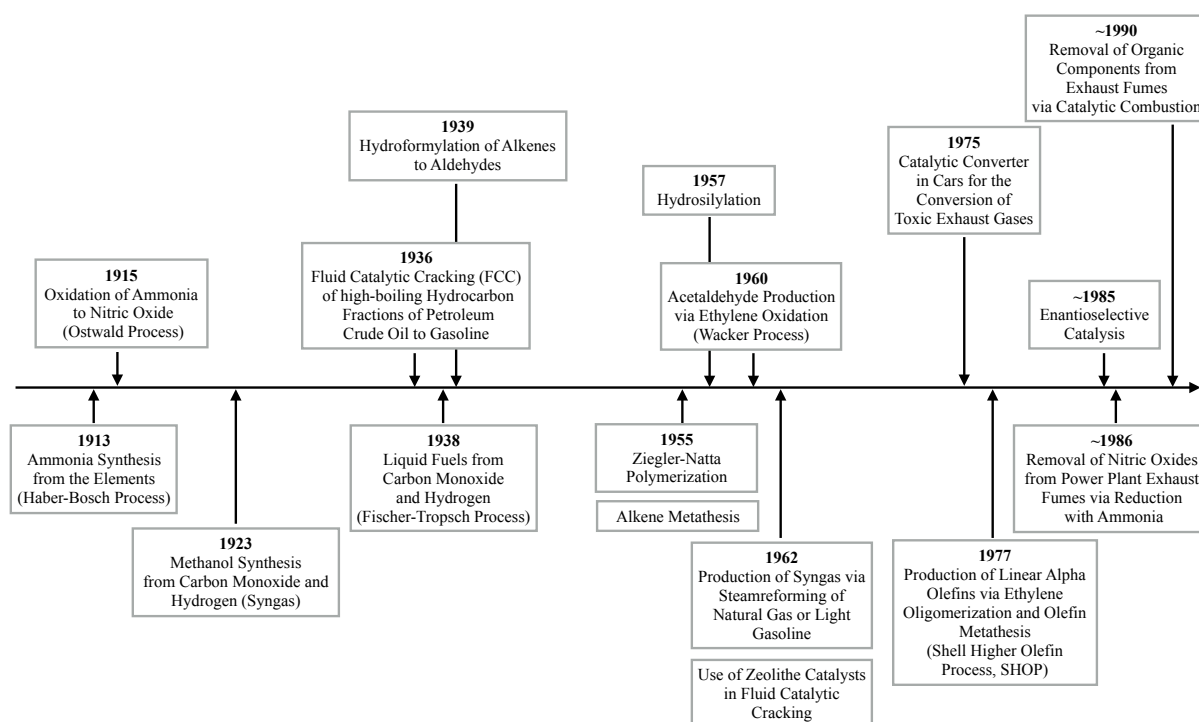


Figure 2. Development of selected industrially important catalytic processes in the past century.³

From an industrial point of view, heterogeneous catalysis is the predominant technology, accounting for 80% of catalytically manufactured products, followed by homogeneous catalysis (15%) and biocatalysis (5%).^{3,15} In analogy to its historical development, heterogeneous catalysis was the first to be applied commercially to a large extent, while biocatalysis constitutes the most recent discipline.¹⁶ Homogeneous catalysis lies in between, accounting for a considerable amount (10^9 tons) of bulk chemicals produced in processes such as hydroformylation, carbonylation, oxidation, hydrogenation, metathesis and hydrocyanation on the one hand, and providing access to fine chemicals with high atom efficiencies and enantiomeric excess (*ee*) on the other hand.¹⁶⁻¹⁹

Recent research efforts in industrial chemistry are often directed towards the incorporation of the principles of *Green Chemistry*, i.e., among others, waste prevention, atom economy, energy efficiency, renewable feedstocks and catalysis.²⁰⁻²⁵ These characteristics are typically showcased by biological reactions, which are generally extremely efficient and selective; moreover, they operate under mild conditions through inherently

'green' processes.^{26,27} Many scientific endeavors aim to understand and exploit the elegant catalytic principles found in nature. Such biomimetic or bioinspired catalyst systems serve as models for innovative approaches to the utilization of alternative raw materials, e.g. methane,^{26,27} lignin^{28,29} and carbon dioxide.^{27,30}

1.2 Homogeneous Industrial Catalysis


Considering that nearly all biological reactions are based on catalysis,¹⁵ the concept of defined metal sites facilitating a specific type of reaction has been used in an enzymatic environment in nature for millions of years, for example in methane monooxygenases or carbonic anhydrases.^{8,31} In a strictly chemical context, the enormous interest in organometallic chemistry since the discovery of ferrocene in the early 1950s is closely related to the advance of homogeneously catalyzed processes for the production of commodity and fine chemicals, coinciding with a marked increase of the volume and value of such products.³² Most advances in homogeneous industrial catalysis are based on the development of transition metal and organometallic complexes¹⁵ rather than homogeneous acid-base catalysts (Figure 3).¹⁶

In general, homogeneous catalysts do not suffer from the typical drawbacks of heterogeneous catalysts such as the pressure gap^I and the lack of a deeper understanding of mechanistic processes due to the difficulty of in situ characterization of relevant species.^{33,34} The major disadvantage of homogeneously catalyzed reactions is the difficult separation of the products from the reaction mixture, since all components of the reaction are, by definition, present in the same phase.^{8,31,32,35} Their key benefit is that their behavior during catalysis is dictated by their molecular architecture; therefore, reaction mechanisms can be rationalized and tuned in a controlled and predictable fashion by specific modification of the catalyst.^{36,37} By virtue of the characteristic selectivity and efficacy of homogeneous catalyst systems, the objectives of *Green Chemistry* are predominantly pursued by means of homogeneous catalysis,¹⁶ which has revolutionized synthetic organic chemistry in both academia and industry.^{35,II} Consequently, the importance of homogeneous catalysis for the production of fine and specialty chemicals such as pharmaceuticals, agrochemicals, flavors and fragrances has been increasing tremendously in recent years.¹⁸ This is illustrated by three Nobel Prizes, which were awarded for merits in this field in the 21st century: (I) the first in 2001 to KNOWLES, NOYORI and SHARPLESS for their work related to asymmetric catalysis,³⁸ (II) the second in 2005 to CHAUVIN, GRUBBS and SCHROCK for their research in the

^I The famous pressure gap problem stems from the fact that industrial catalytic processes are carried out at pressures in the range of 1 to 100 bar, while classical surface science has been restricted to analytical methods applicable between 10⁻⁴ to 10⁻¹⁰ bar.

^{II} It should be noted that the waste production per kg product is much higher in the fine chemicals and pharmaceuticals sector due to the required purity and more complex synthesis of these products in addition to the profit margin structure. This can be illustrated by the *E* factor, which is defined as the amount of by-products produced per kg of product. Typical *E* factors are as follows: bulk chemicals, <1-5; fine chemicals, 5-50; pharmaceuticals, 25-100. However, in absolute numbers, fine chemical and pharmaceutical industry account for only a fraction (<1%) of the total waste production.¹⁹

field of metathesis,³⁹ and (III) the third in 2010 to HECK, SUZUKI and NEGISHI for their investigations of palladium-catalyzed C–C cross-coupling reactions.⁴⁰

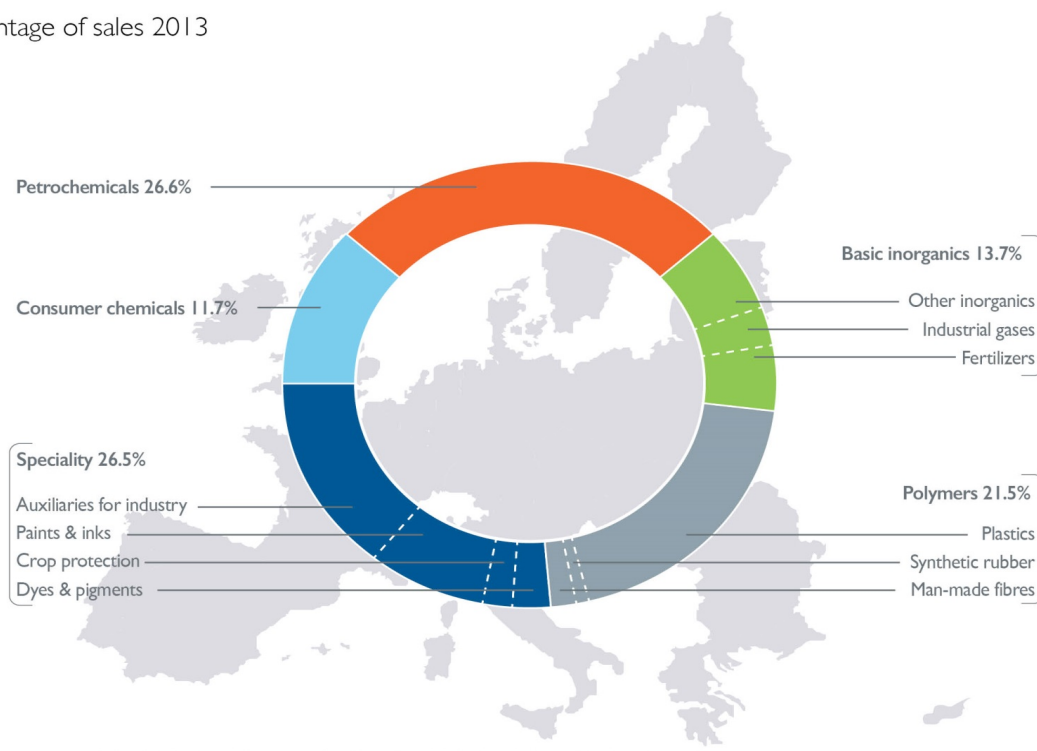


Year	Inventor	Milestone	Metal
2010	R. F. Heck, A. Suzuki, E. Negishi	Nobel Prize (C–C coupling)	Pd
2005	Y. Chauvin, R. H. Grubbs, R. R. Schrock	Nobel Prize (Metathesis)	Ru, Mo
2004	Sasol, Ltd	Selective Ethene Tetramerization	Cr
2003	R. R. Schrock	Homogeneous N ₂ Activation	Mo
2002	BP	Selective Ethene Trimerization	Cr
2001	W. S. Knowles, R. Noyori, K. B. Sharpless	Nobel Prize (Asymmetric Catalysis)	Rh, Ru, Ti, Os
	D. J. Cole-Hamilton	Hydroformylation in supercritical CO ₂ /IL	Rh
1998	G. C. Bazan	LLDPE by Tandem Catalysis	Ti+Zr
	IFP, Y. Chauvin	Difasol Process	(IL)
1997	J.-M. Basset	Alkane Metathesis	Ta
1996	BP	Cativa Process: Acetic Acid	Ir/Ru
1995	S. L. Buchwald, J. F. Hartwig	Amination of Aromatics	Pd
1994	R. Noyori	Supercritical CO ₂ as solvent	
1993	H. U. Blaser	Metolachlor synthesis	Ir
1992	W. A. Herrmann	Carbene Ligands in Catalysis	
1991	Kuraray Company, Ltd.	Telomerization of butadiene/water	Pd
	J.-M. Basset	Surface Organometallic Chemistry	
1986	B. Cornils	Ruhrchemie/Rhône-Poulenc Process	Rh

Figure 3. Milestones in homogeneous transition metal catalysis from 1985 to present.⁸ IFP = Institut Français du Pétrole; BP = British Petroleum plc; IL = ionic liquid; LLDPE = linear low density polyethylene.

The evaluation of the importance of specific catalytic processes can be carried out based on quantity (mass, bulk chemicals) or economic value of the manufactured goods (fine chemicals). With regard to the annual output in tons, the most important industrial applications of homogeneous catalysis include oxidation processes (18 Mt a⁻¹), hydroformylation of alkenes (>7.5 Mt a⁻¹), carbonylation of methanol/methyl acetate (>7.0 Mt a⁻¹), hydroformylation of isooctenes/ethylene oxide (>2.0 Mt a⁻¹) as well as hydrogenations, oligomerization of ethane and hydrocyanations (<2 Mt a⁻¹ each).⁸ All of the above are used for the production of commodity chemicals, which in turn account for roughly 40%⁴¹ of worldwide chemical⁴² and pharmaceutical⁴³ sales of € 3.9 trillion in 2014. When considering the generated value, fine (4%) and specialty chemicals including pharmaceuticals (55%) make up the remaining 60% of the global market, even though the product amount is by far inferior to bulk chemicals.⁴¹ Figure 4 illustrates the segments of the chemical production in Europe in 2013.⁴²

Percentage of sales 2013



Source: Cefic Chemdata International (2014)

*Unless specified, chemical industry excludes pharmaceuticals
Unless specified, EU refers to EU 28*

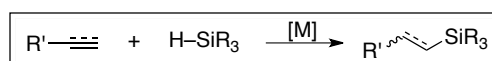
Figure 4. Important areas of production in the chemical industry in Europe in 2013 (excluding pharmaceuticals), which amount to a total of € 527 billion.⁴² Pharmaceutical sales in Europe account for a revenue of € 218 billion.⁴⁴ Reprinted with permission from Cefic Chemdata International 2014. Copyright 2014 Cefic.

Important catalytic reactions employed for the production of fine and specialty chemicals include cross-coupling, hydroformylation, hydrosilylation, epoxidation, asymmetric hydrogenation, and cyanation.¹⁸ Examples for important products are menthol, citral, metolachlor, ibuprofen, propranolol as well as vitamins C and E.⁸

The tremendous economic significance of hydrosilylation, epoxidation and transvinyltion provides the rationale for the focus of this work. These reactions are industrially relevant, homogeneously catalyzed chemical processes, which will be examined in more detail in the following chapters. In addition, the concept of rational design will be explored with respect to the development of new catalyst structural motifs and functional redox-active materials for molecular wires.

1.3 Hydrosilylation

Hydrosilylation is the largest-cost application⁴⁵ and a prime example of industrial catalysis.⁴⁶⁻⁵⁶ It typically comprises the addition of a hydrosilane to a C–C multiple bond, providing access to organofunctional sil(ox)anes and silicones, which are commonly used for the production of a variety of commercially relevant products such as adhesives, crosslinkers and polymers (Scheme 1).⁴⁶⁻⁵⁶



Scheme 1. Transition metal-catalyzed hydrosilylation (M = e.g. Pt, Ir, Pd, Rh).⁴⁵⁻⁵⁹

Consequently, it has emerged as one of the largest-scale applications of homogeneous catalysis.⁵⁷⁻⁵⁹ Depending on the desired utilization, several catalysts based on platinum, palladium, rhodium and iridium are currently employed in industry, with platinum dominating the hydrosilylation catalyst market.^{45,56} These metals are comparatively expensive at an average price of € 495 (Ir), € 630 (Pd), € 870 (Rh) and € 965 (Pt) per oz (1 oz = 29.3 g) in 2015.⁶⁰

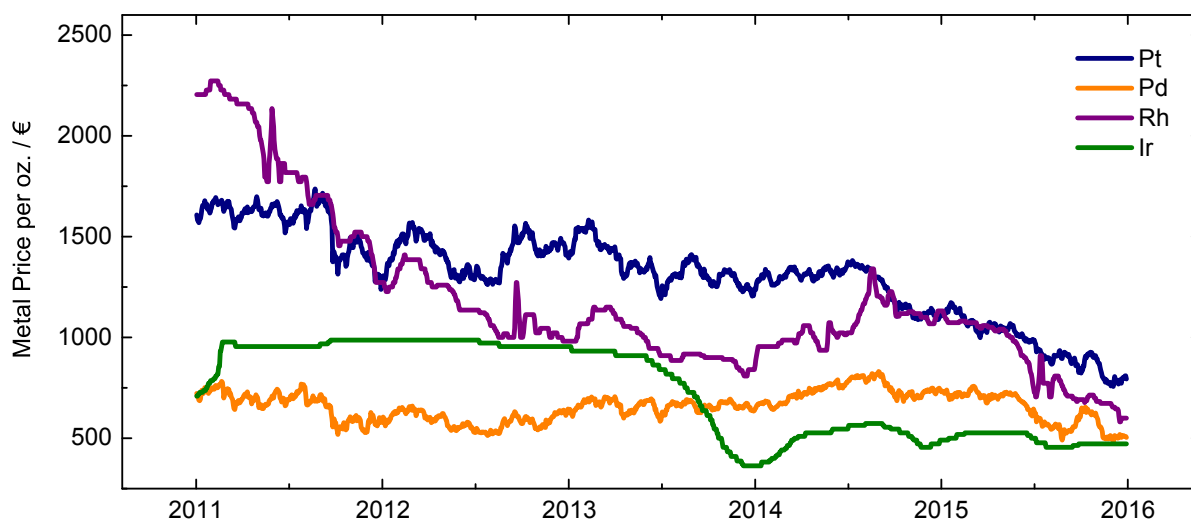


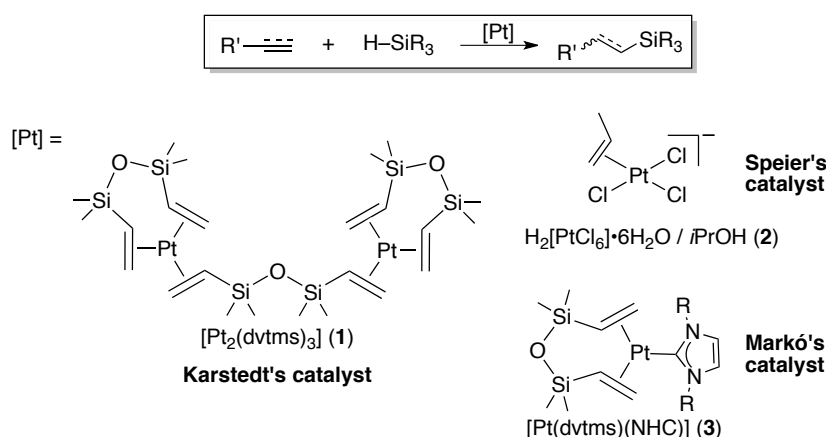
Figure 5. Monthly average metal prices between January 2011 and January 2016 in €/oz (1 oz = 29.3 g). Average Prices: Pt, € 1305, Pd, € 655, Rh, € 1172, Ir, € 728.⁶¹

Owing to the superior properties of these metals, and particularly of platinum in hydrosilylation catalysis, industry tolerates their high cost, which is expected to gradually increase even further due to the difficult separation of catalyst and reaction product in many hydrosilylation processes. As a result, the staggering

amount of 4-6 t of platinum are “lost” annually in the product stream of the catalytic process for the manufacture of cured silicones,⁴⁵ which corresponds to almost the entire platinum demand of the silicones industry⁵⁹ and 23-35% of the platinum demand of the chemical industry,^{62,63} highlighting the profound importance of metal-catalyzed hydrosilylation in chemical industry.

1.3.1 Platinum-catalyzed Hydrosilylation

The key characteristics of hydrosilylation catalysis include its high atom-efficiency, broad substrate scope and widespread application, which allow for a variety of synthetic pathways.^{46-56,64} Even though recent research efforts have been directed towards the design of new commercially viable ignoble metal catalysts,^{56,59,65-67} no match for the traditional platinum catalysts has been developed so far, rendering industrial hydrosilylation still dependent on platinum (Scheme 2).^{56,68-72}



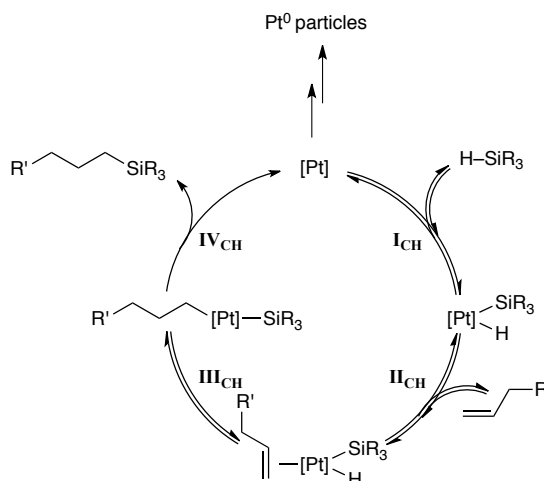
Scheme 2. Platinum-catalyzed hydrosilylation and molecular structures of the industrially relevant Speier's,^{70,71} Karstedt's,^{68,69,73} and Markó's catalyst.^{72,74-76} *i*PrOH = *iso*-propanol, dvtms = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, NHC = *N*-heterocyclic carbene. For Speier's catalyst, the species formed in solution in situ is drawn.⁷⁷

Being the most versatile and established catalyst of these, Karstedt's catalyst $[\text{Pt}_2(\text{dvtms})_3]$ (dvtms = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) continues to serve as benchmark system for newly developed hydrosilylation catalysts.^{56,65,78,79}

Mechanistic Considerations

In light of the fact that this reaction has been commonly practiced for over half a century, the progress in understanding the associated catalytic cycle has been arduous and slow. This can be attributed to the elusive nature of highly reactive intermediates formed by extremely active catalysts such as the ones typically used in

hydrosilylation catalysis.⁵⁷ The current understanding of the reaction still dates back to 1965, when CHALK and HARROD introduced a simple, yet very elegant mechanistic model that remains the widely accepted mechanism for platinum-catalyzed hydrosilylation in the literature even today (Scheme 3).⁸⁰



Scheme 3. Chalk-Harrod (CH) mechanism for the platinum-catalyzed hydrosilylation of alkenes.^{54,79,81} The reaction proceeds along the following steps: I_{CH}, oxidative addition of HSiR₃; II_{CH}, coordination of olefin; III_{CH}, insertion of the olefin into the Pt-H bond; IV_{CH}, reductive elimination of alkylsilane. Steps I_{CH}-III_{CH} are believed to be reversible.

The Chalk-Harrod mechanism proceeds along four basic steps: I_{CH}, oxidative addition of the hydrosilane; II_{CH}, coordination of the olefin; III_{CH}, migratory insertion of the olefin into the Pt-H bond, and IV_{CH}, reductive elimination of the hydrosilylation product (CH = Chalk-Harrod). Step IV_{CH} is considered to be the rate determining, irreversible step, while steps I_{CH}-III_{CH} are assumed to be reversible.^{54,79,81} The formation of Pt⁰ particles has been attributed to catalyst deactivation.^{47,56,79}

Mechanistic studies in this field^{79,81-85} typically focus on the identification of the active catalyst species [Pt], which has been shrouded for a long time. Stein, Lewis et al.⁷⁹ and Roy et al.⁸¹ concluded that it contains Pt-Si and Pt-C bonds, while no evidence for Pt-H bonds has been detected so far. It is believed to resemble the molecular structure depicted in Figure 6:

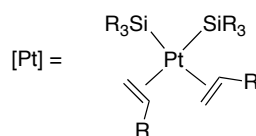


Figure 6. Proposed (generic) structure of the active catalyst species in platinum-catalyzed hydrosilylation according to literature.^{79,81}

The Chalk-Harrod mechanism is in agreement with the mechanistic insights gained by Lewis and Stein,⁷⁹ Roy,⁸¹ and others,⁸²⁻⁸⁵ which provide evidence for the prevalence of the classical Chalk-Harrod mechanism rather than the modified variant^{86,87} comprising the insertion of the olefin into the Pt–Si bond. Several theoretical investigations reach the same conclusion and support the notion that step IV_{CH} is rate limiting.⁸⁸⁻⁹⁰

While the catalytic mechanism of less active transition metals has been the subject of a number of investigations, platinum-based systems have been largely omitted due to their tremendous activity and the related highly sensitive nature of the intermediate species.⁵⁷ The inconvenient characteristics of the industrially most relevant catalyst, Karstedt's catalyst, have contributed further to this negligence. Owing to its tendency to form platinum black without excess olefin ligand, it is usually distributed as a highly diluted solution rather than a solid,^{69,73} typically containing roughly 2 wt% of Pt. This impedes many common laboratory techniques of mechanistic studies such as isolation and characterization of intermediates and renders them painstakingly difficult, if not altogether impossible. As a result, only one recent report employs Karstedt's catalyst as platinum source.⁷⁹ In addition, no in-depth kinetic study of the properties of this pivotal industrial catalyst has been put forth to date, notwithstanding that unraveling the intrinsic rate laws might prove highly advantageous for a better understanding of the catalytic cycle.

Moreover, little attention has been paid to internal alkenes as substrates for hydrosilylation catalysis, which are known to be less prone to undergo hydrosilylation than terminal olefins.^{46,47,56} Previous reports have unanimously ascribed this solely to steric aspects, which does not adequately account for the widely varying reactivity of structurally closely related alkenes. For example, norbornene is prone to hydrosilylation under comparatively mild conditions,⁹¹ while cyclohexene is challenging to hydrosilylate.⁹² This demonstrates that not the internal position of the double bond per se is decisive and that other factors such as coordination ability and electron density at the double bond must exert an influence.

In this context, a detailed mechanistic study of the reaction mechanism of hydrosilylation is presented as part of this work. It comprises both kinetic and isotope labeling experiments and reveals several new principles governing platinum-catalyzed hydrosilylation. The Chalk-Harrod mechanism can be further developed based on the presented results.

Structural Motifs

In addition to the endeavor for novel catalyst systems based on ignoble metals, several new structural motifs of platinum complexes applicable to hydrosilylation catalysis have been presented recently (Figure 7).^{64,65,72,74,76,93-}

106

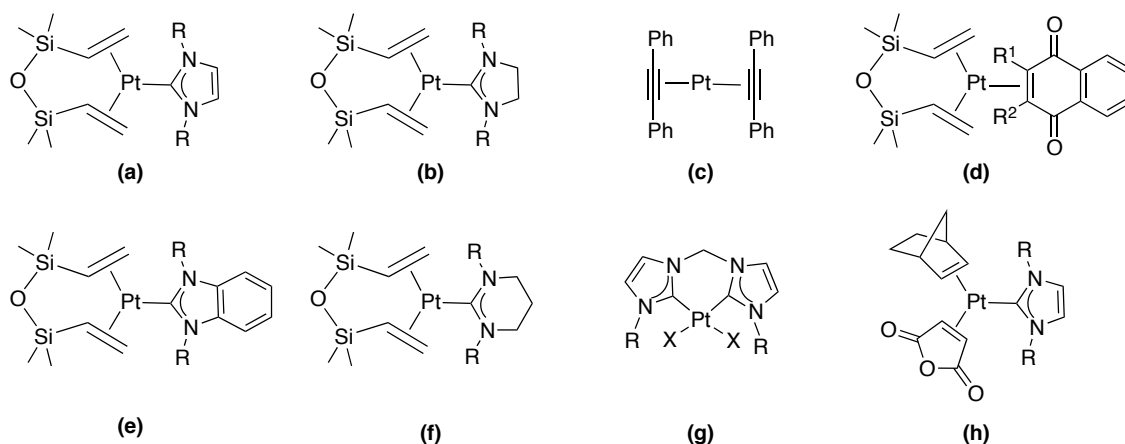


Figure 7. Selected structural motifs of recently reported Pt(0) hydrosilylation catalysts.^{64,65,72,74,76,95,96,99-105}

The underlying idea is to exploit the exceptional reactivity of platinum in hydrosilylation catalysis and develop more stable, hence reusable catalysts at the same time to reduce the enormous platinum consumption. One established way to increase complex stability is the introduction of *N*-heterocyclic carbene (NHC) ligands as spectator ligands, which typically form very strong metal-carbon bonds by virtue of their strong σ -donating and poor π -accepting character.^{74,107} In addition, variation of the NHC allows for stereoelectronic tuning at the metal center.¹⁰⁷⁻¹⁰⁹

Consequently, the use of NHC ligands has greatly extended the scope of Pt(0) complexes in hydrosilylation catalysis.^{64,72,76,93} Complexes of the type [Pt(dvtms)(NHC)] (Markó's catalyst, Scheme 2) are easily synthesized, stable towards both air and moisture, and show remarkable selectivity and efficiency in hydrosilylation of alkenes and alkynes.^{64,72,76,94} Several structurally derived Pt(0) NHC complexes have been reported in recent years,⁹³⁻⁹⁷ all of which venture to exploit the strong Pt-C_{Carbene} bond while maintaining a high reactivity in hydrosilylation catalysis at the same time. It has been established that steric encumbrance caused by bulky aryl substituents is instrumental for achieving high selectivity and catalytic activity.⁷⁴ Imidazo[1,5-*a*]pyridine-3-ylidenes (ImPy-R) are structurally related to 1,3-disubstituted NHCs (Figure 8).

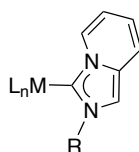
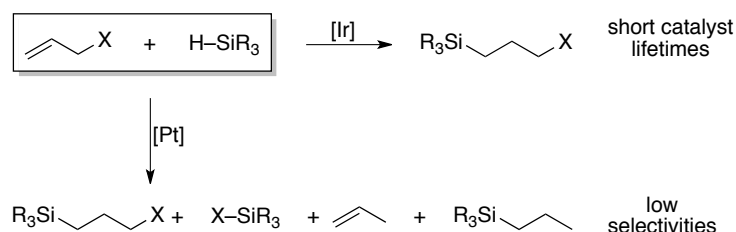


Figure 8. Generic molecular structure of imidazo[1,5-a]pyridine-3-ylidene complexes.

They are among the strongest heteratomic σ -donors and match 1,3-disubstituted imidazolylienes with regard to steric demand.¹¹⁰⁻¹¹² Their bicyclic structure facilitates a unique stereoelectronic environment at the metal center, which may easily be manipulated by varying the substituent R on the free wingtip of the integrated NHC ligand.¹¹⁰⁻¹¹² These characteristics render imidazo[1,5-a]pyridine-3-ylidenes (ImPy-R) promising candidates for the development of derived catalytically active transition metal complexes.^{60,110-114} Their application in novel Pt(0) hydrosilylation catalysts is presented in this work.

1.3.2 Iridium-catalyzed Hydrosilylation

In the context of hydrosilylation, iridium complexes are predominantly employed in the conversion of allyl compounds to yield γ -substituted propylsilanes. These are commercially relevant products due to the multiple functionalities of the obtained products, although their efficient synthesis remains one of the current challenges in hydrosilylation catalysis (Scheme 4).^{56,65,115}



Scheme 4. Ir- and Pt-catalyzed hydrosilylation of allyl compounds.^{56,65,115}

The application of typical platinum-based hydrosilylation catalysts in these transformations initiates several competing reaction pathways associated with considerable byproduct formation and consequently low selectivities.¹¹⁵⁻¹²¹ Particularly the conversion of allyl chloride, the most widely used allyl compound in industry, is prone to byproduct formation.^{56,65} The use of iridium catalysts has emerged and grown explosively in the past decade to circumvent the selectivity issues inherent to platinum catalysis, with the most prominent catalyst precursor being $[\{\text{IrCl}(\text{cod})\}_2]$ (cod = cycloocta-1,5-diene).¹²²⁻¹³⁴ The major drawback of these catalyst systems is their short lifetime, resulting in low yields and the necessity for high metal loadings.^{56,65}

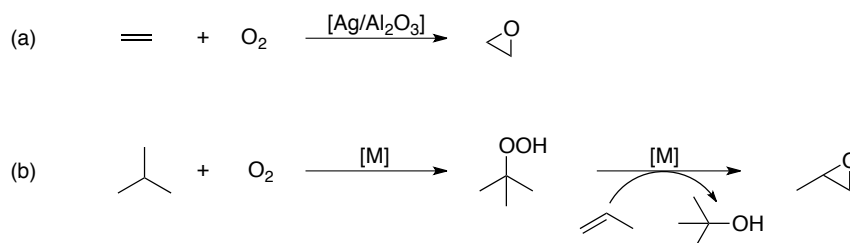
Catalyst loadings can be significantly reduced by the use of additivesⁱⁱⁱ such as cycloocta-1,5-diene (cod); however, a deep mechanistic understanding of the catalytic system on a molecular level has not been established to date, with patent literature constituting the main source of information.¹²²⁻¹³⁴ Thus, part of this work has been dedicated to the in-depth mechanistic study of the iridium-catalyzed hydrosilylation of allyl compounds. It features the results of both stoichiometric and catalytic experiments and also reveals the main deactivation pathways, paving the way toward the design and implementation of more efficient catalyst systems. In addition, the extension of the substrate scope to include allyl acetate has led to the successful direct synthesis of the first $\mu^2\text{-}\eta^2,\eta^2$ -allyl bridged diiridium complex showcasing unique structural features.

ⁱⁱⁱ In the literature on hydrosilylation, cod is often termed a *co-catalyst*, which is misleading since it constitutes merely a replacement for the degenerated (via hydrogenation) cod ligand (vide infra).

1.4 Epoxidation

Epoxidation is an important process in the chemical industry, since epoxides offer a facile access to many functionalizations by ring-opening reactions and thus constitute important building blocks for a variety of polymers such as polyglycols, polyamides and polyurethanes.^{135,136} In addition, the production of various fine chemicals, including e.g. pharmaceuticals, agrochemicals, food additives, flavor and fragrance compounds, depends on epoxide intermediates.¹³⁷⁻¹³⁹ The relevance of asymmetric epoxidation catalysis for the production of enantiomerically pure, biologically active compounds is highlighted by the Nobel prize to B. SHARPLESS in 2001 (vide supra).¹⁴⁰ The most commonly used olefins in epoxidation catalysis are short-chained alkenes extracted from mineral oil, such as ethylene and propylene.^{136,141} Of these, the most important commodity is propylene oxide,¹³⁵ while alternative olefin substrates extracted from sustainable vegetable resources become increasingly important in light of the diminishing fossil resources.¹⁴²

Industrially, the epoxidation of ethene to ethylene oxide is carried out using molecular oxygen as oxidant in the presence of heterogeneous silver contacts. On account of the excessive byproduct formation associated with oxidation of methyl groups by O₂, the strategy of “direct oxidation” has failed for larger substrates such as propene or even longer alkenes to date.^{IV} Instead, an indirect process utilizing alkyl hydroperoxides such as *tert*-butylhydroperoxide (TBHP), the oxirane process, is applied (Scheme 5).⁸



Scheme 5. Selected industrial epoxidation processes.⁸ (a) Industrial production of ethylene oxide, (b) oxirane process for the production of propylene oxide (PO). [M] = Ti(IV)/SiO₂ (heterogeneous, Shell) or Mo (homogeneous catalyst, Halcon/ARCO). The production of PO is also carried out via several other industrial processes, including the chlorohydrin route and the cumene hydroperoxide process according to Sumitomo.¹⁴⁴

The significance of PO as base chemical is illustrated by its worldwide annual supply of just shy of 8 million tonnes in 2012, which is expected to grow even further to beyond 9 million tonnes in 2017.¹⁴⁵ Roughly two thirds of this amount is used for the production of polyether polyols, which are an important intermediate in the production of polyurethanes. The subsequent outlets of PO production include propylene glycols (20%), glycol ethers (5%), isopropanolamines, alkoxyates, cellulose ethers, propylene carbonate, allyl alcohol and

^{IV} The best selectivities reported are in the range of 50-60% at 9% propene conversion.¹⁴³

1,4-butanediol.¹⁴³ The oxirane process as developed by Halcon and ARCO in the 1960s was based on Mo, W, V and Ti catalysts. Metals with low oxidation potentials and high Lewis acidity are superior in epoxidation catalysis, hence reactivity decreases along Mo(VI) > W(VI) > V(V) > Ti(IV).¹⁴⁶ In agreement with this trend, established benchmark systems in homogeneous epoxidation catalysis include molybdenum and rhenium complexes.¹³⁵ Recent research efforts have been directed towards the development of facile syntheses of high valent molybdenum complexes that are active in epoxidation catalysis.¹³⁹ Particularly η^5 -cyclopentadienyl molybdenum complexes have attracted interest in recent years^{135,136,139,147-149} by virtue of the possibility of haptotropic shifts of the Cp moiety in the transition state and the inert behavior of Cp during epoxidation catalysis.¹⁵⁰⁻¹⁵⁶ Two main structural motifs and variations thereof prevail in the literature, namely $[\text{MoCp}(\text{CO})_3\text{X}]$ and $[\text{MoCpO}_2\text{X}]$ (X = e.g. halide, alkyl; Figure 9).¹³⁹

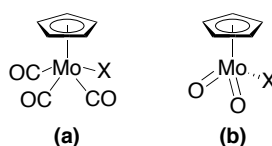
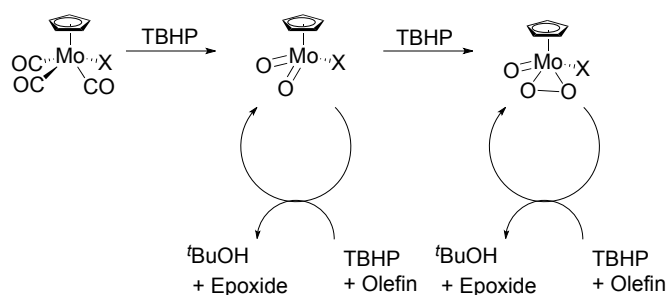


Figure 9. Structural motifs of cyclopentadienyl molybdenum complexes in olefin epoxidation catalysis. X = e.g. halide, alkyl.¹³⁹ Note that substituted Cp derivatives $\text{C}_5\text{R}'_5$, including chiral residues and *ansa* bridges to X are also in use,¹³⁹ but are omitted here for clarity.

The tricarbonyl compounds $[\text{MoCp}(\text{CO})_3\text{X}]$ can be viewed as pre-catalysts, since they are known to oxidize in situ to the active dioxo and oxo-peroxo Mo(VI) species by the hydroperoxide used (Scheme 6).^{139,157-162} Bearing this in mind, the stability and robustness of the ligand X towards oxidative conditions is of particular importance with respect to recyclability and catalyst lifetime (TON), which is a major aspect in the development of industrially relevant catalysts.^{15,161} Ideally, the formation of the catalytically active Mo(VI) species should be facilitated by the Cp and X ligands by stabilization of the corresponding dioxo and oxo-peroxo species.



Scheme 6. Oxidation of $[\text{MoCp}(\text{CO})_3\text{X}]$ pre-catalysts with TBHP.¹⁶² TBHP = *tert*-butylhydroperoxide, *t*BuOH = *tert*-butanol.

In recent years, several ligand spheres have been investigated as part of the η^5 -cyclopentadienyl tricarbonyl molybdenum structural motif.^{139,163-169} In this subclass of molybdenum precatalysts for olefin epoxidation, the *ansa*-bridged cyclopentadienyl Mo complex $[\{\eta^5\text{-C}_5\text{H}_4[\text{CH}(\text{CH}_2)_3\text{-}\eta^1\text{-CH}\}\text{Mo}(\text{CO})_3\text{]}^{170}$ demonstrates the highest activity with a TOF of 11800 h^{-1} in organic solvents¹⁷¹ and TOFs up to 44000 h^{-1} in room temperature ionic liquids (RTILs).¹⁷²

N-heterocyclic carbene (NHC) ligands are often employed as spectator ligands in homogeneous catalysis (vide supra).¹⁰⁷⁻¹⁰⁹ As a consequence of the robust metal-carbon bond originating from their strong σ -donating and poor π -accepting character, their implementation in the complex coordination sphere often facilitates higher complex stability, particularly where high oxidation states of the metal are involved, as is the case in epoxidation catalysis.¹⁰⁷ In addition, variation of the NHC allows for stereoelectronic tuning at the metal center.¹⁰⁷⁻¹⁰⁹ Several complexes with the general formula $[\text{MoCp}(\text{CO})_2(\text{NHC})\text{X}]$ (X = halide, alkyl) have been reported, which can be viewed as structural analogues to $[\text{MoCp}(\text{CO})_3\text{X}]$ with one carbonyl ligand replaced by the NHC.¹⁷³⁻¹⁷⁵ These complexes exhibit indeed longer catalyst lifetimes compared to their tricarbonyl congeners due to their enhanced stability under oxidative conditions, allowing for higher conversions. However, long induction periods and comparatively low turnover frequencies (TOFs) indicate that the stereoelectronic features of the NHC ligand are beneficial for catalyst stability, but detrimental to catalytic activity.¹⁷³⁻¹⁷⁵

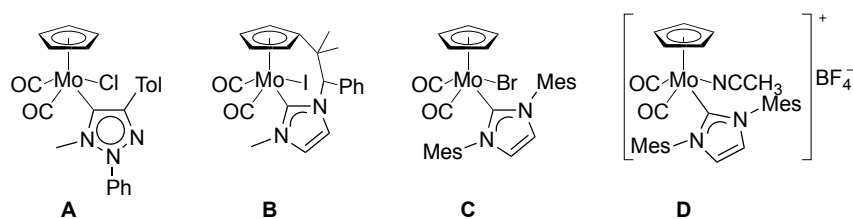


Figure 10. Selected previously reported cyclopentadienyl NHC molybdenum complexes A,¹⁷⁵ B,¹⁷³ C,¹⁷⁴ and D¹⁷⁴ with similar structural motifs. Tol = *para*-tolyl, Ph = phenyl, Mes = mesityl.

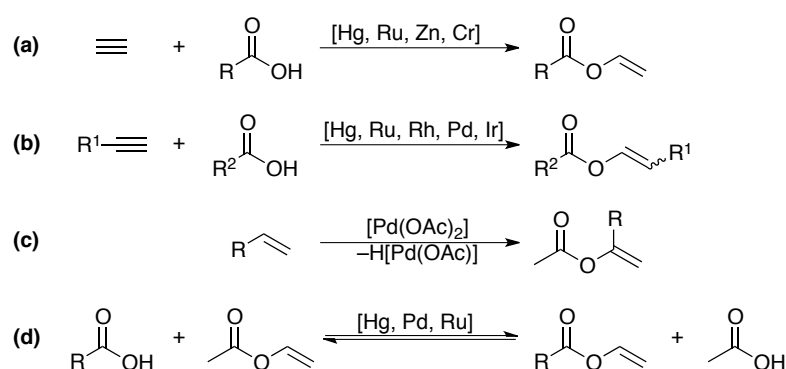
Imidazo[1,5-*a*]pyridine-3-ylidenes (ImPy-R) are structurally related to 1,3-disubstituted imidazolyidenes (Figure 8). Owing to their bicyclic structure, they facilitate a unique stereoelectronic environment at the metal center, which may easily be manipulated by varying the substituent R on the free wingtip of the integrated NHC ligand.¹¹⁰⁻¹¹²

This type of ligand has attracted interest since the synthetic route has been significantly simplified by the group of ARON,¹¹¹ and consequently several imidazo[1,5-*a*]pyridine-3-ylidene transition metal complexes based on Rh,^{60,113,114} Ir,^{110,113} and Pd^{60,110} have been reported for various applications such as allylic substitution,⁶⁰ Suzuki-Miyaura cross-coupling,¹¹⁰ and other cross-coupling reactions.¹¹² They can be

considered promising candidates for the further development of $[\text{MoCp}(\text{CO})_2(\text{NHC})\text{X}]$ type epoxidation catalysts bearing in mind their unique steric and electronic characteristics. Hence, the report of two novel NHC molybdenum complexes, $[\text{CpMo}(\text{CO})_2(\text{ImPyMes})\text{Cl}]$ (**7**) (ImPyMes = 2-mesitylimidazo[1,5-a]pyridine-3-ylidene) and $[\text{CpMo}(\text{CO})_2(\text{ImPyMes})(\text{NCCCH}_3)]\text{BF}_4$ (**8**), and their application as precatalysts in olefin epoxidation is part of this work.

1.5 Transvinylation

Vinyl ester monomers can be used in a wide range of applications and can be converted into a plethora of end product polymers.¹⁷⁶ The industrial applications of vinyl esters include paint synthesis,¹⁷⁷ medical products,¹⁷⁸ paper coatings,¹⁷⁹ and construction materials,¹⁸⁰ as well as organic synthesis and pharmaceutical chemistry.¹⁸¹⁻¹⁸³ In addition, vinyl ester resins are used for the preparation of polymer matrix composites in both military and commercial applications due to their high modulus, high impact strength, high glass transition temperature, low weight and low cost.¹⁸⁴ Owing to the economic interest in vinyl ester monomers, several synthetic strategies have been established for their synthesis (Scheme 7). These include the reaction of carboxylic acids and acetylene,^{185,186} direct addition of carboxylic acids to terminal alkynes catalyzed by mercury salts,¹⁸⁷ Ru-,¹⁸⁸⁻¹⁹² Rh-,¹⁹³ Pd-,¹⁹⁴ or Ir-¹⁹⁵ complexes, and allylic oxidation of olefins¹⁹⁶⁻¹⁹⁸ using $\text{Pd}(\text{OAc})_2$. The synthetic approach via transvinylation of carboxylic acids with vinyl donors has been reported using $\text{Hg}(\text{II})$ -¹⁹⁹ and $\text{Pd}(\text{II})$ -²⁰⁰⁻²⁰³ materials as well as a series of ruthenium precursors such as ruthenium carbonyls, ruthenocene or ruthenium trichloride hydrate.²⁰⁴⁻²⁰⁶



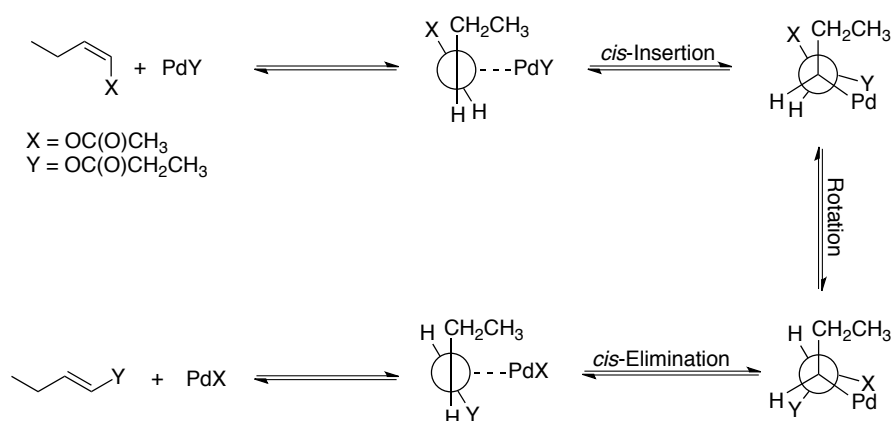
Scheme 7. Catalytic synthetic pathways to vinyl ester monomers.²⁰⁷ (a) Reaction of carboxylic acids and acetylene,^{185,186,208} (b) addition of carboxylic acids to alkynes,^{187-193,195} (c) allylic oxidation of olefins using palladium acetate,^{196,197} (d) transvinylation.¹⁹⁹⁻²⁰⁶

The advantages of catalytic transvinylation compared to the formerly prevalent acetylene route include a significantly increased selectivity and mild reaction conditions. Ruthenium catalyst precursors have proven

particularly useful by virtue of their lower toxicity compared to mercury-based reactions, their higher stability compared to Pd(II) systems as well as the accessibility of thermally labile vinyl esters and functionalized vinyl ester building blocks.^{176,200,202,204-206}

1.5.1 Mechanistic Considerations

Despite the industrial utilization of catalytic transvinylation processes, reports on the mechanistic aspects of this type of reaction are scarce. Previously published studies focus on the mechanism adopted by Pd(II) catalyst precursors, for which – in analogy to olefin oxidation – an intermediate π -complex is proposed.²⁰⁰⁻²⁰² A report by SABEL *et al.* deduces that Pd(II)-catalyzed transvinylation is best described as an equilibrium reaction (1) and comprises the transfer of a vinyl rather than a vinyloxy group (2). In addition, it could be demonstrated that bond formation and bond cleavage take place at the same carbon atom (3) and transvinylation of *cis/trans*-isomers leads to inversion of the stereoconfiguration (4). Based on these experimental findings, the reaction mechanism illustrated in Scheme 8 was proposed by the group of SABEL.



Scheme 8. Mechanism of Pd(II)-catalyzed transvinylation according to SABEL *et al.*²⁰²

Notwithstanding the publication of several patents reporting the application of a variety of ruthenium precursors for ruthenium-catalyzed transvinylation,²⁰⁴⁻²⁰⁶ mechanistic details have been largely disregarded in the literature prior to this work. Thus, part of this study and the preceding Master's Thesis²⁰⁷ has been devoted to a thorough mechanistic investigation of this process.

1.5.2 Structural Motifs

The structural chemistry of ruthenium carbonyl carboxylates is closely related to transvinylation catalysis due to the nature of the catalytically active ruthenium species, which can be described as a mixture of the mono- and dinuclear species $[\text{Ru}(\text{CO})_3(\eta^2\text{-O}_2\text{C-R})(\eta^1\text{-O}_2\text{C-R})]$ and $[\text{Ru}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-O}_2\text{C-R})_2(\text{L})_2]$ ($\text{R-CO}_2^- =$ carboxylate, $\text{L} =$ two-electron donor).¹⁶⁷ Ruthenium complexes of this type have first been described in the literature by CROOKS *et al.*²⁰⁹ and in the course of the past five decades, several catalytic applications apart from transvinylation including isomerization,²¹⁰ hydrogenation,^{211,212} and C–C–bond formation reactions²¹³ have been established. This class of compounds is structurally diverse, comprising mono-,^{214,215} di-,²¹⁶ and tetranuclear^{213,217-227} as well as polymeric structures.²¹⁶ If dicarboxylic acids are used, tetra-,²²⁸ hexa-,²²⁸⁻²³⁰ and octanuclear²³¹ cage structures are accessible (Figure 11).

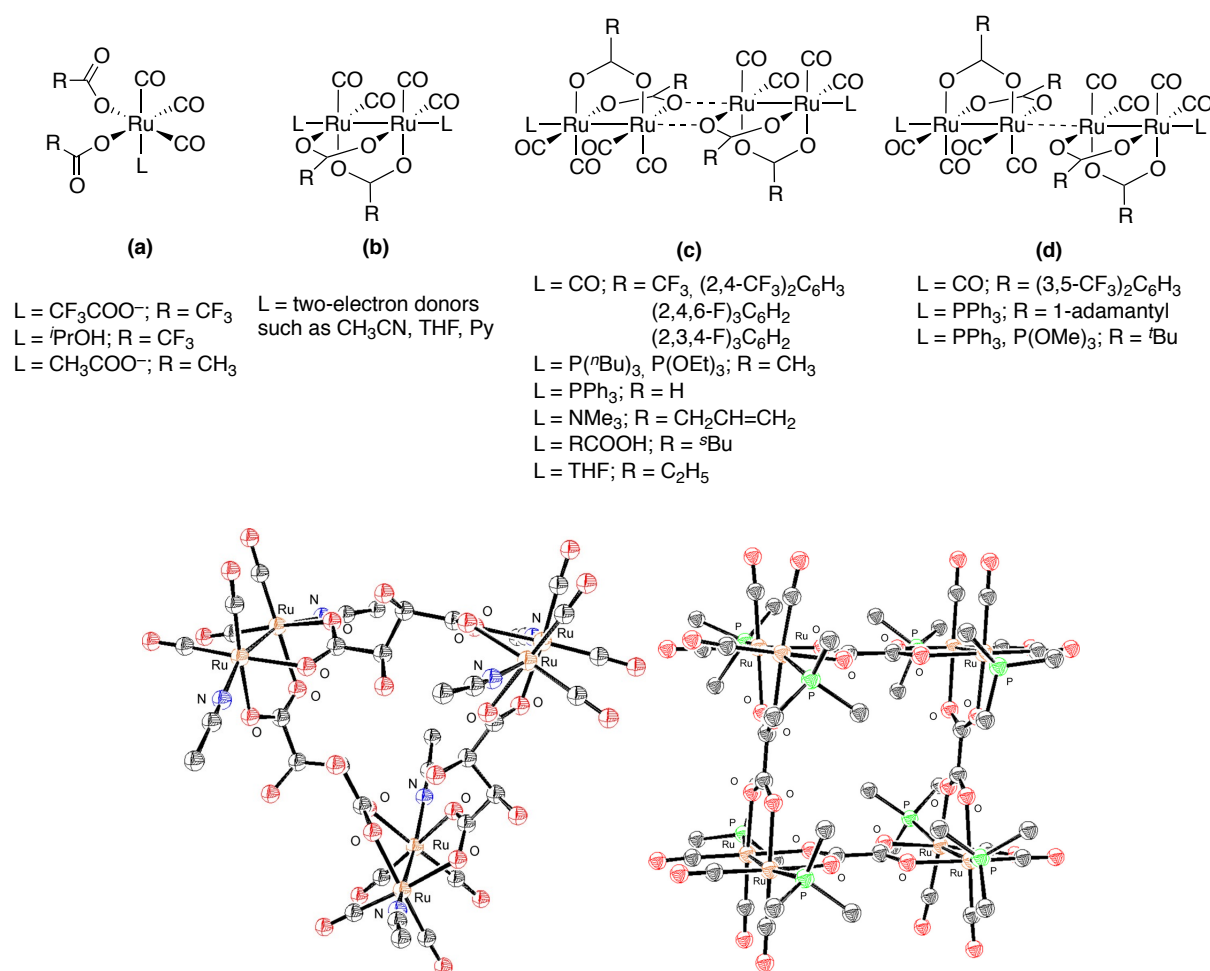


Figure 11. Structural motifs of ruthenium carbonyl carboxylates.²¹³⁻²²⁷ For a detailed review on dinuclear ruthenium sawhorse type complexes see SÜSS-FINK *et al.*²¹⁶

Of these, the by far most diverse and best understood group are dinuclear ruthenium sawhorse type complexes.²¹⁶ Reports of tetranuclear complexes are scarce and frequently require unusual synthetic

techniques. In general, they are composed of two dimeric “ $\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{C-R})_2\text{L}$ ” fragments linked via Ru–O^{213,217-225} or Ru–Ru^{217,226,227} interactions (vide supra). On the other hand, trinuclear ruthenium carbonyl carboxylates have not been reported at all to date. Structurally related complexes typically involve other ligand systems such as thiolates,²³² amino acids,²³³ and formyl²³⁴ in complexes of the general formula $[(\mu^2\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu^2\text{-L})]$ or bridging ligands like *para*-ethynylaniline²³⁵ and alkynoate acetyl salicylic acid esters²³⁶ in $[\text{HRu}_3(\text{CO})_9(\mu^3\text{-L})]$ type complexes. In addition, a number of complexes comprising a “ $(\mu^3\text{-O})(\mu\text{-H})\text{Ru}_3$ ” core have been reported;²³⁷⁻²⁴⁵ however, μ^3 -bridging OH groups connecting three Ru centers are not known in ruthenium carbonyl carboxylates.^V Owing to the rich structural diversity of multinuclear ruthenium carbonyl carboxylates, one component of this work is the report of new complexes of this type.

1.6 Ligand Fine Tuning: Structural Motifs for Molecular Wires

The rich structural chemistry of multinuclear ruthenium compounds not only offers access to numerous catalytic applications, but has also been exploited for the development of functional materials for molecular electronic devices.²⁴⁷⁻²⁴⁹ Even though R. FEYNMAN envisioned the ultimate integrated circuits to be constructed at the molecular or atomic level as early as 1959,^{250,251} *molecular electronics* is a relatively young area of research.^{252,253} It can be defined as technology using single molecules, small groups of molecules, carbon nanotubes, or nanoscale metallic or semiconductor wires to perform electronic functions.²⁵² More specifically, molecular wires are one-dimensional molecules (i.e. chains) with two redox-active termini, which allow for (1) electron transport along the chain and (2) electron exchange with the outside world.²⁵⁴ Much of the early work in this field has been focused on materials based on organic molecules,²⁵⁵ the majority of which feature HOMO-LUMO gaps (E_g) ranging from 2.4 to 5.4 eV, leaving plenty of room for E_g reduction which in turn should lead to higher conductivities (Figure 12).²⁵⁶

^V There has been one report of a complex comprising a similar structural fragment by the group of SÜSS-FINK. It was found that in the tetranuclear cluster $[\text{Ru}_4(\mu^3\text{-OH})(\mu^2\text{-H})_3(\eta^6\text{-C}_6\text{H}_6)_4]$, three of four Ru atoms are connected by a μ^3 -bridging OH.²⁴⁶

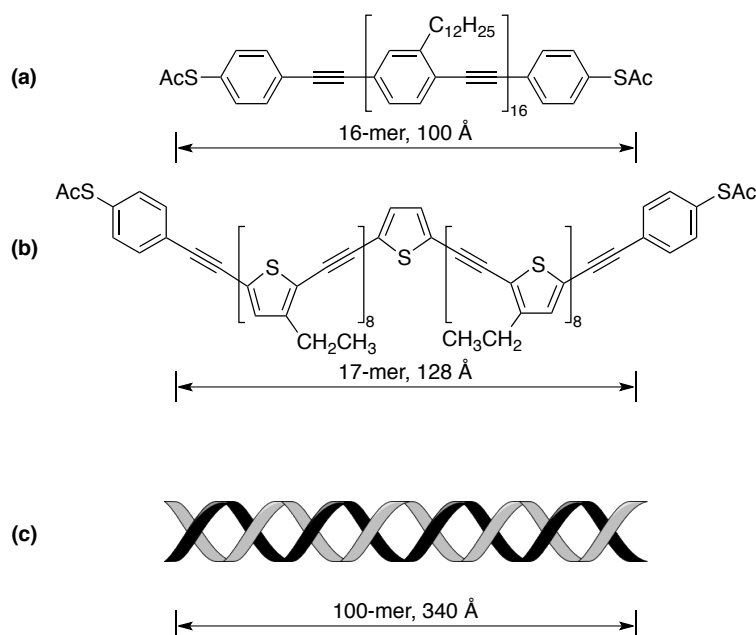


Figure 12. (a-b) Examples of synthetic organic molecular wires (SAc = thioacetate).^{257,258} (c) DNA has also been shown to be a functional molecular wire.^{255,259-261}

One approach is to incorporate metal complex units into the backbone of conjugated organic molecules in such a way that optimum orbital mixings between metal and organic fragments may result in a reduced E_g .²⁴⁷ In this context, diruthenium handles $[\text{Ru}_2]^{n+}$ have been used to cap alkynyl polymer chains, facilitating electron transfer along the chain.^{247,248,262} Contrary to the previously employed mononuclear piano-stool motif employed in organometallic wire termini (see Figure 13a), such dinuclear units $[\text{M}_2]^{n+}$ facilitate the development of oligomers consisting of alternating metal and polymer units (Figure 13d).²⁴⁸

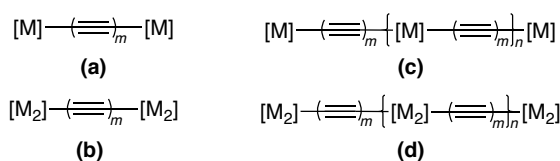


Figure 13. Structural motifs of simple (a, b) and oligomeric (c,d) metallayne wires.²⁴⁸

The *trans* ditopic nature of $[\text{M}_2]^{n+}$ implied by the realization of such a structural motif is highly beneficial to accomplish the key features of scalability and connectivity to external building blocks.^{252,253} In addition, the concept of ligand fine tuning can be exploited in order to tailor the redox properties of the $[\text{M}_2]^{n+}$ for the desired application.

While $[\text{Ru}_2]^{n+}$ moieties were used in the pioneering work by the groups of REN and others,^{247,248,262} a similar structural chemistry has been established for several other transition metals, including Re, Cr, Mo and W.²⁶³⁻²⁷² The properties of these complexes have been studied extensively in relation to the development of supramolecular structures and intrinsic informative electrochemical properties.^{264-266,268,273-282} Apart from research efforts regarding their electronic and photophysical properties²⁸³⁻²⁹⁰ in order to examine potential applications in catalysis²⁹¹⁻²⁹³ and biochemistry,²⁹⁴ synthetic work for the development of molecular wires^{269,295-301} has also been presented. Recent research efforts are focused on the isolated molecular building blocks in order to foster a deep understanding of the electrochemical properties of the $[\text{M}_2]^{n+}$ entities, including the specific influence of the employed ligands and identification of any potential sweet spots for their fine-tuning.^{302,303} When redox-active equatorial ligands such as ferrocenecarboxylate ($\text{Fc}-\text{CO}_2^-$) are employed, the mediating effect of the $[\text{M}_2]^{n+}$ core and possible coupling effects can be observed. A number of studies concentrate on $[\text{Mo}_2]^{4+}$ systems,^{274,287,289,296,304-312} which show great structural diversity when different precursors such as *cis*- $[\text{Mo}_2(\text{DAniF})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ ^{270,280,313-315} and its congener *trans*- $[\text{Mo}_2(\text{DAniF})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ ($\text{DAniF}^- = N,N'$ -di(*p*-anisyl)formamidinate) are used.^{298,316}

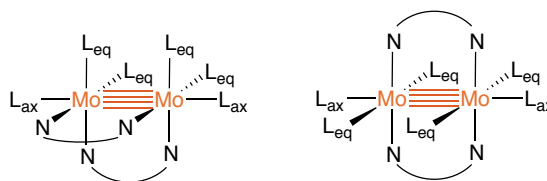


Figure 14. Metal-metal bonded units used in the formation of extended structures ($N \cap N = N,N'$ -di(*p*-anisyl)formamidinate; L_{eq} = equatorial ligand, L_{ax} = axial ligand).³¹⁷

Equatorial and axial ligation can be utilized to attain specifically designed molecular geometries, such as wires, ladders and cyclic structures.³¹⁷ Controllable equatorial ligation offers many advantages with respect to synthesis and application of these redox-active entities. The outcome of the related synthetic routes is largely affected by ligand basicity, which has been found to be proportional to the *trans* effect, hence decreasing in the order $\text{DArF}^- > \text{R}-\text{CO}_2^- > \text{CH}_3\text{CN}$ ($\text{DArF}^- = N,N'$ -diaryformamidinate).³¹⁸ Several series of dinuclear complexes coordinated by two mixed-ligands, $[\text{Ru}_2(\text{DArF})_n(\text{O}_2\text{CCH}_3)_{4-n}\text{Cl}]$ ($n = 4-0$),³¹⁹⁻³²² $[\text{Mo}_2(\text{DArF})_n(\text{NCCH}_3)_{8-2n}][\text{BF}_4]_{4-n}$ ($n = 4-0$),^{318,323-325} and $[\text{Mo}_2(\text{DAniF})_n(\text{O}_2\text{CCH}_3)_{4-n}]$ ($n = 4-0$)^{318,325-327} have been reported,^{280,282,309,326,328-330} which might be applicable as building blocks for supramolecular structures such as molecular wires. Generally speaking, six configurations of $[\text{Mo}_2]^{4+}$ complexes coordinated by two different bridging ligands are feasible (Figure 15).

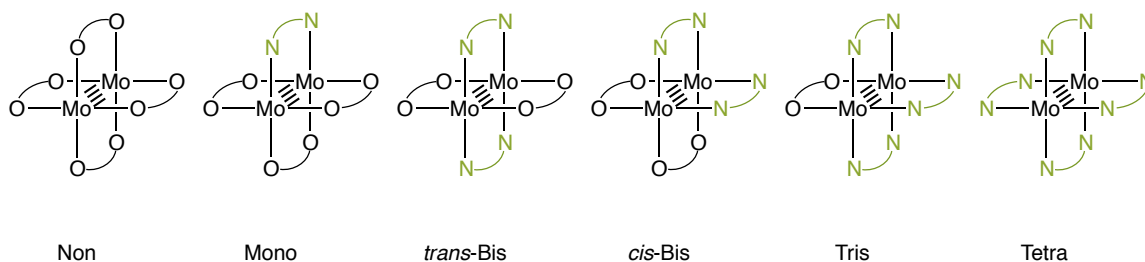
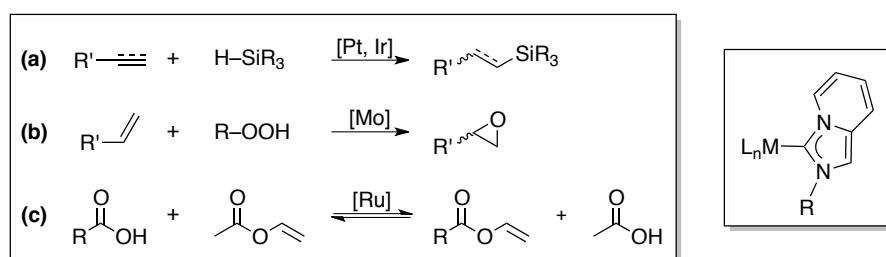


Figure 15. Full series of dinuclear molybdenum complexes with mixed-ligands ($\text{O}\cap\text{O}$ = carboxylate and $\text{N}\cap\text{N}$ = N,N' -diarylfamimidate). The terminologies Tetra, Tris, Bis, Mono, and Non are based on the number of formamidinate ligands.

While there are many examples of the Tetra,³²⁵ Bis,^{295,296,298,318} and Non^{327,331} species, the synthetic accessibility of the Tris and Mono species is limited. Only a few tris-substituted Mo_2 complexes $[\text{Mo}_2(\text{DArF})_3(\text{O}_2\text{C}-\text{R})]$ ^{326,332-336} and one mono-substituted example of the composition $[\text{Mo}_2(o\text{-DMophF})(\text{O}_2\text{C}-\text{Me})_3]$ ($o\text{-DMophF}$ = N,N' -di(2-methoxyphenyl)formamidinate)³³⁷ have been reported to date. However, a full series is required to quantitatively grasp the relative ligand basicity of the ligands involved, particularly DArF^- and $\text{Fc}-\text{CO}_2^-$. Therefore, part of this work has been dedicated to the investigation of the structural and electrochemical characteristics of representatives of the $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C}-\text{Fc})_{4-n}]$ ($n = 4-0$)^{295,325,331} series. By virtue of the different redox activities of these otherwise closely related compounds, they are promising candidates for the synthesis of molecular wires.

2 OBJECTIVE

Platinum-catalyzed hydrosilylation ranks among the most important industrial applications of homogeneous catalysis in terms of both cost and scale of this process. Even though this reaction has been established for over half a century, the development of an understanding for the reaction pathway on a molecular level has been arduous and slow. Bearing this in mind, the prime objective of this thesis is the in-depth mechanistic investigation of platinum-catalyzed hydrosilylation. Owing to its industrial significance, Karstedt's catalyst will be used as platinum source, even though this choice entails several preparative challenges. A combination of isotope labelling, stoichiometric and kinetic experiments will be utilized to reach a deeper understanding of the catalytic cycle. In addition, new structural motifs of Pt(0) NHC complexes will be presented utilizing the ImPy-R ligands, which have only recently become easily accessible (Scheme 9).



Scheme 9. Left: Types of reactions investigated in this work. (a) Hydrosilylation, (b) Epoxidation, (c) Transvinylolation. The denoted transition metals indicate the focus of the respective study. The prime area of research of this work was the investigation of platinum-catalyzed hydrosilylation. **Right:** Generic molecular structure of imidazo[1,5-a]pyridine-3-ylidene (ImPy-R) complexes.

Considering the recent development to employ iridium catalysts for the hydrosilylation of allyl compounds due to their high selectivity compared to conventional catalysts, a mechanistic study of this process will also be presented. In addition, the structural and electronic properties of the first allyl-bridged iridium dimer, which is formed in the stoichiometric reaction of one of the most common iridium catalysts, $[\{\text{IrCl}(\text{cod})\}_2]$, and allyl acetate will be discussed.

On account of the industrial relevance of epoxidation catalysis, new catalyst structural motifs using molybdenum as central metal will be described. To this end, the relatively new ImPy-R ligands will be employed for the further development of complexes of the type $[\text{MoCp}(\text{CO})_2(\text{NHC})]$. Their applicability in epoxidation catalysis will be evaluated.

Ruthenium-catalyzed transvinylolation offers a facile synthetic pathway to vinyl ester monomers, which are frequently used for the production of a plethora of end-use polymers. This process will be examined with respect to the underlying mechanistic principles, and structural motifs of related ruthenium carbonyl carboxylates will be presented. Furthermore, structurally related molybdenum dimers will be reported as potential candidates for the synthesis of functional materials for the manufacture of molecular wires.

3 RESULTS – PAPER

OUTLINES

The individual contributions of T. K. Meister to each of the following publications have been collected in Table A1 (Appendix).

3.1 Molecular Catalysts for Bond Activation – Paving the Way for Alternative Resources

Original Title: Molekulare Katalysatoren zur Bindungsaktivierung – Auf dem Weg zu alternativen Rohstoffquellen

TERESA K. ZIMMERMANN AND FRITZ E. KÜHN

CHEMIE IN UNSERER ZEIT 2015, 49, 248-259

This front page review article is directed at a broad audience including interested laymen and students on the high school level. It focuses on the concept of catalysis as one of the most important value-added processes in chemical industry and provides a short overview of the most important principles and parameters. The importance of the industrial Haber-Bosch Process for the global food production is illustrated. Regardless of the economic and geopolitical significance of catalysis, naturally catalyzed processes remain by far superior to synthetic chemistry with respect to a number of aspects. This is particularly true for the activation of small molecules, which are typically abundant on earth but chemically almost inert. Prominent examples include dinitrogen (N_2) or carbon dioxide (CO_2). The conversion of such molecules to useful building blocks and fuels remains one of the key challenges of catalytic research to date. Consequently, this review describes several biological processes which are currently subject to investigation in the field of biomimetic and bioinspired catalysis by virtue of their high efficiency and efficacy. Special attention is paid to the utilization of alternative resources, since the design of artificial catalysts modeled after natural systems may prove to be a viable approach to solve the global energy problem. In particular, concepts for the exploitation of the following abundant raw materials are presented: methane (1), carbon dioxide (2) and lignin (3).

Methane is the main component of natural gas and is the largest fossil energy source alongside coal. In light of its vast reserves and the high hydrogen to carbon ratio, it is an interesting alternative to oil as main carbon supply. Methane is most notably converted in biological archetypes, i.e. enzymes such as methanemmonoxygenases and cytochromes P450. The latter typically comprise a Fe(II) core in a porphyrinic ring structure, which has served as inspiration for numerous innovative catalyst designs aiming for alkane oxidation. The ultimate dream reaction would be the direct oxidation of methane to methanol, hence providing a versatile fuel and carbon feedstock that is both liquid and comprises a high energy density. Carbon dioxide on the other hand is the building block used in nature for the production of carbohydrates and derived products in photosynthesis. If this process could be appropriated by chemical industry, a nearly unlimited carbon source would be unleashed. Similar considerations apply for the utilization of lignin, a natural polymer occurring mainly in plants. This review provides an overview on concepts and current methodologies for the employment of these potential raw materials, giving a perspective view on each resource candidate.

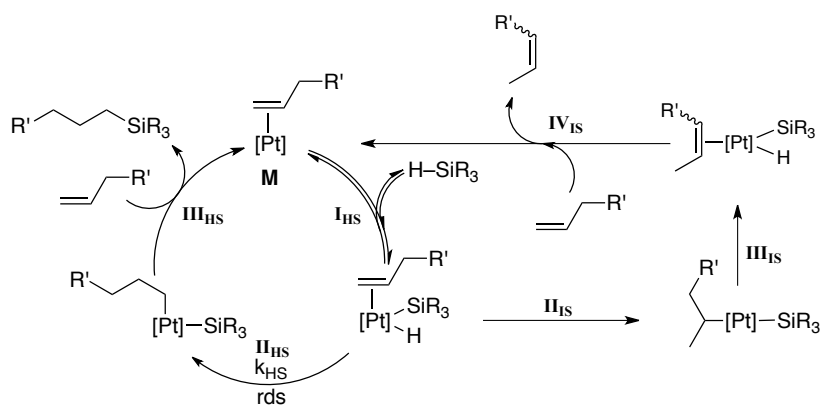
3.2 Platinum Catalysis Revisited – Unraveling Principles of Catalytic Olefin Hydrosilylation

TERESA K. MEISTER, KORBINIAN RIENER, PETER GIGLER, JÜRGEN STOHRER, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

ACS CATALYSIS 2016, 6, 1274-1284

Platinum-catalyzed hydrosilylation ranks among the most important applications of homogeneous catalysis today, with respect to both cost and scale of this process. This industrial process has been established for over half a century and provides access to a number of useful products such as adhesives, crosslinkers, surfactants and molding products via the manufacture of organofunctional sil(ox)anes and silicones. Taking into account that this reaction has been commonly practiced for over 50 years, the development of an understanding of the molecular processes governing this reaction has been arduous and slow. The original model proposed by CHALK and HARROD in 1965 continues to be widely accepted in the literature, providing an elegant yet simple mechanistic approach to this process, yet structural features of the active catalyst species still remain elusive. In addition, the industrially pivotal Karstedt's catalyst has been omitted in past mechanistic studies owing to its disadvantageous features detrimental to common experiments for the elucidation of reaction mechanisms. Furthermore, internal olefins have been largely disregarded as substrates in this process in the past. However, their reactivity cannot be adequately rationalized based on the Chalk-Harrod mechanism.

This paper provides an in-depth mechanistic study of platinum-catalyzed hydrosilylation. To account for its industrial relevance, Karstedt's catalyst was used as platinum source regardless of the ensuing experimental challenges. Based on ^{195}Pt NMR data, ^2H labelling experiments as well as a kinetic study, new insights into this fundamentally important industrial process are provided (Scheme 10).



Scheme 10. Proposed revised mechanism for platinum-catalyzed hydrosilylation using Karstedt's catalyst as platinum source (HS = hydrosilylation, IS = isomerization).

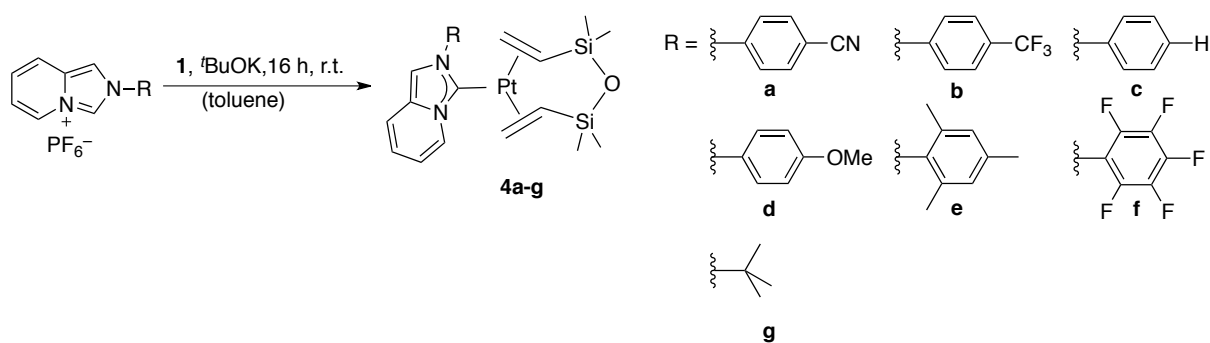
The proposed revised mechanism comprises the following steps (HS = hydrosilylation, IS = isomerization): I_{HS}, oxidative hydrosilane addition, II_{HS}, migratory olefin insertion, III_{HS}, reductive product elimination and recoordination of the olefin. The side reaction leading to olefin isomerization proceeds via I_{IS}, oxidative hydrosilane addition, II_{IS}, migratory olefin insertion, III_{IS}, β-H elimination, and IV_{IS}, loss of the isomerization product and recoordination of olefin. The rate limiting nature of the olefin insertion step II_{HS} was evidenced via the determination of a primary kinetic isotope effect (KIE), characteristic product distributions in labelling experiments, the observation of Pt-²H species as well as the coherence of experimentally determined rate laws and the mechanistic model. In addition to the advances with respect to the catalytic cycle, the dependence of structural features of the catalytically active species on the coordination strength of the chosen olefin substrate could be demonstrated in a ¹⁹⁵Pt NMR study and a series of kinetic experiments.

3.3 Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts

TERESA K. MEISTER, JENS W. KÜCK, KORBINIAN RIENER, ALEXANDER PÖTHIG, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

JOURNAL OF CATALYSIS **2016**, *337*, 157–166

The application of NHC ligands has extended the scope of platinum hydrosilylation catalysts. By virtue of the strong Pt–C bond, platinum(0) carbene complexes are stable towards air and moisture and feature superior stability and selectivity compared to classical catalysts such as Karstedt's and Speier's catalyst. Imidazo[1,5-a]pyridine-3-ylidenes (ImPy–R) provide access to an entire class of NHC complexes featuring a heteroatomic bicyclic ligand structure. They are susceptible to stereoelectronic tuning by variation of the wingtip substituent R. This report endeavors to exploit the unique characteristics of ImPy–R ligands in hydrosilylation catalysis, presenting seven novel complexes [Pt(dvtms)(ImPy–R)] (R = 4-cyanophenyl (**4a**), 4-trifluoromethylphenyl (**4b**), phenyl (**4c**), 4-methoxyphenyl (**4d**), mesityl (**4e**), pentafluorophenyl (**4f**), *tert*-butyl (**4g**), Scheme 11).



Scheme 11. Synthesis of **4a-g**. **1** = [Pt₂(dvtms)₃] (Karstedt's catalyst, see Scheme 2).

The accepted mechanism associated with catalytic hydrosilylation utilizing Pt NHC complexes proceeds in a different manner compared to classical platinum catalysts. The slowest step of the reaction is believed to be the loss of the dvtms ligand, resulting in the formation of a reactive Pt–NHC fragment. The results of detailed investigations of spectroscopic and electrochemical properties of **4a-g** as well as a theoretical study on the B3LYP/6-31G** level of theory suggest that [Pt(ImPy–R)L] complexes follow an analogous reaction pathway. Several parameters influencing catalytic activity could be established in this report. According to Koopman's Theorem, a distinct correlation of HOMO energy levels E_{HOMO} and the oxidation potential E_{Ox} is revealed (Figure 16, left). In addition, the reactivity of **4a-g** can be interpreted by means of the electronics of

the respective substituent R provided that sterics are comparable. More specifically, an increasing electron withdrawing character of the substituent R appears to augment the rate of hydrosilylation, which can be attributed to (1) facilitated loss of the dtvms ligand due to reduced π -backbonding of Pt to dtvms and (2) expedited reductive elimination of the hydrosilylation product by virtue of the corresponding rising E_{Ox} . This can be illustrated by the linear Hammett correlation depicted in Figure 16.

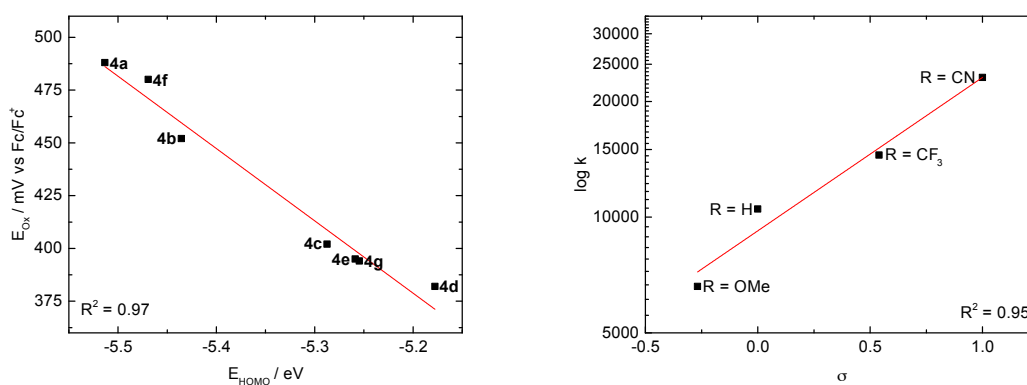


Figure 16. Left: Linear relationship of the experimental oxidation potential E_{Ox} as determined via cyclic voltammetry and HOMO energy levels E_{HOMO} derived from a theoretical investigation of the B3LYP/6-31G** level of the catalyst. **Right:** Hammett plot illustrating the interdependence of electronics and catalytic activity in hydrosilylation of **4a-d**.

In general, **4a-d** are more efficient hydrosilylation catalysts than **4e-g**, suggesting that the steric bulk at the imidazole-N obstructs reaction progress. **4a-g** show remarkable reactivity in hydrosilylation, yielding competitive results to Markó's catalyst in the model hydrosilylation of oct-1-ene with $HSi_3O_2Me_7$.

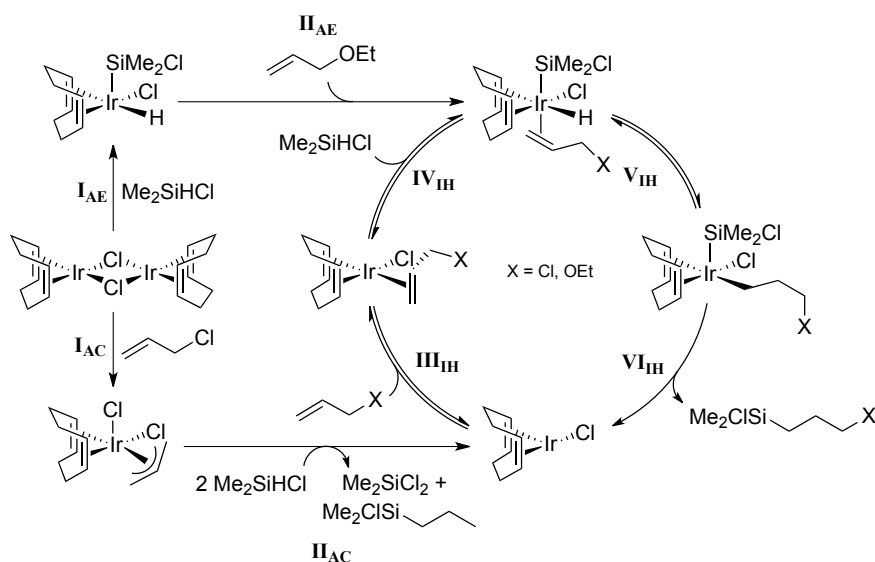
3.4 Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds

KORBINIAN RIENER, TERESA K. MEISTER, PETER GIGLER, WOLFGANG A. HERRMANN, AND FRITZE KÜHN

JOURNAL OF CATALYSIS 2015, 331, 203-209

Iridium catalysis has become increasingly important in industrial hydrosilylation of allyl compounds in recent years owing to the economic significance of the resulting γ -substituted propylsilanes on the one hand, and the remarkable selectivity of Ir catalysts compared to established platinum systems on the other hand. While there are several reports on different aspects of platinum-based procedures, this is the first mechanistic investigation of the more recently developed iridium-variant, which has previously been treated in patent literature only. These feature superior selectivities while generally suffering from short catalyst lifetimes.

A series of stoichiometric and isotope labeling experiments allows for the identification of crucial parameters determining catalytic performance and elucidation of deactivation pathways. The hydrosilylation of allyl chloride, the most widely used allyl compound in industry, with Me_2SiHCl was chosen as model system with $[\{\text{IrCl}(\text{cod})\}_2]$ as catalyst. The developed mechanistic picture is shown in Scheme 12.



Scheme 12. Proposed catalytic pathway of hydrosilylation of allyl compounds using $[\{\text{IrCl}(\text{cod})\}_2]$ as iridium source. AE = activation via allyl ether; AC = activation via allyl chloride; IH = iridium catalyzed hydrosilylation.

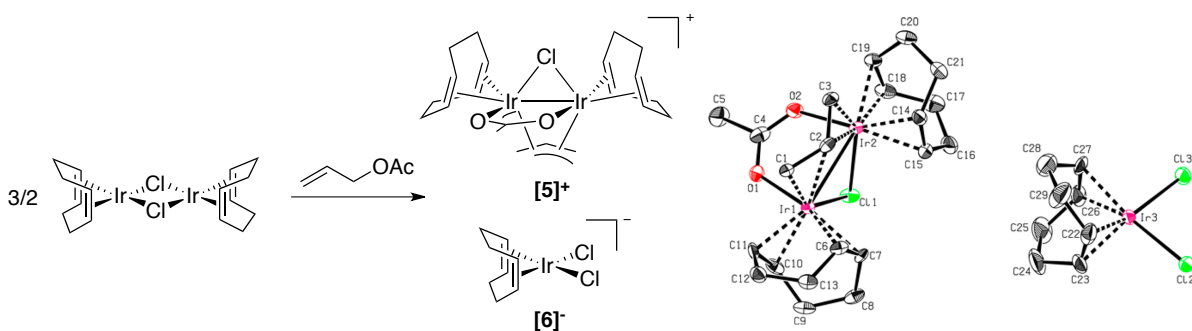
The activation pathway and the corresponding entry point into the catalytic cycle depends on the chosen allyl substrate (I_{AC} and I_{AE}). Starting from the reactive $[IrCl(cod)]$ fragment (Scheme 12, bottom), the reaction proceeds via III_{IH} , allyl substrate coordination, IV_{IH} , oxidative addition of hydrosilane, V_{IH} , migratory insertion of the allyl substrate into the Ir–H bond and VI_{IH} , reductive product elimination. The formation of iridium nanoparticles at high silane concentrations and the hydrogenation of the cod ligand were identified as major deactivation pathways. Their impact can be diminished by continuous silane addition and the employment of cod as additive. In view of these results, new catalyst structural motifs impeding particle formation and ligand hydrogenation can be developed.

3.5 Direct Synthesis and Bonding Properties of the First μ^2 - η^2 , η^2 -Allyl Bridged Diiridium Complex

KORBINIAN RIENER, TERESA K. ZIMMERMANN, ALEXANDER PÖTHIG, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2015, 54, 4600-4602

This report describes the one-step synthesis of the first allyl-bridged diiridium complex $[5]^+$ bearing the uncommon counterion $[6]^+$ and the investigation of the unusual and electronic features of this compound. The reaction proceeds upon treatment of the established hydrosilylation catalyst $[\{\text{IrCl}(\text{cod})\}_2]$ with a potential allyl substrate, allyl acetate (Scheme 13).



Scheme 13. Synthesis and molecular structure (ORTEP plot) of $[5][6]$. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir1–Ir2 2.8736(3), C1–C2 1.441(8), C2–C3 1.454(7), Ir1–C1 2.105(6), Ir1–C2 2.489(5), Ir2–C3 2.111(6), Ir2–C2 2.454(6).

Allyl acetate undergoes C–O bond cleavage, thereby providing the bridging allyl and acetate fragments that are subsequently incorporated into the title compound $[5]^+$. These replace one of the bridging chloride anions, while the other one is retained. The cleaved Cl^- recombines with a $[\text{IrCl}(\text{cod})]$ fragment, yielding the anionic $[6]^-$. The intriguing structural motif can be unequivocally confirmed by single crystal XRD analysis (Scheme 13). $[5][6]$ has been reported to be the first contribution to multinuclear iridium complex chemistry comprising a symmetrically allyl bridged iridium dimer. It features comparatively long Ir–Ir and C–C_{allyl} bonds while showcasing Ir–C_{methylene} bonds that are among the shortest in any Ir–allyl compound reported to date. These structural characteristics are indicative of significant π -backbonding from Ir to the allyl ligand, which could be further evidenced via DFT calculations of the B3LYP/6-311++G** level of theory. The orbital interactions that could be deduced from frontier molecular orbital analysis of $[5]^+$ indicate a σ -like interaction between the iridium centers (Ir–Ir bond) as well as the metal and the allyl ligand (Ir–C_{allyl}). Weakening and elongation of both the C–C_{allyl} and the Ir–Ir bonds results from the population of antibonding

ligand orbitals while strengthening the metal-ligand interactions. This report constitutes a significant contribution to multinuclear iridium chemistry. Future perspectives in this area include the systematic synthesis, characterization and comparison of analogous allyl-bridged compounds bearing other d-block elements.

3.6 Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis

ANDREA SCHMIDT,[#] NIDHI GROVER,[#] TERESA K. ZIMMERMANN,[#] LILIAN GRASER, MIRZA COKOJA, ALEXANDER PÖTHIG, FRITZ E. KÜHN

[#]A. Schmidt, N. Grover and T. K. Zimmermann contributed equally to this work.

JOURNAL OF CATALYSIS 2014, 319, 119-126

Epoxidation catalysis using molybdenum complexes such as $[\text{MoCp}(\text{CO})_3\text{X}]$ ($\text{X} = \text{e.g. Cl}^-, \text{Br}^-$) involves high-valent active species. The stability of such intermediates can often be enhanced by the use of NHC ligands by virtue of their strong σ -donating and poor π -accepting character. Consequently, NHCs have extended the scope of cyclopentadienyl molybdenum complexes in epoxidation catalysis. ImPy–R ligands are an interesting source of NHC moieties comprising a unique annulated bicyclic structure prone to stereoelectronic tuning by variation of the wingtip substituent R. This report presents the synthesis and characterization of two novel complexes **7** and **8** bearing both cyclopentadienyl and ImPy–R spectator ligands as well as their application in epoxidation catalysis (Figure 17).

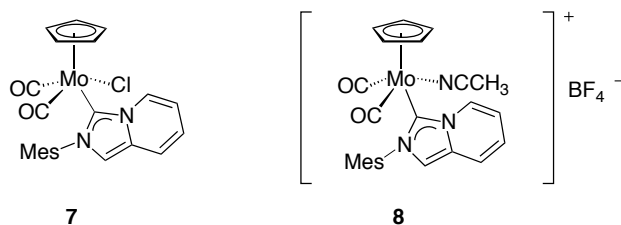


Figure 17. Epoxidation catalysts **7** and **8**.

Synthesis of **7** and **8** proceeds via the silver transmetallation route using the molybdenum precursor $[\text{MoClCp}(\text{CO})_3]$. IR spectroscopic analysis was used to evaluate the degree of π -backbonding of molybdenum to the carbonyl ligands, which can be a useful indicator of the Lewis acidity at the metal. The experimental evidence suggests that electron density at Mo in **8** is higher compared to **7**, which could be further substantiated by a theoretical investigation at the B3LYP/6-31G** level of theory. In addition, ^{95}Mo shielding tensors were calculated for improved analysis of unexpected ^{95}Mo NMR shifts of **7** and **8**. Both **7** and **8** are efficient and selective pre-catalysts in epoxidation of cyclooctene using TBHP (TBHP = *tert*-butylhydroperoxide) as oxidant, outperforming previously reported molybdenum-based epoxidation catalysts

and yielding high TOFs of up to 40,900 h⁻¹ (**7**) and 53,100 h⁻¹ (**8**). This report concludes that the stereoelectronic characteristics of ImPy-R ligands facilitate catalyst stability and activity in epoxidation catalysts. The electronic situation at Mo is decisive for catalytic performance of the respective pre-catalyst, with enhanced Lewis acidity promoting higher activity. Hence, the higher reactivity of **8** over **7** can be rationalized in terms of augmented electron density at Mo.

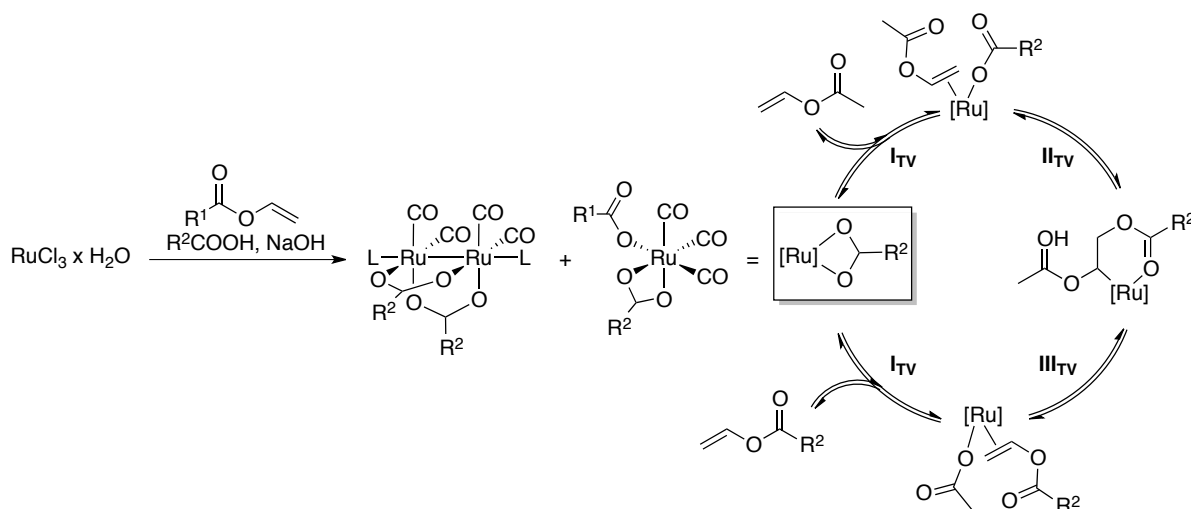
3.7 Ruthenium-Catalyzed Transvinylation – New Insights

JENNIFER ZIRIAKUS,[#] TERESA K. ZIMMERMANN,[#] ALEXANDER PÖTHIG, MARKUS DREES, STEFAN HASLINGER, DOMINIK JANTKE, AND FRITZ E. KÜHN

[#]J. Ziriakus and T. K. Zimmermann contributed equally to this work.

ADVANCED SYNTHESIS & CATALYSIS **2013**, 355, 2845-2859

Vinyl ester monomers are important building blocks for numerous end-use polymers such as medical products, paper coatings and construction materials. They can be produced via ruthenium-catalyzed transvinylation, which has been established since the 1980s. However, the active catalyst species as well as the reaction mechanism has remained elusive in the past. This study presents experimental evidence for the nature of the catalytically active species comprising ruthenium carbonyl carboxylate structural motifs. A combination of IR, ESI-MS and NMR data indicates the presence of both mononuclear and dinuclear ruthenium species in situ (Scheme 14).



Scheme 14. Proposed catalytically active dinuclear Ru(I) (left) and mononuclear Ru(II) (right) species in the active reaction mixture and proposed catalytic cycle of ruthenium-catalyzed hydrosilylation. L = H_2O , Cl^- , CH_3COOH ; R = CH_2CH_3 , CH_3 .

It should be noted that the experimental work related to this paper has been carried out during the Master's Thesis preceding this dissertation²⁰⁷ and in cooperation with J. ZIRIAKUS.³³⁸ The evaluation of the catalytic performance of several mono- and dinuclear ruthenium carbonyl carboxylates indicates that the mononuclear species present in solution accounts for the lion's share of catalytic activity using simple precursors such as RuCl_3 . Hence, a mechanistic model was developed, which was verified and further developed utilizing isotope

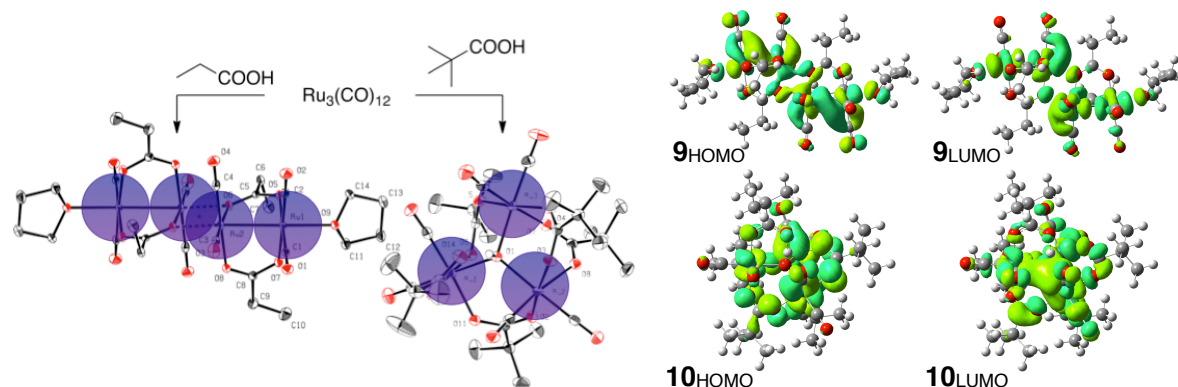
labeling experiments, investigation of stereo- and regioselectivity as well as a theoretical study on the B3LYP/6-31G* level of theory. The resulting proposed cycle is depicted in Scheme 14 and comprises the following steps: I_{TV} , coordination of vinyl ester, II_{TV} , formation of a six-membered ruthenacycle, III_{TV} , vinyl transfer, and IV_{TV} , loss of product and recoordination of vinyl donor (e.g. vinyl acetate, TV = transvinylation). Based on these results, rational design of new transvinylation catalysts mimicking the structural motifs of the active catalyst species is feasible. In addition, replacement of the carbonyl ligands with suitable anchors might allow for catalyst immobilization.

3.8 $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCCH}_2\text{CH}_3)_4(\text{THF})_2]$ and $[\text{Ru}_3(\mu_3\text{-OH})(\text{CO})_6(\mu\text{-OOC}^t\text{Bu})_4(\text{OOC}^t\text{Bu})]$: Novel Multinuclear Ruthenium Carbonyl Carboxylates

TERESA K. ZIMMERMANN, JENNIFER ZIRIAKUS, EBERHARDT HERDTWECK, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

ORGANOMETALLICS 2014, 33, 2667-2670

This paper describes the synthesis of two novel multinuclear ruthenium complexes by reaction of triruthenium dodecacarbonyl $[\text{Ru}_3(\text{CO})_{12}]$ with propionic and pivalic acid, forming $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCCH}_2\text{CH}_3)_4(\text{THF})_2]$ (**9**) and $[\text{Ru}_3(\mu_3\text{-OH})(\text{CO})_6(\mu\text{-OOC}^t\text{Bu})_4(\text{OOC}^t\text{Bu})]$ (**10**, Scheme 15). Ruthenium carbonyl carboxylates have been known since the late 1960s, and particularly dinuclear compounds of the composition $[\text{Ru}_2(\text{CO})_4(\mu\text{-OOCR})_2\text{L}_2]$ (R = alkyl, L = donor ligand, e.g. THF, py) have attracted research interest in the past. Tetranuclear complexes bearing similar building blocks are scarce, while trinuclear complexes of this type have not been reported at all previously. Hence, this report contributes to the structural diversity of ruthenium carbonyl carboxylate chemistry.



Scheme 15. Left: Synthesis of **9** and **10**. Right: Graphical representation of frontier molecular orbitals of **9** and **10** as determined by a computational study on the B3LYP/LANL2DZ level of theory.

It was found that a dynamic equilibrium exists in solution between **9** and its dimeric and oligomeric analogues, $[\text{Ru}_2(\text{CO})_4(\mu\text{-OOCCH}_2\text{CH}_3)_2(\text{THF})_2]$ and $[\{\text{Ru}_2(\text{CO})_4(\mu\text{-OOCCH}_2\text{CH}_3)_2\}_6(\text{THF})_2]$, indicating that **9** is prone to cleavage of the tetranuclear Ru_4 core structure by donor ligands such as THF or pyridine. This is also illustrated by the geometry of this complex' frontier molecular orbitals, which show the localization of the LUMO between the Ru_2 fragments, facilitating a fracture at the weaker axial $\text{Ru}\text{-OOC}\text{-R}$ interactions. The

molecular structure of **10** is quite unique, featuring a μ_3 -bridging hydroxyl group, whose identity could be unequivocally confirmed by refinement of the OH proton in XRD analysis as well as the characteristic low field ^1H NMR shift at $\delta = 14.37$ in CDCl_3 . It is synthesized in an excess of pivalic acid with no additional solvent. Both **9** and **10** reveal remarkable structural characteristics, extending the scope of ruthenium carbonyl carboxylate chemistry.

3.9 Structure and Catalytic Activity of the Ruthenium(I) Sawhorse-Type Complex $[\text{Ru}_2\{\mu, \eta^2\text{-CF}_3(\text{CF}_2)_5\text{COO}\}_2(\text{DMSO})_2(\text{CO})_4]$

TERESA K. ZIMMERMANN, STEFAN HASLINGER, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

ACTA CRYSTALLOGRAPHICA SECTION C **2014**, *C70*, 384-387

The title compound $[\text{Ru}_2\{\mu, \eta^2\text{-CF}_3(\text{CF}_2)_5\text{COO}\}_2(\text{DMSO})_2(\text{CO})_4]$ (**11**) was synthesized using heptanoic acid and $[\text{Ru}_3(\text{CO})_{12}]$ as ruthenium precursor. It is an archetype of ruthenium carbonyl sawhorse type complexes and features the typical μ -bridging coordination mode of the carboxylate ligands (Figure 18).

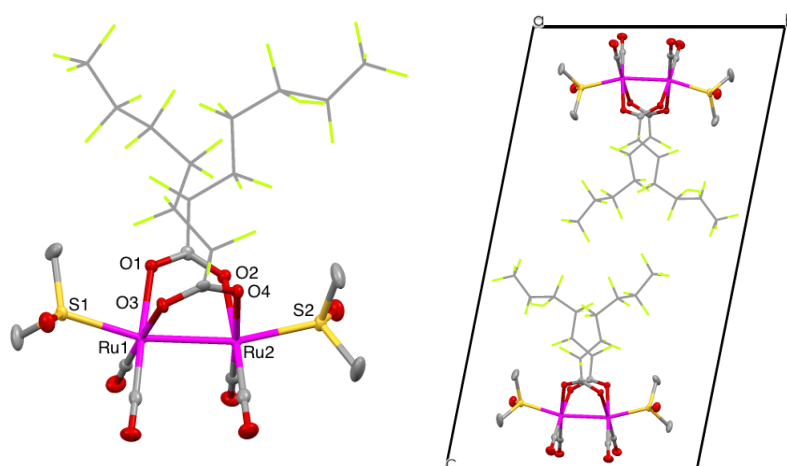


Figure 18. Left: ORTEP-Plot of the molecular structure of **11**. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru1–Ru2 2.6907(4), Ru1–S1 2.4164(8), Ru2–S2 2.4095(7), Ru1–O1 2.1476(17), Ru1–O3 2.1256(18), Ru2–O2 2.1364(18), Ru2–O4 2.1515(17), Ru2–Ru1–S1 165.14(3), Ru1–Ru2–S2 164.70(3), O1–Ru1–O3 81.58(7), O2–Ru2–O4 81.56(7). **Right:** Crystal packing of **11**, highlighting the layered arrangement in the crystal (view along a axis).

Both Ru atoms are coordinated in a distorted octahedral manner, with two DMSO molecules occupying the axial positions along the Ru–Ru axis. The DMSO atoms are tilted with respect to one another and oriented away from the carbonyl groups, thus accounting for the Ru1–Ru2–S2 (164.70(4) deg) and Ru2–Ru1–S1 (165.14(3) deg) torsion angles well below the ideal 180 deg. The examination of the crystal packing reveals a multilamellar structure of bilayers, where sheets of lipophilic fluorinated alkyl chains are intersected by more hydrophilic layers of “ $\text{Ru}_2(\text{DMSO})_2(\text{CO})_4$ ” fragments. The application of **11** in a model vinyl transfer reaction of propionic acid and vinyl acetate to evaluate its reactivity in transvinylation catalysis illustrates that the catalytic performance of **11** compares well with that of structurally similar dinuclear ruthenium carbonyl sawhorse complexes. The obtained data further indicates that the perfluorinated bridging heptanoate exerts a beneficial effect compared to propionate, but overall **11** is still outperformed by mononuclear catalysts. However, it may prove useful to employ perfluorinated carboxylate ligands in the synthesis of mononuclear ruthenium transvinylation catalysts.

3.10 Synthesis and Electrochemical Properties of *cis*- and *trans*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DArF})_2]$ ($\text{O}_2\text{C-Fc}$ = Ferrocenecarboxylate, DArF = *N,N'*-Diarylformamidinate)

XU-MIN CAI, TERESA K. ZIMMERMANN, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2015, 54, 6631-6640

The synthesis of three complexes of the composition $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DArF})_2]$ by reaction of the precursor *cis*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ with three electronically different *N,N'*-diarylformamidinate (DArF) ligands [DArF = *N,N'*-diphenylformamidinate (DPhF), *N,N'*-di(*p*-trifluoromethylphenyl)formamidinate (DTfmpF), and *N,N'*-di(*p*-anisyl)formamidinate (DAniF)] is described. The reaction is performed as a one-pot reaction and generally leads to a mixture of the *cis* and *trans* complexes in the crude product. The preferentially crystallized isomer could be identified unambiguously via single crystal X-ray diffraction in all cases, showcasing the typical molybdenum paddlewheel structures.

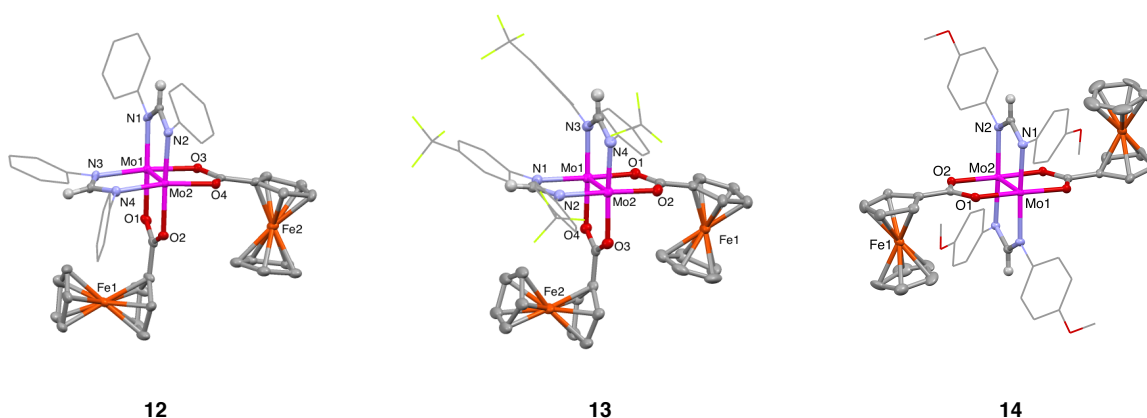


Figure 19. ORTEP plot of the molecular structures of **12**, **13** and **14**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

The new complexes *cis*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DPhF})_2]$ (***cis*-12**), *cis*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DTfmpF})_2]$ (***cis*-13**), and *trans*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DAniF})_2]$ (***trans*-14**) were subjected to electrochemical analysis in order to elucidate their redox properties. On account of the electron-donating character of these DArF ligands, the oxidation of the $[\text{Mo}_2]^{4+}$ occurs prior Fc oxidation, hence inverting the redox sequence previously reported with ligands such as acetonitrile or phosphines. Evidence for the electronic interaction of the redox-active ferrocene carboxylate ligands was found for *trans*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DAniF})_2]$, while the $[\text{Mo}_2]^{5+}/[\text{Mo}_2]^{6+}$ oxidation was observed exclusively with DAniF⁻ as ligand, which can be attributed to the electron-donating character of the

methoxyphenyl substituent. The resemblance of the absorption patterns in UV-vis spectroscopy illustrates the similarity of structural and electronic features of **12-14**. Based on the basicity of the ferrocenecarboxylate and DArF ligands employed in this work, a mechanism for the isomerization of intermediate species during synthesis is presented. This work constitutes an important contribution to the concept of controllable design of structural motifs applicable to the synthesis of molecular wires. Ultimately, this could pave the way for the development of redox-active supramolecular structures. In this context, the directed conversion of the precursor *trans*-[Mo₂(DAniF)₂(NCCH₃)₄][BF₄]₂ to obtain multi redox-active ladder type oligomers utilizing the principles established in this study is of particular interest.

3.11 Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C-Fc})_{4-n}]$ (DArF = *N,N'*-Diarylformamidinate; $\text{O}_2\text{C-Fc}$ = Ferrocenecarboxylate)

XU-MIN CAI, TERESA K. MEISTER, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2015, 55, 858-864

The substitution pattern in complexes of the series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C-Fc})_{4-n}]$ ($n = 4-0$) is demonstrated to be influenced by the electronic properties of the DArF ligand employed for the reaction with the precursor, *cis*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{NCCH}_3)_4][\text{BF}_4]_2$. In particular, when two electronically different *N,N'*-diarylformamidinate (DArF) ligands [DArF = *N,N'*-di(*p*-trifluoromethylphenyl)formamidinate (DTfmpF) and *N,N'*-di(*p*-anisyl)formamidinate (DAniF)] are employed, the respective tris- and mono-substituted complexes $[\text{Mo}_2(\text{DTfmpF})_3(\text{O}_2\text{C-Fc})]$ (**15**) and $[\text{Mo}_2(\text{DAniF})(\text{O}_2\text{C-Fc})_3]$ (**16**) are isolated.

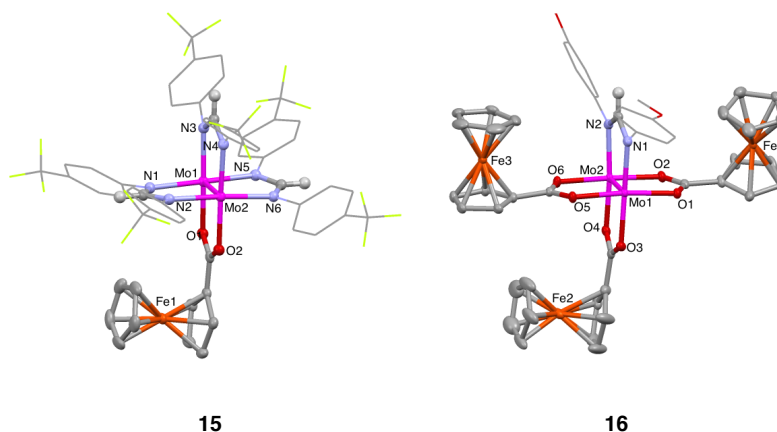
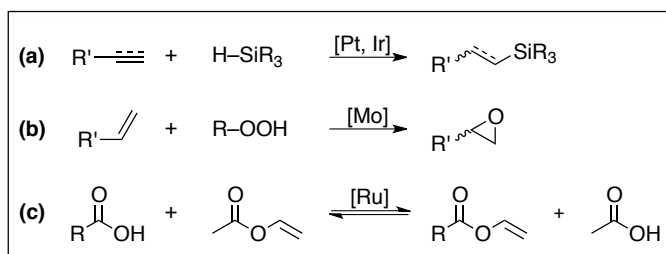


Figure 20. ORTEP plots of the molecular structures of **15** and **16**. Displacement ellipsoids are shown at the 50% probability level. Aryl groups are shown as wireframes, and hydrogen atoms (except for the ones on the DArF bridge) are omitted for clarity.

15 and **16** complete the series of $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C-Fc})_{4-n}]$ ($n = 4-0$) type compounds, thus offering the opportunity of a comprehensive study of the electrochemical properties. Using the characteristic and well-observable oxidation potential $E_{1/2}([\text{Mo}_2]^{4+}/[\text{Mo}_2]^{5+})$, ligand basicity can be quantified and compared in detail. It is concluded that ligand basicity decreases along the series $\text{DAniF}^- > \text{DTfmpF}^- > \text{Fc-CO}_2^- \gg \text{CH}_3\text{CN}$, providing a useful tool for future synthetic approaches aimed at the design of multi redox-active complex building blocks intended for the synthesis of molecular wires.

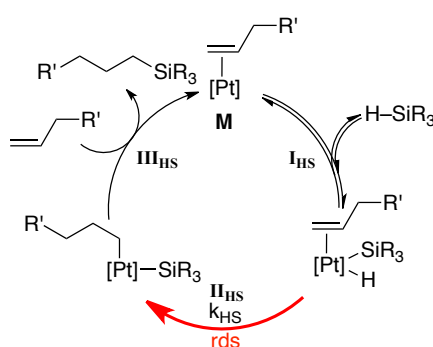
4 CONCLUSION AND OUTLOOK

This work addresses several aspects of homogeneous industrial catalysis. The following three key transformations were selected and examined in more detail on account of their industrial significance: hydrosilylation, epoxidation and transvinylation (Scheme 16).



Scheme 16. Key transformations examined in this work. (a) Hydrosilylation, (b) epoxidation, (c) transvinylation. The denoted transition metals indicate the focus of the respective study. The prime area of research of this work was the investigation of platinum-catalyzed hydrosilylation.

This thesis can be broadly divided into mechanistic studies on the aforementioned reaction types (part I) and the development of novel structural motifs (part II). Most of the experimental work associated with this thesis has been dedicated to the investigation of platinum-catalyzed hydrosilylation (Scheme 16a). As a result of an extensive study comprising isotope labelling experiments, comprehensive NMR investigations and kinetic approaches, an important contribution to the mechanistic understanding of this fundamentally important industrial process using the most widely applied Karstedt's catalyst as platinum source was provided. It was demonstrated that not only reductive elimination, but also olefin insertion is part of the rate limiting step, thereby refining the established Chalk-Harrod mechanism (Chapter 3.2).



Scheme 17. Simplified representation of the revised catalytic cycle of platinum-catalyzed hydrosilylation developed in this work (Chapter 3.2). Contrary to previous reports, it has been proposed that the olefin insertion step is rate limiting.

Furthermore, the first investigation of iridium-catalyzed hydrosilylation of allyl compounds was presented, providing valuable insights into the associated decomposition pathways which account for the observed short catalyst lifetimes (Chapter 3.4). Ruthenium-catalyzed transvinylation (Scheme 16c) was examined in detail

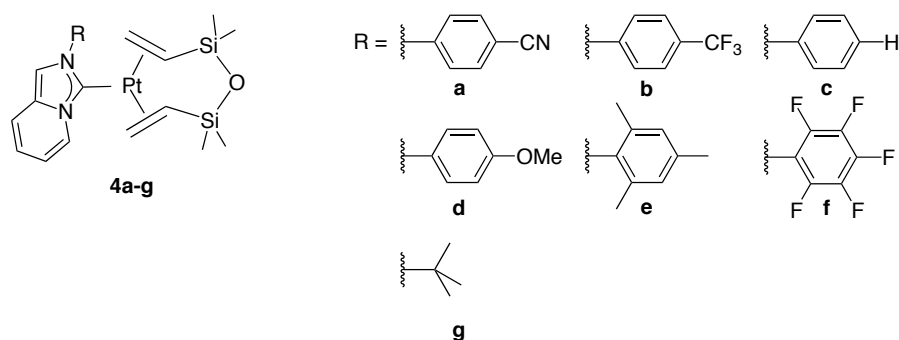
with respect to relevant mechanistic aspects and a likely pathway for the course of the reaction suggested (Chapter 3.7).

The mechanistic investigations of this thesis demonstrate that many reaction mechanisms remain shrouded even in well-established industrial reactions. Their elucidation can provide results that are valuable not only in scientific terms, but can also be utilized for the development and improvement of novel catalyst systems that may actually be put to use.

In addition, new catalyst structural motifs were presented. These can be grouped into (1) carbene complexes comprising ImPy-R ligands and (2) multinuclear structures. Both hydrosilylation and epoxidation catalysts utilizing the newly developed bicyclic ImPy-R ligands were synthesized and tested in model catalytic reactions (Figure 21, Chapter 3.3 and 3.6). The introduction of these ligands proved to be a valuable synthetic strategy with beneficial effects on catalysis in both cases. Furthermore, the investigation of redox properties, HOMO energy levels and TOFs of **4a-g** revealed a distinct correlation of these parameters, illustrating the relevance of electrochemical characteristics for hydrosilylation catalysis. The DFT investigation of **7** and **8** illustrated an increased electron density at Mo compared to previously reported systems, accounting for their remarkable performance in catalysis.

Hence, the application of ImPy-R ligands in catalysts where classical NHC ligands had been established proved to be a worthwhile endeavor. This approach could be extended to other catalyst systems in the future, possibly utilizing the bicyclic ImPy-R structure for asymmetric catalysis.

Hydrosilylation:



Epoxidation:

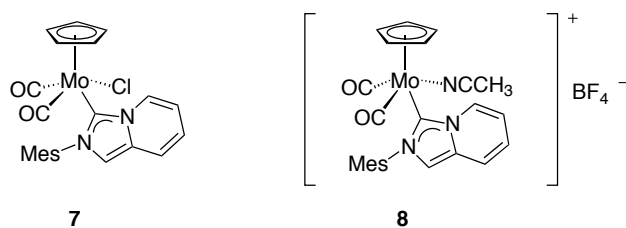


Figure 21. Structural motifs of novel hydrosilylation (top, **4a-g**) and epoxidation (bottom, **7** and **8**) catalysts employing ImPy-R ligands (for more details, see Chapters 3.3 and 3.6).

Novel multinuclear compounds reported in this work include complexes bearing $[\text{Ru}_2]$, $[\text{Ru}_3]$, $[\text{Ru}_4]$, $[\text{Ir}_2]$ and $[\text{Mo}_2]$ cores. These are associated with transvinylation ($[\text{Ru}_2]$, $[\text{Ru}_3]$, $[\text{Ru}_4]$, Chapter 3.8 and 3.9) or hydrosilylation ($[\text{Ir}_2]$, Chapter 3.5) catalysis, respectively, or are of conceptual interest for the synthesis of molecular wires ($[\text{Mo}_2]$, Chapter 3.10 and 3.11). The complexes in this thesis typically bear μ^2 -bridging carboxylate ligands, often feature a paddlewheel or sawhorse type structure and could all be characterized by single crystal XRD (Figure 22)

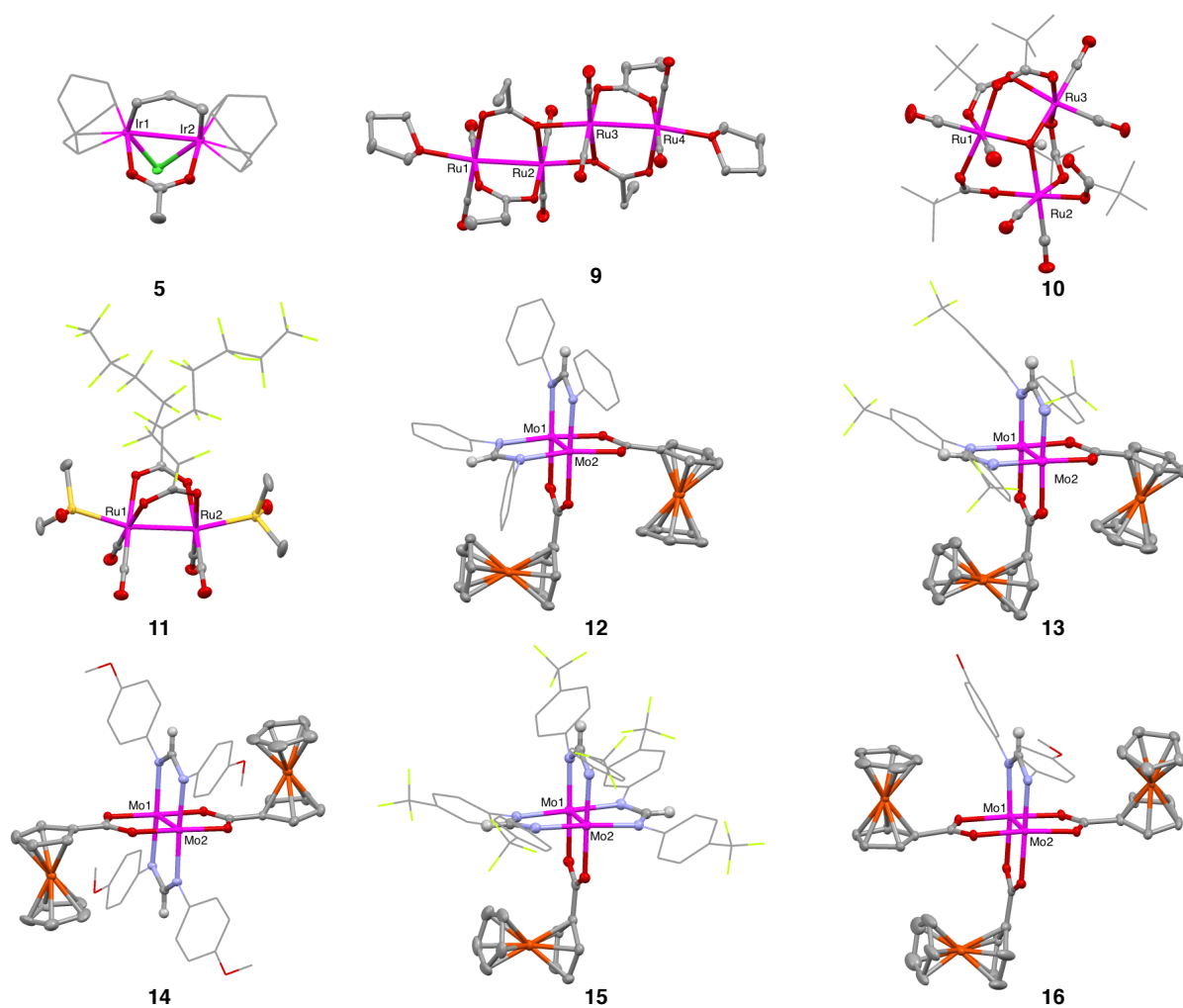


Figure 22. Single crystal structures of multinuclear complexes presented in this work comprising $[\text{Ir}_2]$ (**5**), $[\text{Ru}_2]$ (**11**), $[\text{Ru}_3]$ (**10**), $[\text{Ru}_4]$ (**9**) and $[\text{Mo}_2]$ (**12-16**) core structures. Hydrogen atoms are omitted for clarity except on the *N,N*-diarylformamidinate bridges and the μ_3 -bridging hydroxyl group in **10**. Ellipsoids are shown at the 50% probability level; bulky ligand residues are depicted as wireframes.

These complexes contribute to the rich structural chemistry of multinuclear iridium, ruthenium and molybdenum compounds. The combination of DFT studies, electrochemical investigation and characterization demonstrates different ways to rationalize their composition and reactivity.

5 REPRINT PERMISSIONS

5.1 Molecular Catalysts for Bond Activation – Paving the Way for Alternative Resources

Original Title: Molekulare Katalysatoren zur Bindungsaktivierung – Auf dem Weg zu alternativen Rohstoffquellen

TERESA K. ZIMMERMANN AND FRITZ E. KÜHN

CHEMIE IN UNSERER ZEIT **2015**, 49, 248-259

DOI 10.1002/ciuz.201500716

This Agreement between Teresa K Meister ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	3800371144761
License date	Feb 01, 2016
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Chemie in unserer Zeit
Licensed Content Title	Molekulare Katalysatoren zur Bindungsaktivierung
Licensed Content Author	Teresa K. Zimmermann, Fritz E. Kühn
Licensed Content Date	Aug 4, 2015
Pages	12
Type of use	Dissertation/Thesis
Requestor type	Author of this Wiley article
Format	Print and electronic
Portion	Full article
Will you be translating?	No
Title of your thesis / dissertation	Homogeneous Industrial Catalysis: Hydrosilylation, Epoxidation, Transvinylation
Expected completion date	Mar 2016
Expected size (number of pages)	100
Requestor Location	Teresa K Meister Lichtenbergstr. 4 Garching bei München, Germany 85747 Attn: Teresa K Meister
Billing Type	Invoice
Billing Address	Teresa K Meister Lichtenbergstr. 4

Garching bei München, Germany 85747

Attn: Teresa K Meister

Total 0.00 EUR

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, and any CONTENT (PDF or image file) purchased as part of your order, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS

OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail. WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The Creative Commons Attribution Non-Commercial (CC-BY-NC) License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. (see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The Creative Commons Attribution Non-Commercial-NoDerivs License (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library <http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customer care@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

5.2 Platinum Catalysis Revisited – Unraveling Principles of Catalytic Olefin Hydrosilylation

TERESA K. MEISTER, KORBINIAN RIENER, PETER GIGLER, JÜRGEN STOHRER, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

ACS CATALYSIS 2016, 6, 1274-1284

DOI 10.1021/acscatal.5b02624



RightsLink®

Home

Account Info

Help



Title: Platinum Catalysis Revisited
—Unraveling Principles of
Catalytic Olefin Hydrosilylation

Author: Teresa K. Meister, Korbinian
Riener, Peter Gigler, et al

Publication: ACS Catalysis

Publisher: American Chemical Society

Date: Jan 1, 2016

Copyright © 2016, American Chemical Society

Logged in as:
Teresa Meister
Account #:
3000993792

LOGOUT

Quick Price Estimate

Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

I would like to... ?

reuse in a Thesis/Dissertation

This service provides permission for reuse only. If you do not have a copy of the article you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving Rightslink.

Requestor Type ?

Author (original work)

Portion ?

Full article

Format ?

Print and Electronic

Will you be translating? ?

No

Select your currency

USD - \$

Quick Price

Click Quick Price

QUICK PRICE

CONTINUE

To request permission for a type of use not listed, please contact [the publisher](#) directly.

Copyright © 2016 [Copyright Clearance Center, Inc.](#) All Rights Reserved. [Privacy statement.](#) [Terms and Conditions.](#)
Comments? We would like to hear from you. E-mail us at customer@copyright.com

5.3 Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts

TERESA K. MEISTER, JENS W. KÜCK, KORBINIAN RIENER, ALEXANDER PÖTHIG, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

JOURNAL OF CATALYSIS 2016, 337, 157-166

DOI 10.1016/j.jcat.2016.01.032

This is a License Agreement between Teresa K Meister ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Teresa K Meister
Customer address	Lichtenbergstrasse 4 Garching bei Muenchen, 85747
License number	3842930135481
License date	Apr 06, 2016
Licensed content publisher	Elsevier
Licensed content publication	Journal of Catalysis
Licensed content title	Decoding catalytic activity of platinum carbene hydrosilylation catalysts
Licensed content author	Teresa K. Meister, Jens W. Kück, Korbinian Riener, Alexander Pöthig, Wolfgang A. Herrmann, Fritz E. Kühn
Licensed content date	May 2016
Licensed content volume number	337
Licensed content issue number	n/a
Number of pages	10
Start Page	157

End Page	166
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Homogeneous Industrial Catalysis: Hydrosilylation, Epoxidation, Transvinlylation
Expected completion date	Mar 2016
Estimated size (number of pages)	100
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 EUR
VAT/Local Sales Tax	0.00 EUR / 0.00 GBP
Total	0.00 EUR

Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

- Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
- Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
- Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
- Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
- If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
- Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms

and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for

publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript
 - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
 - directly by providing copies to their students or to research collaborators for their personal use
 - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- - if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (JPA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.

Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.8

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

5.4 Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds

KORBINIAN RIENER, TERESA K. MEISTER, PETER GIGLER, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

JOURNAL OF CATALYSIS **2015**, *331*, 203-209

DOI 10.1016/j.jcat.2015.09.003

This is a License Agreement between Teresa K Meister ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Teresa K Meister
Customer address	Lichtenbergstrasse 4 Garching bei Muenchen, 85747
License number	3796920555468
License date	Jan 27, 2016
Licensed content publisher	Elsevier
Licensed content publication	Journal of Catalysis
Licensed content title	Mechanistic insights into the iridium-catalyzed hydrosilylation of allyl compounds
Licensed content author	Korbinian Riener, Teresa K. Meister, Peter Gigler, Wolfgang A. Herrmann, Fritz E. Kühn
Licensed content date	November 2015
Licensed content volume number	331
Licensed content issue number	n/a
Number of pages	7
Start Page	203
End Page	209

Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Homogeneous Industrial Catalysis: Hydrosilylation, Epoxidation, Transvinylation
Expected completion date	Mar 2016
Estimated size (number of pages)	100
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 EUR
VAT/Local Sales Tax	0.00 EUR / 0.00 GBP
Total	0.00 EUR

Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an

unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author

communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript
 - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
 - directly by providing copies to their students or to research collaborators for their personal use
 - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- - if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (JPA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.

Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.8

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

5.5 Direct Synthesis and Bonding Properties of the First μ^2 - η^2 , η^2 -Allyl Bridged Diiridium Complex

KORBINIAN RIENER, TERESA K. ZIMMERMANN, ALEXANDER PÖTHIG, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2015, 54, 4600-4602

DOI: 10.1021/acs.inorgchem.5b00671



RightsLink®

Home

Account Info

Help



Title: Direct Synthesis and Bonding Properties of the First μ^2 - η^2 , η^2 -Allyl-Bridged Diiridium Complex
Author: Korbinian Riener, Teresa K. Zimmermann, Alexander Pöthig, et al

Logged in as:
Teresa Meister
Account #:
3000993792

LOGOUT

Publication: Inorganic Chemistry
Publisher: American Chemical Society
Date: May 1, 2015
 Copyright © 2015, American Chemical Society

Quick Price Estimate

Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

I would like to... ?	reuse in a Thesis/Dissertation	This service provides permission for reuse only. If you do not have a copy of the article you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving Rightslink.
Requestor Type ?	Author (original work)	
Portion ?	Full article	
Format ?	Print and Electronic	
Will you be translating? ?	No	
Select your currency	EUR - €	
Quick Price	Click Quick Price	

QUICK PRICE

CONTINUE

To request permission for a type of use not listed, please contact [the publisher](#) directly.

Copyright © 2016 Copyright Clearance Center, Inc. All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#).
 Comments? We would like to hear from you. E-mail us at customercare@copyright.com

5.6 Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis

ANDREA SCHMIDT,[#] NIDHI GROVER,[#] TERESA K. ZIMMERMANN,[#] LILIAN GRASER, MIRZA COKOJA, ALEXANDER PÖTHIG, FRITZ E. KÜHN

[#]A. Schmidt, N. Grover and T. K. Zimmermann contributed equally to this work.

JOURNAL OF CATALYSIS 2014, 319, 119-126

DOI 10.1016/j.jcat.2014.08.013

This is a License Agreement between Teresa K Meister ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Teresa K Meister
Customer address	Lichtenbergstrasse 4 Garching bei Muenchen, 85747
License number	3796920316672
License date	Jan 27, 2016
Licensed content publisher	Elsevier
Licensed content publication	Journal of Catalysis
Licensed content title	Synthesis and characterization of novel cyclopentadienyl molybdenum imidazo[1,5-a]pyridine-3-ylidene complexes and their application in olefin epoxidation catalysis
Licensed content author	Andrea Schmidt, Nidhi Grover, Teresa K. Zimmermann, Lilian Graser, Mirza Cokoja, Alexander Pöthig, Fritz E. Kühn
Licensed content date	November 2014
Licensed content volume number	319
Licensed content issue number	n/a

Number of pages	8
Start Page	119
End Page	126
Type of Use	reuse in a thesis/dissertation
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Homogeneous Industrial Catalysis: Hydrosilylation, Epoxidation, Transvinylation
Expected completion date	Mar 2016
Estimated size (number of pages)	100
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 EUR
VAT/Local Sales Tax	0.00 EUR / 0.00 GBP
Total	0.00 EUR

Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

- Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
- Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol / edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
- Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
- Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
- If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
- Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use,

no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on

these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript
 - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
 - directly by providing copies to their students or to research collaborators for their personal use
 - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- - if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.

Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's posting policy for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal

submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.8

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

5.7 Ruthenium-Catalyzed Transvinylolation – New Insights

JENNIFER ZIRIAKUS,[#] **TERESA K. ZIMMERMANN**,[#] ALEXANDER PÖTHIG, MARKUS DREES, STEFAN HASLINGER, DOMINIK JANTKE, AND FRITZ E. KÜHN

[#]J. Ziriakus and T. K. Zimmermann contributed equally to this work.

ADVANCED SYNTHESIS & CATALYSIS **2013**, 355, 2845-2859

DOI 10.1002/adsc.201300447

This Agreement between Teresa K Meister ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	3800390041078
License date	Feb 01, 2016
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Advanced Synthesis & Catalysis
Licensed Content Title	Ruthenium-Catalyzed Transvinylolation – New Insights
Licensed Content Author	Jennifer Ziriakus, Teresa K. Zimmermann, Alexander Pöthig, Markus Drees, Stefan Haslinger, Dominik Jantke, Fritz E. Kühn
Licensed Content Date	Oct 9, 2013
Pages	15
Type of use	Dissertation/Thesis
Requestor type	Author of this Wiley article
Format	Print and electronic
Portion	Full article
Will you be translating?	No
Title of your thesis / dissertation	Homogeneous Industrial Catalysis: Hydrosilylation, Epoxidation, Transvinylolation
Expected completion date	Mar 2016
Expected size (number of pages)	100
Requestor Location	Teresa K Meister Lichtenbergstr. 4 Garching bei München, Germany 85747 Attn: Teresa K Meister
Billing Type	Invoice Teresa K Meister Lichtenbergstr. 4
Billing Address	Garching bei München, Germany 85747 Attn: Teresa K Meister
Total	0.00 EUR

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, and any CONTENT (PDF or image file) purchased as part of your order, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts, You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The Creative Commons Attribution Non-Commercial (CC-BY-NC) License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. (see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The Creative Commons Attribution Non-Commercial-NoDerivs License (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library <http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customer-care@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

5.8 $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCCH}_2\text{CH}_3)_4(\text{THF})_2]$ and $[\text{Ru}_3(\mu_3\text{-OH})(\text{CO})_6(\mu\text{-OOC}^t\text{Bu})_4(\text{OOC}^t\text{Bu})]$: Novel Multinuclear Ruthenium Carbonyl Carboxylates

TERESA K. ZIMMERMANN, JENNIFER ZIRIAKUS, EBERHARDT HERDTWECK, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

ORGANOMETALLICS 2014, 33, 2667-2670

DOI: 10.1021/om500184x



RightsLink®

Home

Account Info

Help



Title: $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCCH}_2\text{CH}_3)_4(\text{THF})_2]$ and $[\text{Ru}_3(\mu_3\text{-OH})(\text{CO})_6(\mu\text{-OOC}^t\text{Bu})_4(\text{OOC}^t\text{Bu})]$: Novel Multinuclear Ruthenium Carbonyl Carboxylates

Logged in as:
Teresa Meister
Account #:
3000993792

LOGOUT

Author: Teresa K. Zimmermann, Jennifer Ziriakus, Eberhardt Herdtweck, et al

Publication: Organometallics

Publisher: American Chemical Society

Date: May 1, 2014

Copyright © 2014, American Chemical Society

Quick Price Estimate

Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

I would like to...

reuse in a Thesis/Dissertation

This service provides permission for reuse only. If you do not have a copy of the article you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving Rightslink.

Requestor Type

Author (original work)

Portion

Full article

Format

Print

Will you be translating?

No

Select your currency

EUR - €

Quick Price

Click Quick Price

QUICK PRICE

CONTINUE

To request permission for a type of use not listed, please contact [the publisher](#) directly.

Copyright © 2016 Copyright Clearance Center, Inc. All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#).
Comments? We would like to hear from you. E-mail us at customer@copyright.com

5.9 Structure and Catalytic Activity of the Ruthenium(I) Sawhorse-Type Complex $[\text{Ru}_2\{\mu, \eta^2\text{-CF}_3(\text{CF}_2)_5\text{COO}\}_2(\text{DMSO})_2(\text{CO})_4]$

TERESA K. ZIMMERMANN, STEFAN HASLINGER, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

ACTA CRYSTALLOGRAPHICA SECTION C **2014**, *C70*, 384-387

DOI 10.1107/S2053229614006354



IUCr Journals
CRYSTALLOGRAPHY JOURNALS ONLINE

[home](#) [submit](#) [subscribe](#) [open access](#)

Author rights after acceptance

Transfer of copyright

Note that for a multi-author article, only one author need sign the Transfer of Copyright Agreement, but that signature is on behalf of all named authors. It is the responsibility of the signing author to obtain the consent of fellow authors to act as their agent in this respect. The rights reserved to authors, listed below, apply equally to *all* the authors of the paper.

Authors retain the following rights to re-use the article, as long as it is not sold or reproduced, in whole or in part, for commercial purposes, *i.e.* for monetary gain on the authors' account or on that of a third party, or for indirect financial gain by a commercial entity. These rights apply **without needing to seek permission** from the IUCr.

Provided that a full bibliographic reference to the article as published in an IUCr journal is made, authors may:

- share print or electronic copies of the article with colleagues;
- use all or part of the article and abstract, without revision or modification, in theses and/or dissertations, in personal compilations or other publications of their own work (and may receive a royalty or other payment for such work);
- use the article within their employer's institution or company for educational or research purposes, including use in course packs;
- post an **authorised electronic reprint** of the article on their own personal website, on their employer's website/repository and on free public servers in their subject area. This includes posting on PubMedCentral and related servers.

The **authorised electronic reprint** stipulated above is automatically **made available to authors** upon publication of their article, or may subsequently be requested from the IUCr. It includes a cover sheet displaying the full bibliographic reference of the published article and conditions of re-use, and is over stamped with an 'electronic reprint' watermark, but is otherwise identical to the final published version of the article as it appears in the journal. Authors are requested to provide a link from their posting to the original article on the IUCr server.

5.10 Synthesis and Electrochemical Properties of *cis*- and *trans*- [Mo₂(O₂C-Fc)₂(DArF)₂] (O₂C-Fc = Ferrocenecarboxylate, DArF = *N,N'*-Diarylformamidinate)

XU-MIN CAI, TERESA K. ZIMMERMANN, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2015, 54, 6631-6640

DOI 10.1021/acs.inorgchem.5b00964



RightsLink®

Home

Account Info

Help



ACS Publications
Most Trusted. Most Cited. Most Read.

Title: Synthesis and Electrochemical Properties of *cis*- and *trans*-[Mo₂(O₂C-Fc)₂(DArF)₂] (O₂C-Fc = Ferrocenecarboxylate; DArF = *N,N'*-Diarylformamidinate)

Logged in as:
Teresa Meister
Account #:
3000993792

LOGOUT

Author: Xu-Min Cai, Teresa K. Zimmermann, Alexander Pöthig, et al

Publication: Inorganic Chemistry

Publisher: American Chemical Society

Date: Jul 1, 2015

Copyright © 2015, American Chemical Society

Quick Price Estimate

Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

I would like to... ?

reuse in a Thesis/Dissertation

This service provides permission for reuse only. If you do not have a copy of the article you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving Rightslink.

Requestor Type ?

Author (original work)

Portion ?

Full article

Format ?

Print and Electronic

Will you be translating? ?

No

Select your currency

EUR - €

Quick Price

Click Quick Price

QUICK PRICE

CONTINUE

To request permission for a type of use not listed, please contact [the publisher](#) directly.

Copyright © 2016 [Copyright Clearance Center, Inc.](#) All Rights Reserved. [Privacy statement.](#) [Terms and Conditions.](#) Comments? We would like to hear from you. E-mail us at customer-care@copyright.com

5.11 Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C}-\text{Fc})_{4-n}]$ (DArF = *N,N'*-Diarylformamidinate; $\text{O}_2\text{C}-\text{Fc}$ = Ferrocenecarboxylate)

XU-MIN CAI, TERESA K. MEISTER, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2015, 55, 858-864

DOI 10.1021/acs.inorgchem.5b02329



RightsLink®



ACS Publications Title:
Most Trusted. Most Cited. Most Read.

Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C}-\text{Fc})_{4-n}]$ (DArF = *N,N'*-Diarylformamidinate; $\text{O}_2\text{C}-\text{Fc}$ = Ferrocenecarboxylate)

Logged in as:
Teresa Meister
Account #:
3000993792

LOGOUT

Author: Xu-Min Cai, Teresa K. Meister, Alexander Pöthig, et al

Publication: Inorganic Chemistry

Publisher: American Chemical Society

Date: Jan 1, 2016

Copyright © 2016, American Chemical Society

Quick Price Estimate

Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

I would like to... ?

reuse in a Thesis/Dissertation

This service provides permission for reuse only. If you do not have a copy of the article you are using, you may copy and paste the content and reuse according to the terms of your agreement. Please be advised that obtaining the content you license is a separate transaction not involving Rightslink.

Requestor Type ?

Author (original work)

Portion ?

Full article

Format ?

Print and Electronic

Will you be translating? ?

No

Select your currency

EUR - €

Quick Price

Click Quick Price

QUICK PRICE

CONTINUE

To request permission for a type of use not listed, please contact [the publisher](#) directly.

Copyright © 2016 [Copyright Clearance Center, Inc.](#) All Rights Reserved. [Privacy statement.](#) [Terms and Conditions.](#) Comments? We would like to hear from you. E-mail us at customercare@copyright.com

5.12 Figures and Schemes

Figure 1 is reprinted with permission from *Nat. Geosci.* **2008**, *1*, 636-639. Copyright 2008 Nature Publishing Group.



RightsLink®

Home

Account Info

Help



Title: How a century of ammonia synthesis changed the world
Author: Jan Willem Erisman, Mark A. Sutton, James Galloway, Zbigniew Klimont, Wilfried Winiwarter

Publication: Nature Geoscience
Publisher: Nature Publishing Group
Date: Sep 28, 2008

Copyright © 2008, Rights Managed by Nature Publishing Group

Logged in as:
Teresa Meister
Account #:
3000993792

LOGOUT

Order Completed

Thank you very much for your order.

This is a License Agreement between Teresa K Meister ("You") and Nature Publishing Group ("Nature Publishing Group"). The license consists of your order details, the terms and conditions provided by Nature Publishing Group, and the [payment terms and conditions](#).

[Get the printable license.](#)

License Number	3801240874921
License date	Feb 03, 2016
Licensed content publisher	Nature Publishing Group
Licensed content publication	Nature Geoscience
Licensed content title	How a century of ammonia synthesis changed the world
Licensed content author	Jan Willem Erisman, Mark A. Sutton, James Galloway, Zbigniew Klimont, Wilfried Winiwarter
Licensed content date	Sep 28, 2008
Type of Use	reuse in a dissertation / thesis
Volume number	1
Issue number	10
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
High-res required	no
Figures	Figure 1
Author of this NPG article	no
Your reference number	None
Title of your thesis / dissertation	Homogeneous Industrial Catalysis: Hydrosilylation, Epoxidation, Transvinilation
Expected completion date	Mar 2016
Estimated size (number of pages)	100
Total	0.00 EUR

ORDER MORE...

CLOSE WINDOW

Copyright © 2016 Copyright Clearance Center, Inc. All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#). Comments? We would like to hear from you. E-mail us at customercare@copyright.com

Scheme 2 and 17 are adapted and Figure 6 and Scheme 3 are reprinted with permission from *ACS Catalysis*, **2016**, *6*, 1274-1284. Copyright 2016 American Chemical Society.

Figure 10 and Scheme 6 are reprinted from *Journal of Catalysis*, *319* (2014), A. Schmidt, N. Grover, T. K. Zimmermann, L. Graser, M. Cokoja, A. Pöthig, F. E. Kühn, Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis, p. 119-126, Copyright (2014), with permission from Elsevier.

Scheme 4 and Scheme 12 are reprinted from *Journal of Catalysis*, *331* (2015), K. Riener, T. K. Meister, P. Gigler, W. A. Herrmann, F. E. Kühn, Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds, p. 203-209, Copyright (2015), with permission from Elsevier.

Figure 15 is adapted with permission from *Inorganic Chemistry* **2015**, *55*, 858-864. Copyright 2015 American Chemical Society.

Figure 16 and Scheme 11 are reprinted from *Journal of Catalysis*, *337* (2016), T. K. Meister, J. W. Kück, K. Riener, A. Pöthig, W. A. Herrmann, F. E. Kühn, Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts, p. 157-166, Copyright (2016), with permission from Elsevier.

Scheme 8 is reprinted with permission from *Advanced Synthesis & Catalysis* **2013**, *355*, 2845-2859. Copyright 2013 John Wiley & Sons, Inc.

Scheme 13 is adapted with permission from *Inorganic Chemistry* **2015**, *54*, 4600-4602. Copyright 2015 American Chemical Society.

Scheme 15 is reprinted with permission from *Organometallics* **2014**, *33*, 2667-2670. Copyright 2014 American Chemical Society.

Figure 19 is adapted with permission from *Inorganic Chemistry* **2015**, *54*, 6631-6640. Copyright 2015 American Chemical Society.

Figure 20 is adapted with permission from *Inorganic Chemistry* **2015**, *55*, 858-864. Copyright 2015 American Chemical Society.

6 BIBLIOGRAPHIC DATA OF
COMPLETE LIST OF
PUBLICATIONS

Molecular Catalysts for Bond Activation – Paving the Way for Alternative Resources

Original Title: Molekulare Katalysatoren zur Bindungsaktivierung – Auf dem Weg zu alternativen Rohstoffquellen

TERESA K. ZIMMERMANN AND FRITZ E. KÜHN

CHEMIE IN UNSERER ZEIT **2015**, 49, 248-259

DOI 10.1002/ciuz.201500716

Reprinted with Permission from *Chemie in Unserer Zeit* **2015**, 49, 248-259. Copyright 2015 John Wiley & Sons, Inc.

Platinum Catalysis Revisited – Unraveling Principles of Catalytic Olefin Hydrosilylation

TERESA K. MEISTER,^{a,b} KORBINIAN RIENER,^{b,c} PETER GIGLER,^d JÜRGEN STOHRER,^d WOLFGANG A. HERRMANN,^c AND FRITZ E. KÜHN^{a,c,*}

ACS CATALYSIS **2016**, *6*, 1274-1284

^a Molecular Catalysis, ^b Institut für Siliciumchemie, ^c Chair of Inorganic Chemistry, Department of Chemistry, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching b. München, Germany

^d Wacker Chemie AG, Consortium für elektrochemische Industrie, Zielstattstraße 20, 81379 München, Germany

DOI 10.1021/acscatal.5b02624

Reprinted with permission from *ACS Catalysis* **2016**, *6*, 1274-1284. Copyright 2016 American Chemical Society.

Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts

TERESA K. MEISTER,^{a,b} JENS W. KÜCK,^b KORBINIAN RIENER,^{b,c} ALEXANDER PÖTHIG,^d WOLFGANG A. HERRMANN,^c AND FRITZ E. KÜHN^{a,c,d*}

JOURNAL OF CATALYSIS **2016**, *337*, 157–166

^aMolecular Catalysis, ^bInstitut für Siliciumchemie, ^cChair of Inorganic Chemistry, Department of Chemistry, ^dCatalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Strasse 1, 85747 Garching b. München. E-mail: fritz.kuehn@ch.tum.de

DOI 10.1016/j.jcat.2016.01.032

Reprinted from *Journal of Catalysis*, *337* (2016), T. K. Meister, J. W. Kück, K. Riener, A. Pöthig, W. A. Herrmann, F. E. Kühn, Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts, p. 157-166, Copyright (2016), with permission from Elsevier.

Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds

KORBINIAN RIENER,^a TERESA K. MEISTER,^a PETER GIGLER,^b WOLFGANG A. HERRMANN,^a AND FRITZ E. KÜHN^{a,*}

JOURNAL OF CATALYSIS **2015**, *331*, 203-209

^a Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center and Department of Chemistry, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching b. München, Germany

^b Wacker Chemie AG, Consortium für elektrochemische Industrie, Zielstattstraße 20, 81379 München, Germany

DOI 10.1016/j.jcat.2015.09.003

Reprinted from *Journal of Catalysis*, *331* (2015), K. Riener, T. K. Meister, P. Gigler, W. A. Herrmann, F. E. Kühn, Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds, p. 203-209, Copyright (2015), with permission from Elsevier.

Direct Synthesis and Bonding Properties of the First μ^2 - η^2 , η^2 -Allyl Bridged Diiridium Complex

KORBINIAN RIENER, TERESA K. ZIMMERMANN, ALEXANDER PÖTHIG, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2015, 54, 4600-4602

Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Department of Chemistry, Technische Universität München, Lichtenbergstraße 4, 85747 Garching bei München, Germany

DOI: 10.1021/acs.inorgchem.5b00671

Reprinted with permission from *Inorganic Chemistry* 2015, 54, 4600-4602. Copyright 2015 American Chemical Society.

Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis

ANDREA SCHMIDT,^{a,*} NIDHI GROVER,^{a,*} TERESA K. ZIMMERMANN,^{a,b,*} LILIAN GRASER,^a MIRZA COKOJA,^a ALEXANDER PÖTHIG,^a FRITZ E. KÜHN^{a,*}

*A. Schmidt, N. Grover and T. K. Zimmermann contributed equally to this work.

JOURNAL OF CATALYSIS **2014**, *319*, 119-126

^a Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center and Department of Chemistry, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

^b WACKER Institut für Siliciumchemie, Department of Chemistry, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

DOI 10.1016/j.jcat.2014.08.013

Reprinted from *Journal of Catalysis*, *319* (2014), A. Schmidt, N. Grover, T. K. Zimmermann, L. Graser, M. Cokoja, A. Pöthig, F. E. Kühn, Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis, p. 119-126, Copyright (2014), with permission from Elsevier.

Ruthenium-Catalyzed Transvinylation – New Insights

JENNIFER ZIRIAKUS,^{a,b,#} TERESA K. ZIMMERMANN,^{a,#} ALEXANDER PÖTHIG,^a MARKUS DREES,^a STEFAN HASLINGER,^a DOMINIK JANTKE,^a AND FRITZ E. KÜHN^{a,*}

[#]J. Ziriakus and T. K. Zimmermann contributed equally to this work.

ADVANCED SYNTHESIS & CATALYSIS **2013**, 355, 2845-2859

^a Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

^b WACKER Institut für Siliciumchemie, Department of Chemistry, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

DOI 10.1002/adsc.201300447

Reprinted with Permission from *Advanced Synthesis & Catalysis* **2013**, 355, 2845-2859. Copyright 2013 John Wiley and Sons, Inc.

[Ru₄(CO)₈(μ-OOCCH₂CH₃)₄(THF)₂] and [Ru₃(μ₃-OH)(CO)₆(μ-OOC^tBu)₄(OOC^tBu)]: Novel Multinuclear Ruthenium Carbonyl Carboxylates

TERESA K. ZIMMERMANN,^{a,b} JENNIFER ZIRIAKUS,^{a,b,c} EBERHARDT HERDTWECK,^a ALEXANDER PÖTHIG,^a AND FRITZ E. KÜHN^{a,*}

ORGANOMETALLICS **2014**, *33*, 2667-2670

^a Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

^b WACKER Institut für Siliciumchemie, Department of Chemistry, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

^c TUM Asia/German Institute of Science and Technology, 10 Central Exchange Green, Singapore 138649

DOI: 10.1021/om500184x

Reprinted with permission from *Organometallics* **2014**, *33*, 2667-2670. Copyright 2014 American Chemical Society.

Structure and Catalytic Activity of the Ruthenium(I) Sawhorse-Type Complex $[\text{Ru}_2\{\mu, \eta^2\text{-CF}_3(\text{CF}_2)_5\text{COO}\}_2(\text{DMSO})_2(\text{CO})_4]$

TERESA K. ZIMMERMANN,^a STEFAN HASLINGER,^b ALEXANDER PÖTHIG,^{b,*} AND FRITZ E. KÜHN^{b,*}

ACTA CRYSTALLOGRAPHICA SECTION C **2014**, *C70*, 384-387

^a WACKER Institut für Siliciumchemie and Catalysis Research Center, Department of Chemistry/Molecular Catalysis, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

^b Catalysis Research Center, Department of Chemistry/Molecular Catalysis, Technische Universität München, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

DOI 10.1107/S2053229614006354

Reprinted with permission from *Acta Crystallographica Section C* **2014**, *C70*, 384-387. Copyright 2014 International Union of Crystallography.

Synthesis and Electrochemical Properties of *cis*- and *trans*-[Mo₂(O₂C–Fc)₂(DArF)₂] (O₂C–Fc = Ferrocenecarboxylate, DArF = *N,N'*-Diarylformamidinate)

XU-MIN CAI,^a TERESA K. ZIMMERMANN,^a ALEXANDER PÖTHIG,^b AND FRITZ E. KÜHN^{a,*}

INORGANIC CHEMISTRY **2015**, *54*, 6631-6640

^a Molecular Catalysis, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85747 Garching b. München, Germany

^b Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

DOI 10.1021/acs.inorgchem.5b00964

Reprinted with permission from *Inorganic Chemistry* **2015**, *54*, 6631-6640. Copyright 2015 American Chemical Society.

Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C}-\text{Fc})_{4-n}]$ (DArF = *N,N'*-Diarylformamidinate; $\text{O}_2\text{C}-\text{Fc}$ = Ferrocenecarboxylate)

XU-MIN CAI,^a TERESA K. MEISTER,^a ALEXANDER PÖTHIG,^b AND FRITZ E. KÜHN^{a,*}

INORGANIC CHEMISTRY **2015**, *55*, 858-864

^a Molecular Catalysis, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85747 Garching b. München, Germany

^b Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, 85747 Garching b. München, Germany

DOI 10.1021/acs.inorgchem.5b02329

Reprinted with permission from *Inorganic Chemistry* **2015**, *55*, 858-864. Copyright 2015 American Chemical Society.

7 REFERENCES

- (1) van der Eijk, J., The Next Feedstock Transition. In *Catalytic Process Development for Renewable Materials*, Imhof, P.; van der Waal, J. C., Eds. Wiley-VCH: Weinheim, 2013.
- (2) Sa, J.; Szlachetko, J.; Sikora, M.; Kavcic, M.; Safonova, O. V.; Nachtegaal, M., *Nanoscale* **2013**, *5*, 8462-8465.
- (3) Weitkamp, J.; Gläser, R., Methodische Grundlagen. In *Chemische Technik: Prozesse und Produkte*, Dittmeyer, R.; Keim, W.; Kreysa, G.; Oberholz, A., Eds. Wiley-VCH: Weinheim, 2004.
- (4) Tyrell, J. A., *Fundamentals of Industrial Chemistry: Pharmaceuticals, Polymers, and Business*. 2014.
- (5) Rovner, S. L., *Chem. Eng. News* **2013**, *91*, 9-13.
- (6) Lloyd, L., *Handbook of Industrial Catalysis*. Springer: New York, 2011.
- (7) Kühn, F. E.; Herrmann, W. A., *Coord. Chem. Rev.* **2011**, *255*, 1439.
- (8) Behr, A.; Neubert, P., *Applied Homogeneous Catalysis*. Wiley-VCH: Weinheim, 2012.
- (9) *World Catalysts - Demand and Sales Forecast, Market Share, Market Size, Market Leaders. Industry Study 3217*; The Freedonia Group, Inc.: Cleveland, Ohio, 2014.
- (10) Röper, M., *Chem. Unserer Zeit* **2006**, *40*, 126-136.
- (11) van Santen, R., Future Perspectives in Catalysis, Dutch National Research School Combination - Catalysis Controlled by Chemical Design (NRSC-Catalysis) Eindhoven, 2009.
- (12) Schüth, F., *Chem. Unserer Zeit* **2006**, *40*, 92-103.
- (13) Heveling, J., *J. Chem. Educ.* **2012**, *89*, 1530-1536.
- (14) Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winiwarter, W., *Nat. Geosci.* **2008**, *1*, 636-639.
- (15) Hagen, J., *Industrial Catalysis: A Practical Approach*. 2nd ed.; Wiley-VCH: Weinheim, 2006.
- (16) Cornils, B.; Herrmann, W. A., *J. Catal.* **2003**, *216*, 23-31.
- (17) Cornils, B.; Herrmann, W. A.; Rasch, M., *Angew. Chem.* **1994**, *106*, 2219-2238.
- (18) *Organometallics as Catalysts in the Fine Chemical Industry*. Springer: Berlin, 2012.
- (19) Sheldon, R. A., *J. Chem. Technol. Biotechnol.* **1997**, *68*, 381-388.
- (20) Sanderson, K., *Nature* **2011**, *469*, 18-20.
- (21) Anastas, P. T.; Kirchhoff, M. M., *Acc. Chem. Res.* **2002**, *35*, 686-694.
- (22) Poliakoff, M.; Fitzpatrick, J. M.; Farren, T. R.; Anastas, P. T., *Science* **2002**, *297*, 807-810.
- (23) Horváth, I. T.; Anastas, P. T., *Chem. Rev.* **2007**, *107*, 2169-2173.
- (24) Poliakoff, M.; Anastas, P., *Nature* **2001**, *413*, 257-257.
- (25) Anastas, P. T.; Warner, J. C., *Green Chemistry: Theory and Practice*. Oxford University Press: 1998.
- (26) Que, L. J.; Tolman, W. B., *Nature* **2008**, *455*, 333-340.
- (27) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielsen, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W., *Chem. Rev.* **2001**, *101*, 953-996.
- (28) Besson, M.; Gallezot, P.; Pinel, C., *Chem. Rev.* **2014**, *114*, 1827-1870.
- (29) Zakzeski, J.; Bruijninx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M., *Chem. Rev.* **2010**, *110*, 3552-3599.
- (30) Aresta, M.; Dibenedetto, A.; Quaranta, E., Reaction Mechanisms in the Direct Carboxylation of Alcohols, Polyols, Cyclic Ethers, and Cyclic Amines to Afford Monomeric Compounds and Polymeric Materials. In *Reaction Mechanisms in Carbon Dioxide Conversion*, Springer Berlin Heidelberg: 2016.
- (31) van Leeuwen, P. W. N. M., *Homogeneous Catalysis. Understanding the Art*. Kluwer Academic Publishers: Dordrecht, 2004.
- (32) Whyman, R., *Applied Organometallic Chemistry and Catalysis*. Oxford University Press: Oxford, 2001.
- (33) Zhang, S.; Nguyen, L.; Zhu, Y.; Zhan, S.; Tsung, C.-K.; Tao, F., *Acc. Chem. Res.* **2013**, *46*, 1731-1739.
- (34) Oosterbeek, H., *Phys. Chem. Chem. Phys.* **2007**, *9*, 3570-3576.
- (35) van Leeuwen, P. W. N. M.; Chadwick, J. C., *Homogeneous Catalysts. Activity-Stability-Deactivation*. Wiley-VCH: Weinheim, 2011.
- (36) Thomas, A.; Driess, M., *Angew. Chem. Int. Ed.* **2009**, *48*, 1890-1892.
- (37) Cornils, B.; Herrmann, W. A., Introduction. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley-VCH: 2008.
- (38) The Nobel Prize in Chemistry 2001.
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2001/ (accessed December 21st 2015).

- (39) The Nobel Prize in Chemistry in 2005.
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/ (accessed December 21st 2015).
- (40) The Nobel Prize in Chemistry 2010.
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2010/ (accessed December 21st 2015).
- (41) Pollak, P., Market Size and Structure. In *Fine Chemicals*, John Wiley & Sons, Inc.: 2007.
- (42) *The European Chemical Industry - Facts & Figures 2015*; Cefic, the European Chemical Industry Council: 2014.
- (43) Revenue of the worldwide pharmaceutical market from 2001 to 2014 (in billion U.S. dollars).
<http://www.statista.com/statistics/263102/pharmaceutical-market-worldwide-revenue-since-2001/> (accessed December 21st 2015).
- (44) *The Pharmaceutical Industry in Figures - Key Data 2014*; efpia - European Federation of Pharmaceutical Industries and Associations: Brussels, 2014.
- (45) *The Role of the Chemical Sciences in Finding Alternatives to Critical Resources: A Workshop Summary*; National Research Council (US) Chemical Sciences Roundtable: Washington (DC), 2012.
- (46) Marciniak, B., *Comprehensive Handbook on Hydrosilylation*. Pergamon Press: 1992.
- (47) Marciniak, B., *Hydrosilylation: A Comprehensive Review on Recent Advances*. Springer Netherlands: 2009.
- (48) Marciniak, B., *Silicon Chem.* **2003**, *1*, 155-175.
- (49) Marciniak, B., *Coord. Chem. Rev.* **2005**, *249*, 2374-2390.
- (50) Marciniak, B., *Coord. Chem. Rev.* **2005**, *249*, 2374-2390.
- (51) Reichl, J. A.; Berry, D. H., *Adv. Organomet. Chem.* **1999**, *43*, 197-265.
- (52) Ojima, I., The Hydrosilylation Reaction. In *Organic Silicon Compounds (1989)*, Patai, S.; Rappoport, Z., Eds. John Wiley & Sons, Ltd: 2004.
- (53) Ojima, I.; Li, Z.; Zhu, J., Recent Advances in the Hydrosilylation and Related Reactions. In *The Chemistry of Organic Silicon Compounds*, Rappoport, Z.; Apeloig, Y., Eds. John Wiley & Sons, Ltd: 2003.
- (54) Marciniak, B., Hydrosilylation and Related Reactions of Silicon Compounds. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Herrmann, W. A.; Cornils, B., Eds. Wiley-VCH Verlag GmbH: 2008.
- (55) Brook, M. A., *Silicon in Organic, Organometallic and Polymer Chemistry*. John Wiley & Sons: Chichester, 2000.
- (56) Troegel, D.; Stohrer, J., *Coord. Chem. Rev.* **2011**, *255*, 1440-1459.
- (57) Roy, A. K., *Adv. Organomet. Chem.* **2007**, *55*, 1-59.
- (58) Noels, A. F.; Hubert, A. J., *Industrial Applications of Homogeneous Catalysis*. D. Reidel Publishing Company: Amsterdam, 1985.
- (59) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J., *Science* **2012**, *335*, 567-570.
- (60) Roseblade, S. J.; Ros, A.; Monge, D.; Alcarazo, M.; Álvarez, E.; Lassaletta, J. M.; Fernández, R., *Organometallics* **2007**, *26*, 2570-2578.
- (61) Price Charts. <http://www.platinum.matthey.com/prices/price-charts> (accessed January 11th 2016).
- (62) World Platinum Investment Council Ltd: London, 2015.
- (63) *Platinum Quarterly*; SFA (Oxford) Ltd. for World Platinum Investment Council Ltd.: London, 2015.
- (64) Berton-Gelloz, G.; Buisine, O.; Brière, J.-F.; Michaud, G.; Stérin, S.; Mignani, G.; Tinant, B.; Declercq, J.-P.; Chapon, D., *J. Organomet. Chem.* **2005**, *690*, 6156-6168.
- (65) Nakajima, Y.; Shimada, S., *RSC Adv.* **2015**, *5*, 20603-20616.
- (66) Mérel, D. S.; Do, M. L. T.; Gaillard, S.; Dupau, P.; Renaud, J.-L., *Coord. Chem. Rev.* **2015**, *288*, 50-68.
- (67) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P., *ChemCatChem* **2015**, *7*, 190-222.
- (68) Karstedt, B. D., US3775452, 1973, to General Electric Co.
- (69) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F., *Organometallics* **1987**, *6*, 191-192.
- (70) Speier, J. L.; Webster, J. A.; Barnes, G. H., *J. Am. Chem. Soc.* **1957**, *79*, 974-979.
- (71) Speier, J. L.; Hook, D. E., US2823218, 1958, to Dow Corning Corp.
- (72) Markó, I. E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P., *Science* **2002**, *298*, 204-206.
- (73) Hitchcock, P. B.; Lappert, M. F.; Warhurst, N. J. W., *Angew. Chem.* **1991**, *103*, 439-441.
- (74) De Bo, G.; Berthon-Gelloz, G.; Tinant, B.; Markó, I. E., *Organometallics* **2006**, *25*, 1881-1890.

- (75) Berthon-Gelloz, G.; Schumers, J.-M.; De Bo, G.; Markó, I. E., *J. Catal.* **2008**, *73*, 4190-4197.
- (76) Markó, I. E.; Stérin, S.; Buisine, O.; Berthon, G.; Michaud, G.; Tinant, B.; Declercq, J.-P., *Adv. Synth. Catal.* **2004**, *346*, 1429-1434.
- (77) Benkeser, R. A.; Kang, J., *J. Organomet. Chem.* **1980**, *185*, C9-C12.
- (78) Lewis, L. N.; Stein, J.; Gao, Y.; Colborn, R. E.; Hutchings, G., *Platinum Metals Review* **1997**, *41*, 66-75.
- (79) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. a., *J. Am. Chem. Soc.* **1999**, *121*, 3693-3703.
- (80) Chalk, A. J.; Harrod, J. F., *J. Am. Chem. Soc.* **1965**, *87*, 16-21.
- (81) Roy, A. K.; Taylor, R. B., *J. Am. Chem. Soc.* **2002**, *124*, 9510-9524.
- (82) Caseri, W.; Pregosin, P. S., *J. Organomet. Chem.* **1988**, *356*, 259-269.
- (83) Caseri, W.; Pregosin, P. S., *Organometallics* **1988**, *7*, 1373-1380.
- (84) Coqueret, X., *Organometallics* **1991**, *10*, 3139-3145.
- (85) Brand, D., *J. Prakt. Chem.* **1994**, *336*, 218-224.
- (86) Schroeder, M. A.; Wrighton, M. S., *J. Organomet. Chem.* **1977**, *128*, 345-358.
- (87) Mitchener, J. C.; Wrighton, M. S., *J. Am. Chem. Soc.* **1981**, *103*, 975-977.
- (88) Eichinger, B.; Stein, J., *Polym. Prepr.* **2001**, *42*, 251.
- (89) Sakaki, S.; Mizoe, N.; Sugimoto, M.; Musashi, Y., *Coord. Chem. Rev.* **1999**, *190-192*, 933-960.
- (90) Sakaki, S.; Mizoe, N.; Musashi, Y.; Sugimoto, M., *J. Mol. Struct. Theochem.* **1999**, *461-462*, 533-546.
- (91) Hambley, T. W.; Maschmeyer, T.; Masters, A. F., *Appl. Organomet. Chem.* **1992**, *6*, 253-260.
- (92) Belyakova, Z. V.; Chernyshev, E. A.; Storozhenko, P. A.; Knyazev, S. P.; Turkel'taub, G. N.; Parshina, E. V.; Kisin, A. V., *Russ. J. Gen. Chem.* **2006**, *76*, 925-930.
- (93) Hu, J. J.; Li, F.; Hor, A., *Organometallics* **2009**, *28*, 1212-1220.
- (94) Silbestri, G. F.; Flores, J. C.; de Jesús, E., *Organometallics* **2012**, *31*, 3355-3360.
- (95) Taige, M. A.; Ahrens, S.; Strassner, T., *J. Organomet. Chem.* **2011**, *696*, 2918-2927.
- (96) Sprengers, J. W.; Mars, M. J.; Duin, M. A.; Cavell, K. J.; Elsevier, C. J., *J. Organomet. Chem.* **2003**, *679*, 149-152.
- (97) Poyatos, M.; Maise-François, A.; Bellemin-Laponnaz, S.; Gade, L. H., *Organometallics* **2006**, *25*, 2634-2641.
- (98) Bernhammer, J. C.; Huynh, H. V., *Organometallics* **2014**, *33*, 1266-1275.
- (99) De Bo, G.; Berthon-Gelloz, G.; Tinant, B.; Markó, I. E., *Organometallics* **2006**, *25*, 1881-1890.
- (100) Berthon-Gelloz, G.; Buisine, O.; Brière, J.-F.; Michaud, G.; Stérin, S.; Mignani, G.; Tinant, B.; Declercq, J.-P.; Chapon, D.; Markó, I. E., *J. Organomet. Chem.* **2005**, *690*, 6156-6168.
- (101) Steffanut, P.; Osborn, J. A.; DeCian, A.; Fisher, J., *Chem. Eur. J.* **1998**, *4*, 2008-2017.
- (102) Hu, J. J.; Li, F.; Hor, A., *Organometallics* **2009**, *28*, 1212-1220.
- (103) Buisine, O.; Berthon-Gelloz, G.; Briere, J.-F.; Sterin, S.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P.; Markó, I. E., *Chem. Commun.* **2005**, 3856-3858.
- (104) Hopf, A.; Dötz, K. H., *J. Mol. Catal. A: Chem.* **2000**, *164*, 191-194.
- (105) Huber, C.; Kokil, A.; Caseri, W. R.; Weder, C., *Organometallics* **2002**, *21*, 3817-3818.
- (106) Marciniak, B., *Hydrosilylation: A Comprehensive Review on Recent Advances*. Springer: Berlin, 2009.
- (107) Herrmann, W. A., *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309.
- (108) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L., *Coord. Chem. Rev.* **2009**, *253*, 687-703.
- (109) Jain, K. R.; Herrmann, W. A.; Kühn, F. E., *Curr. Org. Chem.* **2008**, *12*, 1468-1478.
- (110) Burstein, C.; Lehmann, C. W.; Glorius, F., *Tetrahedron* **2005**, *61*, 6207-6217.
- (111) Hutt, J. T.; Aron, Z. D., *Org. Lett.* **2011**, *13*, 5256-5259.
- (112) Würtz, S.; Glorius, F., *Acc. Chem. Res.* **2008**, *41*, 1523-1533.
- (113) Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernández, R.; Brown, J. M.; Lassaletta, J. M., *J. Am. Chem. Soc.* **2005**, *127*, 3290-3291.
- (114) Fürstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W., *J. Am. Chem. Soc.* **2007**, *129*, 12676-12677.
- (115) Gigler, P.; Drees, M.; Riener, K.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E., *J. Catal.* **2012**, *295*, 1-14.
- (116) Marciniak, B.; Maciejewski, H.; Duczmal, W.; Fiedorow, R.; Kityński, D., *Appl. Organomet. Chem.* **2003**, *17*, 127-134.
- (117) Jankowiak, M.; Maciejewski, H.; Gulinski, J., *J. Organomet. Chem.* **2005**, *690*, 4478-4487.
- (118) Belyakova, Z. V.; Chernyshev, E. A.; Storozhenko, P. A.; Knyazev, S. P.; Turkel'taub, G. N.; Parshina, E. V.; Kisin, A. V., *Russ. J. Gen. Chem.* **2006**, *76*, 925-930.

- (119) Wawrzyńczak, A.; Dutkiewicz, M.; Guliński, J.; Maciejewski, H.; Marciniak, B.; Fiedorow, R., *Catal. Today* **2011**, *169*, 69-74.
- (120) Igarashi, M.; Matsumoto, T.; Kobayashi, T.; Sato, K.; Ando, W.; Shimada, S.; Hara, M.; Uchida, H., *J. Organomet. Chem.* **2014**, *749*, 421-427.
- (121) Igarashi, M.; Kobayashi, T.; Sato, K.; Ando, W.; Matsumoto, T.; Shimada, S.; Hara, M.; Uchida, H., *J. Organomet. Chem.* **2013**, *725*, 54-59.
- (122) Bauer, A.; Schäfer, O.; Kriegbaum, M.; Brader, L.; Pachaly, B.; Frey, V., US6388119, 2002, to Consortium für elektrochemische Industrie GmbH.
- (123) Tonomura, Y.; Kubota, T.; Endo, M., US6359161, 2002, to Shin-Etsu Chemical Co., Ltd.
- (124) Bauer, A.; Brader, L.; Frey, V.; Kriegbaum, M.; Pachaly, B.; Schäfer, O., EP1201671B1, 2003, to Consortium für elektrochemische Industrie GmbH.
- (125) Baumann, F.; Hoffmann, M., DE102004052424A1, 2006, to Wacker Chemie AG.
- (126) Tonomura, Y.; Kubota, T.; Endo, M., EP1156052B1, 2006, to Shin-Etsu Chemical Co., Ltd.
- (127) Baumann, F., DE102005030581A1, 2007, to Wacker Chemie AG.
- (128) Kornek, T.; Bauer, A.; Senden, D., US7208618, 2007, to Wacker Chemie AG.
- (129) Ramdani, K.; Vogin, B.; Guennount, N., US7659418, 2010, to Rhodia Operations.
- (130) Ramdani, K.; Vogin, B.; Guennouni, N., US7655813, 2010, to Rhodia Chimie.
- (131) Ramdani, K.; Vogin, B.; Guennouni, N., EP1515977B1, 2007, to Rhodia Chimie SA.
- (132) Ramdani, K.; Guennouni, N.; Vogin, B., EP1637534B1, 2009, to Rhodia Chimie.
- (133) Guennouni, N.; Galland, J.-C., US7884225, 2011, to Rhodia Chimie.
- (134) Igarashi, M.; Matsumoto, T.; Kobayashi, T.; Sato, K.; Ando, W.; Shimada, S.; Hara, M.; Uchida, H., *J. Organomet. Chem.* **2014**, *752*, 141-146.
- (135) Hauser, S. A.; Cokoja, M.; Kühn, F. E., *Cat. Sci. Tech.* **2013**, *3*, 552-561.
- (136) Müller, C.; Grover, N.; Cokoja, M.; Kühn, F. E., Chapter Two - Homogeneous Catalytic Olefin Epoxidation with Molybdenum Complexes. In *Adv. Inorg. Chem.*, Rudi van, E.; Colin, D. H., Eds. Academic Press: 2013; Vol. Volume 65, pp 33-83.
- (137) Huber, S.; Cokoja, M.; Kühn, F. E., *J. Organomet. Chem.* **2014**, *751*, 25-32.
- (138) Jorgensen, K. A., *Chem. Rev.* **1989**, *89*, 431-458.
- (139) Grover, N.; Kühn, F. E., *Curr. Org. Chem.* **2012**, *16*, 16-32.
- (140) Xia, Q. H.; Ge, H. Q.; Ye, C. P.; Liu, Z. M.; Su, K. X., *Chem. Rev.* **2005**, *105*, 1603-1662.
- (141) Oyama, S. T., *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*. Elsevier: Amsterdam, 2008.
- (142) Farias, M.; Martinelli, M.; Bottega, D. P., *Applied Catalysis A: General* **2010**, *384*, 213-219.
- (143) Clerici, M. G.; Ricci, M.; Strukul, G., Formation of C-O Bonds by Oxidation. In *Metal-Catalysis in Industrial Organic Processes*, Chiusoli, G. P.; Maitlis, P. M., Eds. The Royal Society of Chemistry: Cambridge, 2006.
- (144) Russo, V.; Tesser, R.; Santacesaria, E.; Di Serio, M., *Ind. Eng. Chem. Res.* **2013**, *52*, 1168-1178.
- (145) World Propylene Oxide Supply to Exceed 9.2 Million Tons in 2017, According to New Report by Merchant Research & Consulting. <http://www.prweb.com/releases/2014/02/prweb11552989.htm> (accessed January 07th 2016).
- (146) Oxidation. In *Fine chemicals through heterogeneous catalysis*, Sheldon, R. A.; van Bekkum, H., Eds. Wiley-VCH: Weinheim; New York, 2001.
- (147) Kühn, F. E.; Santos, A. M.; Herrmann, W. A., *Dalton Trans.* **2005**, 2483-2491.
- (148) Kühn, F. E.; Santos, A. M.; Abrantes, M., *Chem. Rev.* **2006**, *106*, 2455-2475.
- (149) Freund, C.; Abrantes, M.; Kühn, F. E., *J. Organomet. Chem.* **2006**, *691*, 3718-3729.
- (150) O'Connor, J. M.; Casey, C. P., *Chem. Rev.* **1987**, *87*, 307-318.
- (151) Nguyen Trong, A.; Elian, M.; Hoffmann, R., *J. Am. Chem. Soc.* **1978**, *100*, 110-116.
- (152) Veiros, L. F., *J. Organomet. Chem.* **1999**, *587*, 221-232.
- (153) Veiros, L. F., *Organometallics* **2000**, *19*, 5549-5558.
- (154) Romão, C. C.; Veiros, L. F., *Organometallics* **2007**, *26*, 1777-1781.
- (155) Simanko, W.; Sapunov, V. N.; Schmid, R.; Kirchner, K.; Wherland, S., *Organometallics* **1998**, *17*, 2391-2393.
- (156) Romão, C. C., *Appl. Organomet. Chem.* **2000**, *14*, 539-548.
- (157) Trost, M. K.; Bergmann, R. G., *Organometallics* **1991**, *10*, 1172-1178.

- (158) Valente, A. A.; Seixas, J. D.; Goncalves, I. S.; Abrantes, M.; Pillinger, M.; Romao, C. C., *Catal. Lett.* **2005**, *101*, 127–130.
- (159) Abrantes, M.; Santos, A. M.; Mink, J.; Kühn, F. E.; Romão, C. C., *Organometallics* **2003**, *22*, 2112–2118.
- (160) Zhao, J.; Santos, A. M.; Herdtweck, E.; Kühn, F. E., *J. Mol. Catal. A: Chem.* **2004**, *222*, 265–271.
- (161) Crabtree, R. H., *J. Organomet. Chem.* **2014**, *751*, 174–180.
- (162) Al-Ajlouni, A. M.; Veljanovski, D.; Capapé, A.; Zhao, J.; Herdtweck, E.; Calhorda, M. J.; Kühn, F. E., *Organometallics* **2009**, *28*, 639–645.
- (163) Zhao, J.; Sakthivel, A.; Santos, A. M.; Kühn, F. E., *Inorg. Chim. Acta* **2005**, *358*, 4201–4207.
- (164) Freund, C.; Abrantes, M.; Kühn, F. E., *J. Organomet. Chem.* **2006**, *691*, 3718–3729.
- (165) Abrantes, M.; Sakthivel, A.; Romão, C. C.; Kühn, F. E., *J. Organomet. Chem.* **2006**, *691*, 3137–3145.
- (166) Zhao, J.; Jain, K. R.; Herdtweck, E.; Kühn, F. E., *Dalton Trans.* **2007**, 5567–5571.
- (167) Raith, A.; Altmann, P.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E., *Coord. Chem. Rev.* **2010**, *254*, 608–634.
- (168) Abrantes, M.; Paz, F. A. A.; Valente, A. A.; Pereira, C. C. L.; Gago, S.; Rodrigues, A. E.; Klinowski, J.; Pillinger, M.; Gonçalves, I. S., *J. Organomet. Chem.* **2009**, *694*, 1826–1833.
- (169) Hauser, S. A.; Cokoja, M.; Drees, M.; Kühn, F. E., *J. Mol. Catal. A: Chem.* **2012**, *363–364*, 237–244.
- (170) Capapé, A.; Raith, A.; Kühn, F. E., *Adv. Synth. Catal.* **2009**, *351*, 66–70.
- (171) Capapé, A.; Raith, A.; Herdtweck, E.; Cokoja, M.; Kühn, F. E., *Adv. Synth. Catal.* **2010**, *352*, 547–556.
- (172) Betz, D.; Raith, A.; Cokoja, M.; Kühn, F. E., *ChemSusChem* **2010**, *3*, 559–562.
- (173) Kandepi, V. V. K. M.; da Costa, A. P.; Peris, E.; Royo, B., *Organometallics* **2009**, *28*, 4544–4549.
- (174) Li, S.; Kee, C. W.; Huang, K.-W.; Hor, T. S. A.; Zhao, J., *Organometallics* **2010**, *29*, 1924–1933.
- (175) Schaper, L.-A.; Graser, L.; Wei, X.; Zhong, R.; Öfele, K.; Pöthig, A.; Cokoja, M.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E., *Inorg. Chem.* **2013**, *52*, 6142–6152.
- (176) Murray, R. E.; Lincoln, D. M., *Catal. Today* **1992**, *13*, 93–102.
- (177) Neff, R. E.; Ryles, R. G., EP 0311799 A1, 1988, to American Cyanamid Company.
- (178) Nunez, I. M.; Linhardt, J. G.; McGee, J. A.; Hunt, J.; Alton, M.; Shipp, D. A.; Kunzler, J. F.; Ammon, D. M., WO 2010/147864 A2, 2010, to Bausch & Lomb Incorporated.
- (179) Ahlgren, J.; Bruun, N.; Buutinen, V., WO 2010/058087 A1, 2010, to Kemira Oyj.
- (180) Ko, C.-B.; Kim, Y.-M.; Song, K.-J.; Lee, K.-H., US 2010/0048077 A1, 2010, to Lg Chem, Ltd.
- (181) Kerr, W. J.; McLaughlin, M.; Pauson, P. L.; Robertson, S. M., *J. Organomet. Chem.* **2001**, *630*, 104–117.
- (182) Yang, H.; Henke, E.; Bornscheuer, U. T., *J. Org. Chem.* **1999**, *64*, 1709–1712.
- (183) Snuparek, J. J.; Mleziva, J., *Angew. Makromol. Chem.* **1970**, *12*, 145–156.
- (184) La Scala, J. J.; Orlicki, J. A.; Winston, C.; Robinette, E. J.; Sands, J. M.; Palmese, G. R., *Polymer* **2005**, *46*, 2908–2921.
- (185) Cywinski, N. F., US 3372198, 1968, to Phillips Petroleum Co.
- (186) Drent, E., EP 0512656A2, 1992, to Shell Internationale Research Maatschappij B.V.
- (187) Hudrlik, P. F.; Hudrlik, A. M., *J. Org. Chem.* **1973**, *38*, 4254–4258.
- (188) Rotem, M.; Shvo, Y., *Organometallics* **1983**, *2*, 1689–1691.
- (189) Bruneau, C.; Dixneuf, P. H., *J. Chem. Soc., Chem. Commun.* **1997**, 507–512.
- (190) Kita, Y.; Maeda, H.; Omori, K.; Okuno, T.; Tamura, Y., *J. Chem. Soc. Perkin Trans. 1* **1993**, 2999–3005.
- (191) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H., *J. Org. Chem.* **1995**, *60*, 7247–7255.
- (192) Rotem, M.; Shvo, Y., *J. Organomet. Chem.* **1993**, *448*, 189–204.
- (193) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Bruneau, C.; Dixneuf, P. H., *Organometallics* **1990**, *9*, 1155–1160.
- (194) Wakabayashi, T.; Ishii, Y.; Murata, T.; Mizobe, Y.; Hidai, M., *Tetrahedron Lett.* **1995**, *36*, 5585–5588.
- (195) Nakagawa, H.; Okimoto, Y.; Sakaguchi, S.; Ishii, Y., *Tetrahedron Lett.* **2003**, *44*, 103–106.
- (196) Kitching, W.; Rapport, Z.; Winstein, S.; Young, W. G., *J. Am. Chem. Soc.* **1966**, *88*, 2054–2055.
- (197) Nicolau, I.; Colling, P. M.; Johnson, L. R., WO 94/08714, 1994.
- (198) Lu, X.; Zhu, G.; Ma, S., *Tetrahedron Lett.* **1992**, *33*, 7205–7206.
- (199) Adelman, R., *J. Org. Chem.* **1949**, *14*, 1057–1077.
- (200) Mc Keon, J. E.; Pfitton, P.; Griswold, A. A., *Tetrahedron* **1972**, *28*, 227–232.

- (201) Mc Keon, J. E.; Fitton, P., *Tetrahedron* **1971**, *28*, 233-238.
- (202) Sabel, A.; Smidt, J.; Jira, R.; Prigge, H., *Chem. Ber.* **1969**, *102*, 2939-2950.
- (203) Smidt, J.; Hafner, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sabel, A., *Angew. Chem.* **1962**, *74*, 93-128.
- (204) Murray, R. E., US 5155253 A, 1991, to Union Carbide Chemicals & Plastics Technology Corporation.
- (205) Murray, R. E., EP 0506070 A2, 1992, to Union Carbide Chemicals & Plastics Technology Corporation.
- (206) Murray, R. E., EP 0351603A2, 1989, to Union Carbide Corporation.
- (207) Zimmermann, T. K. Untersuchungen zur Immobilisierung von Umvinlyierungskatalysatoren. Master's Thesis, Technische Universität München, Munich, 2013.
- (208) Imperial Chemical Industries, L., GB581501(A), 1946, to.
- (209) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G.; Gamlen, G., *J. Chem. Soc. A* **1969**, 2761-2766.
- (210) Salvini, A.; Frediani, P.; Piacenti, F., *J. Mol. Catal. A: Chem.* **2000**, *159*, 185-195.
- (211) Salvini, A.; Frediani, P.; Rivalta, E., *Inorg. Chim. Acta* **2003**, *351*, 225-234.
- (212) Salvini, A.; Frediani, P.; Giannelli, C.; Rosi, L., *J. Organomet. Chem.* **2005**, *690*, 371-382.
- (213) Sevryugina, Y.; Weaver, B.; Hansen, J.; Thompson, J.; Davies, H. M. L.; Petrukhina, M. A., *Organometallics* **2008**, *27*, 1750-1757.
- (214) Fachinetti, G.; Funaioli, T.; Lecci, L.; Marchetti, F., *Inorg. Chem.* **1996**, *35*, 7217-7224.
- (215) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B., *Polyhedron* **1989**, *8*, 597-602.
- (216) Therrien, B.; Süß-Fink, G., *Coord. Chem. Rev.* **2009**, *253*, 2639-2664.
- (217) Petrukhina, M. A.; Sevryugina, Y.; Andreini, K. W., *J. Cluster Sci.* **2004**, *15*, 451-467.
- (218) Sevryugina, Y.; Olenev, A. V.; Petrukhina, M. A., *J. Cluster Sci.* **2005**, *16*, 217-229.
- (219) Bianchi, M.; Frediani, P.; Matteoli, U.; Menchi, G.; Piacenti, F.; Petrucci, G., *J. Organomet. Chem.* **1983**, *259*, 207-214.
- (220) Bianchi, M.; Matteoli, U.; Frediano, P.; Piacenti, F.; Nardelli, M.; Pelizzi, G., *Chim. Ind. (Milan)* **1981**, *63*, 475-481.
- (221) Bianchi, M.; Frediani, P.; Nardelli, M.; Pelizzi, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1981**, *37*, C236.
- (222) Rotem, M.; Shvo, Y.; Goldberg, I.; Shmueli, U., *Organometallics* **1984**, *3*, 1758-1759.
- (223) Rotem, M.; Goldberg, I.; Shmueli, U.; Shvo, Y., *J. Organomet. Chem.* **1986**, *314*, 185-212.
- (224) Morris, D. J.; Clarkson, G. J.; Wills, M., *Organometallics* **2009**, *28*, 4133-4140.
- (225) Reibenspies, J. H.; Fontal, B.; Darensbourg, D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *49*, 1619-1621.
- (226) Oh, S. P.; Chor, B. Y.; Fan, W. Y.; Li, Y.; Leong, W. K., *Organometallics* **2011**, *30*, 6774-6777.
- (227) Chor, B. Y.; Ganguly, R.; Leong, W. K., *J. Organomet. Chem.* **2016**, *802*, 15-20.
- (228) Auzias, M.; Therrien, B.; Süß-Fink, G., *Inorg. Chem. Commun.* **2007**, *10*, 1420-1424.
- (229) Süß-Fink, G.; Wolfender, J.-L.; Neumann, F.; Stoeckli-Evans, H., *Angew. Chem.* **1990**, *102*, 447-449.
- (230) Shiu, K.-B.; Lee, H.-C.; Lee, G.-H.; Ko, B.-T.; Wang, Y.; Lin, C.-C., *Angew. Chem. Int. Ed.* **2003**, *42*, 2999-3001.
- (231) Shiu, K.-B.; Lee, H.-C.; Lee, G.-H.; Wang, Y., *Organometallics* **2002**, *21*, 4013-4016.
- (232) Li, C.; Leong, W. K., *J. Organomet. Chem.* **2008**, *693*, 1292-1300.
- (233) Süß-Fink, G.; Jenke, T.; Heitz, H.; Pellinghello, M. A.; Tiripicchio, A., *J. Organomet. Chem.* **1989**, *379*, 311-323.
- (234) Kampe, C. E.; Kaesz, H. D., *Inorg. Chem.* **1984**, *23*, 4646-4653.
- (235) Deeming, A. J.; Hogarth, G.; Lee, M.-y. V.; Saha, M.; Redmond, S. P.; Taya, H.; Orpen, A. G., *Inorg. Chim. Acta* **2000**, *309*, 109-122.
- (236) Rubner, G.; Bendorf, K.; Wellner, A.; Kircher, B.; Bergemann, S.; Ott, I.; Gust, R., *J. Med. Chem.* **2010**, *53*, 6889-6898.
- (237) Vieille-Petit, L.; Therrien, B.; Süß-Fink, G., *Eur. J. Inorg. Chem.* **2003**, *2003*, 3707-3711.
- (238) Vieille-Petit, L.; Therrien, B.; Süß-Fink, G., *Inorg. Chim. Acta* **2003**, *355*, 394-398.
- (239) Vieille-Petit, L.; Therrien, B.; Süß-Fink, G.; Ward, T. R., *J. Organomet. Chem.* **2003**, *684*, 117-123.
- (240) Vieille-Petit, L.; Su, G.; Therrien, B.; Ward, T. R.; Stoeckli-Evans, H.; Labat, G.; Karmazin-Brelot, L.; Neels, A.; Bürgi, T.; Finke, R. G.; Hagen, C. M., *Organometallics* **2007**, *24*, 6104-6119.
- (241) Vieille-Petit, L.; Karmazin-Brelot, L.; Labat, G.; Süß-Fink, G., *Eur. J. Inorg. Chem.* **2004**, *2004*, 3907-3912.

- (242) Therrien, B.; Vieille-Petit, L.; Süss-Fink, G., *Inorg. Chim. Acta* **2004**, *357*, 3289-3294.
- (243) Therrien, B.; Vieille-Petit, L.; Süss-Fink, G.; Sei, Y.; Yamaguchi, K., *J. Organomet. Chem.* **2004**, *689*, 2820-2826.
- (244) Therrien, B.; Vieille-Petit, L.; Süss-Fink, G., *J. Mol. Struct.* **2005**, *749*, 183-186.
- (245) Vieille-Petit, L.; Therrien, B.; Süss-Fink, G., *Inorg. Chim. Acta* **2004**, *357*, 3437-3442.
- (246) Chérioux, F.; Maise-François, A.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G., *J. Chem. Soc., Dalton Trans.* **2001**, *4*, 2184-2187.
- (247) Blum, A. S.; Ren, T.; Parish, D. A.; Trammell, S. A.; Moore, M. H.; Kushmerick, J. G.; Xu, G.-L.; Deschamps, J. R.; Pollack, S. K.; Shashidhar, R., *J. Am. Chem. Soc.* **2005**, *127*, 10010-10011.
- (248) Xu, G.-L.; Zou, G.; Ni, Y.-H.; DeRosa, M. C.; Crutchley, R. J.; Ren, T., *J. Am. Chem. Soc.* **2003**, *125*, 10057-10065.
- (249) Cao, Z.; Xi, B.; Jodoin, D. S.; Zhang, L.; Cummings, S. P.; Gao, Y.; Tyler, S. F.; Fanwick, P. E.; Crutchley, R. J.; Ren, T., *J. Am. Chem. Soc.* **2014**, *136*, 12174-12183.
- (250) Toumey, C., *Nat. Nanotechnol.* **2009**, *4*, 783-784.
- (251) *Nat. Nanotechnol.* **2009**, *4*, 781-781.
- (252) Carroll, R. L.; Gorman, C. B., *Angew. Chem. Int. Ed.* **2002**, *41*, 4378-4400.
- (253) Tour, J. M., *Acc. Chem. Res.* **2000**, *33*, 791-804.
- (254) Paul, F.; Lapinte, C., *Coord. Chem. Rev.* **1998**, *178-180*, 431-509.
- (255) Mas-Ballesté, R.; Castillo, O.; Miguel, P. J. S.; Olea, D.; Gómez-Herrero, J.; Zamora, F., *Eur. J. Inorg. Chem.* **2009**, 2885-2896.
- (256) Salomon, A.; Cahen, D.; Lindsay, S.; Tomfohr, J.; Engelkes, V. B.; Frisbie, C. D., *Adv. Mater.* **2003**, *15*, 1881-1890.
- (257) Pearson, D. L.; Tour, J. M., *J. Org. Chem.* **1997**, *62*, 1376-1387.
- (258) Jones, L.; Schumm, J. S.; Tour, J. M., *J. Org. Chem.* **1997**, *62*, 1388-1410.
- (259) Wohlgamuth, C. H.; McWilliams, M. A.; Slinker, J. D., *Anal. Chem.* **2013**, *85*, 8634-8640.
- (260) Slinker, J. D.; Muren, N. B.; Renfrew, S. E.; Barton, J. K., *Nat. Chem.* **2011**, *3*, 228-233.
- (261) Livshits, G. I.; Stern, A.; Rotem, D.; Borovok, N.; Eidelshtein, G.; Migliore, A.; Penzo, E.; Wind, S. J.; Di Felice, R.; Skourtis, S. S.; Cuevas, J. C.; Gurevich, L.; Kotlyar, A. B.; Porath, D., *Nat. Nanotechnol.* **2014**, *9*, 1040-1046.
- (262) Ying, J.-W.; Liu, I. P.-C.; Xi, B.; Song, Y.; Campana, C.; Zuo, J.-L.; Ren, T., *Angew. Chem. Int. Ed.* **2010**, *49*, 954-957.
- (263) Cotton, F. A.; Curtis, N. F.; Harris, C. B.; Johnson, B. F. G.; Lippard, S. J.; Mague, J. T.; Robinson, W. R.; Wood, J. S., *Science* **1964**, *145*, 1305-1307.
- (264) Cotton, F. A.; Murillo, C. A.; Walton, R. A., *Multiple Bonds Between Metal Atoms*. Springer Science and Business Media Inc.; New York; 3rd ed.: 2005.
- (265) Cai, X.-M.; Höhne, D.; Köberl, M.; Cokoja, M.; Pöthig, A.; Herdtweck, E.; Haslinger, S.; Herrmann, W. A.; Kühn, F. E., *Organometallics* **2013**, *32*, 6004-6011.
- (266) Höhne, D.; Herdtweck, E.; Pöthig, A.; Kühn, F. E., *Dalton Trans.* **2014**, *43*, 15367-74.
- (267) Köberl, M.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E., *Dalton Trans.* **2011**, *40*, 6834-59.
- (268) Köberl, M.; Cokoja, M.; Bechlars, B.; Herdtweck, E.; Kühn, F. E., *Dalton Trans.* **2011**, *40*, 11490-6.
- (269) Fritsch, N.; Wick, C. R.; Waidmann, T.; Dral, P. O.; Tucher, J.; Heinemann, F. W.; Shubina, T. E.; Clark, T.; Burzlaff, N., *Inorg. Chem.* **2014**, *53*, 12305-14.
- (270) Chisholm, M. H.; Patmore, N. J.; Reed, C. R.; Singh, N., *Inorg. Chem.* **2010**, *49*, 7116-7122.
- (271) Xue, W.-M.; Kühn, F. E.; Herdtweck, E.; Li, Q., *Eur. J. Inorg. Chem.* **2001**, 213-221.
- (272) Xue, W.-M.; Kühn, F. E., *Eur. J. Inorg. Chem.* **2001**, 2041-2047.
- (273) Cao, Z.; Xi, B.; Jodoin, D. S.; Zhang, L.; Cummings, S. P.; Gao, Y.; Tyler, S. F.; Fanwick, P. E.; Crutchley, R. J.; Ren, T., *J. Am. Chem. Soc.* **2014**, *136*, 12174-12183.
- (274) Wilkinson, L. A.; McNeill, L.; Patmore, N. J., *J. Am. Chem. Soc.* **2013**, *135*, 1723-1726.
- (275) Forrest, W. P.; Cao, Z.; Hassel, K. M.; Ren, T., *Inorg. Chem.* **2012**, *51*, 3261-3269.
- (276) Cai, X.-M.; Zhang, X.-Y.; Savchenko, J.; Cao, Z.; Ren, T.; Zuo, J.-L., *Organometallics* **2012**, *31*, 8591-8597.
- (277) Xi, B.; Xu, G.-L.; Fanwick, P. E.; Ren, T., *Organometallics* **2009**, *28*, 2338-2341.
- (278) Cotton, F. A.; Murillo, C. A.; Villagrán, D.; Yu, R., *J. Am. Chem. Soc.* **2006**, *128*, 3281-3290.

- (279) Xu, G.-L.; Crutchley, R. J.; DeRosa, M. C.; Pan, Q.-J.; Ren, T., *J. Am. Chem. Soc.* **2005**, *127*, 13354-13363.
- (280) Cotton, F. A.; Lin, C.; Murillo, C. A., *Inorg. Chem.* **2001**, *40*, 478-484.
- (281) Cotton, F. A.; Lin, C.; Murillo, C. A., *J. Am. Chem. Soc.* **2001**, *123*, 2670-2671.
- (282) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A., *Inorg. Chem.* **2001**, *40*, 1234-1244.
- (283) Chisholm, M. H.; Durr, C. B.; Gustafson, T. L.; Kender, W. T.; Spilker, T. F.; Young, P. J., *J. Am. Chem. Soc.* **2015**, *137*, 5155-5162.
- (284) Chisholm, M. H.; Brown-Xu, S. E.; Spilker, T. F., *Acc. Chem. Res.* **2015**, *48*, 877-885.
- (285) Chisholm, M. H., *Coord. Chem. Rev.* **2015**, *282-283*, 60-65.
- (286) Brown-Xu, S. E.; Chisholm, M. H.; Durr, C. B.; Spilker, T. F.; Young, P. J., *Chem. Sci.* **2015**, *6*, 1780-1791.
- (287) Brown-Xu, S. E.; Chisholm, M. H.; Durr, C. B.; Lewis, S. A.; Spilker, T. F.; Young, P. J., *Chem. Sci.* **2014**, *5*, 2657-2666.
- (288) Brown-Xu, S. E.; Chisholm, M. H.; Durr, C. B.; Lewis, S. A.; Naseri, V.; Spilker, T. F., *Chem. Sci.* **2013**, *4*, 2105-2116.
- (289) Brown-Xu, S. E.; Chisholm, M. H.; Durr, C. B.; Gustafson, T. L.; Naseri, V.; Spilker, T. F., *J. Am. Chem. Soc.* **2012**, *134*, 20820-6.
- (290) Bunting, P.; Chisholm, M. H.; Gallucci, J. C.; Lear, B. J., *J. Am. Chem. Soc.* **2011**, *133*, 5873-81.
- (291) Tsurugi, H.; Hayakawa, A.; Kando, S.; Sugino, Y.; Mashima, K., *Chem. Sci.* **2015**, *6*, 3434-3439.
- (292) Tsurugi, H.; Yamada, K.; Majumdar, M.; Sugino, Y.; Hayakawa, A.; Mashima, K., *Dalton Trans.* **2011**, *40*, 9358-9361.
- (293) Rach, S. F.; Kühn, F. E., *Chem. Rev.* **2009**, *109*, 2061-2080.
- (294) Li, Z.; David, A.; Albani, B. A.; Pellois, J.-P.; Turro, C.; Dunbar, K. R., *J. Am. Chem. Soc.* **2014**, *136*, 17058-17070.
- (295) Cai, X.-M.; Zimmermann, T. K.; Pöthig, A.; Kühn, F. E., *Inorg. Chem.* **2015**, *54*, 6631-6640.
- (296) Cai, X.-M.; Riener, K.; Herdtweck, E.; Pöthig, A.; Kühn, F. E., *Inorg. Chem.* **2015**, *54*, 3272-3280.
- (297) Fischer, N. V.; Alam, M. S.; Jum'ah, I.; Stocker, M.; Fritsch, N.; Dremov, V.; Heinemann, F. W.; Burzclaff, N.; Müller, P., *Chem. Eur. J.* **2011**, *17*, 9293-9297.
- (298) Brown, D. J.; Chisholm, M. H.; Gallucci, J. C., *Dalton Trans.* **2008**, 1615-1624.
- (299) Mahapatro, A. K.; Ying, J.; Ren, T.; Janes, D. B., *Nano Lett.* **2008**, *8*, 2131-2136.
- (300) Lin, C.; Kagan, C. R., *J. Am. Chem. Soc.* **2003**, *125*, 336-337.
- (301) Cotton, F. A.; Lin, C.; Murillo, C. A., *Chem. Commun.* **2001**, 11-12.
- (302) Cai, X.-M.; Meister, T. K.; Pöthig, A.; Kühn, F. E., *Inorg. Chem.* **2015**.
- (303) Berry, J. F.; Cotton, F. A.; Murillo, C. A.; Roberts, B. K., *Inorg. Chem.* **2004**, *43*, 2277-2283.
- (304) Wilkinson, L. A.; McNeil, L.; Scattergood, P. A.; Patmore, N. J., *Inorg. Chem.* **2013**, *52*, 9683-9691.
- (305) Xiao, X.; Liu, C.-Y.; He, Q.; Lu, X., *Inorg. Chem.* **2013**, *52*, 12624-12633.
- (306) Cotton, F. A.; Murillo, C. A.; Zhao, Q., *Inorg. Chem.* **2009**, *48*, 11755-11766.
- (307) Cotton, F. A.; Li, Z.; Murillo, C. A., *Inorg. Chem.* **2009**, *48*, 11847-11852.
- (308) Cotton, F. A.; Lin, C.; Murillo, C. A., *Acc. Chem. Res.* **2001**, *34*, 759-771.
- (309) Han, M. J.; Liu, C. Y.; Tian, P. F., *Inorg. Chem.* **2009**, *48*, 6347-6349.
- (310) Tan, Z. F.; Liu, C. Y.; Li, Z.; Meng, M.; Weng, N. S., *Inorg. Chem.* **2012**, *51*, 2212-2221.
- (311) Han, L. J.; Fan, L. Y.; Meng, M.; Wang, X.; Liu, C. Y., *Dalton Trans.* **2011**, *40*, 12832-12838.
- (312) Shu, Y.; Lei, H.; Tan, Y. N.; Meng, M.; Zhang, X. C.; Liu, C. Y., *Dalton Trans.* **2014**, *43*, 14756-14765.
- (313) Cotton, F. A.; Lin, C.; Murillo, C. A., *Inorg. Chem.* **2001**, *40*, 472-477.
- (314) Cotton, F. A.; Lin, C.; Murillo, C. A., *Inorg. Chem.* **2001**, *40*, 575-577.
- (315) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A., *J. Am. Chem. Soc.* **1999**, *121*, 4538-4539.
- (316) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B., *J. Am. Chem. Soc.* **1991**, *113*, 8709-8724.
- (317) Cotton, F. A.; Lin, C.; Murillo, C. A., *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 4810-4813.
- (318) Cotton, F. A.; Liu, C. Y.; Murillo, C. A., *Inorg. Chem.* **2004**, *43*, 2267-2276.
- (319) Angaridis, P.; Cotton, F. A.; Murillo, C. A.; Villagrán, D.; Wang, X.-P., *Inorg. Chem.* **2004**, *43*, 8290-8300.
- (320) Stephenson, T. A.; Wilkinson, G., *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285-2291.

- (321) Angaridis, P.; Berry, J. F.; Cotton, F. A.; Lei, P.; Lin, C.; Murillo, C. A.; Villagrán, D., *Inorg. Chem. Commun.* **2004**, *7*, 9-13.
- (322) Ren, T.; DeSilva, V.; Zou, G.; Lin, C.; Daniels, L. M.; Campana, C. F.; C. Alvarez, J., *Inorg. Chem. Commun.* **1999**, *2*, 301-304.
- (323) Chisholm, M. H.; Cotton, F. A.; Daniels, L. M.; Folting, K.; Huffman, J. C.; Iyer, S. S.; Lin, C.; Macintosh, A. M.; Murillo, C. A., *J. Chem. Soc., Dalton Trans.* **1999**, 1387-1392.
- (324) Cotton, F. A.; Wiesinger, K. J., *Inorg. Chem.* **1991**, *30*, 871-873.
- (325) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T., *Inorg. Chem.* **1996**, *35*, 6422-6428.
- (326) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Villagrán, D.; Wang, X., *J. Am. Chem. Soc.* **2003**, *125*, 13564-13575.
- (327) Stephenson, T. A.; Bannister, E.; Wilkinson, G., *J. Chem. Soc.* **1964**, 2538-2541.
- (328) Cotton, F. A.; Li, Z.; Liu, C. Y.; Murillo, C. A.; Villagrán, D., *Inorg. Chem.* **2006**, *45*, 767-778.
- (329) Cotton, F. A.; Li, Z.; Liu, C. Y.; Murillo, C. A., *Inorg. Chem.* **2006**, *45*, 9765-9770.
- (330) Cotton, F. A.; Liu, C. Y.; Murillo, C. A.; Villagrán, D.; Wang, X., *J. Am. Chem. Soc.* **2004**, *126*, 14822-14831.
- (331) Cotton, F. A.; Falvello, L. R.; Reid, A. H.; Tocher, J. J. H., *J. Organomet. Chem.* **1987**, *319*, 87-97.
- (332) Han, L.-J., *Acta Cryst.* **2011**, *E67*, m256.
- (333) Albert Cotton, F.; Jin, J.-Y.; Li, Z.; Liu, C. Y.; Murillo, C. A., *Dalton Trans.* **2007**, 2328-2335.
- (334) Yamaguchi, Y.; Ozaki, S.; Hinago, H.; Kobayashi, K.; Ito, T., *Inorg. Chim. Acta* **2005**, *358*, 2363-2370.
- (335) Cotton, F. A.; Donahue, J. P.; Murillo, C. A., *J. Am. Chem. Soc.* **2003**, *125*, 5436-5450.
- (336) Cotton, F. A.; Ilsley, W. H.; Kaim, W., *Inorg. Chem.* **1981**, *20*, 930-934.
- (337) Wu, Y.-Y.; Chen, J.-D.; Liou, L.-S.; Wang, J.-C., *Inorg. Chim. Acta* **2002**, *336*, 71-79.
- (338) Ziriakus, J. Ruthenium katalysierte Umvinylierung. Dissertation, Technische Universität München, Munich, 2012.

8 COMPLETE LIST OF PUBLICATIONS

- [11] **T. K. Zimmermann**, F. E. Kühn, Molekulare Katalysatoren zur Bindungsaktivierung – Auf dem Weg zu alternativen Rohstoffquellen. *Chemie in Unserer Zeit* **2015**, *49*, 248-259.
- [10] **T. K. Meister**, K. Riener, P. Gigler, J. Stohrer, W. A. Herrmann, F. E. Kühn, Platinum Catalysis Revisited – Unraveling Principles of Catalytic Olefin Hydrosilylation. *ACS Catalysis* **2016**, *6*, 1274-1284.
- [9] **T. K. Meister**, J. Kück, K. Riener, A. Pöthig, W. A. Herrmann, F. E. Kühn, Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts. *Journal of Catalysis* **2016**, *337*, 157-166.
- [8] K. Riener, **T. K. Meister**, P. Gigler, W. A. Herrmann, F. E. Kühn, Mechanistic Insights into the Iridium-Catalyzed Hydrosilylation of Allyl Compounds. *Journal of Catalysis* **2015**, *331*, 203-209.
- [7] K. Riener, **T. K. Zimmermann**, A. Pöthig, W. A. Herrmann, F. E. Kühn, Direct Synthesis and Bonding Properties of the First μ^2 - η^2 , η^2 -Allyl-Bridged Diiridium Complex. *Inorganic Chemistry* **2015**, *54*, 4600-4602.
- [6] A. Schmidt,[#] N. Grover,[#] **T. K. Zimmermann**,[#] L. Graser, M. Cokoja, A. Pöthig, F. E. Kühn, Synthesis and Characterization of Novel Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis. *Journal of Catalysis* **2014**, *319*, 119-126.
- [5] J. Ziriakus,[#] **T. K. Zimmermann**,[#] A. Pöthig, M. Drees, S. Haslinger, D. Jantke, F. E. Kühn, Ruthenium Catalyzed Transvinylation – New Insights. *Advanced Synthesis & Catalysis* **2013**, *355*, 2845–2859.
- [4] **T. K. Zimmermann**, J. Ziriakus, E. Herdtweck, A. Pöthig, F. E. Kühn, $[\text{Ru}_4(\text{CO})_8(\mu\text{-OOCCH}_2\text{CH}_3)_4(\text{THF})_2]$ and $[\text{Ru}_3(\mu_3\text{-OH})(\text{CO})_6(\mu\text{-OOC}^t\text{Bu})_4(\text{OOC}^t\text{Bu})]$: Novel Multinuclear Ruthenium Carbonyl Carboxylates. *Organometallics* **2014**, *33*, 2667-2670.
- [3] **T. K. Zimmermann**, S. Haslinger, A. Pöthig, F. E. Kühn, Structure and Application of the Ruthenium(I) Sawhorse-Type Complex $[\text{Ru}_2(\mu, \eta^2\text{-CF}_3(\text{CF}_2)_5\text{COO})_2(\text{DMSO})_2(\text{CO})_4]$. *Acta Crystallographica, Section C* **2014**, *C70*, 384-387.
- [2] X.-M. Cai, **T. K. Zimmermann**, A. Pöthig, F. E. Kühn, Synthesis and Electrochemical Properties of *cis*- and *trans*- $[\text{Mo}_2(\text{O}_2\text{C-Fc})_2(\text{DArF})_2]$ ($\text{O}_2\text{C-Fc}$ = Ferrocenecarboxylate, DArF = *N,N'*-Diarylformamidinate). *Inorganic Chemistry* **2015**, *54*, 6631-6640.
- [1] X.-M. Cai, **T. K. Meister**, A. Pöthig, F. E. Kühn, Filling a Gap: Electrochemical Property Comparison of the Completed Compound Series $[\text{Mo}_2(\text{DArF})_n(\text{O}_2\text{C-Fc})_{4-n}]$ (DArF = *N,N'*-Diarylformamidinate; $\text{O}_2\text{C-Fc}$ = Ferrocenecarboxylate). *Inorganic Chemistry* **2015**, *55*, 858-864.

[#] Equally contributing co-authors.

9 APPENDIX

Table A1. Contribution of Ph.D. candidate T. K. Meister to individual publications. * = contributed equally as first author (refers to publications in Chapters 3.6 and 3.7).

Bibliographic Data	Chapter	Author	Contribution
<i>Chem. Unserer Zeit</i> 2015 , <i>49</i> , 248-259	3.1	1 st	research, conception and writing of manuscript
<i>ACS Catal.</i> 2016 , <i>6</i> , 1274-1284	3.2	1 st	conceptual approach, experimental work, conception and writing of manuscript
<i>J. Catal.</i> 2016 , <i>337</i> , 157-166	3.3	1 st	conceptual approach, experimental work, DFT study, conception and writing of manuscript
<i>J. Catal.</i> 2015 , <i>331</i> , 203-209	3.4	2 nd	support of 1 st author (K. Riener) in conception and wording of manuscript
<i>Inorg. Chem.</i> 2015 , <i>54</i> , 4600-4602	3.5	2 nd	experimental work and related data interpretation, support of first author (K. Riener) in conception and wording of manuscript
<i>J. Catal.</i> 2014 , <i>319</i> , 119-126	3.6	3 rd *	DFT study and related data interpretation, contribution to conception and writing of the manuscript
<i>Adv. Synth. Catal.</i> 2013 , <i>355</i> , 2845-2859	3.7	2 nd *	conceptual approach, experimental work and related data interpretation, conception and writing of manuscript
<i>Organometallics</i> 2014 , <i>33</i> , 2667-2670	3.8	1 st	conceptual approach, experimental work and related data interpretation, DFT study, conception and writing of manuscript
<i>Acta Cryst. C</i> 2014 , <i>C70</i> , 384-387	3.9	1 st	conceptual approach, experimental work and related data interpretation, conception and writing of manuscript
<i>Inorg. Chem.</i> 2015 , <i>54</i> , 6631-6640	3.10	2 nd	experimental work and related data interpretation, support of 1 st author (X.-M. Cai) in conception and wording of manuscript
<i>Inorg. Chem.</i> 2015 , <i>55</i> , 858-864	3.11	2 nd	experimental work and related data interpretation, support of 1 st author (X.-M. Cai) in conception and wording of manuscript