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Carbocyclic Carbenes and Beyond: Functionalised Cycloheptatriene Systems as Versatile Ligands in Palladium Chemistry

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It is by logic that we prove, but by intuition that we discover.

Jules Herni Poincaré (1854–1912)

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Abstract

Carbocyclic carbenes represent a relatively unknown class of carbene ligands compared to N-heterocyclic carbenes (NHCs), which have firmly established themselves as one of the most versatile ligand classes in organometallic chemistry. Nevertheless, the group of Pd-cycloheptatrienylidene(CHT) complexes proved to be a highly interesting motif and in this thesis a diverse structural chemistry could be developed around them. In continuation of former studies, the reactivity of the CHT ligand towards N-nucleophiles and the associated rearrangement of the carbene ligand to an allyl binding mode was utilised as the key step to prepare a broad variety of imidazolium- and pyridinium-substituted η^3-cycloheptatrienide-Pd complexes. Unlike previously proposed, the resulting complexes were shown to have a monomeric structure of the type $[PdBr_2(\eta^3\text{-}C_7H_6\text{-Im/pyr})]$ due to the zwitterionic nature of the organometallic ligand. Computational studies revealed a highly dynamic equilibrium between different regioisomers of the allyl bond in solution and the β-isomer (with regard to the distance of the central allyl-C atom from the substituent) was found to be most favourable, in agreement with crystallographic results.

In order to overcome the drawback of their poor solubility, partial exchange of bromide ligands for non-coordinating anions was identified as a suitable way to obtain dimeric halide-bridged complexes of type $[Pd(\mu\text{-}Br)(\eta^3\text{-}C_7H_6\text{-Im/pyr})]_2(BF_4)_2$ with greatly enhanced solubility. In the case of the derivative $\{[PdBr(\eta^3\text{-}C_7H_6\text{-Im-DiPP})](BF_4)\}_n$ it could be demonstrated that the dimer co-exists in an equilibrium with a tetramer featuring a Pd_4Br_4-macrocycle, which might not only have implications for this class of compounds, but also for dimeric Pd complexes with halide bridges in general. In the course of these structural studies, also the γ-isomer could be crystallographically observed in a few cases, mainly due to packing effects favouring it over the otherwise more stable β-isomer. Further investigation of anion exchange reactions showed that a complete removal of bromide leads back to a monomeric structure with coordinating solvent molecules, $[Pd(MeCN)_2(\eta^3\text{-}C_7H_6\text{-Im/pyr})](BF_4)_2$. With respect to further synthetic utilisation, particular attention was paid to dimers with a Pd:Br ratio of 2:3, $[\{PdBr(\eta^3\text{-}C_7H_6\text{-Im/pyr})\}_2(\mu\text{-}Br)](BF_4)$, featuring two terminal and one bridging bromide ligand, which causes a close Pd-Pd interaction. Although their isolation and full characterisation was only possible in one case, their existence in an equilibrium with a mixture of monomers and Pd:Br = 2:2 dimers made it possible to use such a mixture of readily available compounds instead.

Imidazolium- and pyridinium-substituted η^3-cycloheptatrienide-Pd complexes represent a highly interesting platform for Pd chemistry with functionlised cycloheptatriene-based ligand systems. As such, they were successfully employed in the synthesis of functionalised trinuclear

Pd sandwich complexes of type [$Pd_3Br_3(C_7H_6$-Im/pyr$)_2$](Br/BF_4), for which several strategies were tested. A generally applicable route was developed based on the dimeric precursors with a Pd:Br ratio of 2:3, the particular aptitude of which can be attributed to the metal-metal interaction, which prearranges the Pd atoms for the cluster formation. For such a precursor or intermediate the term “pre-cluster” was introduced. Electrochemical and computational studies gave insights into the electronic structure of the Pd_3 sandwich cluster motif, indicating formally triply anionic seven-membered rings and a non-integer formal oxidation state of +2.666 for the Pd atoms. Significant differences in the coordination environments and electron densities allowed the conclusion that the most accurate description based on integer formal oxidation states is a mixed valence cluster of one Pd(II) and two Pd(III) ions. The intermediate formal oxidation state makes them promising candidates for future applications in catalysis. Additionally, the imidazolium-substituted derivatives offer the chance to convert the imidazolium sidearms to NHCs and thus introduce further metal atoms on the sidearms. As a proof of principle, this was performed with Pd, resulting in a Pd_3 sandwich cluster complex extended by a fourth Pd(II) between the two NHC sidearms. Electrochemical characterisation showed two different reduction potentials, thus confirming the interpretation that the formal oxidation state of the Pd_3 cluster is more positive than for the Pd(II) ion bound on the sidearms. This structural motif could also allow the combination of Pd_3 clusters with other metals, which would create a universal platform for heterobimetallic Pd_3M systems.

The scope of relevant target structures accessible from imidazolium-substituted η^3-cycloheptatrienide-Pd complexes is, of course, not limited to functionalised sandwich clusters. They could also be utilised as precursors in the synthesis of the first hybrid carbocyclic/N-heterocyclic carbene ligand by a two-step deprotonation/hydride abstraction sequence. In the first step, the imidazolium sidearm of the monomeric complex [$PdBr_2(\eta^3$-C_7H_6-Im-DiPP)] was transformed into an NHC which prompted an intramolecular coordination to Pd and a rearrangement of the allyl-bound cycloheptatrienide ligand to an alkyl binding mode. This crucial rearrangement allowed the abstraction of the alkyl-H atom as a hydride in the second step, thus converting the cycloheptatrienyl- into a cycloheptatrienylidene-ligand. Spectroscopic and crystallographic data indicate an electronic interaction between the two carbene moieties and allowed the first direct comparison of their properties in a single complex. Reactivity studies revealed a surprising behaviour of the hybrid CHT/NHC-Pd complex towards iodine, leading to dimerisation upon removal of one bromide ligand, which represents an unprecedented reaction of a coordination compound with iodine.

As this thesis is fundamentally based on the area of CHT complexes, it also addressed the open questions concerning the ligand precursors of the formula $C_7H_6X_2$ (X = Cl, Br), which had mostly been regarded as 7,7-dihalocycloheptatrienes so far. In fact, this turned out to be the only unfounded representation, whereas all other possible structures, namely the covalent 1,7-, 2,7- and 3,7-dihalocycloheptatriene isomers and the ionic halotropylium halide form, are relevant. In the solid state, crystallographic analysis found the ionic structure exclusively. In solution, however, NMR spectroscopic and computational studies showed a dynamic equilibrium between the three covalent isomers which interconvert via the halotropylium halide structure. With increasing polarity of the solvent, the ionic structure becomes more and more stabilised, so that it actually turns from a minor species functioning as an intermediate to the main species in very polar solvents. The knowledge of the behaviour of these compounds will now permit a better understanding of their reactivity and applications. In the course of these studies, also the crystal structure of hydroxytropylium chloride was obtained serendipitously as a decomposition product and this represents the first crystallographic characterisation of an unstabilised hydroxytropylium ion. This also confirms that such a hydroxytropylium halide species is the intermediate in the hydrolytic decomposition pathway of halotropylium halides to tropone.

In continuation of the studies of organometallic Pd clusters, a side project was dedicated to the re-investigation of a protocol from 1964 on the reaction of a Pd(II) salt with triphenylcyclopropenium chloride and ethylene. The true structure of the product was identified as a Pd_6Cl_8 cluster capped by μ^3-η^1:η^1:η^3-C_3Ph_3 ligands and with triphenylcyclopropenium counterions: $[C_3Ph_3]_2[Pd_6Cl_8(C_3Ph_3)_2]$. The formation of the ligands could be explained by a partial reduction of Pd(II) to Pd(0) by ethylene and a subsequent ring-opening oxidative addition of the triphenylcyclopropenium ions on Pd(0) leading to the rare binding mode of the capping ligands, which combines two η^1(alkyl)-coordinations and one η^3(allyl)-coordination. The cluster formation then proceeds via self-assembly with excess Pd(II) salt and triphenylcyclopropenium chloride. This cluster from 1964 in fact represents the first isolated organometallic Pd cluster, even though its structure was not recognised until now.

Zusammenfassung

Carbocyclische Carbene stellen eine relativ unbekannte Klasse von Carben-Liganden dar im Vergleich zu den N-heterocyclischen Carbenen (NHCs), welche als eine der vielfältigsten Ligandenklassen der Organometallchemie etabliert sind. Nichtsdestoweniger stellte sich die Gruppe der Pd-Cycloheptatrienyliden(CHT)-Komplexe als ein hochinteressantes Motiv heraus und im Rahmen dieser Arbeit konnte auf ihrer Basis eine vielseitige Strukturchemie entwickelt werden. In Fortsetzung vorangegangener Arbeiten wurden die Reaktivität des CHT-Liganden gegenüber N-Nucleophilen und die damit einhergehende Umlagerung des Carben-Liganden zu einem Allyl-Bindungsmodus als Schlüsselschritt genutzt, um eine Vielzahl an Imidazolium- und Pyridinium-substituierten η^3-Cycloheptatrienid-Pd-Komplexen darzustellen. Es konnte gezeigt werden, dass die resultierenden Komplexe – anders als bislang vorgeschlagen – eine monomere Struktur des Typs [$PdBr_2(\eta^3$-C_7H_6-Im/pyr)] aufweisen, was auf die zwitterionische Natur der metallorganischen Liganden zurückgeführt werden konnte. Computerchemische Studien deckten ein hochdynamisches Gleichgewicht zwischen verschiedenen Regioisomeren der Allyl-Bindung in Lösung auf und das β-Isomer (bezogen auf den Abstand des zentralen Allyl-C-Atoms vom Substituenten) stellte sich in Einklang mit kristallographischen Ergebnissen als das günstigste heraus.

Um den Nachteil ihrer niedrigen Löslichkeit zu überwinden, erwies sich ein teilweiser Austausch der Bromid-Liganden gegen nichtkoordinierende Anionen als geeignete Methode. Dies führt zu dimeren, Halogenid-verbrückten Komplexen des Typs [Pd(μ-Br)(η^3-C_7H_6-Im/pyr)]$_2(BF_4)_2$ mit beträchtlich verbesserter Löslichkeit. Im Fall des Derivats {[PdBr(η^3-C_7H_6-Im-DiPP)](BF_4)}$_n$ konnte gezeigt werden, dass sich das Dimer in Koexistenz mit einem Tetramer befindet, welches einen Pd_4Br_4-Makrocyclus aufweist. Dies könnte nicht nur Bedeutung für diese Verbindungsklasse haben, sondern auch ganz generell für dimere Pd-Komplexe mit Halogenid-Brücken. Im Zuge der Strukturuntersuchungen konnte auch in wenigen Fällen das γ-Isomer kristallographisch beobachtet werden, was auf Packungseffekte zurückzuführen war, die es gegenüber dem ansonsten stabileren β-Isomer begünstigen. Weitergehende Studien der Anionenaustausch-Reaktionen zeigten, dass ein komplettes Entfernen der Bromide zurück zu einer monomeren Struktur mit koordinierenden Lösungsmittel-Molekülen, [Pd(MeCN)$_2$(η^3-C_7H_6-Im/pyr)](BF_4)$_2$, führt. Mit Blick auf weiteren synthetischen Nutzen wurde besonderes Augenmerk auf Dimere mit einem Pd:Br-Verhältnis von 2:3, [{PdBr(η^3-C_7H_6-Im/pyr)}$_2$(μ-Br)](BF_4), gelegt, welche zwei terminale und einen verbrückenden Bromid-Liganden aufweisen und damit eine enge Pd-Pd-Wechselwirkung bewirken. Obwohl sich deren Isolierung und vollständige Charakterisierung nur in einem Fall bewerkstelligen lies, ermöglichte es die Tatsache, dass sie in einem Gleichgewicht mit einer

Mischung aus Monomeren und Dimeren mit Pd:Br = 2:2 existieren, stattdessen eine solche Mischung leicht zugänglicher Verbindungen zu verwenden.

Imidazolium- und Pyridinium-substituierte η^3-Cycloheptatrienid-Pd-Komplexe stellen eine hochinteressante Plattform für Pd-Chemie mit funktionalisierten Cycloheptatrien-basierten Liganden dar. In diesem Sinne wurden sie erfolgreich für die Synthese von funktionalisierten trinuclearen Pd-Sandwich-Komplexen des Typs $[Pd_3Br_3(C_7H_6\text{-Im/pyr})_2](Br/BF_4)$ verwendet, wofür mehrere Strategien erprobt wurden. Eine universell einsetzbare Route wurde auf Basis der dimeren Vorstufen mit einem Pd:Br-Verhältnis von 2:3 entwickelt, deren besondere Eignung der Metall-Metall-Wechselwirkung zugeschrieben werden kann, welche die Pd-Atome für die Clusterbildung prä-organisiert. Für derartige Vorstufen oder Intermediate wurde der Begriff „Prä-Cluster“ eingeführt. Elektrochemische und theoretische Studien gewährten Einblicke in die elektronische Struktur des Pd_3-Sandwich-Cluster-Motivs und wiesen auf einen formal dreifach anionischen Charakter des Siebenrings und einen nicht-ganzzahligen formalen Oxidationszustand der Pd-Atome von +2.666 hin. Signifikante Unterschiede der Koordinationsumgebungen und Elektronendichten erlaubten die Schlussfolgerung, dass die zutreffendste Beschreibung anhand ganzzahliger formaler Oxidationsstufen in einem gemischt valenten Cluster aus einem Pd(II)- und zwei Pd(III)-Ionen besteht. Der intermediäre formale Oxidationszustand macht sie zu einem vielversprechenden Forschungsgegenstand für künftige Anwendungen in der Katalyse. Zusätzlich bieten die Imidazolium-substituierten Derivate die Chance, den Imidazolium-Seitenarm zu einem NHC umzusetzen und dadurch weitere Metallatome an den Seitenarmen einzuführen, was kooperative Effekte hervorbringen könnte. Zur Bestätigung des Konzepts wurde dies mit Pd durchgeführt, was zu einem Pd_3-Sandwich-Cluster-Komplex führte, der um ein viertes Pd(II)-Zentrum zwischen den beiden NHC-Seitenarmen erweitert ist. Die elektrochemische Charakterisierung zeigte zwei unterschiedliche Reduktionspotentiale und bestätigt damit die Interpretation, dass die formale Oxidationsstufe des Pd_3-Clusters positiver ist als die des an die Seitenarme gebundenen Pd(II)-Ions. Dieses Strukturmotiv könnte auch die Kombination des Pd_3-Clusters mit weiteren Metallen erlauben, wodurch sich eine universelle Plattform für hetrobimetallische Pd_3M-Systeme schaffen ließe.

Der Umfang bedeutender Zielstrukturen, die ausgehend von Imidazolium-substituierten η^3-Cycloheptatrienid-Pd-Komplexen zugänglich sind, ist natürlich nicht auf funktionalisierte Sandwich-Cluster beschränkt. Sie konnten auch als Ausgangsverbindungen in der Synthese des ersten gemischten carbocyclisch/N-heterocyclichen Carben-Liganden mittels einer zweistufigen Sequenz aus Deprotonierung und Hydridabstraktion eingesetzt werden. Im ersten Schritt wurde der Imidazolium-Seitenarm des monomeren Komplexes $[PdBr_2(\eta^3\text{-}C_7H_6\text{-}$

Im-DiPP)] in ein NHC überführt, was eine intramolekulare Koordination an Pd und eine Umlagerung des allyl-gebundenen Cycloheptatrienid-Liganden hin zu einem Alkyl-Bindungsmodus bewirkte. Diese entscheidende Umlagerung erlaubte im zweiten Schritt die Abstraktion des Alkyl-H-Atoms als Hydrid, wodurch der Cycloheptatrienyl- in einen Cycloheptatrienyliden-Liganden umgewandelt wurde. Spektroskopische und kristallographische Daten weisen auf eine elektronische Wechselwirkung zwischen den beiden Carben-Einheiten hin und erlaubten erstmals einen direkten Vergleich ihrer Eigenschaften in einem einzigen Komplex. Reaktivitätsstudien zeigten ein überraschendes Verhalten des hybriden CHT/NHC-Pd-Komplexes gegenüber Iod, was zu einer Dimerisierung durch Entfernen eines Bromid-Liganden führte. Dies stellt eine bislang unbekannte Reaktion einer Koordinationsverbindung mit Iod dar.

Da diese Arbeit wesentlich auf dem Themengebiet von CHT-Komplexen aufbaut, befasste sie sich auch mit offenen Fragen bezüglich der Ligand-Vorstufen mit der Formel $C_7H_6X_2$ (X = Cl, Br), die bislang zumeist als 7,7-Dihalogencycloheptatriene aufgefasst wurden. Dies stellte sich jedoch in der Tat als die einzige unzutreffende Darstellung heraus, während alle anderen möglichen Strukturen, nämlich die kovalenten 1,7-, 2,7- und 3,7-Dihalogencycloheptatrien-Isomere, sowie die ionische Halogentropyliumhalogenid-Form eine relevante Rolle spielen. Im Festkörper wiesen kristallographische Analysen ausschließlich die ionische Struktur nach. In Lösung dagegen zeigten NMR-spektroskopische und computerchemische Studien ein dynamisches Gleichgewicht zwischen den drei kovalenten Isomeren, welche sich über die Halogentropyliumhalogenid-Form ineinander umwandeln. Mit steigender Polarität des Lösungsmittels wird die ionische Struktur zunehmend stabilisiert, so dass sie in hochpolaren Lösungsmitteln sogar von einer Nebenspezies, die als Intermediat fungiert, zur Hauptspezies wird. Das Wissen um das Verhalten dieser Verbindungen erlaubt nun ein besseres Verständnis ihrer Reaktivität und Anwendungen. Im Zuge dieser Studien wurde auch zufällig als Zersetzungsprodukt die Kristallstruktur des Hydroxytropyliumchlorids erhalten, was die erste kristallographische Charakterisierung eines unstabilisierten Hydroxytropylium-Ions darstellt. Dies beweist auch, dass solch eine Hydroxytropyliumhalogenid-Spezies als Intermediat in der hydrolytischen Zersetzung von Halogentropyliumhalogeniden zu Tropon auftritt.

In Fortsetzung der Studien metallorganischer Pd-Cluster wurde eine Nebenprojekt der erneuten Untersuchung einer Versuchsvorschrift über die Reaktion eines Pd(II)-Salzes mit Triphenylcyclopropeniumchlorid und Ethen aus dem Jahr 1964 gewidmet. Die tatsächliche Struktur des Produkts wurde als ein Pd_6Cl_8-Cluster mit μ^3-η^1:η^1:η^3-C_3Ph_3-Liganden und Triphenylcyclopropenium-Gegenionen, $[C_3Ph_3]_2[Pd_6Cl_8(C_3Ph_3)_2]$, identifiziert. Die Bildung der

Liganden konnte durch eine partielle Reduktion von Pd(II) zu Pd(0) durch Ethen und eine anschließende ringöffnende oxidative Addition an Pd(0) erklärt werden, was zu dem seltenen Bindungsmodus führt, in dem zwei η^1(Alkyl)-Koordinationen und eine η^3(Allyl)-Koordination kombiniert sind. Die Bildung des Clusters erfolgt dann durch Selbstassemblierung mit überschüssigem Pd(II)-Salz und Triphenylcyclopropeniumchlorid. Dieser Cluster aus dem Jahr 1964 stellt in der Tat den ersten isolierten metallorganischen Pd-Cluster dar, auch wenn seine Struktur erst jetzt erkannt wurde.

List of Abbreviations

Ac	acetyl
ADP	anisotropic displacement parameter
aNHC	abnormal N-heterocyclic carbene
Ar	aryl
BAC	bis(amino)cyclopropenylidene
BAr_f	tetrakis(pentafluorophenyl)borate
Bn	benzyl
btsa	bis(trimethylsilyl)amide
cat	catalyst
CHT	cycloheptatrienylidene
CHT(allyl)	η^3-cycloheptatrienide
CHT(alkyl)	η^1-cycloheptatrienyl
CHTE	cycloheptatetraene
cod	cycloocta-1,5-diene
coe	cyclooctene
COSY	correlation spectroscopy
cot	cyclooctatetraene
Cp	cyclopentadienyl/cyclopentadienide
CPr	cyclopropenylidene
CM	cross metathesis
CV	cyclic voltammetry
Cy	cyclohexyl
dba	dibenzylideneacetone
DCM	dichloromethane
DFT	density functional theory
DiPP	2,6-diisopropylphenyl
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
ECP	effective core potential

eq	equivalent(s)
ESR	electron spin resonance
Et	ethyl
Et_2O	diethyl ether
ESI	electrospray ionisation
FAB	fast atom bombardment
HSQC	heteronuclear single quantum correlation
HMBC	heteronuclear multiple-bond correlation
Im	imidazole/imidazolium
^{i}Pr	isopropyl
IR	infrared (spectroscopy)
L	ligand
LDA	lithium diisopropylamide
LED	light emitting diode
M	metal
Me	methyl
MeCN	acetonitrile
Mes	mesityl (= 2,4,6-trimethylphenyl)
MOF	metal-organic framework
MS	mass spectrometry
^{n}Bu	*n*-butyl
NHDC	N-heterocyclic dicarbene
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser enhancement spectroscopy
OAc	acetate
OTf	triflate (= trifluoromethanesulfonate)
PEPPSI	pyridine-enhanced precatalyst preparation, stabilisation and initiation
Ph	phenyl
p-Tol	*para*-methylphenyl

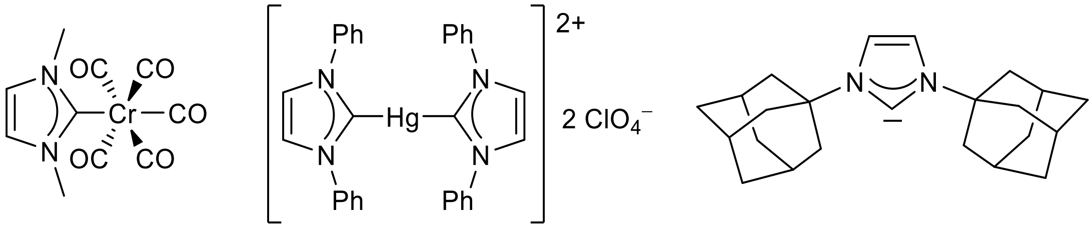
pyr	pyridine/pyridinium
R	organic rest
RCM	ring closing metathesis
rNHC	remote N-heterocyclic carbene
ROMP	ring opening metathesis polymerisation
RT	room temperature
^{t}Bu	tertiary butyl
TEP	Tolman electronic parameter
THF	tetrahydrofuran
TrxR	mitochondrial thioredoxin reductase
TS	transition state
X	halogen (if not specified otherwise)

Content

1. Introduction

1.1 N-Heterocyclic Carbenes

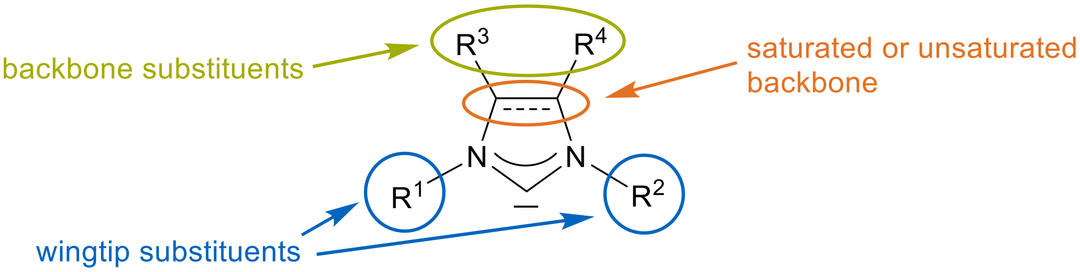
The first N-heterocyclic carbene (NHC) complexes were discovered in 1968 by Öfele and Wanzlick (see Scheme 1, left and centre).[1,2] At first, however, this class of ligands attracted only little attention. This changed dramatically, when Arduengo isolated the first stable free NHC in 1991 (see Scheme 1, right).[3] The following decades saw a rapid development of NHC chemistry and they are now established as one of the most valuable and versatile ligand classes in the toolkit of organometallic chemistry.[4-8]



Scheme 1: First NHC complexes by Öfele (left) and Wanzlick (centre). First free NHC by Arduengo (right).[1-3]

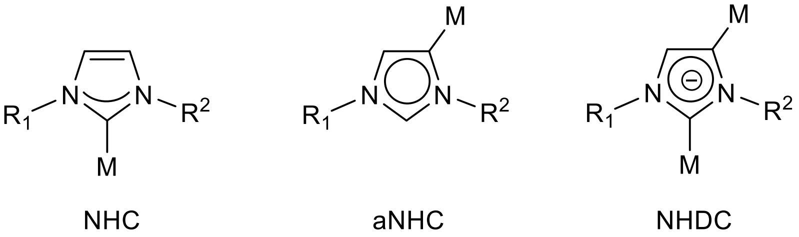
1.1.1 Structures

Among NHCs, the group of 1,3-disubstituted imidazol-4-in-2-ylidenes – as described in the first reports by Öfele and Wanzlick (see above) is by far the most abundant.[4-7] This corresponds to $R^3 = R^4 = H$, R^1 & R^2 = organic groups and an unsaturated backbone in the general structure as depicted in Scheme 2. All these structural features can be specifically tailored to fine-tune the properties of NHC ligands (see next paragraph), which underlines the versatility that made them an integral part of modern organometallic chemistry.[4-8] Variations of all the parameters highlighted in Scheme 2 are feasible and common practice in NHC ligand design, but it can be stated that the wingtip substituents are the most important factor and therefore the one with the most variety in literature.[4-9]



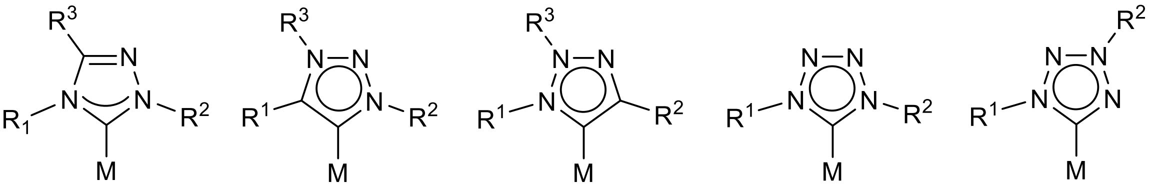
Scheme 2: General structure of an imidazole-based N-heterocyclic carbene (normal binding mode).

But not only the substituents can be varied, also the carbene position itself can be changed to a different position. Besides the common normal carbene biding mode, where the carbene C is located between the N-heteroatoms (Scheme 2 and Scheme 3, left), there is also an abnormal (aNHC) binding mode, where the carbene C is located in the backbone (Scheme 3, centre).[10] The normal and abnormal carbene mode can even be combined in the same ligand moiety yielding a structure as depicted in Scheme 3, right, which is called an anionic dicarbene or N-heterocyclic dicarbene (NHDC) and was first reported in 2006.[11,12]



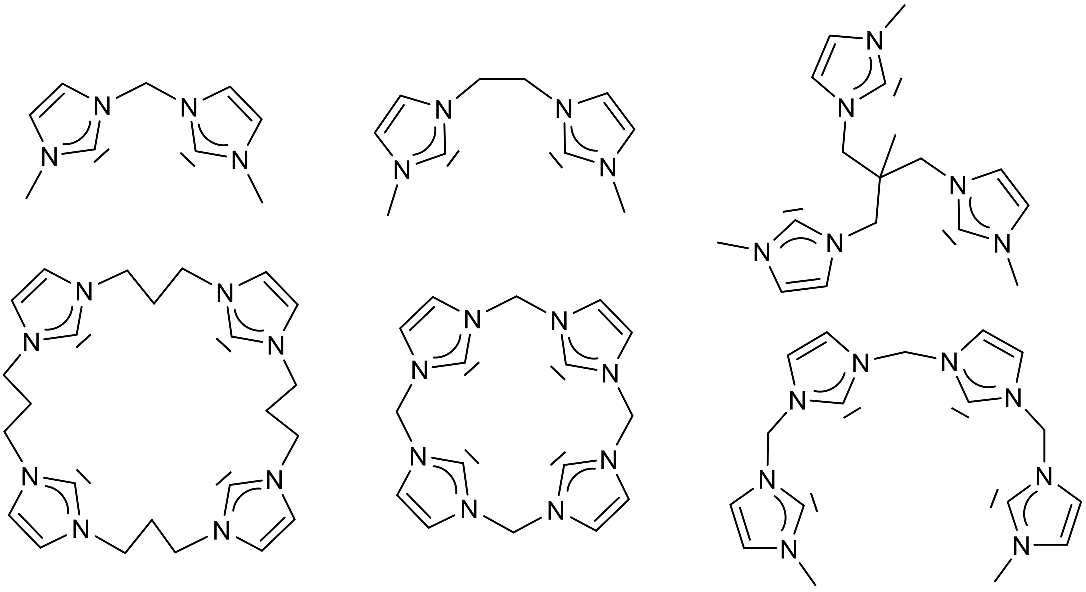
Scheme 3: General structures of a normal carbene (left), abnormal carbene (centre) and anionic dicarbene (right) metal complex based on imidazolylidenes.[10-12]

The group of N-heterocyclic carbenes is, of course, not limited to imidazole-based ligands (or the similar benzimidazole ligands): Analogous carbene ligands can also be obtained from various triazoles or tetrazoles (see Scheme 4 for examples).[6-8] [13-15] The different donor properties of such carbene ligands and the possibility of “skipping” a wingtip substituent (as e.g. in 1,3-disubstituted tetrazolylidenes, see Scheme 4, far right) can make them interesting alternatives to classic NHCs in some cases.[7] [13] [15,16] For completeness, it must be mentioned that other N-heterocycles of various size and also such with only one N atom and another heteroatom like O or S can form carbene ligands.[6-8] [17-19] As such structures are less common, they will not be discussed in detail. The same applies to N-heterocyclic carbene ligands where the carbene C is not directly attached to a heteroatom, so-called remote NHCs (rNHCs).[10] This introduction instead focusses on normal imidazole-based NHCs in the following.



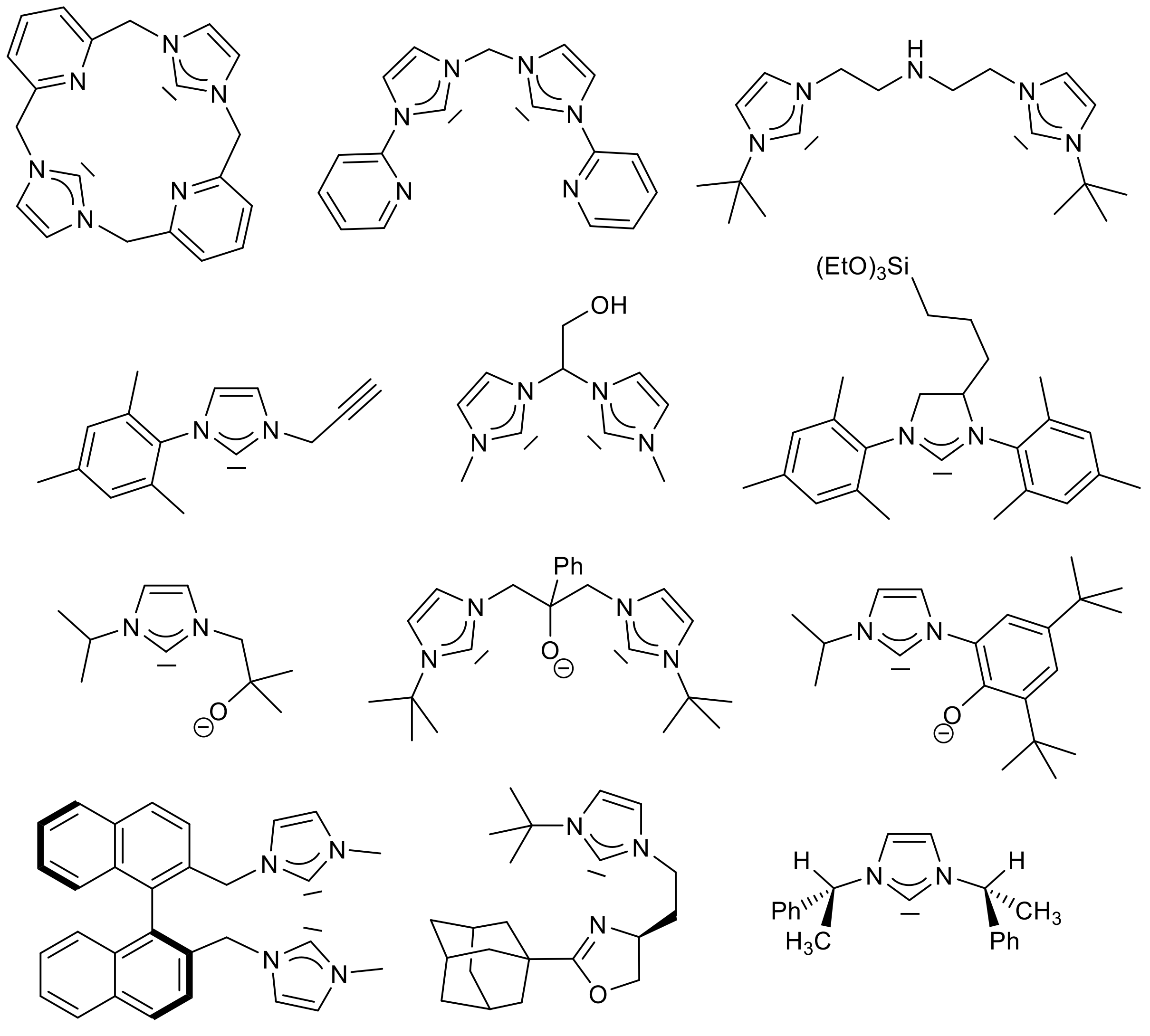
Scheme 4: General structures of triazole (left) and tetrazole (right) based NHC complexes with different heteroatom and substitution patterns.[6-8] [13-15]

As mentioned, the wingtip substituents are the main focus in NHC ligand design. Particularly interesting are other coordinating moieties on the wingtip groups, which can even be further NHCs. In this way a plethora of bi- and polydentate NHC ligand scaffolds has been synthesised up to now and a selection is shown in Scheme 5.[20-25] Especially the multidentate NHC ligands give rise to a broad variety of structures of the resulting metal complexes, ranging from simple mononuclear square planar complexes to multinuclear molecular boxes or helices.[26-28]



Scheme 5: Selection of some bi- and polydentate NHC-ligands.[20-25]

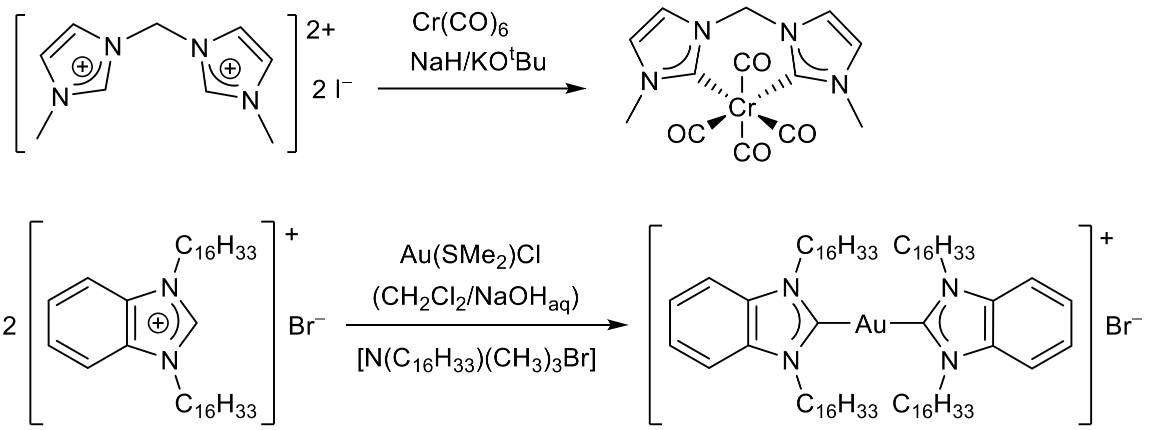
NHC ligands can also be combined with basically any other ligand motif or functional group depending on the desired purpose. As there are countless possibilities of such combinations, only a small selection will be shown in the following (see Scheme 6). As the first example, polydentate NHC ligands can not only be constructed purely from NHC ligands (as shown in Scheme 5), but also from a combination of NHC moieties and other coordinating groups, e.g. N-donors (see Scheme 6, first row).[29-31] But functional groups can also be utilised for other purposes than coordination, like the immobilisation on a solid support material, which brings about several advantages for practical applications.[32] Suitable groups for grafting the complex to a solid support can both be introduced on the wingtip substituents and on the backbone (see Scheme 6, second row).[33-35] The functional groups can also be chosen to tailor NHC ligands for specific groups of metals, which otherwise form only labile bonds to NHCs, like for example lanthanides; in this case, hard anionic groups which form strong bonds to hard lanthanide centres can help as tethers to stabilise the NHC-metal bond.[36] This concept has been realised e.g. by introducing alcoholate or aryloxide (phenolate) functionalities (see Scheme 6, third row).[37-39] As the final example, substituents can also be used to introduce chiral information (see Scheme 6, fourth row).[40-42] This small selection underlines the versatility of the class of NHC ligands and why they have found their way into so many fields of coordination chemistry.



Scheme 6: Examples of functionalized NHC complexes, first row: polydentate NHC/N-donor ligands.[29-31] Second row: NHC ligands with functional groups for immobilisation.[33-35] Thirds row: alcoholate/aryloxide-tethered NHC ligands.[37-39] Fourth row: chiral NHC ligands.[40-42]

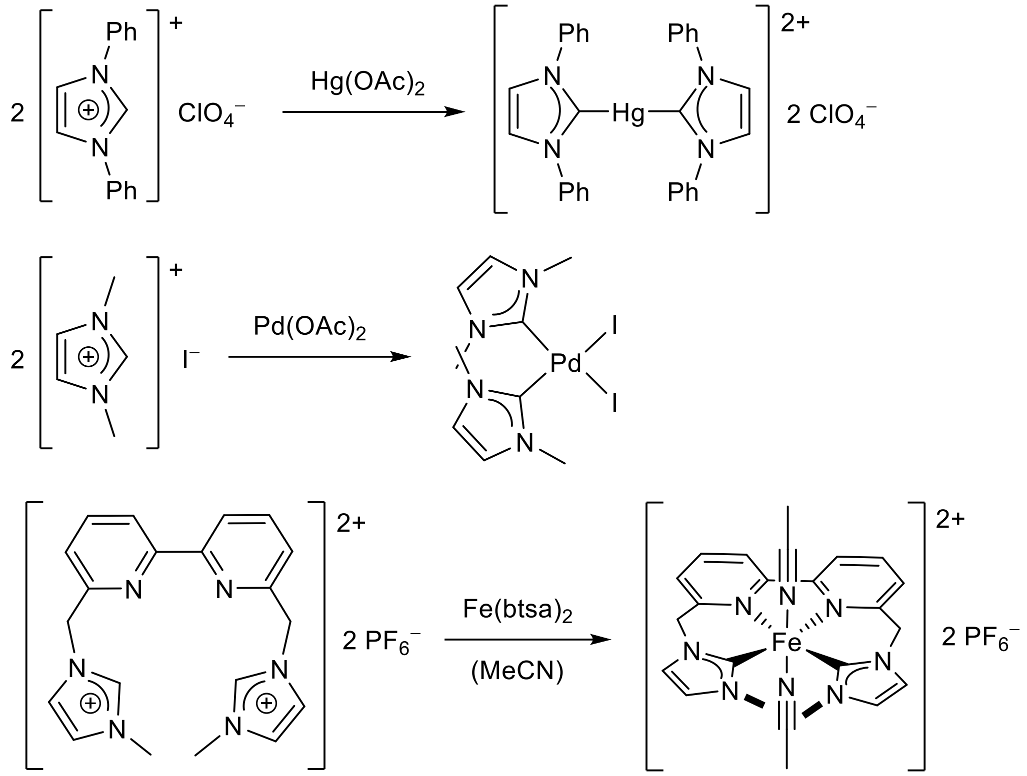
1.1.2 Synthesis

The vast majority of NHC complexes is synthesised from the respective imidazolium ions as these are usually the easiest accessible precursors.[6] [7] [43] The carbene ligand is then formed by deprotonation of the acidic C-H bond by a base, for which there are generally two possibilities: Either an external base is used or an internal base, i.e. a ligand on the employed metal precursor that can serve as a base. Examples for the use of external bases are depicted in Scheme 7: For this route the metal precursor should bear ligands that can easily be replaced by the NHC, e.g. phosphines, cod (1,5-cyclooctadiene), CO or dimethyl sulfide.[43-45] In the second example in Scheme 7 (bottom) a phase transfer catalyst is necessary, which illustrates that this route is not without difficulties in some cases.[45] Furthermore, having to use two reactants (metal precursor + base) usually implies the formation or more by-products as compared to only one reactant in the case of an internal base.



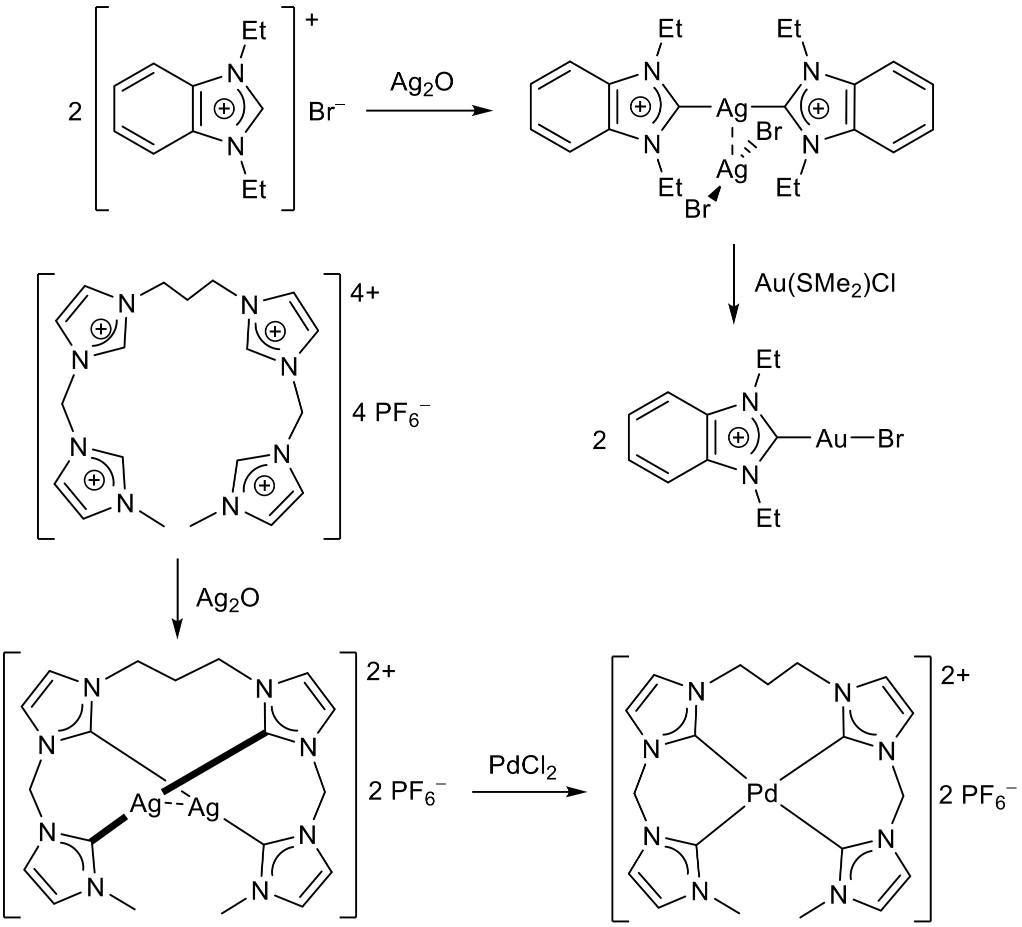
Scheme 7: Examples for syntheses of NHC complexes from imidazolium/benzimidazolium ions by use of an external base.[44,45]

Therefore, the internal base route is advantageous in many cases (see Scheme 8 for examples). This is also the strategy that was already used by Wanzlick, who used acetate ligands as the internal base (Scheme 8, top).[2] Besides acetate, alcoholates, acetylacetonate or amides (see Scheme 8, bottom) proved to be valuable bases, just to name some examples.[43] [46] Obviously, the base is ideally chosen to afford an easily separable corresponding acid. For this route, the choice of counterions of the imidazolium ion can be very significant: Halides (see Scheme 8, middle) tend to bind to the obtained metal complex, whereas this can be avoided by using non-coordinating anions (see Scheme 8, top and bottom). It can also be the case that an external base pre-coordinates to the metal and therefore acts as an in-situ-formed internal base.[43] [47] However, this is only interesting from the mechanistic point of view as the advantage of avoiding by-products is lost.



Scheme 8: Examples for syntheses of NHC complexes from imidazolium ions by use of metal precursors with internal bases.[2] [48] [46]

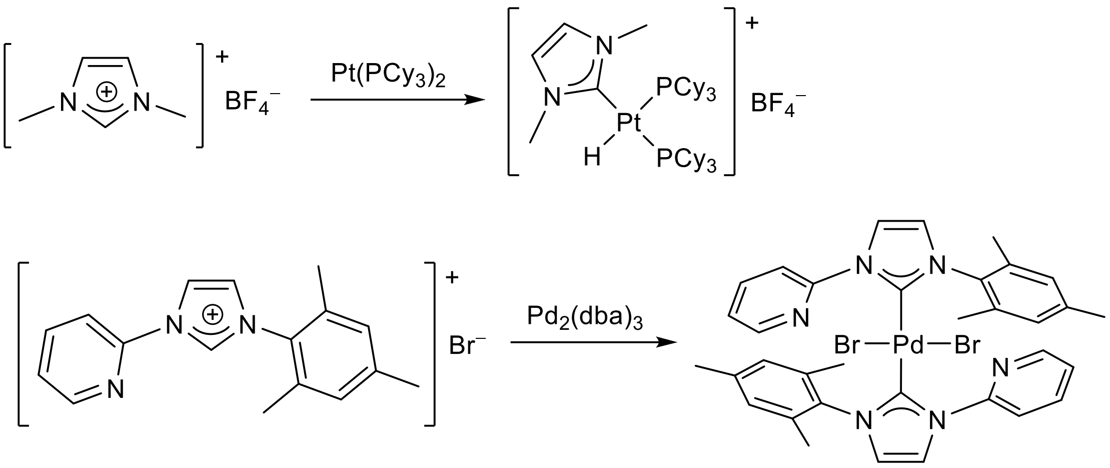
Another widely applicable synthetic strategy is the transmetalation from Ag-NHC complexes (see Scheme 9 for examples). It is based on the observation that the carbene bond of Ag-NHC complexes is rather labile as compared to many other transition metals; additionally, a suitable transition metal precursor should contain halide ligands to allow the formation of silver halide as another driving force and to ensure the quantitative precipitation of silver from the reaction mixture.[49,50] Other reasons for the success of this strategy are the stability and facile synthesis of the intermediate Ag-NHC complexes from the respective imidazolium ion and silver oxide – which is also another example for the internal base route and therefore counted among syntheses based on imidazolium ions (see Scheme 9).[49,50] Silver oxide is by far the most common precursor for the formation of Ag-NHC complexes, but other methods can be used as well, e.g. other basic silver salts as Ag(OAc) and Ag_2CO_3 or $NaOH_{aq}$, silver salt and a phase transfer catalyst.[50,51] The intermediate Ag-NHC complex does not necessarily need to be isolated (as in the examples in Scheme 9), but can also be formed in situ to directly transmetalate in a one-pot-reaction.[49,50] A limitation of this route are lanthanides and some early transition metals which form significantly weaker bonds to NHC ligands than Ag: In these cases, for example NHC-adducts of alkali metals (which are far more sensitive) can be employed as transmetalation agents.[52,53] Other metals can, of course, also form suitable NHC complexes for transmetalation, but none find nearly as widespread use as Ag.[50,51]



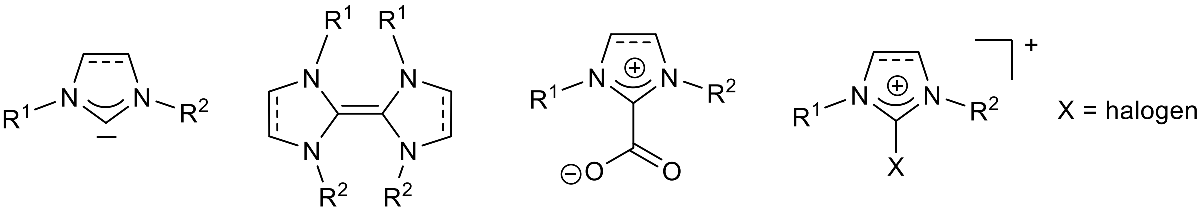
Scheme 9: Examples for syntheses of NHC complexes via transmetalation from Ag-NHC complexes.[49] [25] [27]

Another possibility to form NHC complexes from imidazolium ions is the direct activation of the acidic C-H bond without a base present (see Scheme 10 for examples).[54,55] As the examples show, this is limited to electron-rich metal precursors which are capable of undergoing an oxidative addition to the C-H bond, but nevertheless it is an interesting option.

As mentioned, imidazolium ions are the most common precursors for NHC ligands, but they are, of course, not the only compounds that can be used to form NHC complexes, as some selected examples show in Scheme 11.[6,7] First, NHC complexes can obviously be synthesized from isolable free carbenes.[6,7] Second, the dimerization products of NHCs (tetraaminoethylenes) can also serve as precursors for some metal compounds which can cleave the C-C double bond that connects the two NHC fragments.[56] Third, imidazolium-2-carboxylates can be decarboxylated in the presence of a metal complex to from NHC complexes.[57] As the final examples here, the C-X bond (X = halogen) of 2-halo-substituted imidazolium ions can undergo oxidative addition reactions with electron rich metals easier than described above for C-H bonds, so they can also be suitable NHC precursors.[58] There are more types of carbene adducts or imidazole derivatives that can serve as precursors for free NHCs or NHC complexes, but due to their rarer occurrence they will not be discussed here.[6,7] [43]



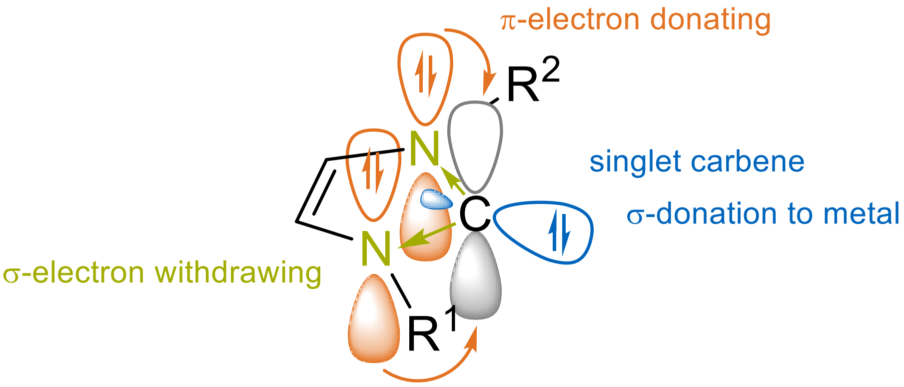
Scheme 10: Examples for syntheses of NHC complexes from imidazolium ions by direct activation of the acidic C-H bond.[54,55]



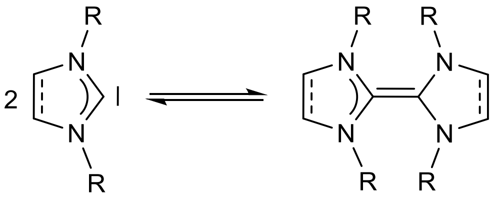
Scheme 11: Examples of precursors for the formation of NHC complexes other than simple imidazolium ions.[6,7]

1.1.3 Properties

Free NHCs have a singlet ground state with a formally sp^2-hybridised carbene-C.[3] [5,6] [8] The main reason for the stabilisation of the carbene-C is the π-electron donation by the adjacent N atoms, which simultaneously have a σ-electron withdrawing effect (see Scheme 12).[5,6] [8] [59] In the case of unsaturated NHCs, the aromaticity adds an additional small stabilisation.[8] [59] Cyclicity is not a necessary prerequisite for stability as is illustrated by the fact that also acyclic diaminocarbenes can be isolated as free carbenes.[8] [60] NHCs tend to dimerise and from tetraaminoethylenes/tetraazafulvalenes and the relation between free NHC and its dimer became known as the "Wanzlick-equilibrium" (see Scheme 13).[61] Therefore, in order to isolate a free NHC, bulky wingtip substituents (e.g. adamantyl in the case of Arduengo´s first isolated NHC) are usually employed to prevent dimerization, but they are not essential as some free NHCs have also been isolated without such bulky groups.[3,4] When coordinated to a metal, NHC ligands act mainly as σ-donors with only minor contributions of π-backbonding.[8] [59] However, in recent years a few studies showed that in some cases there can be significant π-backbonding, which actually influences the chemical behaviour of the complexes.[59] [62] In general, their bonding properties are very similar to phosphines – an analogy which was recognised early by Herrmann and pathed their way to applications in homogeneous catalysis (see below).[5] Determinations of bond dissociation energies were employed for a direct comparison of phosphines and NHCs and showed that at least for the investigated examples the NHC ligands exhibited stronger bonds to Ni(0) and Ru(II).[7]



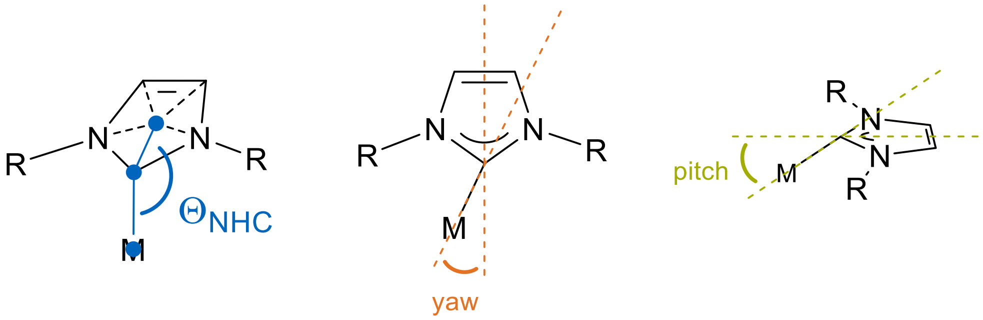
Scheme 12: Illustration of the electronic structure of an NHC ligand.



Scheme 13: General formulation of the "Wanzlick-equilibrium".[61]

As initially said, there are many ways to modify NHC ligands, so a number of parameters has been developed to quantify their steric and electronic properties and compare them to other ligands and among themselves. For the steric demand of an NHC ligand, the buried volume (usually given in percent: $\%V_{\mathrm{Bur}}$) was introduced, which visually corresponds to the fraction of a hypothetical sphere around the metal which is occupied by the ligand.[63,64] For the donor strength of NHC ligands, the Tolman electronic parameter (TEP) has established itself as the most common measure: It corresponds to the stretching vibration wave-number of a *trans*-located CO ligand.[7,8] [65] Whereas the initial model for the determination of TEPs were Ni(0) complexes of type $[\mathrm{Ni(CO)_3L}]$, toxicity and stability issues have led to these being replaced by Ir(I) and Rh(I) complexes, *cis*-$[\mathrm{IrCl(CO)_2L}]$ and *cis*-$[\mathrm{RhCl(CO)_2L}]$.[7] [65-67] Other parameters based on redox potentials and ^{13}C NMR shifts have been developed as well, but have not found as widespread use as the TEP.[7] [68,69]

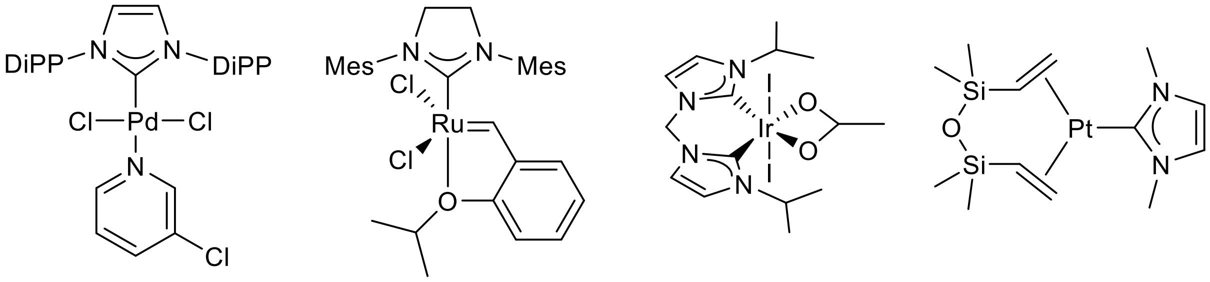
In order to describe distortions of the NHC-metal bond, the NHC tilting angle Θ_{NHC} has been introduced, which is defined as the angle between metal, carbene-C and the centroid of the NHC (see Scheme 14).[70] The ideal coordination geometry then corresponds to $\Theta_{\mathrm{NHC}} = 180°$ and more than 80% of all NHC complexes are within 10° deviation from this value.[70] The distortion can be divided into two fractions: in-plane ("yaw angle") and out-of-plane ("pitch angle") as illustrated in Scheme 14.[70] Among the two types of distortion, the pitching displacement has a considerably flatter potential energy surface than yawing, so the in-plane (yawing) displacement is energetically more unfavourable.[70]



Scheme 14: Graphical definition of angles used to describe the distortion of NHC-metal bonds.[70]

1.1.4 Applications

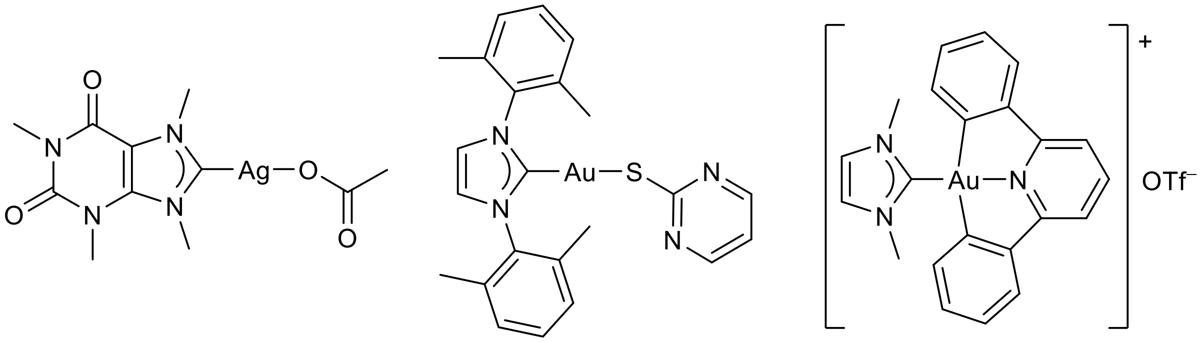
In recent years, NHCs have found applications in various fields of chemical research, but the widest of these is still catalysis.[8] The first catalytic application of NHC complexes was published in 1995 by Herrmann, who employed Pd-NHC complexes in the Heck reaction.[20] This report, their stability and structural versatility and the aforementioned analogy between NHCs and phosphine ligands were the foundation for their further development, in which they rose to one of the most abundant classes of steering ligands that can now be encountered in basically every field of homogeneous catalysis.[5-8] A small range of representative example catalysts for different applications is depicted in Scheme 15 and two of them will be discussed in more detail. To start with, the field of Pd-catalysed cross coupling reactions with its high synthetic relevance has been one of the main playfields for the development of novel NHC-based catalysts and produced a wide variety of highly active Pd-NHC complexes even for challenging substrates.[71,72] It was also the field, in which the PEPPSI (pyridine-enhanced precatalyst preparation, stabilisation and initiation) concept first came up: A substituted pyridine-ligand *trans* to the NHC was not only found to be beneficial for the stability of the precatalyst, but also to be easily cleaved upon activation of the precatalyst by reduction of Pd(II) to Pd(0) (see example first from the left, in Scheme 15).[73] Another field, in which great improvements were achieved by the introduction of NHC ligands, is olefin metathesis: Replacing a phosphine ligand in the original Grubbs-type metathesis catalysts by an NHC increased the substrate affinity by several orders of magnitude.[8] Similar to the PEPPSI concept, a labile group *trans* to the NHC was found to be advantageous as can be seen in the Hoveyda-Grubbs catalyst shown in Scheme 15 (second from the left).[8] [74] The strong *trans*-effect caused by the high σ-donor strength of NHCs is therefore seen as another factor for their success as it facilitates the formation of free coordination sites for substrate binding.[75,76] There are also some types of functionalisations to point out which are particulary interesting for catalysts to further tailor their properties. One is the immobilisation of NHC complexes to achieve the heterogenisation of homogeneous catalysts in order to facilitate the separation



Scheme 15: Examples for NHC complexes applied in various catalytic transformations (from the left: cross coupling, olefin metathesis, transfer hydrogenation, hydrosilylation).[73,74] [77,78]

of products and the recycling of the catalyst.[32] Other important strategies are the introduction of ionic groups (e.g. sulfonates) to render NHC complexes water-soluble and the use of chiral NHC complexes for asymmetric catalysis.[8] [79] Besides NHC metal complexes, free NHCs have also gained a lot of attention as organocatalysts.[8] The foundation for their utilisation in this field is the nucleophilic reactivity of free NHCs, which enables them to attack electrophilic C atoms in groups as esters, aldehydes or Michael-acceptors and thus activate them for further transformations.[80,81] Possible reactions then are for instance transesterifications, Stetter reactions, cycloadditions or cross-benzoin reactions.[8] [80,81]

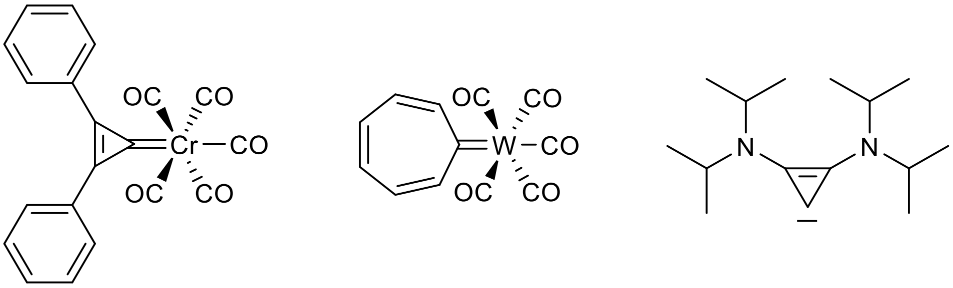
Another field of growing interest aside from catalysis are medicinal applications of NHC complexes, particularly of Ag and Au (see examples in Scheme 16).[8] Ag-NHC compounds were found to be effective as antimicrobials, but in this case not the complexes themselves, but silver ions liberated upon decomposition are seen as the active species, so for maximum efficiency the stability of the complexes under physiological conditions can be adjusted towards a slow long-term release of silver ions.[82-85] Antimicrobial activity was also observed for some Au-NHC complexes, but they have drawn even more attention as antitumor agents.[84-86] As one of their targets, mitochondrial thioredoxin reductase (TrxR) was identified and the NHC ligand is currently seen as a tool to tune both the lipophilicity of the Au complex, which influences the ability to pass mitochondrial membranes, and the selectivity to bind to the selenocysteine active sites of TrxR.[83,84] [85] [87] In this context, the luminescence of various Au-NHC complexes is another interesting feature as it can be utilised to study the Au-uptake and distribution in cells.[88] Luminescent materials are also a field of interest for NHC complexes in general, showing promise for organic LEDs, solar cells or water splitting.[89] Further applications of NHC complexes to be mentioned are liquid crystals, organometallic polymers as building units for molecular electronics, functionalised metal-organic frameworks (MOFs), and molecular recognition.[8] [45] [90-93]



Scheme 16: Examples for NHC complexes applied in medicinal research as antimicrobials or anticancer agents.[82-85]

1.2 Carbocyclic Carbenes

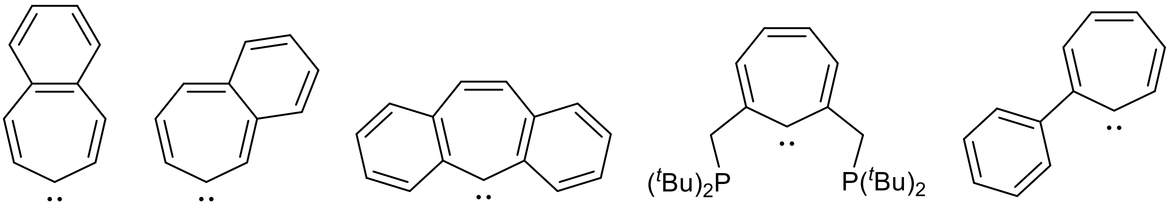
The year 1968 does not only mark the beginning of the history of N-heterocyclic carbenes, but also the discovery of the first carbocyclic carbene complex pentacarbonyl(2,3-diphenylcyclopropenylidene)chromium(0) by Öfele (see Scheme 17, left).[94] The first complexes of cycloheptatrienylidene, which is the class of carbocyclic carbenes relevant in this thesis, were reported ten years later by Jones and co-workers (see Scheme 17, middle).[95] Similar to NHCs, also a free carbocyclic carbene 2,3-bis(diisopropylamino)-cyclopropenylidene was isolated in 2006 by Bertrand and co-workers (see Scheme 17, right) and the corresponding class of amino-substituted cyclopropenylidene ligands became known as bis(amino)cyclopropenylidenes (BACs).[96,97] Although in many respects similar to their N-heterocyclic relatives (see properties below), carbocyclic carbenes have never gotten as much attention in chemical research, so there is still a lot of room for further development and their full potential is certainly not unlocked yet.



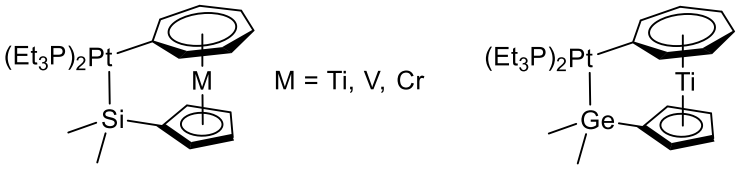
Scheme 17: First carbocyclic carbene complex by Öfele (left), one of the first cycloheptatrienylidene complexes by Jones (middle) and first isolated free cyclopropenylidene derivative by Bertrand.[94-96]

1.2.1 Structures

The two most important classes of carbocyclic carbenes are cyclopropenylidenes (CPrs) and cycloheptatrienylidenes (CHTs), the latter of which will be the main focus of this introduction.[98] As a drawback of carbocyclic carbenes in comparison to NHCs, the scope of available substitutions is rather limited so far: In the case of CHTs, some benzannulated systems, one example of a phosphine-functionalised pincer ligand and one example of a mono-*α*-substituted ligand have been reported (see Scheme 18).[98-100] Notably, there is an isomeric form of cycloheptatrienylidene, cycloheptatetraene (CHTE), which is also capable of coordinating to metals, but no interconversion of these binding modes has been observed yet.[98] Ligands of the CHT analogous formula C_7H_6 are also able to form heterobimetallic complexes by binding both in the ligand plane and as a *π*-complex (see Scheme 19), but in these cases neither the bond lengths nor the ^{13}C NMR shifts of the “carbene-C” are in the typical range, so these ligands cannot be regarded as actual CHTs.[98] [101-103] Metals known in combination with CHT ligands are only Cr, Mn, Fe, W, Ru, Ir, Pd, Pt and Au – another evidence that their chemistry is definitely underdeveloped in comparison to NHCs.[98] [104]

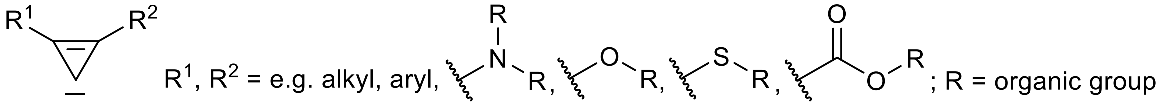


Scheme 18: Known substituted CHT ligand systems.[98-100]



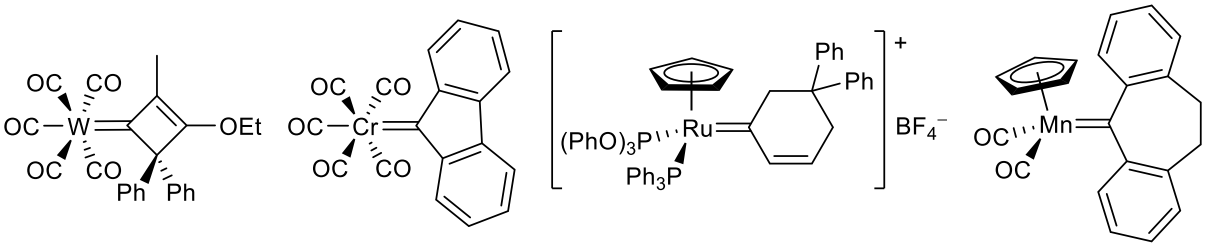
Scheme 19: Examples of heterobimetallic complexes featuring C_7H_6 ligands which do not behave as typical CHTs.[101-103]

For CPr ligands, both the scope of available metals and ligand substitutions are considerably broader than for CHTs and an overview of reported ligand variations is given in Scheme 20; it should also be noted that an unsubstituted CPr ligand (i.e. $R^1 = R^2 = H$) is unknown.[98] [105] The drawback of the functionalisations of CPr ligands is that the substituents point away from the metal centre, so their influence is rather limited in terms of sterics.[98]

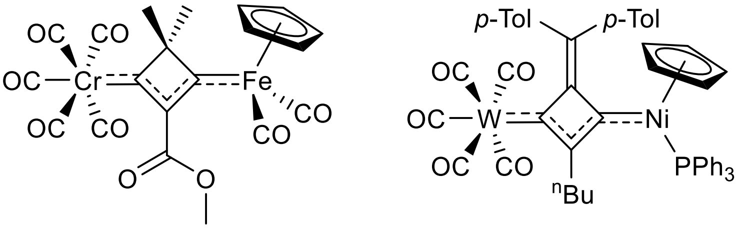


Scheme 20: Known substituted CPr ligand systems.[98]

Aside from CHTs and CPrs, carbocyclic carbene complexes have also been synthesised with a range of ligands that involve carbocycles of other sizes from four to seven, representative examples for which are depicted in Scheme 21.[106-109] Unlike CHTs and CPrs, the carbene-C is not incorporated in an aromatic ring in these cases, which leads to different properties of these classes of carbocyclic carbenes.[98] The most numerous class among these non-aromatic carbocyclic carbenes are the cyclobutenylidenes, which are fairly versatile with respect to their substitution patterns and can even serve as a bridging dicarbene moieties between two metals (see examples in Scheme 22).[98] [110,111]



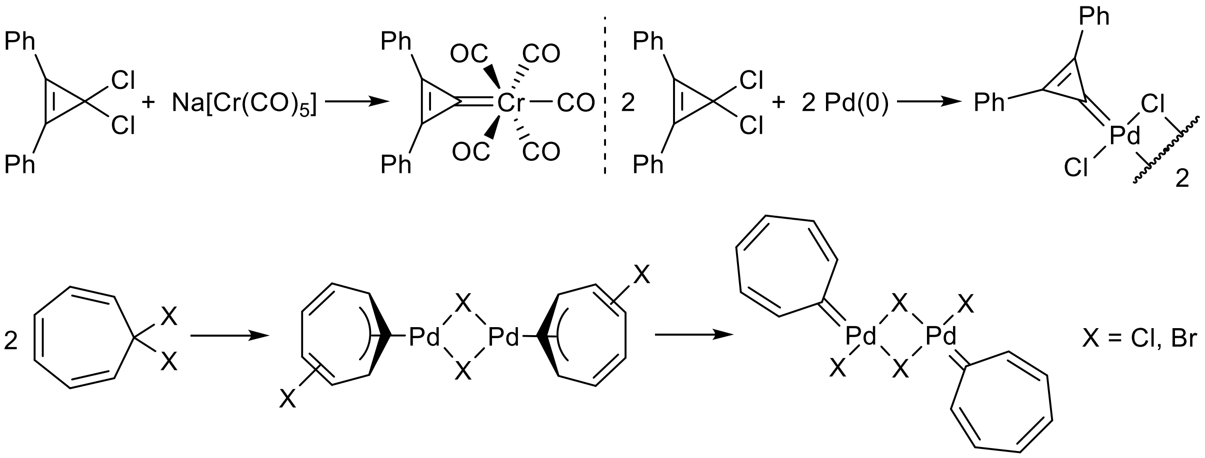
Scheme 21: Examples of complexes bearing carbocyclic carbene ligands of different ring sizes other than CPrs and CHTs.[106-109]



Scheme 22: Examples for heterobimetallic complexes with bridging four-membered carbocyclic carbene moieties.[110,111]

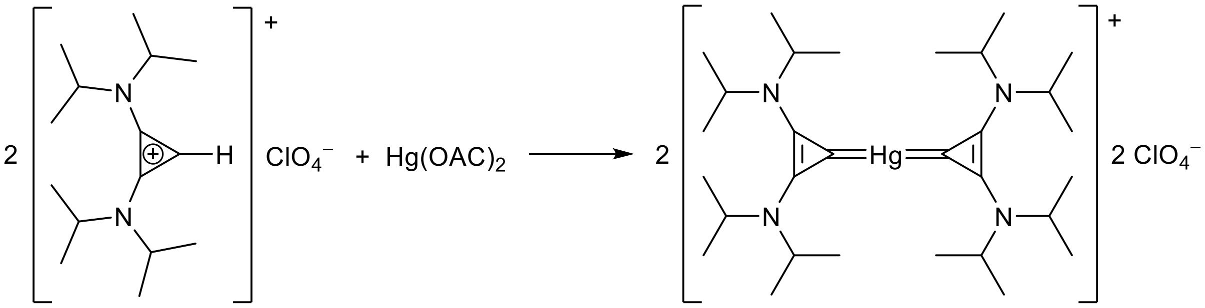
1.2.2 Synthesis

In contrast to NHC complexes, for which imidazolium ions are a universal precursor, suitable for the vast majority of syntheses (see above), carbocyclic carbene metal complexes require different synthetic strategies depending on the target ligand and the metal involved. The strategy employed by Öfele in the synthesis of the first CPr complex was based upon the oxidative addition of a geminal dihalide (the structure of which is actually questionable as explained later) to sodium pentacarbonylchromate (see Scheme 23, top left).[94] This reaction is also viable for other electron-rich metal precursors or metal powders, which are capable of performing an oxidative addition, in particular for Pd(0) (see Scheme 23, top right).[98] [112] The analogous strategy was applied to synthesise Pd-CHT complexes and in this case an intermediate of the reaction could be isolated, in which the seven-membered rings still bear one chloro-substituent and are bound in an allyl mode, indicating that the second step of the reaction is the formation of the carbene bond by insertion of Pd(II) into the C-Cl bond (see Scheme 23, bottom).[113] Concerning Pd complexes, it proved to be advantageous to use Pd(0) complexes like $Pd_2(dba)_3$ instead of Pd metal.[114,115]



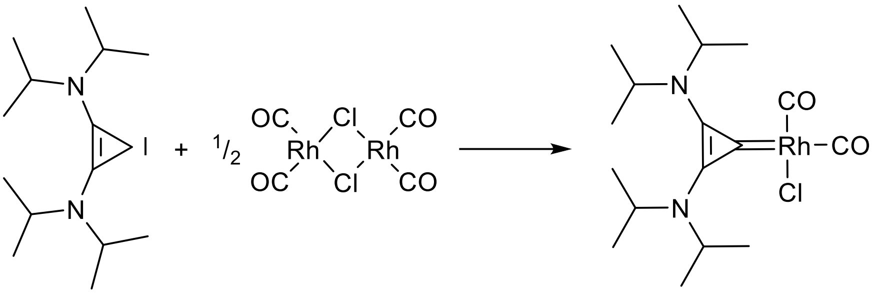
Scheme 23: Examples for the synthesis of CPr and CHT complexes from geminal dihalide precursors (questionable structure as explained later), including an isolated intermediate (for X = Cl) in the latter case.[94] [112,113]

The strategy most similar to NHC complex synthesis is the deprotonation of cyclopropenium ions in the presence of a metal precursor as illustrated by the example in Scheme 24.[116] In the same way, free CPrs can be obtained in the absence of a metal, if the substitution pattern allows a stable free carbene.[96] Substituted cyclopropenium ions with a functional group (Cl or OEt) instead of a proton are also viable CPr-precursors.[98] It should be noted that up to now no successful deprotonation of a tropylium ion to form a CHT complex has been reported, so at the moment this strategy is limited to CPr systems.



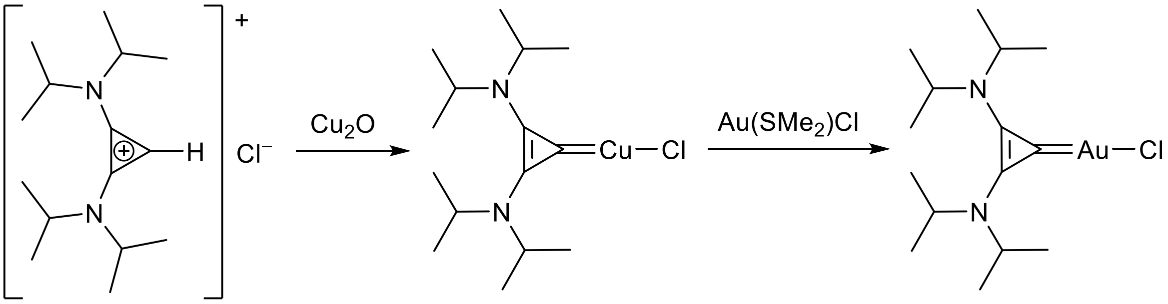
Scheme 24: Example for the synthesis of a CPr complex by deprotonation of the respective cyclopropenium ion.[116]

Not very much unlike the route before, during which the carbene is generated in situ, CPr complexes can also be prepared from free carbenes (see example in Scheme 25).[97] In this reaction, CPr can either cleave dimeric metal precursors or replace other ligands like phosphines, amines or cod.[97] Inherently, this strategy is limited to BACs or potentially similar systems, which form isolable carbenes.[98]



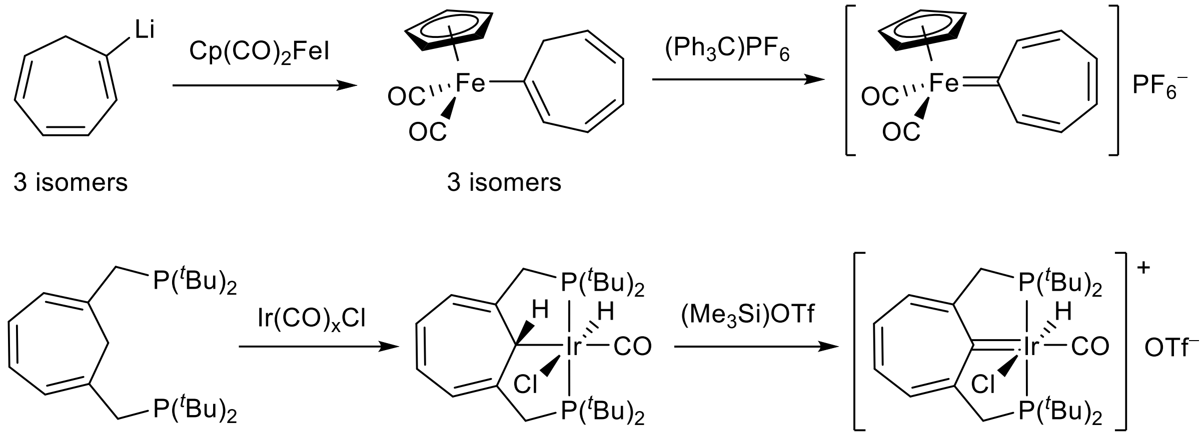
Scheme 25: Example for the synthesis of a CPr complex from the respective free carbene.[97]

Another strategy very similar to NHC chemistry is the recently reported transmetalation of BAC ligands by a Cu complex, which can be synthesised from the respective cyclopropenium ion and copper(I) oxide (see Scheme 26).[105] Suitable metal precursors for the transmetalation route should ideally bear a labile ligand (e.g. cod) as stated for the free CPr route, but an advantage in comparison to that route is the air- and moisture-stability of the Cu-transmetalation reagent.[105]



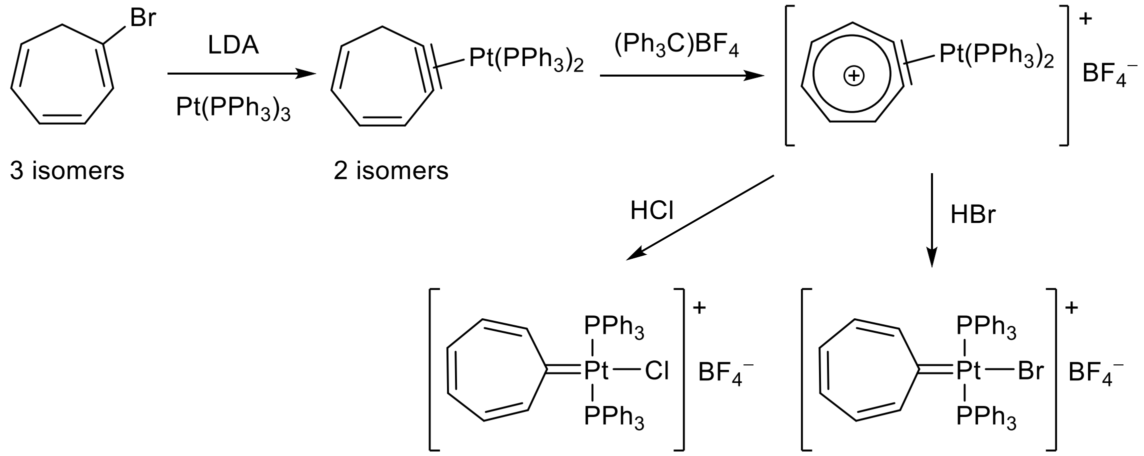
Scheme 26: Synthesis of a Cu-BAC complex and its application as transmetalation agent.[105]

The next route, which was used in the synthesis of the first CHT complexes by Jones, is the abstraction of a hydride from a metal-cycloheptatrienyl complex obtained by transmetalation via a lithium cycloheptatrienyl reagent (see Scheme 27, top).[95] The Li-transmetalation agent can either be obtained from different bromocycloheptatriene isomers or from 1-(trimethylstannyl)-cycloheptatriene, where the latter was found to significantly improve the yield of the final product.[98] Another interesting variation was published for a very specific example: Starting from a bis-phosphine functionalised cycloheptatriene, a direct C-H activation could be performed by an Ir(I) complex yielding the necessary cycloheptatrienyl intermediate for the subsequent hydride abstraction (see Scheme 27, bottom).[99] [117] Hydride abstraction is also a viable strategy for the synthesis of cyclobutenylidene complexes.[98]



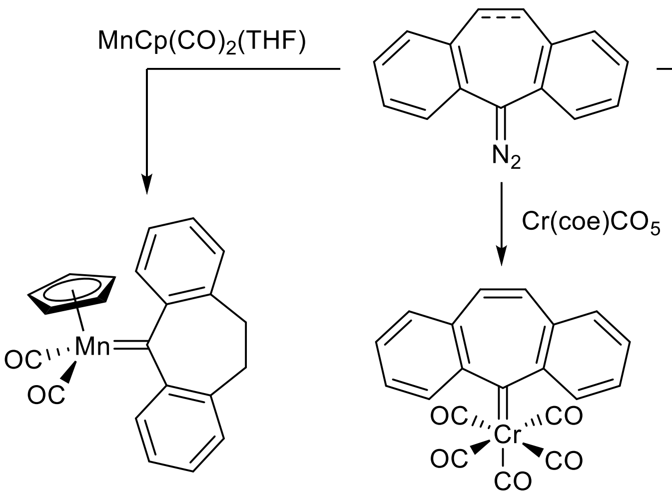
Scheme 27: Synthetic strategy used by Jones for the synthesis of the first CHT complexes (top) and synthesis of a phosphine-pincer-CHT complex with a modified preparation of the cycloheptatrienyl intermediate.[95] [99] [117]

Another very special sequence proceeds via protonation of a cycloheptadienynylium/ tropynylium-Pt complex, which seems to prompt an oxidation of Pt and the formation of a CHT ligand (see Scheme 28).[118] Notably, the products can also be obtained by the hydride abstraction route described above.[119]



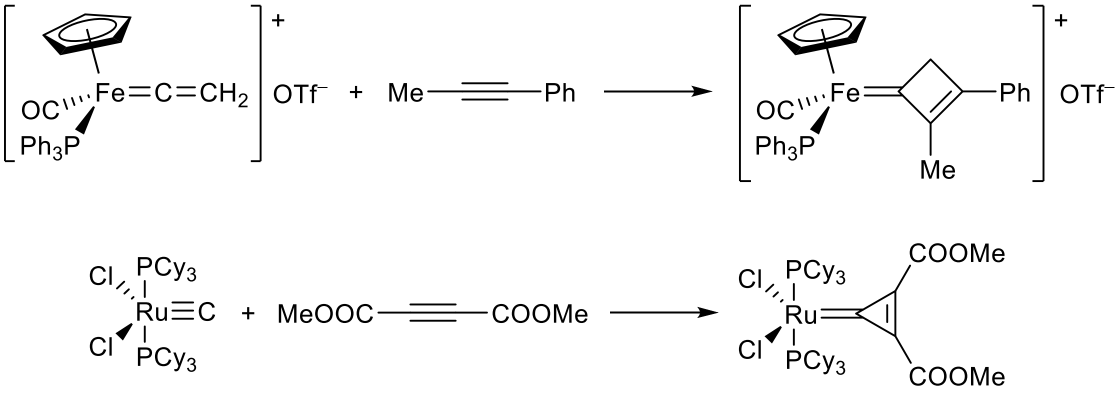
Scheme 28: Reaction sequence for the preparation of CHT complexes via a tropynylium complex.[118]

A more general route is based on diazo-precursors, examples for which are depicted in Scheme 29.[109] [120,121] This route has not only been used both for benzannulated CHT ligands and non-aromatic seven-membered ring carbenes as shown in Scheme 20, but is also viable for carbocyclic carbenes of other ring sizes.[98] As mentioned for many syntheses, the metal precursor should bear ligands which are easily replaced by the carbene formed upon cleavage of dinitrogen from the diazo-precursor.[98]



Scheme 29: Examples for the synthesis of carbocyclic carbene complexes via the diazo-route.[109] [120,121]

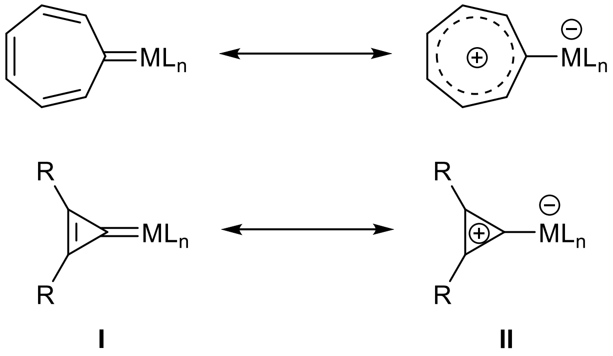
A totally different strategy is represented by building up the ligand carbocycle “on-site”, i.e. directly on the metal, which is the main route to cyclobutenylidene complexes.[98] In this case, the carbocycle is formed by a cycloaddition reaction of a substituted acetylene to a vinylidene or allenylidene complex (see Scheme 30, top).[98] [122] A cycloaddition reaction has also been reported between a carbido complex and a substituted acetylene leading to a CPr complex (see Scheme 30, bottom).[123] Besides the synthetic strategies presented so far, a few more exist, which mostly pertain to the less important non-aromatic carbocyclic carbene complexes and therefore will not be discussed here; reference [98] gives an excellent overview of the reported synthetic routes.



Scheme 30: Examples for the on-site synthesis of carbocyclic carbene complex by cycloaddition reactions.[122-123]

1.2.3 Properties

There are essentially two groups of carbocyclic carbene complexes with different properties: Those which are aromatic like CHTs and CPrs, and non-aromatic carbocyclic carbenes. The latter mostly behave as Schrock-type carbenes if they do not bear specific substituents that would effect a Fischer carbene character.[98] More interesting in the context of this work are CHTs and CPrs, in which the carbene-C is stabilised by the incorporation into an aromatic ring as illustrated by resonance structure **II** in Scheme 31.[98] Several investigations have shown this resonance form to be predominant. Comparison of the stretching vibrations of [W(CHT)(CO)$_5$] to similar complexes indicates only weak *π*-backbonding to the CHT ligand, which is further supported by measurements of the dipole moments.[95] [124] An evaluation of all reported crystal structures of (unsubstituted) CHT complexes shows that the seven-membered rings are planar with very similar C-C bond lengths, which further corroborates the idea of aromatic carbocycles.[98] [100] [104] [113] [115] [119] [125-127] Finally, the high downfield shift of the CHT NMR signals reported in all relevant references also agrees very well with the positive formal charge of the aromatic ring in **II**. For convenience, however, resonance structure **I** is most commonly used in literature and this will also be adopted here. These statements made for CHT complexes also apply to CPr systems, where it has to be said that in a direct comparison *π*-backbonding is generally stronger in CPr complexes, so effectively they act as weaker donors.[98] [124] [128]



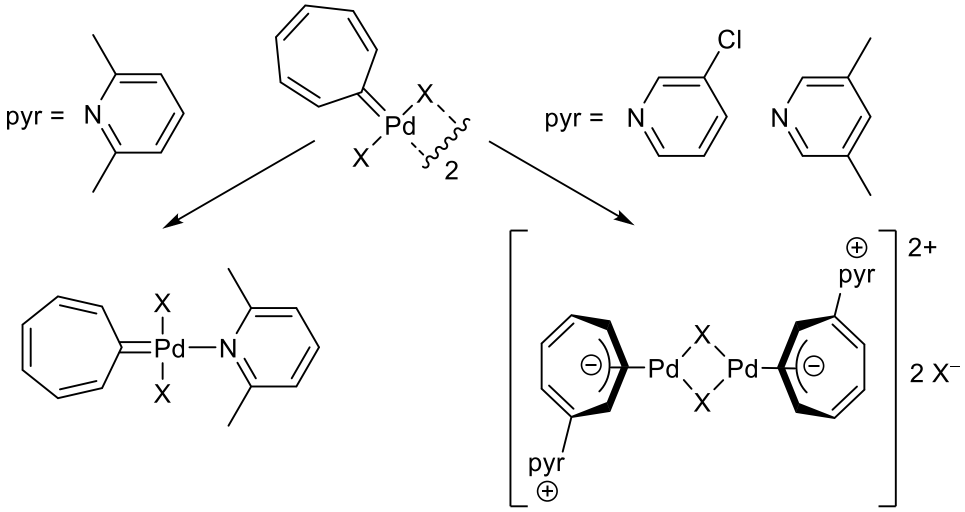
Scheme 31: Key resonance structures of CHT and CPr complexes.

From the above bonding properties, it can be concluded that CHT and CPr ligands mainly act as *σ*-donors which makes them very similar to NHC ligands (see above): Indeed it has been observed that the metal-carbene bond lengths and the influence on the bond lengths of *trans*-located ligands exerted by these ligand classes are very similar.[98] [121] Another similarity is the usually very high stability of the complexes formed with these carbene ligands.[98] [113] As mentioned, free carbenes have been isolated both from the classes of NHCs and CPrs and a singlet ground state has been established in both cases.[3] [96] In contrast, a free CHT has not been isolated so far, so the C_7H_6 system was subject to intensive theoretical studies, which concluded that the absolute minimum on the potential energy surface of C_7H_6 is neither singlet nor triplet cycloheptatrienylidene, but instead cycloheptatetraene.[129-131] For the less favourable cycloheptatrienylidene, theoretical predictions did not agree on whether the singlet or triplet state would be more stable, but more studies argue in favour of the triplet.[129-132] Experimentally, low temperature matrix ESR spectroscopy studies indeed detected triplet cycloheptatrienylidene as a meta-stable species upon photolysis of diazocycloheptatriene.[133,134] Furthermore, a triplet ground state was also found for dibenzo[a,d]cycloheptatrienylidene (third from the left in Scheme 18).[135] Concerning the latter, it is also noteworthy that it does not behave as a classical CHT when coordinated to a metal, but tends more towards a diphenylcarbene (judging by carbene NMR shifts, bond lengths and IR spectroscopy of CO complexes), whereas monobenzannulated or other substituted CHT ligands are not significantly affected in their bonding by the derivatisation.[98] [100] [121]

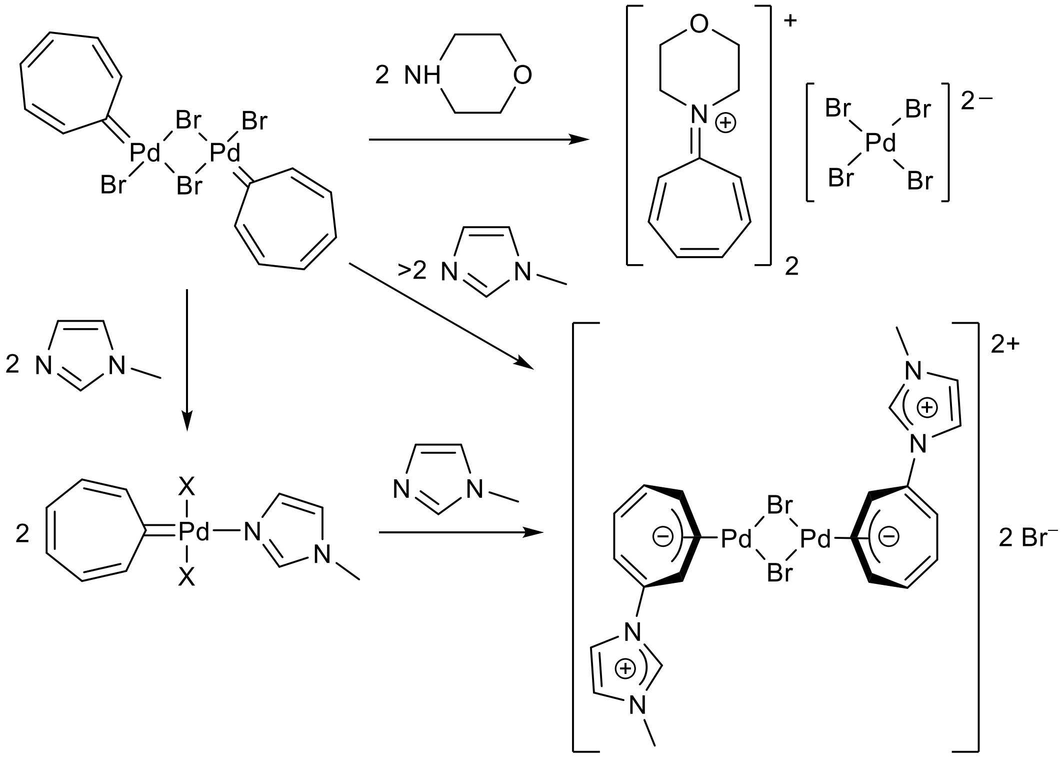
1.2.4 Reactivity of Pd-CHT Complexes towards Nucleophiles

NHC ligands attached to most transition metals are usually considered to be strongly bound and rather inert (exceptions are some early transition metals).[5-7] [36] So a feature that sets carbocyclic carbene complexes apart from NHC complexes is the reactivity of the carbene centre, even though it is by far not fully explored yet. Reported reactions are e.g. insertions into the carbene bond or carbocycle, cleavage of the carbene ligand by reagents like sulphur or iodine and exchange of the substituents on CPr complexes.[98] [104] Probably the most interesting reactivity has been observed for Pd-CHT complexes: By attack of pyridines on the carbene-C, the CHT ligand can be converted to a pyridinium-functionalised allyl-bound cycloheptatrienide ligand (see Scheme 32, right).[127] Only in the case of sterically hindered 2,6-lutidine, this reaction did not proceed and instead only a cleavage of the dimeric halide-bridged Pd complex was observed (see Scheme 32, left).[127] Similar dimer cleavage is also the type of reaction with acetonitrile or phosphines, where the latter prefer the *cis*-isomer in contrast to N-donors.[100] [113] [115] With methylimidazole, the nucleophilic attack on the carbene was reported to proceed only with an excess of nucleophile; using stoichiometric amounts only dimer cleavage was reported, but the *trans*-CHT/methylimidazole complex could still be reacted further by adding more methylimidazole (see Scheme 33, bottom).[127] A different reaction was observed with morpholine: In this case, the CHT ligand was cleaved off the metal, thus forming an aminotropylium/tropylideniminium ion with tetrabromopalladate as counterion

(Scheme 33, top right).[127] It was postulated that this reaction also proceeds via nucleophilic attack at the carbene-C and an intermediate allyl-cycloheptatrienide complex.[127] These reactions are important for two reasons. First, they open up a path to functionalised cycloheptatriene-based ligand systems and in particular imidazolium-substituents as NHC precursors could be interesting.[131] And second, when using Pd-CHT complexes in catalysis (see below) such reactions can take place in the presence of nucleophilic bases, which raises questions about the active species in such transformations.[127]



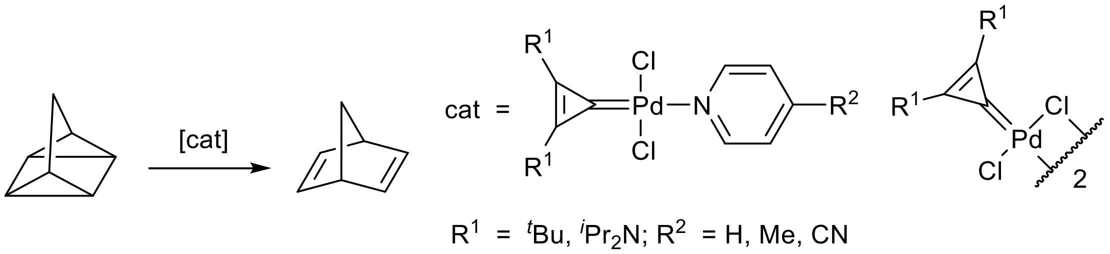
Scheme 32: Reported reactions of Pd-CHT complexes towards pyridines.[127]



Scheme 33: Reported reactions of a Pd-CHT complex towards methylimidazole and morpholine.[127]

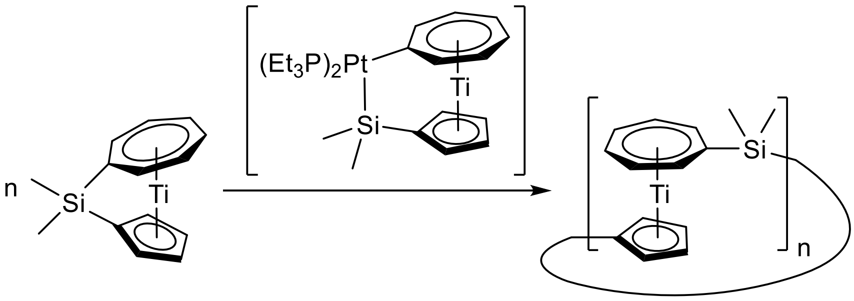
1.2.5 Applications

Their similarity to NHC ligands (see above) suggests that carbocyclic carbene ligands could be equally promising steering ligands and thus it is not surprising that carbocyclic carbene ligands have been employed in catalysis as well, although only to a very limited extent so far. In 1988, Yoshida and co-workers published the first catalytic application of Pd-CPr complexes in the isomerisation of quadricyclane to norbornadiene (see Scheme 34).[136] Mechanistic investigations indicated that the active species is a Pd complex with a free coordination site *trans* to CPr and therefore a correlation was drawn between the dissociation of the *trans*-pyridine ligand and the catalytic activity – a situation not very much unlike the PEPPSI-concept later introduced for NHC-based catalysts.[98] [136]



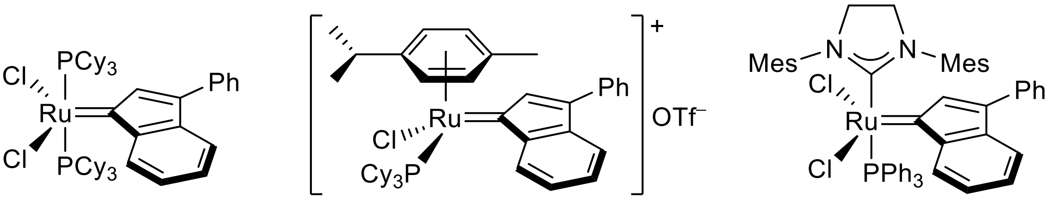
Scheme 34: First catalytic application of Pd-CPr complexes in the isomerisation of quadricyclane to norbornadiene.[136]

A rather special application has been reported for the type of non-classic heterobimetallic CHT complexes discussed before (Scheme 19): They are able to catalyse the ring opening polymerisation of related strained Si-bridged *ansa*-metallocenes (see Scheme 35).[137]



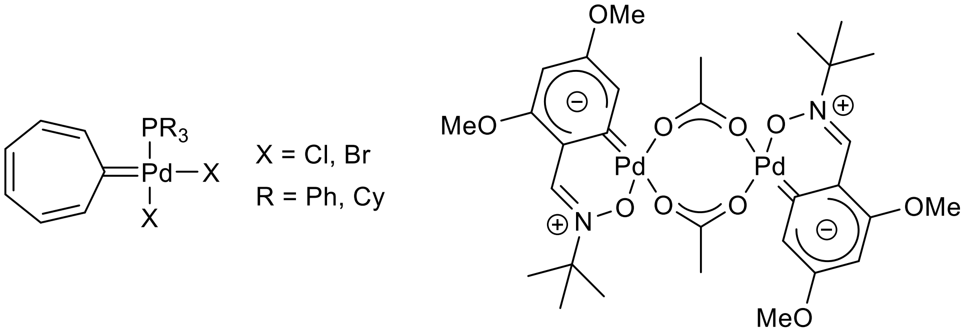
Scheme 35: Catalytic ring opening polymerisation of strained ansa-metallocenes.

A field in which carbocyclic carbene ligands have gained considerable attention, are metathesis reactions, as indenylidene ligands have been shown to act as possible replacement for the benzylidene ligand in the various generations of Grubbs-type Ru complexes (see examples in Scheme 36).[138-140] Such Ru-indenylidene complexes have been shown to be of comparable activity in several types of metathesis reactions, like cross metathesis (CM), ring closing metathesis (RCM) or ring opening metathesis polymerisation (ROMP).[139] [141] Benefits are their easy accessibility, robustness and high tolerance towards functional groups.[138,139] Furthermore, this class of catalysts is also active in addition reactions and hydrosilylations of alkynes.[139]



Scheme 36: Examples for Ru-indenylidene complexes active as metathesis catalysts.[138-140]

The first application of carbocylic carbene ligands in cross coupling reactions was reported by Herrmann and co-workers who used Pd-CHT complexes for Heck and Suzuki reactions (see example catalyst in Scheme 37, left).[113] This work highlighted that carbocyclic carbene complexes can be equal and in some cases even superior to established NHC (pre-)catalysts.[113] Pd-CPr complexes were also found to be active in C-C coupling reactions, but in comparison to the analogous CHT complexes slightly less efficient.[128] [142] The most efficient catalyst based on carbocyclic carbene ligands so far features six-membered rings with nitrone half-pincer groups (see Scheme 38, right).[143] The scope of catalytic reactions with Pd-carbocyclic carbene complexes was also expanded to C-N coupling (Hartwig-Buchwald reaction) and again CHT ligands proved to be superior to CPr ligands.[114,115] For the reactions with CHT and CPr ligands, no induction periods were observed, but no detailed studies on the



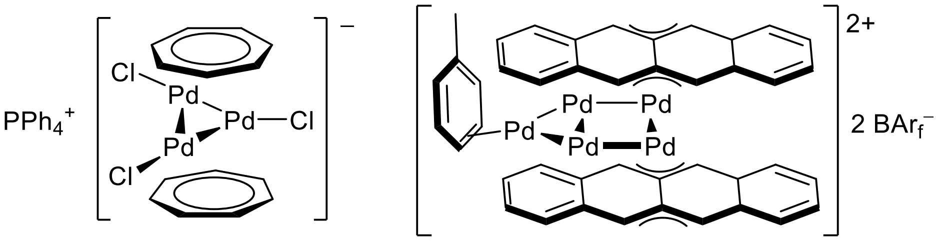
Scheme 37: Pd-CHT complexes first employed in cross coupling reactions (left) and most active carbocyclic carbene-based cross coupling catalyst so far (right).[113] [143]

active species have been performed yet, so it remains uncertain if the carbocyclic carbene ligand remains attached to Pd during the catalysis.[113] [115] [128] [142] With respect to the reactivity towards N-nucleophiles reported for CHT complexes, it is not unlikely that the active species is no longer a carbocyclic carbene complex, particularly in C-N coupling reactions or when a nucleophilic base or solvent is used.[127]

Finally, free BACs have also found applications in organocatalysis. Similar to NHC-based organocatalysis, substrates are activated by a nucleophilic attack (e.g. on a carbonyl group) causing an umpolung of their reactivity, which has so far been utilised in BAC-catalysed Stetter reactions, (aza)-benzoin reactions, conjugate addition reactions and aza-Morita-Baylis-Hilman reactions.[144-148] Attempts towards using chiral BACs for asymmetric catalysis yielded only moderate enantiomeric excess, which can most probably be attributed to the chiral substituents pointing away from the substrate binding site.[144,145] [148] Whereas the orientation of the substituents is clearly a drawback for asymmetric catalysis, it also makes BACs the sterically least hindered isolable carbenes, so they will certainly have a spot in further catalytic research.[148,149]

1.3 Pd Metal Sheet Sandwich Complexes

Pd metal sheet sandwich complexes are a relatively new area in organometallic chemistry as the first representatives were only published in 2006 by Murahashi, Kurosawa and co-workers (see Scheme 38).[150] The prototypic compound most relevant for further research consists of a triangular Pd_3 cluster sandwiched by seven-membered rings (Scheme 38, left) and with respect to the pioneer in this field complexes of this type will be called Murahashi complexes in the following. The motif of the pentanuclear metal sheet complex sandwiched by tetracene ligands (Scheme 38, right) has so far not been pursued any further than in the initial publication.

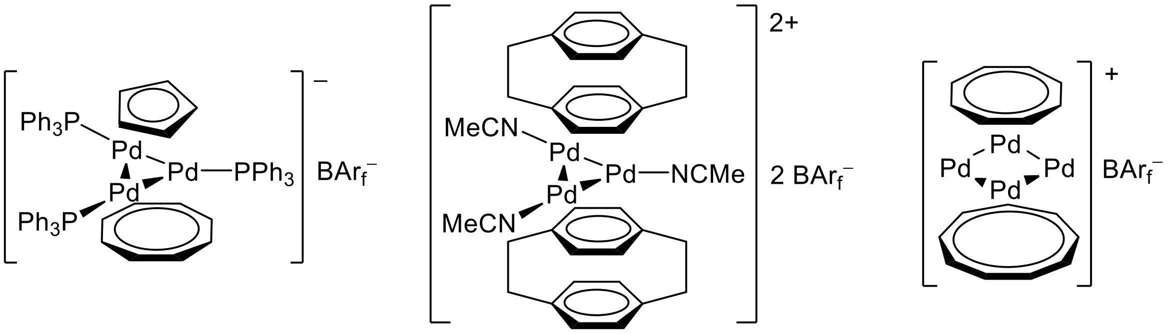


Scheme 38: The first Pd metal sheet sandwich complexes by Murahashi ($[BAr_f]^-$ = $[B(C_6F_5)_4]^-$).[150]

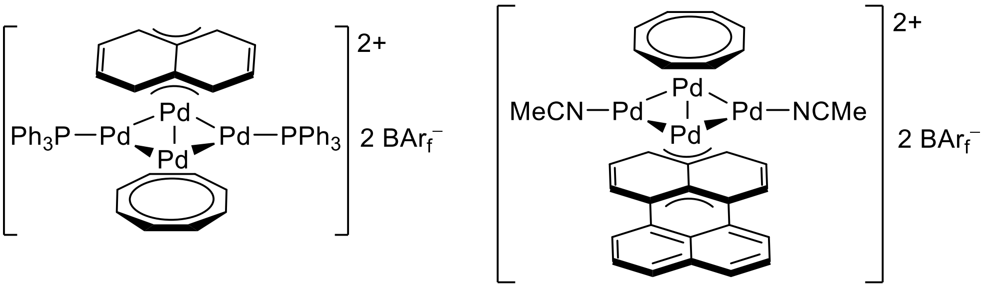
As this field is concerned with clusters, it is necessary to give a short definition. According to the IUPAC definition a cluster is “a number of metal centres grouped close together which can have direct metal bonding interactions or interactions through a bridging ligand, but are not necessarily held together by these interactions”.[151] However, this definition is coined for bioinorganic chemistry, so a more specific definition for metal clusters will be needed here. The first definition that found general acceptance was made by Cotton who defined “metal atom clusters” as “those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster”.[152] Whereas Cotton´s definition also includes diatomic groups, there have been arguments to define a minimum size of three atoms, which seems very reasonable as according to the non-scientific meaning of the word and according to the meaning of the word in other areas a pair would not usually be considered to be a cluster.[153-155] For the present work, another differentiation shall be made: In linear chains the metal atoms cannot really be considered as “clustered”, so for metal clusters in the narrower sense the condition shall be added to Cotton´s definition that each metal atom features multiple (i.e. at least two) metal-metal bonds. This also inherently excludes diatomic groups. According to this definition, metal triangles as in Murahashi complexes represent the smallest possible metal cluster unit. Linear metal clusters then should be regarded as a special case of metal clusters in the wider sense.

1.3.1 Structures

Besides the original trinuclear cluster sandwiched by seven-membered rings, a lot of variations of the Pd-sandwich-cluster motif have been synthesised so far, involving capping ligands of ring sizes from five to nine and Pd clusters of three and four Pd atoms (see examples in Scheme 39).[156-159] Four atoms seem to be the limit for a single carbocycle as capping ligand as the only example of a pentanuclear cluster so far requires polycyclic capping ligands (see Scheme 38, right).[150] But polycyclic systems can also serve as capping ligands for tetranuclear clusters (see examples in Scheme 40).[160,161]



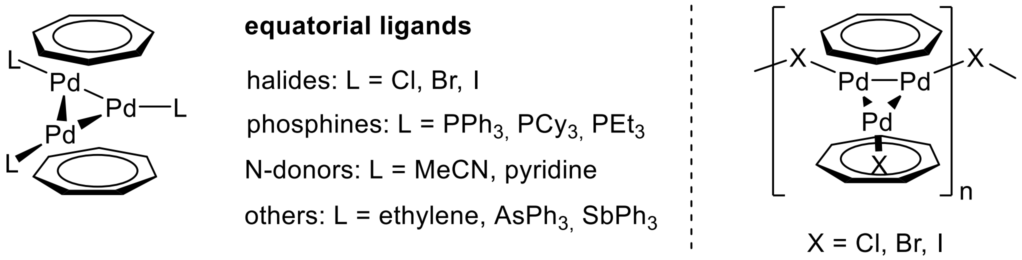
Scheme 39: Examples for derivatives of Murahashi complexes bearing capping ligands of ring sizes other than seven and cores of three and four Pd atoms.[156-158]



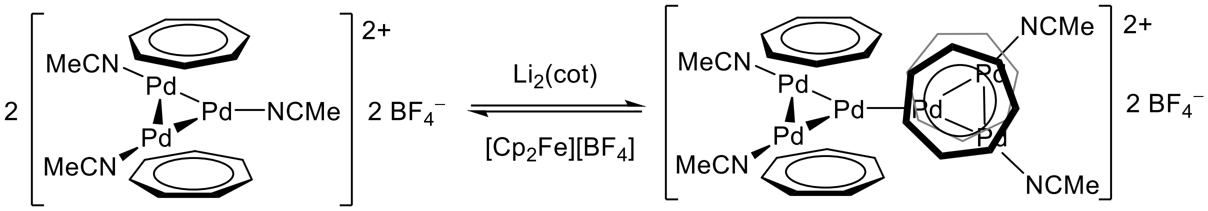
Scheme 40: Examples for tetranuclear Pd sandwich cluster complexes bearing polycyclic capping ligands.[160-161]

Not only the capping ligands, but also the equatorial ligands of Murahashi complexes can be varied: An overview of reported ligands is given in Scheme 41, left.[150] [161-164] In the trinuclear type, usually all equatorial positions are occupied, but in the case of tetranuclear complexes, a maximum of two Pd atoms bear a ligand in the equatorial plane and examples without any equatorial ligands are known as well.[157] [159-161] A very interesting phenomenon related to the equatorial ligands was reported by Hurst and co-workers, who were able to polymerise trinuclear sandwich complexes via bridging halides (see Scheme 41, right).[162] The group of Murahashi also demonstrated that sandwich cluster complexes can be coupled in the equatorial plane through metal-metal bonds by reaction with a strong reducing agent (see

Scheme 42); cleavage of the coupled dimer by an oxidant was also possible, so this reaction is reversible.[165]

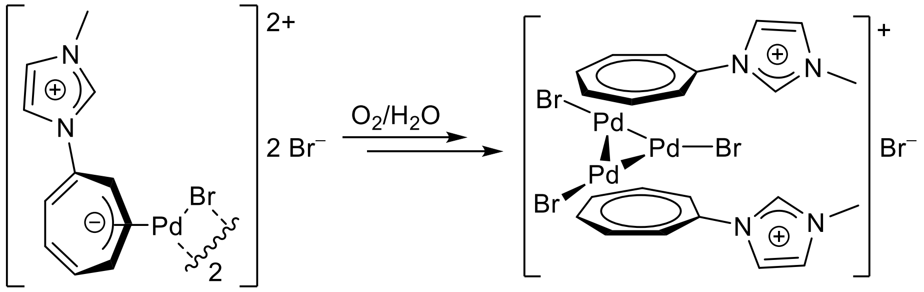


Scheme 41: Overview of reported equatorial ligands in Murahashi complexes (left) and structure of polymeric Murahashi complexes (right).[150] [161-164]



Scheme 42: Reversible reductive coupling of Murahashi complexes.[165]

Other than with Pd, metal sheet sandwich complexes have only been reported for Pt so far.[164] Interestingly, a method was also found to selectively construct mixed Pd_2Pt and $PdPt_2$ cluster sandwich complexes (see below).[166] Finally, a functionalised Murahashi complex has been discovered serendipitously by Kühn and co-workers: From an aqueous solution of an imidazolium-substituted allyl-bound cycloheptatrienide-Pd complex they obtained a Murahashi complex bearing imidazolium-groups on the seven-membered rings (see Scheme 43).[127] It was postulated that its formation proceeded via partial decomposition to Pd(0) which then reacted with the remaining complex and that therefore the addition of a Pd(0) source

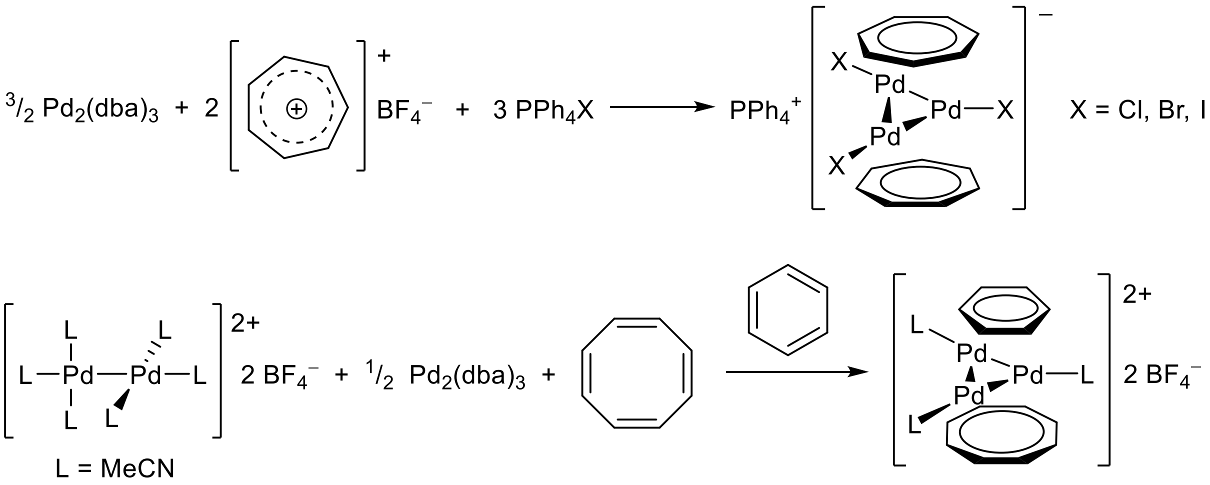


Scheme 43: Formation of the first functionalised Murahashi complex.[127]

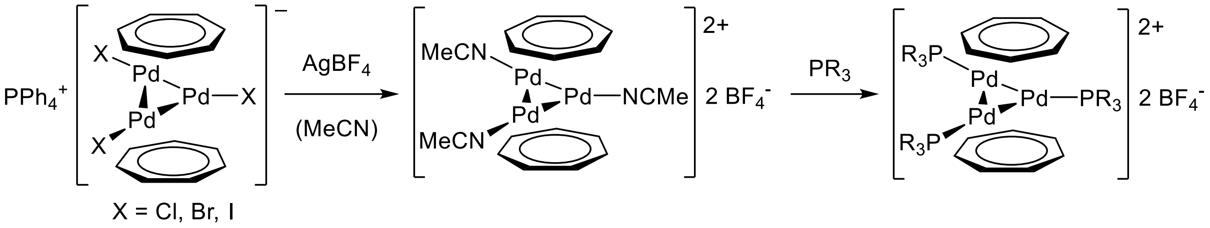
also accomplishes the formation of the cluster complex.[127] However, this postulated synthesis could not be reproduced and the structure of the precursor was not established unambiguously, either.[131]

1.3.2 Synthesis

The synthesis of trinuclear sandwich cluster complexes is usually performed by reaction of Pd(0)-precursors with tropylium tetrafluoroborate in the presence of tetraphenylphosphonium halide, if equatorial halide ligands are desired (see Scheme 44, top).[150] [162] If no halide source is added, the equatorial positions are occupied by solvent ligands, commonly acetonitrile.[165] For syntheses involving even ring sizes and polycyclic capping ligands, the respective neutral arenes serve as starting material and either a dimeric Pd(I) precursor or a mixture of Pd(0) and Pd(I) precursors is used (see example in Scheme 44, bottom).[150] [156] [159] [161] There is also a minor class of complexes with cycloheptatriene ligands, which do not feature a conjugated system in contrast to all other compounds discussed here; these capping ligands are also introduced as neutral alkenes and not as tropylium ions.[165] Exchange reactions of the equatorial ligands are easily feasible starting from complexes with equatorial acetonitrile ligands, which can readily be replaced, e.g. by phosphines (see Scheme 45, right).[150] [163] As mentioned, the necessary acetonitrile complexes can be prepared directly, but also by precipitation of halide ligands in acetonitrile solution (see Scheme 45, left).[150] [163]

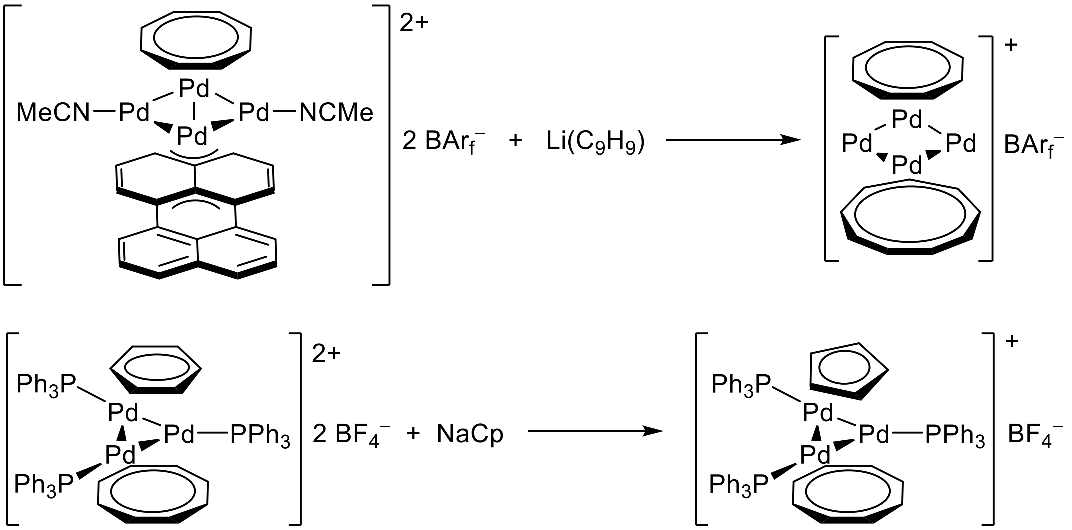


Scheme 44: Examples for syntheses of Pd metal sheet sandwich complexes.[150] [161,162]

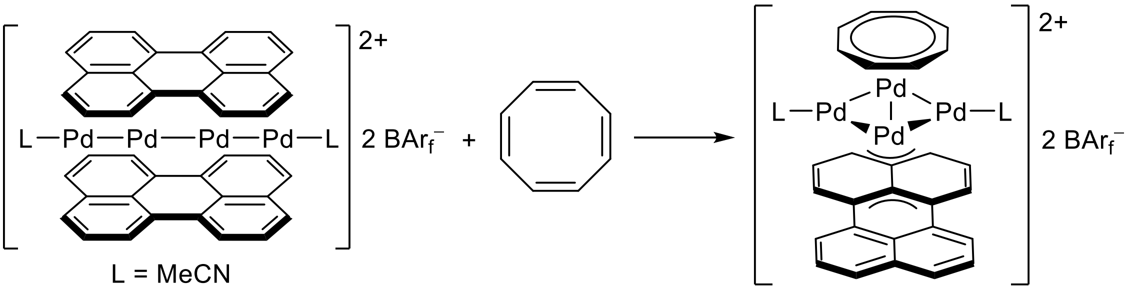


Scheme 45: Examples for exchange reactions of the equatorial ligands.[150] [163]

Exchange reactions are also possible with the capping ligands, and in the case of five-membered and nine-membered rings this is so far the only viable route to introduce them as ligands (see Scheme 46).[157,158] Closely related to this is another strategy for the synthesis of Murahashi-type complexes: By exchanging capping ligands a rearrangement of sandwiched Pd chain complexes to Pd sheet complexes can be achieved (see Scheme 47).[160]

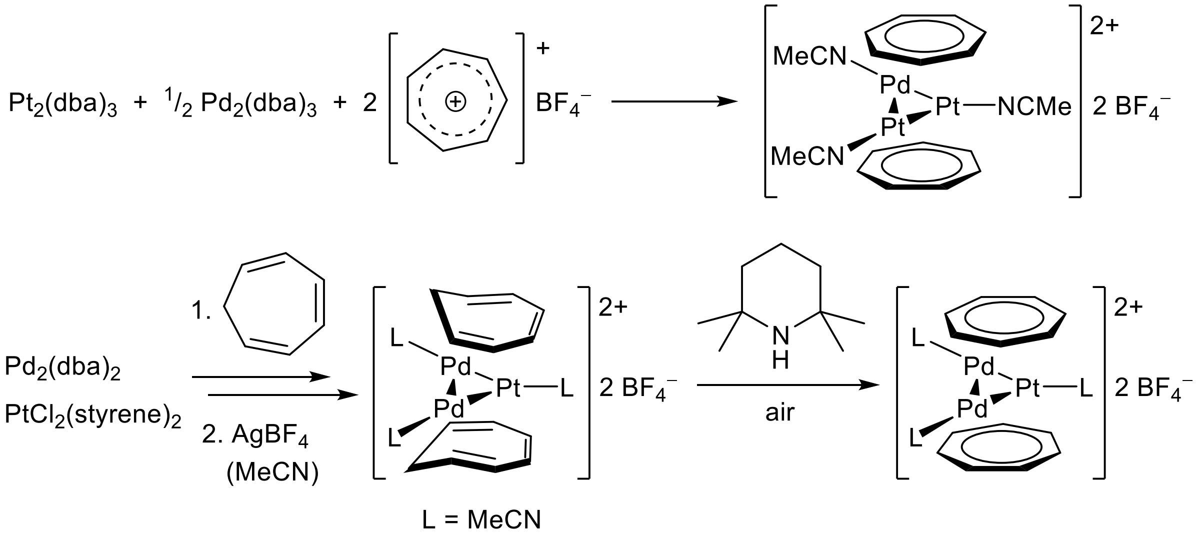


Scheme 46: Examples for exchange reactions of the capping ligands.[157,158]



Scheme 47: Rearrangement of a Pd chain to a Pd sheet complex by exchange of a capping ligand.[160]

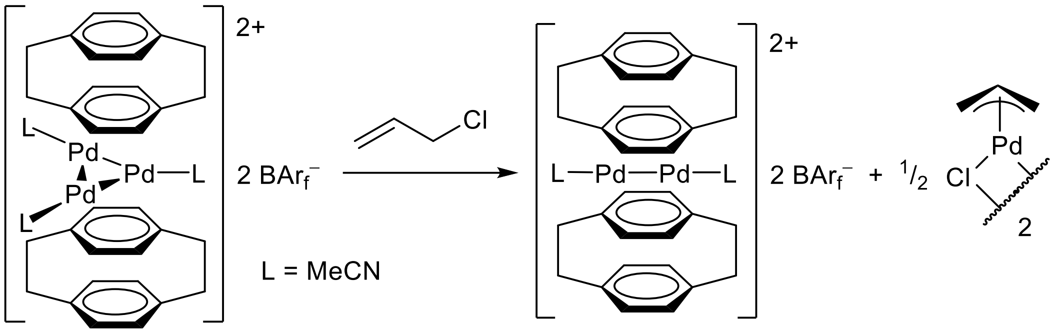
Trinuclear Pt sandwich cluster complexes can be obtained in the same way as their Pd analogues.[164] For mixed Pd/Pt clusters the route depends on the target cluster composition. For $PdPt_2$ clusters, the same strategy as for Pd_3 clusters can be applied using a 1:2 mixture of Pd(0) and Pt(0) precursor: The sandwich complex with a $PdPt_2$ cluster is then formed with high selectivity and only minor amounts of the other possible clusters (Pd_3, Pd_2Pt, Pt_3) are observed (see Scheme 48, top).[166] For the Pd_2Pt cluster a two-step synthesis is necessary: First, a Pd_2Pt sandwich complex with cycloheptatriene ligands is prepared, which can then be converted to the cycloheptatrienyl sandwich complex by reaction with tetramethylpiperidine on air (see Scheme 48, bottom).[166]



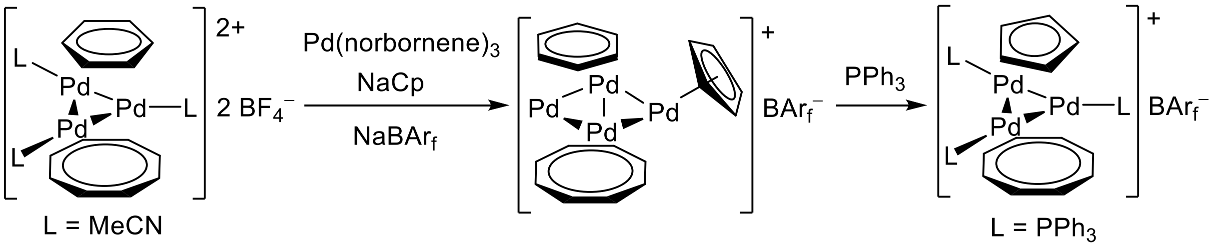
Scheme 48: Selective synthesis of $PdPt_2$ and Pd_2Pt metal sheet sandwich complexes.[166]

1.3.3 Properties and Applications

So far there is no complete picture of the properties of Murahashi complexes. They are described as air-stable in most, but not all cases.[150] [165,166] The polymerisation via bridging halides mentioned before was achieved simply by heating the samples, so the compounds cannot be considered as inert.[162] Exchange reactions of equatorial and capping ligands as well as the reductive coupling of cluster complexes have already been covered above. There is also an example of a controlled disassembly of a trinuclear cluster complex by addition of allyl chloride, which leads to a dinuclear sandwich complex (see Scheme 49).[156] Another interesting reactivity was reported by the group of Murahashi, who was able to extend a trinuclear Pd sandwich complex to a tetranuclear complex by formally adding a $[PdCp]^-$ group (see Scheme 50, left).[158] The extended cluster complex could then be converted back to a trinuclear cluster e.g. by triphenylphosphine (see Scheme 50, right).[158]



Scheme 49: Controlled disassembly of a trinuclear Pd sandwich cluster complex.[156]



Scheme 50: Reaction sequence showing the reversible extension of a trinuclear to a tetranuclear Pd sandwich cluster complex.[158]

Some theoretical studies of $[Pd_3Cl_3(C_7H_7)]^-$ and related systems have also been performed. They showed that in agreement with crystallographic bond distances there is significant bonding between the Pd atoms and that, unsurprisingly, the capping ligands have a high degree of aromaticity.[150] [167] The bonds of the cycloheptatrienyl ligands to the cluster can formally be divided into two η^2-(alkenyl) and one η^3-(allyl) coordination, but due to constant ring whizzing the ligands appear to be fully symmetric in solution (as observed e.g. in NMR spectra).[150] [167] Concerning oxidation states and formal charges, the Pd_3 clusters have been described as Pd(0) and the C_7H_7-ligands have been interpreted as cationic tropylium ligands by all authors so far.[150] [162] [167]

As yet, the only reported application of Pd sandwich cluster complexes was published by Murahashi, Kurosawa and co-workers in their initial publication, where they stated the compounds to be active as catalysts in Suzuki-Miyaura coupling reactions.[150] They have also been proposed as model compounds for transformations of aromatic hydrocarbons on metal surfaces or building units for molecular electronics, but none of these applications have been realised so far.[150] [158] [163]

2. Objectives of this Thesis

The research performed in this thesis evolves around Pd complexes of carbocyclic carbenes, more specifically CHTs, and their reaction with N-nucleophiles (as described in 1.2.4) leading to imidazolium- and pyridinium-substituted η^3-cycloheptatrienide-Pd complexes.[127] This class of compounds represents a potential starting point for synthetic studies towards highly interesting ligand motifs based on functionalised seven-membered rings. However, to start with, it will be necessary to explore the reactivity of Pd-CHT complexes towards imidazoles and pyridines in more detail as preliminary studies indicate that the dimeric structures proposed so far for the primary reaction products are most probably inaccurate.[131] To firmly establish the class of imidazolium- and pyridinium-substituted η^3-cycloheptatrienide-Pd complexes, a broad variety of derivatives with different substituents is to be synthesised and structurally characterised. The experimental studies shall be supplemented by DFT calculations to gain insight into mechanistic details of their formation and their properties.

The serendipitous discovery of an imidazolium-functionalised Murahashi complex (see above) highlights that substituted η^3-cycloheptatrienide-Pd complexes are promising precursors for this type of cluster complexes. Very recently, a (non-sandwich) Pd_3 cluster supported by phosphine ligands was introduced as a robust and efficient catalyst for Suzuki reactions, so defined molecular Pd clusters certainly are promising candidates for catalytic applications.[168] So, once the chemistry of the precursors is sufficiently explored, the main goal of this work is the development of a rational synthesis of functionalised sandwich cluster complexes. Access to a broad variety of substitutions would not only introduce a tool to tune the properties of the complexes. In the case of imidazolium substituents it also opens up a chance to metalate the sidearms by converting them to NHCs. This would provide a unique platform for the combination of Pd_3 clusters with basically any other metal. As such, cooperative effects of the metals could be utilised for novel catalytic transformations or bifunctional catalysis. The bifunctionality might be particularly interesting for CO_2 activation as free NHCs have been demonstrated to reversibly bind CO_2, so it is conceivable to perform this on the NHC sidearms of a Murahashi complex and enable further transformations at the cluster site.[169,170]

There are also still questions about the electronic situation in Murahashi complexes: The current interpretation as Pd(0) clusters capped by cationic tropylium ligands (see above) seems quite counterintuitive. For one, halides, which are a frequent equatorial ligand, are not expected to bind to Pd(0). Moreover, the reported NMR shifts of the cycloheptatrienyl ligands indicate rather electron-rich seven-membered rings, which is incompatible with a cationic charge.[150] [162,163] Therefore, an important aspect of the characterisation will be the elucidation of the charge distribution within the $[Pd_3(C_7H_7)]^{2+}$ fragment by experimental and computational methods. This knowledge is vital as the oxidation state of Pd is a key feature in catalysis, which commonly involves oxidative and reductive steps at the Pd centre.[75]

Aside from functionalised Murahashi complexes, the structure of imidazolium-substituted η^3-cycloheptatrienide-Pd complexes also inspires another interesting target motif. If the allyl-bound cycloheptatrienide ligand could be transformed back to a carbene binding mode while also turning the imidazolium group into an NHC, this would allow the first combination of a carbocyclic and an N-heterocyclic carbene in a single ligand framework. Owing to their similar origin, this is interesting from a historical point of view on the one hand, but on the other hand it also allows a direct comparison of these two carbene classes and potentially the utilisation of their different properties. Formally, the formation of the envisioned CHT-NHC ligand only requires the abstraction of a proton from the imidazolium moiety and a hydride from the cycloheptatrienide ring. First experiments in this direction have already shown promising results.[131]

With Pd-CHT complexes being the starting point of the planned chemistry, some attention should also be paid to the ligand precursors (shown in Scheme 23, bottom). $C_7H_6Cl_2$ and $C_7H_6Br_2$ were already reported by Föhlisch and co-workers in 1968 and in recent years, $C_7H_6Cl_2$ has found applications in organic synthesis as mild halogenating agent and activator in Swern-type oxidations.[171-174] It is therefore quite surprising that their solid state structure has not been determined yet, so their structure still remains uncertain. They have mostly been referred to as 7,7-dihalocycloheptatrienes, although it was recognised early that other covalent isomers could also play a role and that an ionic halotropylium halide structure is possible as well.[98] [113] [115] [171-175] As the active species in synthetic applications is considered to be the chlorotropylium ion, the structural information is important for a deeper mechanistic understanding and potential further development.[172-174] Besides crystallographic determination of the solid state structure, the behaviour in solution shall be studied by means of computational chemistry in order to gain insights into a potential interconversion and equilibria of different isomers, which are difficult to grasp experimentally.

Finally, a side project will deal with a reaction of potassium tetrachloropalladate, ethylene and triphenylcyclopropenium chloride, reported in 1964, but without structural characterisation.[176] The structure proposed back then is rather unusual and in the light of the reactants it does not seem unlikely that a Pd cluster, potentially with sandwiching triphenylcyclopropenium ligands, is formed. If this assumption is true, another route towards defined Pd cluster complexes could be developed to supplement the Murahashi systems.

3. Experimental Methods

3.1 Syntheses

All reactions involving sensitive compounds were performed under Argon (99,996%, *Westfalen*) using standard Schlenk techniques or in a glove box (labmaster 130, *MBraun*). Dry solvents were obtained from an MB SPS (*MBraun*) and stored over molecular sieves (3Å or 4Å as appropriate for the respective solvent) under argon atmosphere. NMR solvents were purchased from *Eurisotop* and dried over molecular sieves, if necessary. Chemicals were purchased from commercial suppliers and used without further purification, if not stated otherwise in the relevant section in the Appendix. A sample of the product from reference [176] for re-investigation was supplied by Dr. Karl Öfele. Characterisation of novel substances was performed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry as well as X-ray crystallographic analysis of representative compounds.

3.2 NMR Spectroscopy

Standard NMR spectra in solution were recorded on a *Bruker* AVIII 400US spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C) equipped with a broad-band probe head and a gradient coil. Variable temperature ^{1}H spectra and extended duration ^{13}C spectra were recorded on a *Bruker* DRX400 spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C) equipped with a broad-band probe head. ^{13}C spectra are proton-decoupled. Chemical shifts (δ) are referenced to the solvent residual signals with respect to tetramethylsilane. ^{1}H NMR data are reported as follows: chemical shift in ppm (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, virt. = virtual, br. = broad, n. r. = not resolved), coupling constant in Hz, integral, assignment). If necessary, 2D spectra (COSY, HSQC, HMBC, NOESY) were used to aid in peak assignment. Solid state MAS-NMR spectra were recorded on a *Bruker* AV300 spectrometer (75.47 MHz for ^{13}C) with the samples finely ground and packed into a 4 mm ZrO_2-rotor. The rotational frequency is given where the spectra are reported. ^{13}C spectra were measured with cross polarisation technique and signals are referenced to the external standard adamantane with respect to tetramethylsilane. Processing and analysis of data as well as preparation of graphical material were performed using the MestReNova software package.[177]

3.3 Elemental Analysis

Elemental analyses were carried out by the microanalytical laboratory of the Technical University Munich and values are given in percent by weight.

3.4 Mass Spectrometry

FAB mass spectra were recorded on an MAT 90 spectrometer (*finnigan MAT*). ESI mass spectra were recorded on an LTQ TF Ultra spectrometer (*Thermo Scientific*) or a Q-TOF micro spectrometer (*micromass*) with the samples prepared as solution in acetonitrile. m/z is reported in atomic units per elementary charge.

3.5 Electrochemistry

Electrochemical experiments were carried out by J. R. Pankhurst at the University of Edinburgh and the details are given in the relevant section in the Appendix.

3.6 Computational Chemistry

All calculations were performed using the Gaussian09 software package.[178] The semi-empirical method PM6, the density functionals ωB97X-D, M06, M06-2X, PBE0 and B3LYP as well as the basis sets 6-31G*, 6-31+G*, LANL2DZ (including an ECP for metals) and TZVP were employed as implemented in this software package.[179-190] The basis sets def2-TZVP (including a corresponding ECP for metals) and def2-TZVPD were obtained from EMSL Basis Set Exchange.[191-195] For calculations simulating the situation in solution, the implicit solvent model SMD was used and the calculation of the cavity was performed with UFF radii and scaling factors as defaulted in Gaussian09, if not stated otherwise.[178] [196] The deviations in one case are discussed in detail in the relevant section of the Appendix.

Starting points for geometry optimisations were taken from crystal structures, if available. Otherwise a chemically reasonable structural guess was pre-optimised on the PM6 level of theory. Starting points for the determination of transition states were obtained from scans of distances or angles along the reaction coordinate. Several density functionals and basis sets were initially tested for the accurate reproduction of structural features of a carbocyclic carbene model compound, the details of which can be found in the Appendix. In agreement with other studies on a larger basis of test compounds, the ωB97X-D functional was found to perform best.[197,198] As a result, the ωB97X-D functional with a triple-zeta basis set (TZVP for first and second row elements, def2-TZVPD for other non-metals and def2-TZVP with a corresponding ECP for metals) was used for all final calculations. In the case of large molecules, the optimisation was performed in two steps, first using a double-zeta basis set (6-31G* for first and second row elements, 6-31+G* for other non-metals and LANL2DZ with a corresponding ECP for metals) and then the above triple-zeta basis set.

Calculations of vibrational frequencies were employed to determine the nature of stationary points and thermodynamic properties as enthalpies or Gibbs free energies. If in doubt, transition states were additionally verified by step-wise following the reaction coordinate in both directions until the expected minima were reached. A correction for low vibrations was applied to all Gibbs free energy values by replacing the entropy contributions of all vibrations with wavenumbers lower than 50 cm^{-1} by the contribution of a vibration of 50 cm^{-1} (which equals $4.82\,\frac{cal}{K\cdot mol}$) in order to account for the inaccuracy of the harmonic oscillator model in the case of low energy vibrations.[199,200] If a continuum solvent model was employed, both the geometry optimisation and the frequency calculation were performed using the solvent model as recommended by Truhlar and Cramer.[200] As an exception, in cases where the optimisation did not converge while using a solvent model, the geometry and thermodynamic values were taken from a gas phase calculation and the energy of solvation was determined by a single point calculation with the solvent model. For reaction data in solution, concentrations were converted to the standard concentration of 1 mol/L, if not stated otherwise. If large differences in concentrations needed to be accounted for, the chemical potential based on the formula $\mu = G + RT \ln c$ (where the concentration c is used as an approximation for the activity) was used. Graphical material of computationally obtained structures was created with CYLview.[201]

3.7 Single Crystal X-Ray Diffraction

Data were collected on *Bruker* single crystal X-ray diffractometers equipped with one of the following setups, all using Mo-K_α radiation (λ = 0.71073 Å):

1) a CCD detector (APEX II, κ-CCD), a fine-focus sealed tube and a graphite monochromator
2) a CCD detector (APEX II, κ-CCD), a fine-focus sealed tube and a Triumph monochromator

3) a CCD detector (APEX II, *κ*-CCD), an FR591 rotating anode and a Montel mirror optic
4) a CMOS detector (APEX III, *κ*-CMOS), an IMS microsource and a Helios optic
5) a CMOS detector (APEX III, *κ*-CMOS), a TXS rotating anode and a Helios optic

Setups 1), 2) and 3) used the APEX II software package and setups 4) and 5) used the APEX III software package.[202,203] Crystal samples were prepared in perfluorinated ether, examined under a microscope and well-formed single crystals were selected, fixed on a glass fibre or kapton micro sampler, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters, ensure the quality of the crystal and develop an adequate data collection strategy. Upon integration, reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[204] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[204]

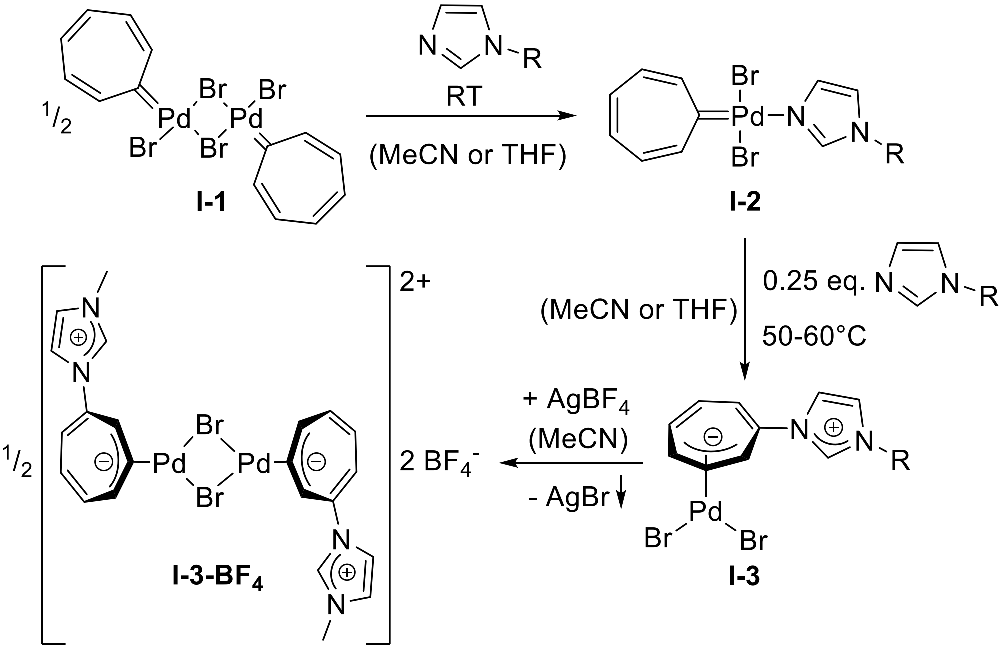
The assignment of space groups was based on systematic absences, *E* statistics, and successful refinement of the structures based on *R* values, residual electron densities and anisotropic displacement parameters. Structures were solved using SHELXS-97 or SHELXT with the aid of successive difference Fourier maps.[205,206] Structures were refined against all data (excluding reflections affected by systematic errors, e.g. due to absorption by the beamstop) using SHELXL-97 or SHELXL-2014 in conjunction with SHELXLE.[205] [207,208] Full-matrix least-squares refinements were carried out by minimizing $\sum \omega (F_o^2 - F_c^2)^2$ with the SHELXL weighting scheme and neutral atom scattering factors for all atoms and anomalous dispersion corrections for non-hydrogen atoms were taken from *International Tables for Crystallography* as defaulted in the refinement software.[207] [209] If not stated otherwise, hydrogen atoms were calculated in ideal positions as follows: Methyl H atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso}(H) = 1.5 \cdot U_{eq}(C)$. Methylene, aromatic and other H atoms were refined using a riding model with C–H distances of 0.99 Å, 0.95 Å and 1.00 Å, respectively, and $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Split-layer refinements were used for disordered groups, anions or solvent molecules. If necessary, additional similarity restraints for distances and ADPs (SHELX keywords SAME and SIMU) as well as rigid body restraints (SHELX keyword DELU) were introduced to ensure convergence of the refinements within chemically reasonable and physically meaningful limits. In the case of disordered solvent molecules which could not be properly refined, these were treated as a diffuse contribution to the overall scattering without specific atom positions using the SQUEEZE procedure implemented in the PLATON software package.[210,211] Graphical material was created using the programs PLATON and Mercury.[211,212] Other publication material was prepared using PLATON, enCIFer and publCIF.[211] [213,214] For specific details on particular crystal structures (e.g. setup, crystallisation procedure, treatment of H atoms and disordered solvent molecules) see the relevant sections in the Appendix.

4. Summary and Discussion of Publications

4.1 Structure and Dynamics of Imidazolium- and Pyridinium-substituted η^3-Cycloheptatrienide-Pd Complexes

As a starting point for the consecutive projects, the recently discovered class of imidazolium- and pyridinium-substituted η^3-cycloheptatrienide-Pd complexes was investigated in more detail.[127] A broad variety of derivatives could be synthesised by reaction of different N-nucleophiles with CHT-Pd complex **I-1** as depicted in Scheme 51 for the case of imidazoles; the reaction with pyridines works analogously. A drawback of compounds of type **I-3** turned out to be their poor solubility. As a suitable strategy to increase the solubility, an exchange of one bromide ligand for a non-coordinating tetrafluoroborate anion was found, which produces dimeric structures of type **I-3-BF$_4$** (see Scheme 51, bottom).



Scheme 51: Reaction pattern for the formation of imidazolium-substituted η^3-cycloheptatrienide-Pd complexes by reaction of Pd-CHT complexes with substituted imidazoles and their conversion to dimers by anion exchange.

All structural motifs shown in Scheme 51 could be confirmed by X-ray crystallography. Of particular interest is the monomeric structure of **I-3**, which previously had been postulated to be a dimer.[127] The reason for this unexpected structure is the zwitterionic nature of the ligands consisting of a formally anionic cycloheptatrienide-moiety and a cationic imidazolium/pyridinium-substituent. For this strategy of using a zwitterionic ligand to obtain a monomeric $LPdX_2$ complex, there is only one precedent, but without crystallographic characterisation.[215] The cationic substituents also form strong intramolecular hydrogen bonds to the bromide ligands, the geometry of which was found to be dependent both on the polarity of the solvent and the steric bulk of the substituent in the case of imidazolium-groups.

The structure of the title compounds proved to be even more complex in solution, where there is a highly dynamic equilibrium between different isomers which interconvert by the migration of Pd along the seven-membered ring. This behaviour was studied in detail by means of DFT calculations, which produced the energy profile depicted in Figure 1. This was rationalised by the interplay of two effects: On the one hand, a maximum distance of the electron-rich allyl-bond from the electron-withdrawing substituent is advantageous; on the other hand, the internal hydrogen bond requires a heavy structural distortion in the case of the *γ*-isomer (denomination with respect to the distance between the substituent and the central allyl-carbon). As a result, the *β*-isomer was obtained as the most favourable geometry in agreement with the crystal structures. The very low activation barriers between the different isomers confirm the rapid interconversion of isomers, which was still observed at low temperature (-90 °C) in NMR studies.

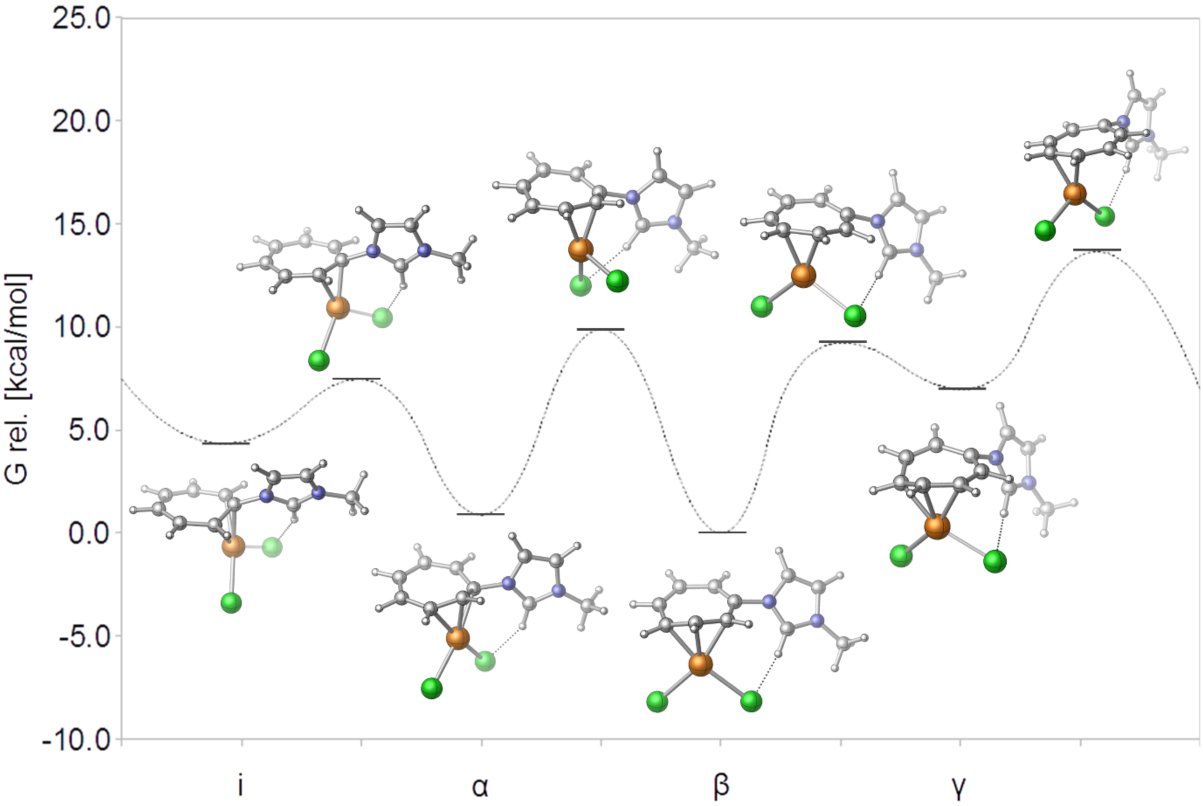


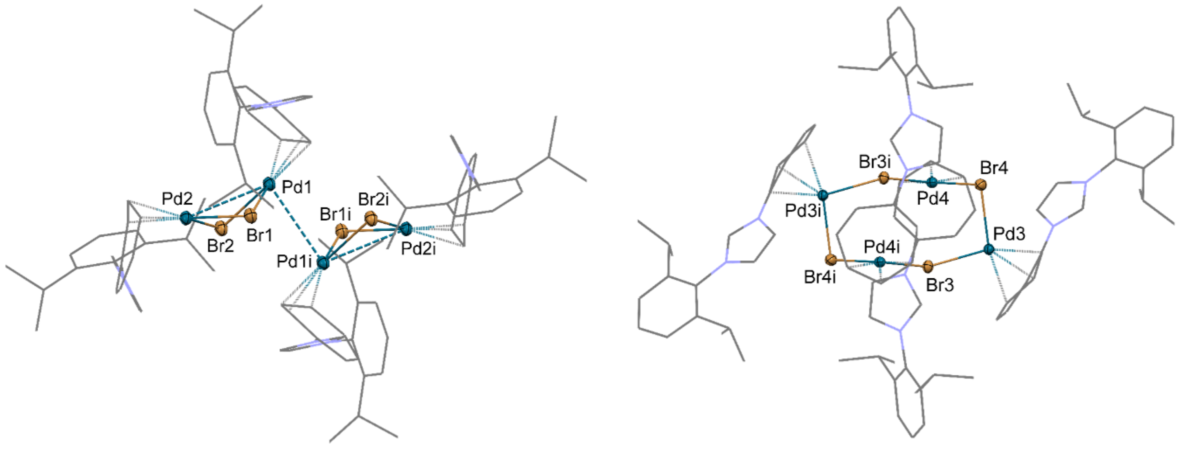
*Figure 1: Graphical representation of the Gibbs free energy profile for the migration of Pd along the cycloheptatrienide ring of complex **I-3** (R = Me) in solution.*

Finally, the mechanism of formation of the title compounds was also elucidated in a DFT study of the imidazolium-derivatives: First, the intermediate **I-2** is formed in a dissociative mechanism. Then, an additional imidazole molecule attacks on the carbene-C forming an alkyl-bound cycloheptatrienyl complex as a short-lived intermediate. After dissociation of the *trans*-bound imidazole, the organometallic ligand rearranges to the allyl-binding mode found in complexes of type **I-3**. This mechanism explains the catalytic function of excess nucleophile, but also points out the flexibility of the ligand motif with respect to binding modes of the seven-membered ring, which could be exploited in further studies.

Reference: C. Jandl, K. Öfele, F. E. Kühn, W. A. Herrmann, A. Pöthig, *Organometallics* **2014**, *33*, 6398–6407, doi: 10.1021/om500738d.

4.2 A Pd_4Br_4 Macrocycle trapped by Cocrystallization from a Highly Dynamic Equilibrium of η^3-Cycloheptatrienide Complexes

In continuation of the structural studies of imidazolium-functionalised η^3-cycloheptatrienide-Pd complexes after partial exchange of bromide ligands, a co-crystal of the derivative bromido{η^3-[3-(2,6-diisopropylphenyl)imidazolium-1-yl]cycloheptatrienido}palladium(II) tetrafluoroborate **II-1** provided further insights into the dynamic behaviour of this class of complexes in solution. In this crystal, half of the complexes (based on the monomer count) form dimers **II-1a**, which are linked via Pd-Pd interactions to pseudo-tetramers (see Figure 2, left), whereas the other half forms actual tetramers **II-1b** featuring an eight-membered Pd_4Br_4 macrocycle as the core-structure (see Figure 2, right). This static ratio of dimers and tetramers in the crystalline state corresponds to the equilibrium in solution as could be shown by low-temperature NMR spectroscopy. The tetramer also features both the β- and the γ-binding mode of the substituted cycloheptatrienide ligands, which allows a better crystal packing than a potential geometry with only the β-binding mode, which otherwise is the most favourable position of the allyl-bond. The co-crystal therefore represents a crystallographic snapshot of two different dynamic processes in solution: The migration of Pd along the cycloheptatrienide ring, which is also found in the respective monomeric complexes, and additionally an equilibrium between the previously reported dimeric motif and a new tetrameric structure.



II-1a **II-1b**

*Figure 2: Molecular structures of two interacting dimers **II-1a** (left) and the tetramer **II-1b** (right) from the co-crystal of **II-1** with ellipsoids at the 50% probability level. Hydrogen atoms, counterions and co-crystallised solvent molecules are omitted for clarity and the organic ligands are simplified as wireframes.*

In the light of these results and the common occurrence of dimeric Pd complexes with bridging halide ligands, such an equilibrium with higher oligomers seems possible in many cases where currently only the dimeric structure is considered. So far, a few other complexes with $(PdX)_n$-core structures (in one case with an additional capping halide) are known, and one of these articles also reported an equilibrium with dimers.[216-219] Such equilibria between dimers and different oligomers would have consequences for the understanding of the structural chemistry of Pd coordination compounds and their applications, so an interesting field for further research could open up here.

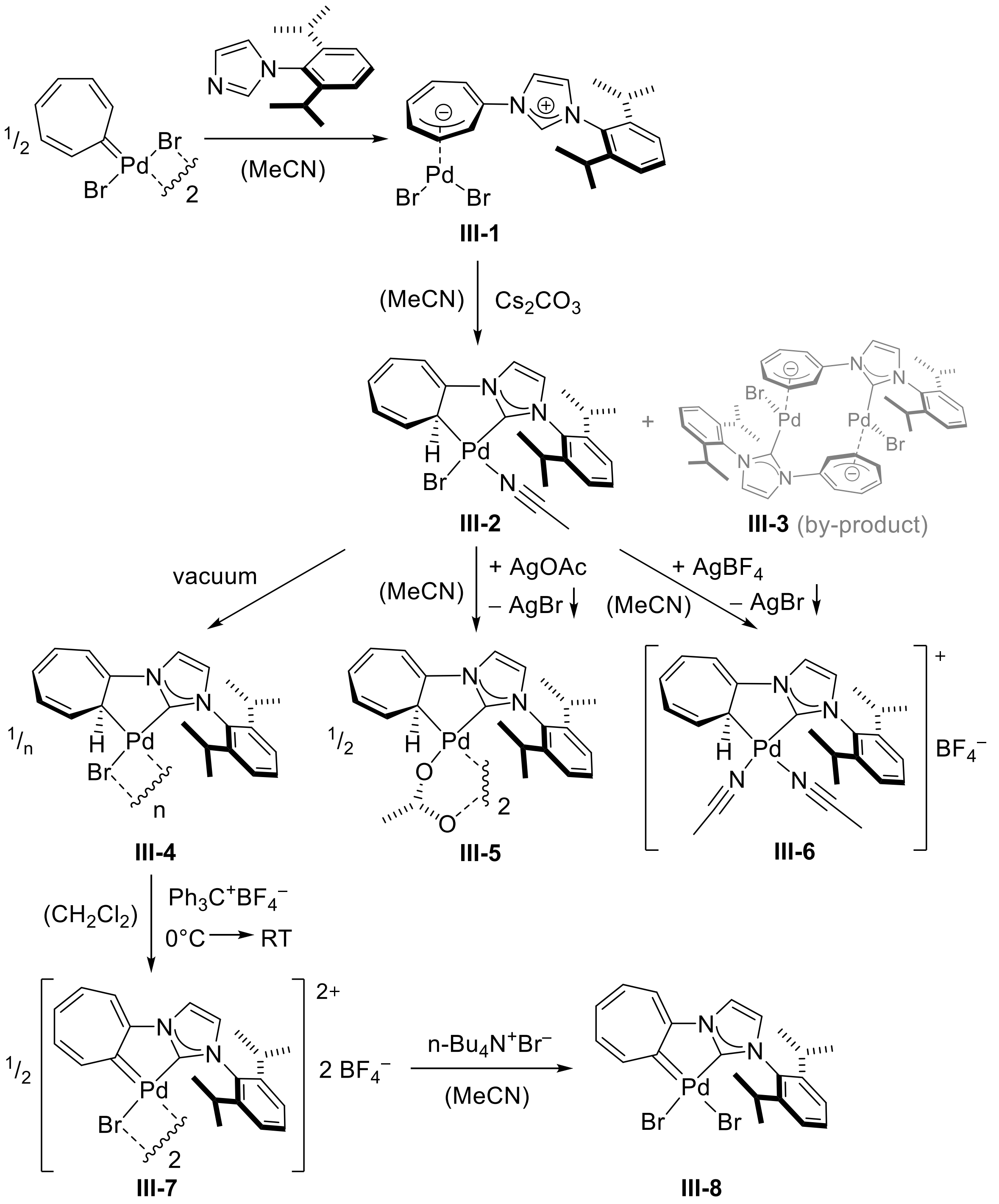
Reference: C. Jandl, S. Stegbauer, A. Pöthig, *Acta Crystallogr., Sect. C* **2016**, *72*, 509–513, doi: 10.1107/S2053229616008275.

4.3 A Hybrid Carbocyclic/N-heterocyclic Carbene Ligand

As proposed in chapter 2, the motif of imidazolium-functionalised η^3-cycloheptatrienide-Pd complexes indeed proved to be a suitable starting point for a mixed carbocyclic/N-heterocyclic carbene ligand by a two-step deprotonation/hydride abstraction sequence (see Scheme 52). In the first step, the imidazolium-sidearm was converted to an NHC-ligand by reaction with caesium carbonate, which caused the allyl-bound cycloheptatrienide ligand to rearrange to an alkyl-binding mode in **III-2**. This crucial rearrangement, which makes the further route possible, was also studied in more detail by means of DFT calculations. It is worthwhile adding that this reaction was also attempted in the presence of carbon dioxide to test for potential carbon dioxide fixation on the NHC, but none of the like could be observed. This can be attributed to the very short half-life of the free NHC before coordinating to Pd(II) as deduced from the DFT studies. In this reaction, also a dimeric by-product **III-3** could be isolated, in which the allyl-binding mode is retained, showing that there are two competing reaction pathways: an intramolecular and an intermolecular coordination of the free NHC to Pd(II), so the steric bulk of the DiPP-substituent is important in slowing down the intermolecular side-reaction.

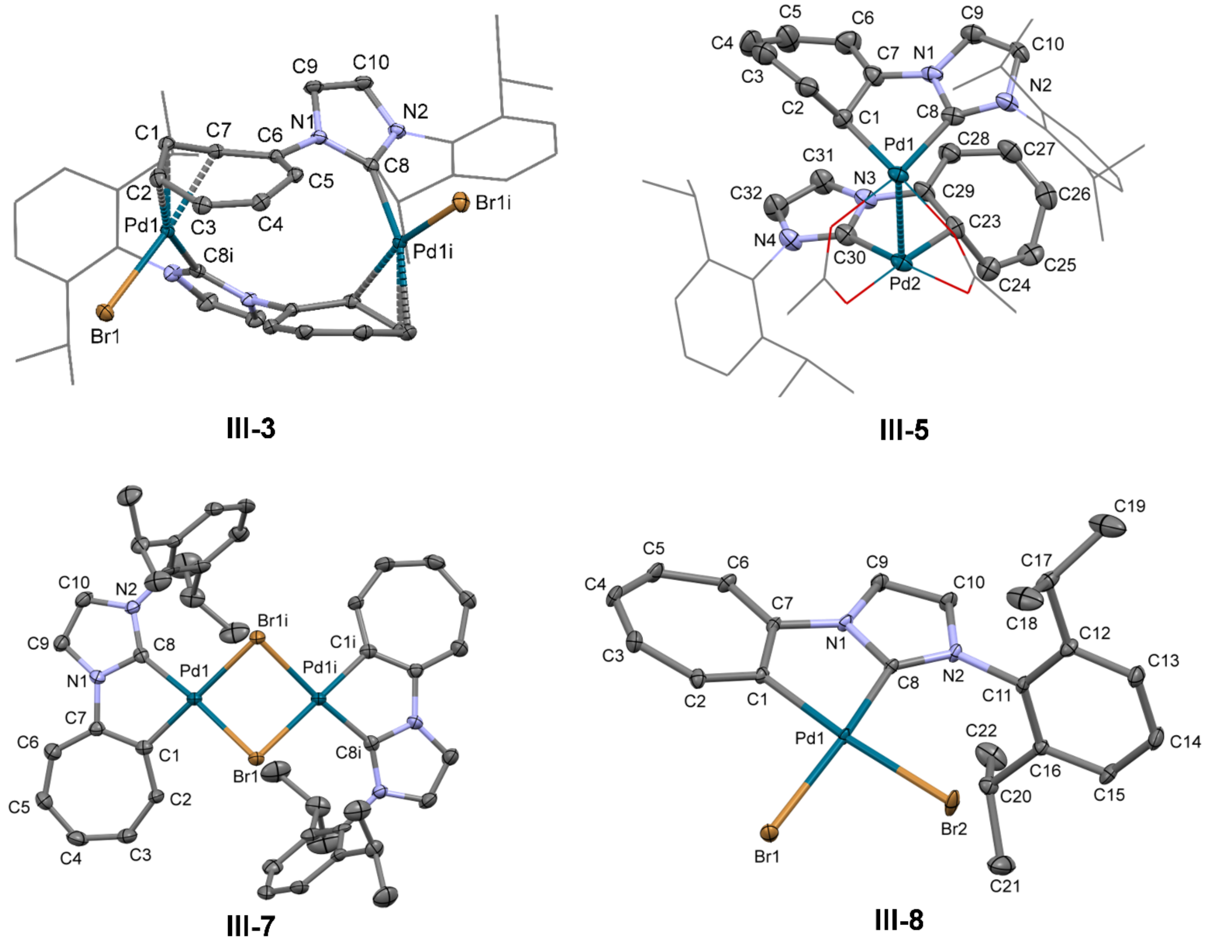
In the next step, the alkyl-bound cycloheptatrienyl ligand was transformed into a carbene-bound CHT ligand by hydride abstraction with tritylium tetrafluoroborate – similar to the original CHT-synthesis by Jones and co-workers.[95] The dimeric product **III-7** could be converted to monomeric **III-8** by addition of a bromide salt. **III-7** and **III-8** represent the first complexes featuring a hybrid CHT/NHC ligand, so these two classes of carbene ligands, which have a lot in common, but have developed quite differently in the almost 50 years since their discovery, could finally be combined in a single ligand motif.[1,2] [4-8] [94,95] [98]

All stages of the synthetic route could be verified by crystallographic analysis. In the case of the CHT(alkyl)/NHC intermediate, derivatisation was necessary, because neither **III-2** nor **III-4** could be properly crystallised as **III-2** loses the acetonitrile ligand upon crystallisation and **III-4** exists as a mixture of oligomers. Exchange of the bromide ligands by reaction with the respective silver salts produced the acetate derivative **III-5** and the tetrafluoroborate derivative with solvent ligands **III-6**. Crystal structures were obtained of compounds **III-5**, **III-7**, and **III-8** and the by-product **III-3** (see Figure 3). The CHT(alkyl)/NHC ligand in **III-5** features a distinct boat-shape of the seven-membered ring with alternating C-C bond lengths and an interesting stacked arrangement of the Pd coordination planes enabling a strong Pd-Pd interaction. In the novel CHT/NHC ligand of **III-7** and **III-8**, both carbene moieties are coplanar, suggesting aromaticity of both ring systems and an electronic communication between them. As a consequence of the electronic interaction with the NHC, the CHT-carbene bonds are significantly elongated and the ^{13}C NMR signals of the carbene C atoms appear strongly upfield shifted. Aside from that, the steric requirements of the chelating mixed carbene ligand cause significant distortions of the carbene bond geometries, which mainly affects the NHC group, suggesting that the CHT carbene bond is more rigid in direct comparison. The direct comparison also indicates that the CHT moiety exerts a stronger *trans*-influence than the NHC.



Scheme 52: Synthetic route towards the Pd complexes of the first hybrid carbocyclic/N-heterocyclic carbene ligand, including relevant derivatisations and by-products as well as the precursor synthesis from chapter 4.1.

Finally, the reaction sequence illustrates the remarkable flexibility of cycloheptatriene-based ligand systems as the seven-membered ring switches its binding mode several time: First, from the η^1-carbene mode in $[PdBr_2(CHT)]_2$ to the η^3-allyl mode in **III-1**, then to the η^1-alkyl mode in **III-2** and **III-4**, and finally back to the η^1-carbene mode in the target CHT/NHC ligand of **III-7** and **III-8**.



III-3

III-5

III-7

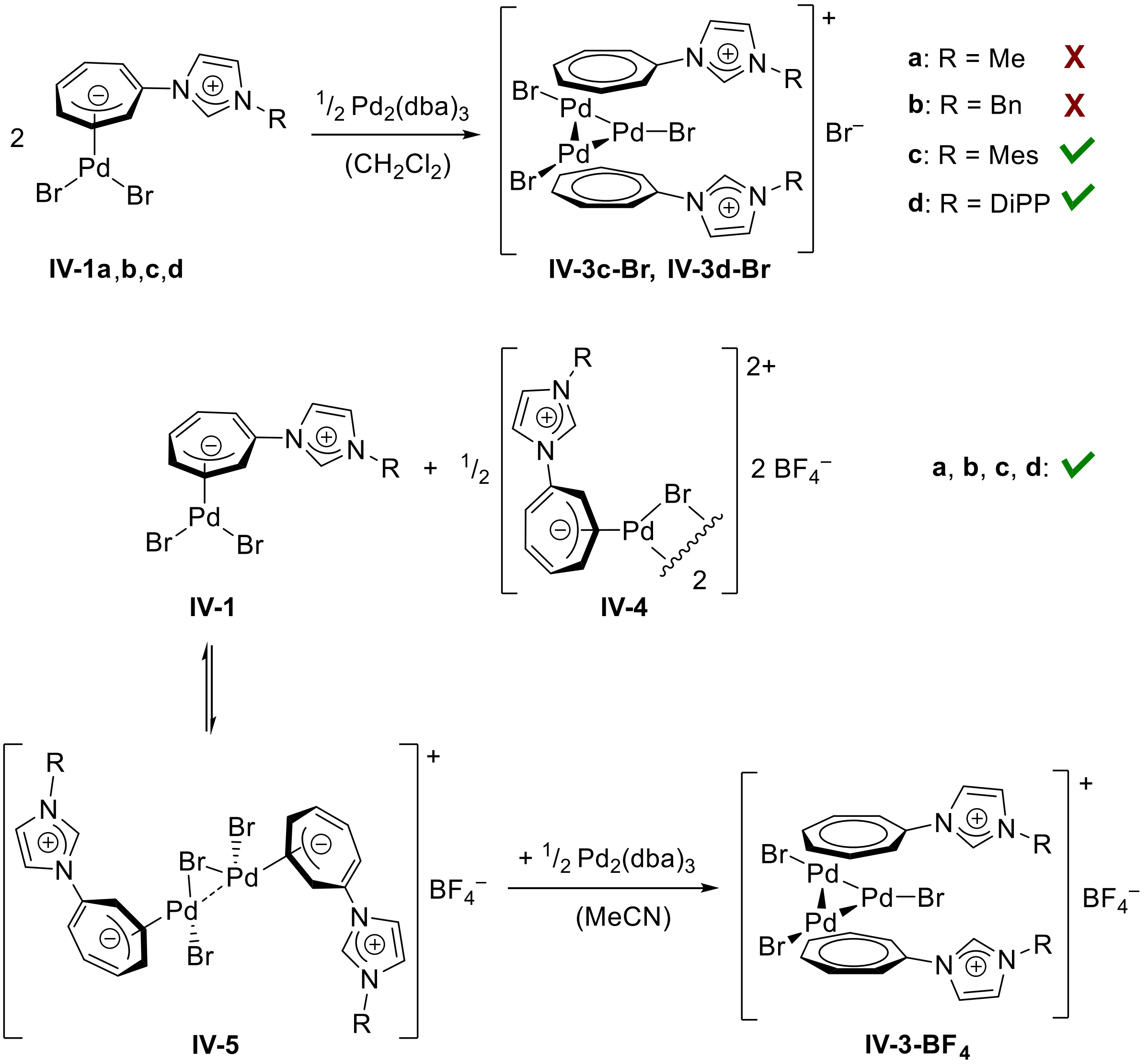
III-8

*Figure 3: Molecular structures of CHT(allyl)/NHC complex **III-3**, CHT(alkyl)/NHC complex **III-5** and CHT(carbene)/NHC complexes **III-7** and **III-8** with ellipsoids at the 30% (**III-5**) and 50% (**III-3**, **III-7**, **III-8**) probability level. Hydrogen atoms, counterions and co-crystallised solvent molecules are omitted for clarity and DiPP as well as acetate groups are simplified as wireframes if necessary.*

Reference: C. Jandl, A. Pöthig, *Chem. Commun.* **2017**, *53*, 2098–2101,
doi: 10.1039/C6CC08468K.

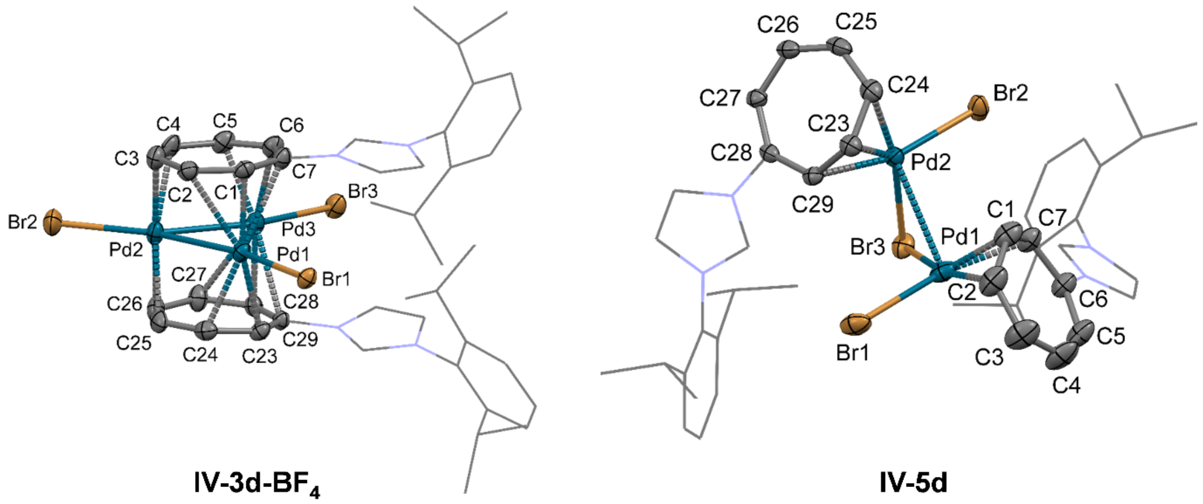
4.4 Rational Synthesis and Electronic Structure of Functionalized Trinuclear Pd Metal Sheet Sandwich Complexes

On the basis of the studies of imidazolium- and pyridinium-functionalised η^3-cycloheptatrienide-Pd complexes (chapter 4.1) and the serendipitous discovery of the first imidazolium-substituted Murahashi complex, a general route to functionalised Pd_3 sandwich complexes could be established.[127] The simple direct conversion of monomeric precursors **IV-1** by reaction with a Pd(0) source turned out to be viable only for bulky substituents on the imidazolium group (see Scheme 53, top). For other substitution patterns, an improved synthesis based on the in-situ-formation of dimeric “pre-clusters” from a mixture of dimeric and



Scheme 53: Synthesis of imidazolium-substituted Pd_3 sandwich complexes directly from monomeric precursors (top) and via dimeric “pre-clusters” (bottom).

monomeric precursors was developed (see Scheme 53, bottom). This route is also applicable to pyridinium-substituted derivatives. The structure of the resulting functionalised Pd_3 sandwich clusters could also be confirmed by several crystal structures, one example of which is depicted in Figure 4, left. Isolation of the “pre-cluster” complex could be achieved in case of the very bulky DiPP derivative **IV-5d** and crystallographic analysis revealed a core of two Pd atoms with one bridging and two terminal bromide ligands (see Figure 4, right). As can easily be seen, this complex bears all components of the target trinuclear sandwich complex except one more Pd atom and therefore formally requires only the addition of another Pd source. Additionally, the interaction between the two Pd atoms prearranges them for the incorporation of the third Pd and thus facilitates the formation of the cluster, so the term “pre-cluster” was introduced for such a type of structure. Other routes based solely on dimeric precursors of type **IV-4** were also tested and found viable, but required the addition of an external bromide source, which then caused by-product formation and thus made this synthetic path less preferable for preparative purposes. But from the mechanistic point of view, this strategy provided insights into the reaction pathway leading to unsubstituted Murahashi complexes, indicating that this also proceeds via η^3-cycloheptatrienide intermediates.[150] [162] This is similar to a mechanism postulated by Murahashi and co-workers for reactions in a halide-free environment, although the intermediates could not be isolated in this case.[166]



IV-3d-BF$_4$ **IV-5d**

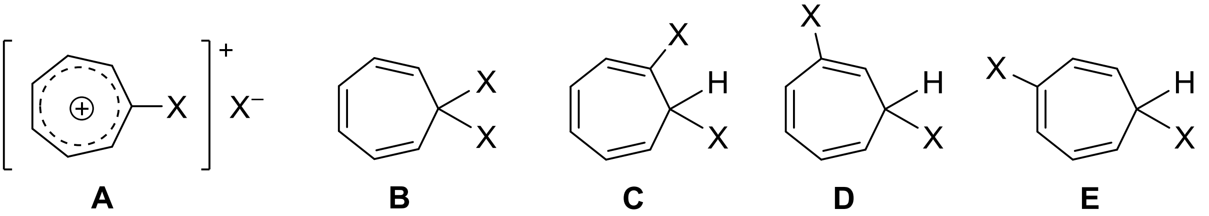
*Figure 4: Molecular structures of imidazolium-functionalised Pd_3 sandwich complex **IV-3d-BF$_4$** and “pre-cluster” **IV-5d** with ellipsoids at the 50% probability level. Hydrogen atoms, counterions and co-crystallised solvent molecules are omitted for clarity and DiPP groups are simplified as wireframes.*

As mentioned in chapter 2, the oxidation state of Pd in the trinuclear sandwich complexes had not been satisfactorily explained beforehand, so computational and electrochemical studies were undertaken and compared to suitable reference compounds to elucidate the electronic situation in complexes of type **IV-3**. The results clearly disproved the previous interpretation of Murahashi complexes as Pd(0) compounds with cationic tropylium ligands and instead indicated formally triply anionic cycloheptatrienide ligands and an intermediate formal oxidation state of +2.666 for Pd.[150] [167] The reaction of the Pd(II) precursors with an additional Pd(0) therefore formally represents an oxidative step. Closer analysis revealed distinctive differences between the charge densities on the three Pd atoms, which was further supported by small, but significant and systematic differences of the coordination environments of the Pd atoms in the crystal structures. From all the observations it could be concluded that the most accurate description based on integer oxidation states is a mixed valence cluster of one Pd(II) and two Pd(III) ions. However, due to the fluxionality, only an averaged apparent oxidation state is observed by electrochemical and spectroscopic methods in solution. As a point of interest, which was not included in the publication, it should be added that the imidazolium-functionalised Pd_3 sandwich complexes were also tested in CO_2-fixation and activation, but did not show any activity.

Reference: C. Jandl, J. R. Pankhurst, J. B. Love, A. Pöthig, *Organometallics* **2017**, *36*, 2772–2783, doi: 10.1021/acs.organomet.7b00276.

4.5 The Ambivalent Nature of Halogenated Tropone Derivatives: Dihalocycloheptatriene versus Halotropylium Halide

A detailed computational and crystallographic study was dedicated to the structure of the cycloheptatrienylidene precursor compounds $C_7H_6Cl_2$ (**V-1**) and $C_7H_6Br_2$ (**V-2**). All possible isomers depicted in Scheme 54 were given consideration. In the solid state, both compounds exist as ionic halotropylium halides (see Figure 5). Bromotropylium bromide additionally features halogen bonding (see Figure 5, right), while chlorotropylium chloride only shows a weak halogen bond-like contact.[220]



*Scheme 54: Relevant ionic (**A**) and covalent (**B**-**E**) isomers of chlorotropylium chloride and bromotropylium bromide; X = Cl, Br.*

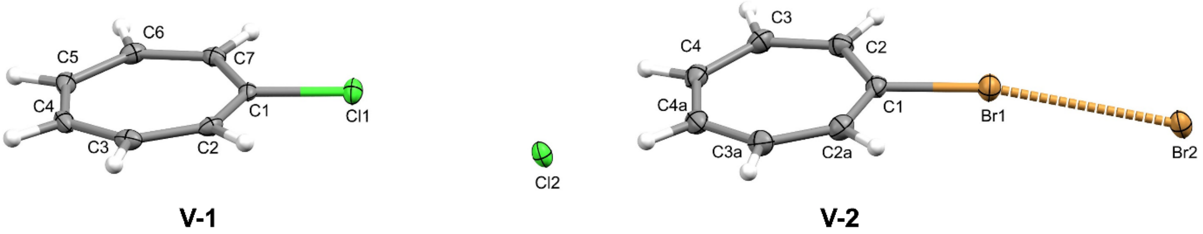
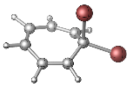
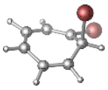
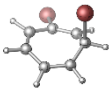
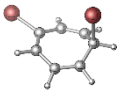
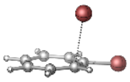
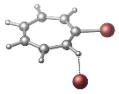
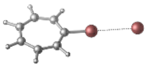


*Figure 5: Molecular structures of **V-1** (left) and **V-2** (right) in the solid state with ellipsoids at the 50% probability level.*

In solution, all possible geometries of interaction between halotropylium ion and halide ion were evaluated, namely an ionic interaction with the halide placed above the plane of the tropylium ring, a hydrogen bond with the halide in the same plane as the halotropylium ion and a halogen bond (X-bond) as observed in the solid state structure of bromotropylium bromide. For each type of interaction, the different possible geometries (e.g. hydrogen bonds with the α-, β-, γ-protons or in between) turned out to differ only very slightly in energy. The same was observed for the covalent isomers **C**-**E**, which were found to be effectively thermoneutral, whereas the geminal dihalide structure **B** – which previously had been the most frequent representation in the literature – was found to be several kcal/mol higher in energy and therefore could be excluded.[98] [113] [115] [172-174] One can assume that in analogy to this, the geminal dihalide structure of the CPr precursors shown in chapter 1.2.2 is also questionable. The halogen bond interaction is also too high in energy to be relevant in solution, so it only seems to exist in the solid state. An overview is given in Table 1 for the example of the $C_7H_6Br_2$ system. It can be seen that in dichloromethane as the less polar solvent, the covalent isomers are more favourable than any of the ionic structures. In the more polar acetonitrile, this turns around, so that the bromotropylium bromide structure with an H-bond is lowest in energy. This predicted behaviour could in fact be observed NMR spectroscopically. In the case of **V-1**, the covalent isomers are the dominant form in both solvents. In order to study the interconversion between covalent dihalocycloheptatrienes and halotropylium halides, the transition states for the halide attack on the halotropylium ion (respectively halide expulsion from the dihalocycloheptatriene) were calculated. The energy barriers were found to be very low, so all thermodynamically relevant species are also easily accessible kinetically. It can be concluded that in solution there is a highly dynamic equilibrium between the three dihalocycloheptatriene isomers **C**, **D**, and **E**, which interconvert via the ionic halotropylium halide structure. With increasing polarity of the solvent, the ratio of ionic species grows, which can even turn it from a short-lived intermediate to the major species in highly polar solvents. As mentioned before, this might help in the optimisation of their catalytic and synthetic applications as the halotropylium ion is considered to be the active species.[172-174]

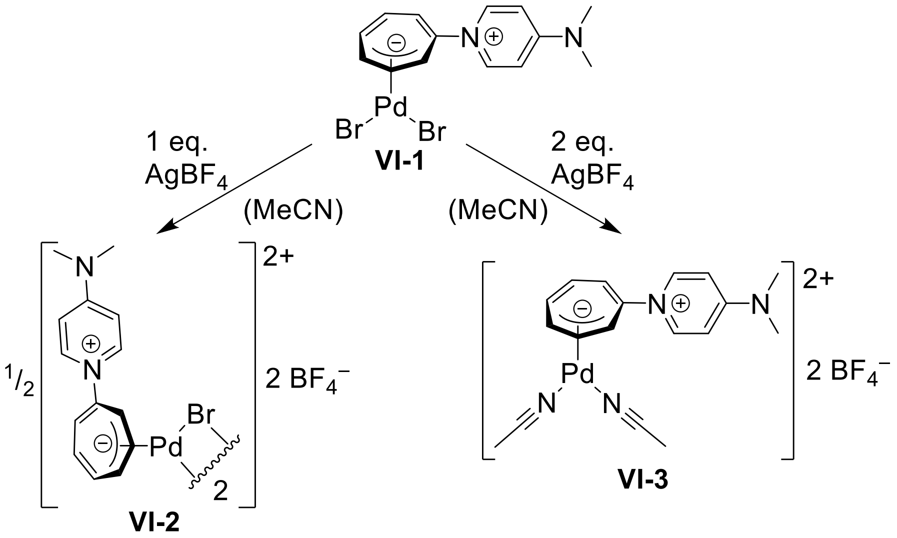
*Table 1: Relative Gibbs free energies for covalent isomers **B**-**E** and different types of interaction for the ionic form **A** of **V-2** in dichloromethane (DCM) and acetonitrile (MeCN). For the ionic and H-bond interaction only the most favourable geometry has been included. All data relative to structure **E** in the respective solvent.*

isomer/ interaction	**B**		**C**		**D**		**E**		**A: ionic**		**A: H-bond**		**A: X-bond**	
geometry														
solvent	DCM	MeCN	DCM	MeCN	DCM	MeCN	DCM	MeCN	DCM	MeCN	DCM	MeCN	DCM	MeCN
$G_{rel.}$	6.29	6.31	0.05	0.12	0.30	0.33	0.00	0.00	2.70	0.15	2.33	-0.73	4.93	6.31

<u>Reference:</u> C. Jandl, D. C. Mayer, A. Pöthig, *Eur. J. Org. Chem.* **2017**, 4255–4259, doi: 10.1002/ejoc.201700692.

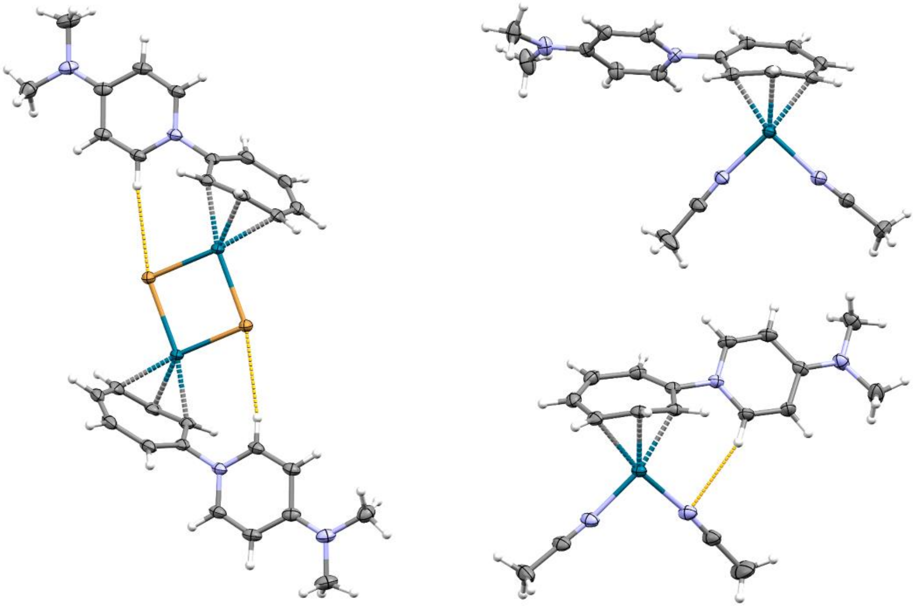
4.6 A Halide-free Pyridinium-substituted η^3-Cycloheptatrienide-Pd Complex

As the studies of substituted η^3-cycloheptatrienide-Pd complexes with different Pd:Br ratios had produced a great variety of structures ranging from monomers (Pd:Br = 1:2), over dimers (Pd:Br = 2:2 and Pd:Br = 2:3) to tetramers (Pd:Br = 4:4) (see the above chapters), the question arose which shape the complexes would assume upon complete removal of bromide ligands. This was also envisioned as a possible route to complexes with metal-metal interactions which then could serve as useful precursors similar to the concept of "pre-clusters" (see chapter 4.4). Similar to the synthesis of dimeric complexes (see chapter 4.1 and **VI-2** in Scheme 55, left), the halide free compound **VI-3** could be synthesised from the monomeric complex **VI-1** by reaction with two equivalents of silver tetrafluoroborate (see Scheme 55, right). Single crystals could be obtained of both complexes **VI-2** and **VI-3** (see Figure 6). The structure of compound **VI-2** is analogous to related dimeric complexes with a Pd:Br ratio of 2:2. The halide free complex **VI-3** has a monomeric structure, in which acetonitrile solvent ligands occupy the empty coordination sites on Pd. Attempted crystallisation from a non-coordinating solvent resulted in decomposition, indicating that the envisioned metal-metal contacts were indeed formed, but were not stable and thus initiated decomposition to elemental Pd. **3** crystallised with two independent molecules in the asymmetric unit, which differ in the orientation of the pyridinium-substituent so that only one of the molecules features an intramolecular H bond.



*Scheme 55: Synthesis of dimeric and monomeric pyridinium-substituted η^3-cycloheptatrienide complexes **VI-2** and **VI-3** by exchange of bromide ligands for tetrafluoroborate ions.*

Still both molecules crystallise as the *β*-isomer, which previously had been explained by internal hydrogen bonds between the cationic substituents and bromide ligands. In this case, the effect could be attributed to crystal packing and electronic effects. Although the importance of hydrogen bonds for halide-containing derivatives is not disproved by this, it shows that other factors play a significant role as well.



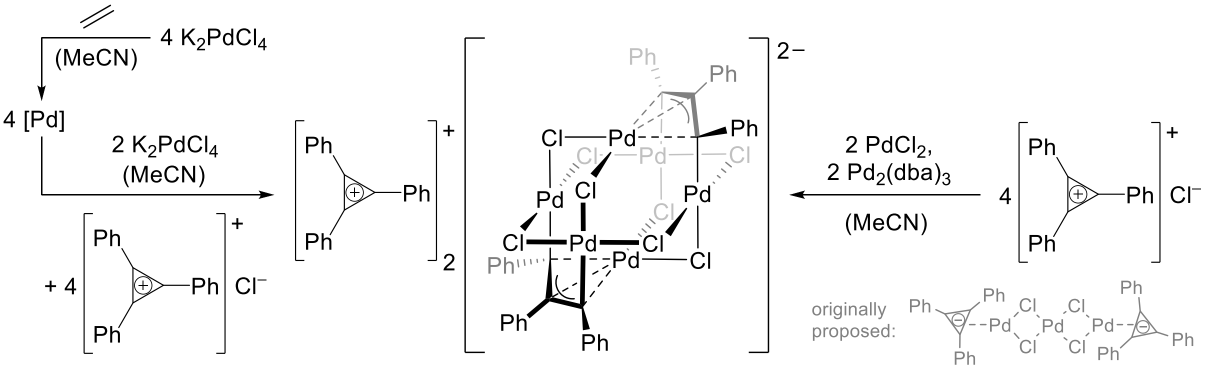
VI-2 **VI-3**

*Figure 6: Molecular structures of complexes **VI-2** (left) and **VI-3** (right, two molecules in the asymmetric unit) with ellipsoids at the 50% probability level. Counterions and co-crystallised solvent molecules are omitted for clarity.*

Reference: C. Jandl, S. Stegbauer, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 754–759, doi: 10.1107/S2053229617012244.

4.7 A Pd Halide Cluster from 1964: Pd_6Cl_8 Capped by Ring-Opened C_3Ph_3 Ligands from Oxidative Addition of Cyclopropenium Ions

As proposed earlier, a re-investigation of a protocol from 1964 on the reaction of potassium tetrachloropalladate, triphenylcyclopropenium chloride and ethylene was undertaken.[176] It could be shown that instead of the originally proposed structure (see Scheme 56, bottom right), a Pd_6Cl_8 cluster with capping C_3Ph_3 ligands is formed, the structure of which could be elucidated by X-ray crystallography (see Scheme 56 and Figure 7). The structure can be derived from the β-$PdCl_2$ structure, Pd_6Cl_{12}, in which Pd(II) occupies the centres of all faces and chloride the centres of all edges of a cube.[221-224] In the cluster fragment $[Pd_6Cl_8(C_3Ph_3)_2]^{2-}$, each two chlorides on opposite vertices are replaced by the capping ligands, which feature the rare μ^3-η^1:η^1:η^3-binding mode with two alkyl and one allyl bond. The Pd atoms form a heavily distorted octahedron with Pd-Pd distances ranging from weak contacts to strong interactions. The formation of $[C_3Ph_3]_2[Pd_6Cl_8(C_3Ph_3)_2]$ can be explained by a three-step mechanism: First, Pd(II) is partially reduced by ethylene leading to an intermediate Pd(0) species. Then, a ring-opening oxidative addition of the triphenylcyclopropenium ions takes place on Pd(0) and finally the clusters are formed by self-assembly with residual $PdCl_2$ from K_2PdCl_4 (see Scheme 56, left). Unreacted triphenylcyclopropenium ions serve as counterions. The partial reduction/oxidative addition sequence could be confirmed by performing the synthesis directly from a Pd(0)/Pd(II) mixture (see Scheme 56, right). An interesting observation was made in a crystal structure obtained from undried DMSO: The triphenylcyclopropenium ions obviously decomposed under these conditions and instead, the counterions of the $[Pd_6Cl_8(C_3Ph_3)_2]^{2-}$ cluster were found to be DMSO-dimers bridged by a proton between the O atoms, which represents the first crystallographic characterisation of such a $[(DMSO)_2H]^+$ species. As the



Scheme 56: Formation of cluster compound $[C_3Ph_3]_2[Pd_6Cl_8(C_3Ph_3)_2]$ by a partial reduction/oxidative addition pathway in the original reaction (left) and direct synthesis from a Pd(0)/Pd(II) mixture (right); structure of the originally proposed product (bottom right).

title compound dates back to 1964, it represents the first organometallic Pd cluster compound, although its structure was not recognised at that time. It also represents the first occurrence of the ring-opening oxidative addition reactivity of a cyclopropenium ion and the μ^3-η^1:η^1:η^3-binding mode.[225-234] These findings are not only interesting from a historical point of view, but are also relevant for future research on the controlled synthesis of metal clusters.

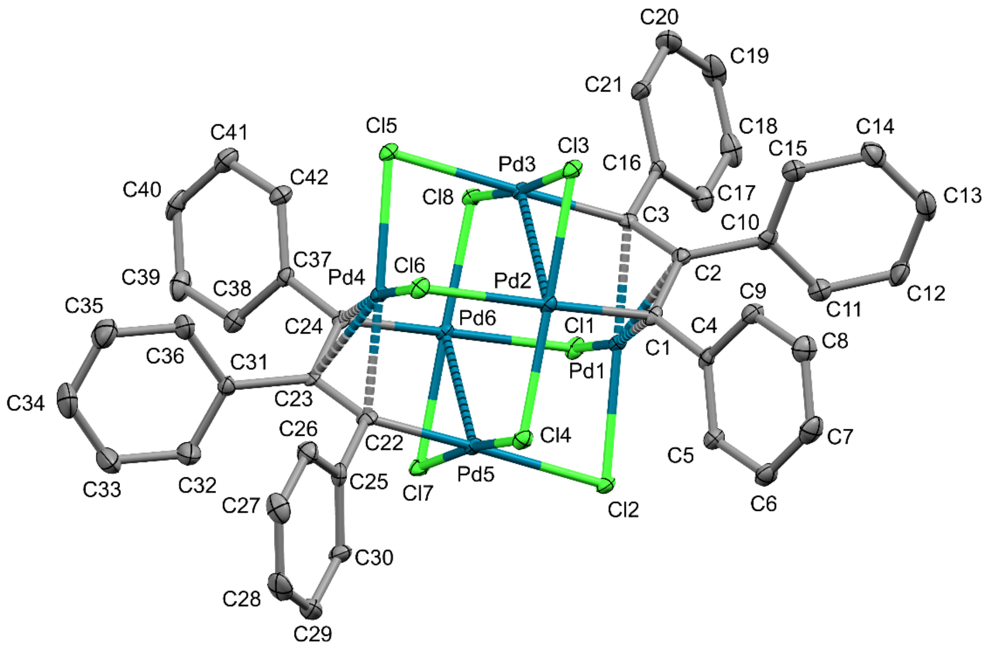


Figure 7: Molecular structure of the cluster fragment from $[C_3Ph_3]_2[Pd_6Cl_8(C_3Ph_3)_2]$ *with ellipsoids at the 50% probability level. Hydrogen atoms, counterions and co-crystallised solvent molecules are omitted for clarity.*

Reference: C. Jandl, K. Öfele, A. Pöthig, *Organometallics* **2017**, *36,* 4348–4350,
doi: 10.1021/acs.organomet.7b00525.

4.8 Hydroxytropylium Chloride: First Crystal Structure of an Unfunctionalized Hydroxytropylium Ion

In the course of the studies of halotropylium halides (see chapter 4.5), single crystals of hydroxytropylium chloride were obtained serendipitously from a decomposed sample of chlorotropylium chloride. Although this compound had first been discovered in 1951 and other hydroxytropylium salts are known as well, no crystal structure of any of these simple and fundamental organic salts has been reported so far.[235-239] The only available crystal structure involves 1,6-methano[10]annulene-fused hydroxytropylium perchlorate, but the quality is questionable.[240] The crystal structure of hydroxytropylium chloride (see Figure 8) features an almost perfectly planar seven-membered ring, thus supporting the aromatic character. However, there is a small, but significant alternation between the C-C bond lengths following the pattern of single and double bonds in the Lewis structure of tropone. Although this does not justify a full separation into single and double bonds, it shows that besides the dominating aromatic hydroxytropylium resonance structure, there are also contributions from the resonance structure of a protonated tropone (see Scheme 57, centre). The structure also gives rise to interesting packing effects as it allows both the formation of strong hydrogen bonds from the OH-group and weaker hydrogen bonds from the tropylium-protons, which creates two-dimensional networks within a layered structure. In the light of the applications of halotropylium halides mentioned earlier, the way in which the crystals were obtained also provides relevant information about their decomposition pathway. The formation of hydroxytropylium chloride can be attributed to a partial hydrolysis of chlorotropylium chloride, the full hydrolysis of which is known to lead to tropone.[171] This allows the conclusion that hydroxytropylium salts in general are the key intermediate in the hydrolytic decomposition of halotropylium halides.

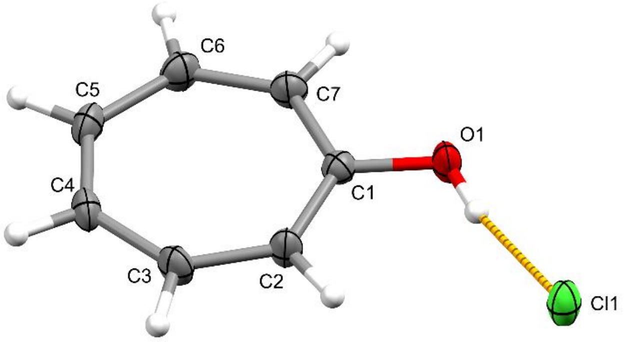
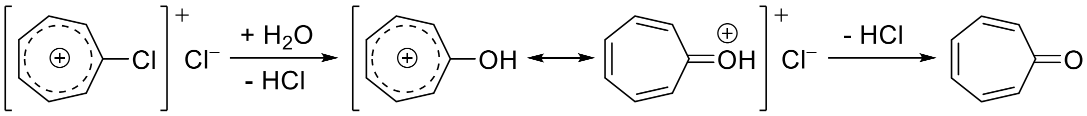


Figure 8: Molecular structure of hydroxytropylium chloride in the solid state with ellipsoids at the 50% probability level, with illustration of the strong hydrogen bonding.



Scheme 57: Hydrolytic decomposition pathway of chlorotropylium chloride to tropone via hydroxytropylium chloride, including the resonance structures of the hydroxytropylium ion.

Reference: C. Jandl, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 810–813, doi: 10.1107/S2053229617013183.

4.9 Dimerization of a Mixed-Carbene Pd^{II} Dibromide Complex by Elemental Iodine

Having established the hybrid CHT/NHC ligand motif (see chapter 4.3), further studies were conducted to elucidate the reactivity of its metal complexes. A surprising product was obtained when reacting the respective Pd(II) dibromide complex **IX-1** with an excess of elemental iodine: A dimeric bromide-bridged CHT/NHC-Pd complex similar to the one described in chapter 4.3, but with pentaiodide counterions (see Figure 9). Such a bromide removal is usually performed with silver salts (see chapter 4.1) and has not been reported with iodine so far. To explain this behaviour, the mechanism depicted in Scheme 58 was proposed. The initial attack of iodine on a bromide ligand leads to complex **IX-3**, which was found to be unstable in this case, but in the literature there are examples for complexes with a coordinated diiodobromide ion.[241,242] The formation of the observed dimer then liberates the BrI_2^- ion and it rearranges with an excess of iodine to mixed Br/I polyhalides. From crystallographic data mining it could be deduced that such systems have a tendency to from bromine-enriched species, which in an iodine-rich environment also brings about the formation of pure polyiodides. Due to favourable crystal packing only the pentaiodide ion was found in the crystal structure. Although it would be premature to attribute this novel type of reaction with iodine solely to the influence of the CHT/NHC ligand, this ligand system has certainly proved itself to be an interesting motif for further research.

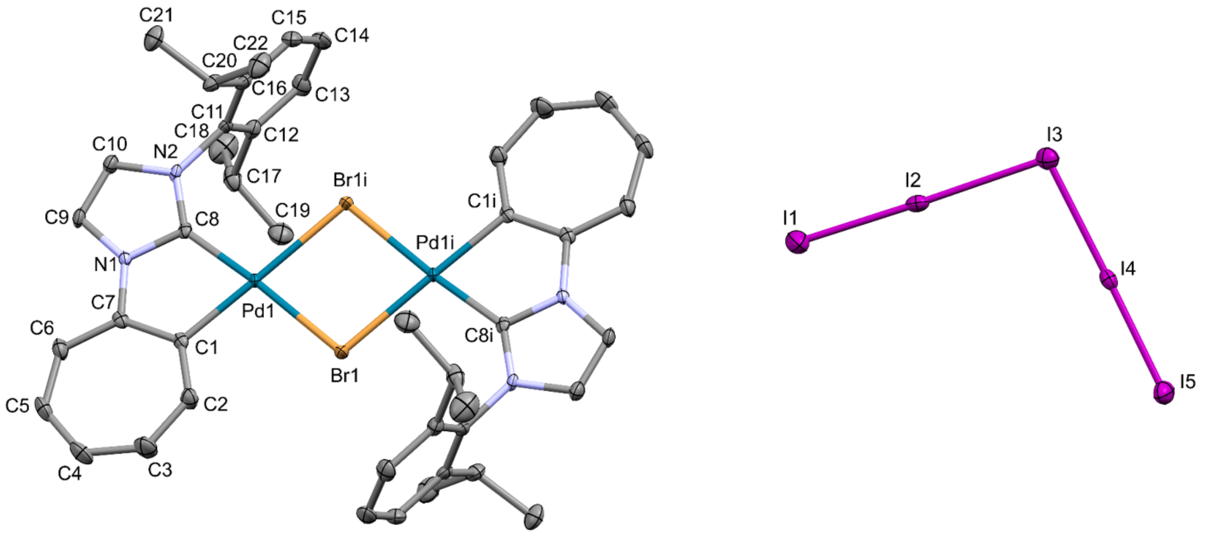
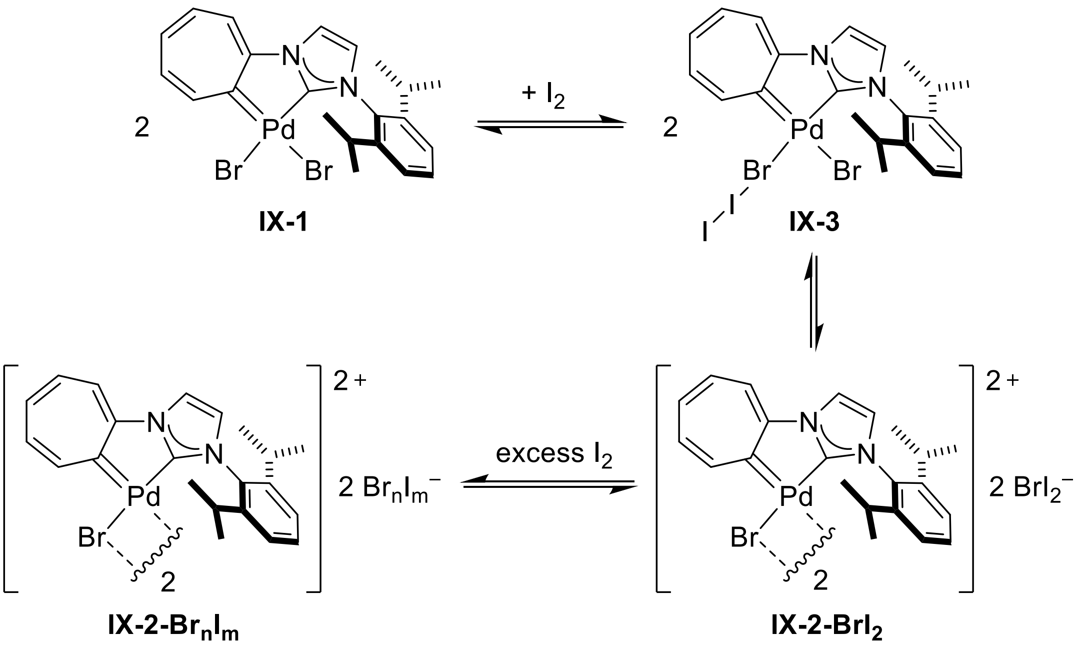


*Figure 9: Solid-state molecular structures of the dimerised complex **IX-2** (left) and one pentaiodide counterion (right) obtained from the reaction of complex **IX-1** with excess iodine. Ellipsoids are displayed at the 50% probability level and hydrogen atoms as well as co-crystallised solvent molecules are omitted for clarity.*

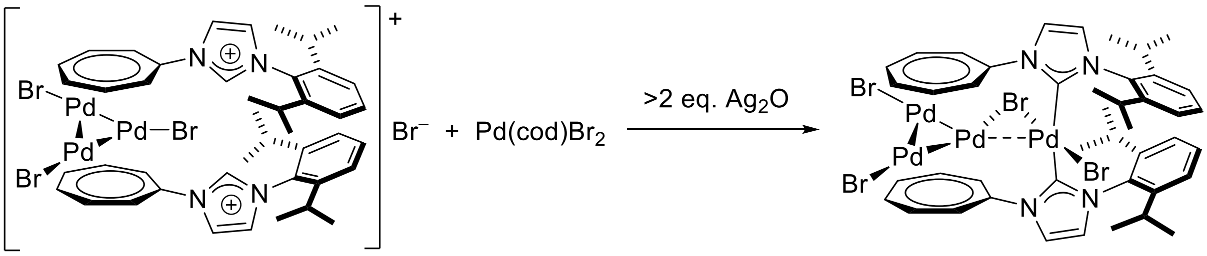


Scheme 58: Proposed mechanism for the iodine-induced dimerisation of complex ***IX-1****.*

Reference: C. Jandl, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 1131–1136, doi: 10.1107/S2053229617016412.

4.10 Unpublished Results: Extended Pd_3 Sandwich Cluster Complexes

With the facile access to imidazolium-functionalised Pd_3 sandwich cluster complexes (see chapter 4.4), the utilisation of the sidearms as NHC-precursors in order to introduce an additional metal is probably the most promising direction for further development. Initial attempts to introduce Ag(I) on the sidearms and thus obtain a universal transmetalation agent were only partly successful: Even though the desired species could be observed NMR spectroscopically in the reaction mixture, it was found to be unstable and could not be isolated. Therefore, the transmetalation was conducted in situ as shown in Scheme 59, producing the prototypic extended Murahashi complex **$[Pd_4Br_4(C_7H_6\text{-NHC-DiPP})_2]$** with a fourth Pd centre between the NHC substituents. Interestingly, even with two equivalents of the Pd(II) source only the product with one Pd between the NHCs and none of the possible Murahashi complex with one Pd on each of the NHC sidearms could be obtained. It was also noted that a large excess of silver oxide is necessary for a full conversion to take place.



Scheme 59: Synthesis of extended Murahashi complex ***$[Pd_4Br_4(C_7H_6\text{-NHC-DiPP})_2]$****.*

Crystallographic analysis confirmed the structure of **$[Pd_4Br_4(C_7H_6\text{-NHC-DiPP})_2]$** (see Figure 10, for more details including bond lengths and angles see A4.6 in the Appendix). The geometric parameters of the Pd_3 cluster are comparable to the compounds described in chapter 4.4, indicating that the additional metal does not cause a significant change in the bonding properties of the cluster. The Pd—Pd distance to the external Pd(II) (Pd1—Pd4 = 2.8184(9) Å) confirms an interaction with the additional metal, although the bond is slightly longer than the bonds within the Pd_3 cluster. An intermediate from the reaction could also be trapped crystallographically (see Figure 11). In the intermediate, only half of the imidazolium groups are deprotonated and two Murahashi complexes are connected via $PdBr_2$ units between the NHCs and equatorial bromide ligands to form an organometallic macrocycle. Whether this is a productive intermediate on the way to **$[Pd_4Br_4(C_7H_6\text{-NHC-DiPP})_2]$** or unproductive, because it leads to polymeric side-products, cannot be decided yet. However, this already points towards nanoarchitectures, which represent a potential application of Murahashi complexes as mentioned before.

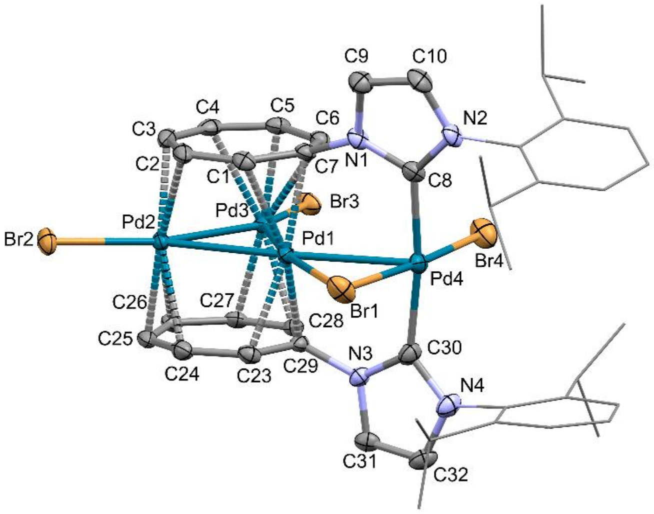


Figure 10: Molecular structure of ***[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP)$_2$]*** *in the solid state with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity and DiPP-substituents are simplified as wireframes.*

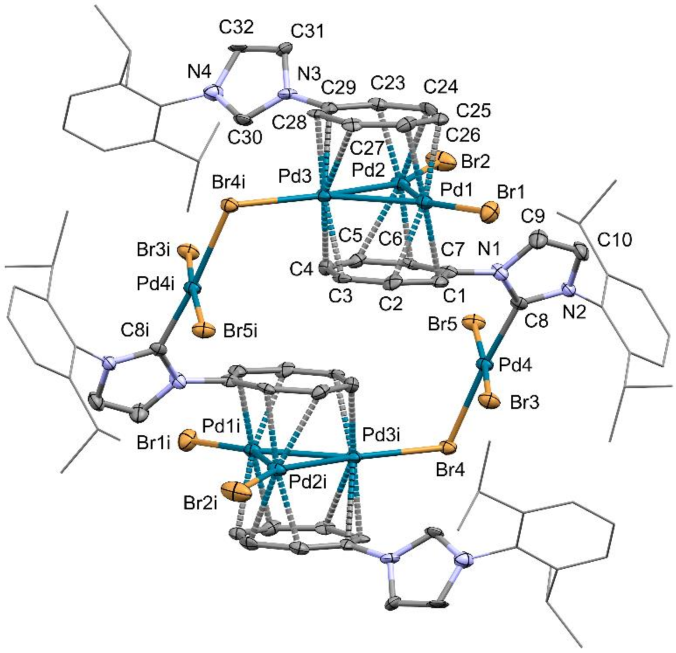


Figure 11: Molecular structure of the intermediate from the synthesis of ***[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP)$_2$]*** *in the solid state with ellipsoids at the 50% probability level. Hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and DiPP-substituents are simplified as wireframes.*

The interesting aspect of introducing exactly Pd(II) on the sidearms is the verification of the interpretation of the formal oxidation state of Pd in the trinuclear cluster. CV and SWV data clearly show an additional, more negative reduction wave in comparison to the Pd$_3$ complexes described before (see Figure 12 and the Appendix). This fully agrees with the proposed higher positive charge density of the Pd_3 cluster as compared to Pd(II). In addition to that, DFT calculations afforded NBO charges which are also more positive for the Pd_3 cluster than for the Pd(II) bound between the NHCs (see Figure 13). These results strongly corroborate the conclusions made in chapter 4.4 on the electronic structure of Murahashi complexes. The structure also shows that imidazolium-functionalised Murahashi complexes can serve as a platform to introduce additional metals in an interacting position with the Pd_3 cluster. As mentioned, an extension of a Pd_3 to a Pd_4 cluster has already been achieved for an unfunctionalised complex by Murahashi and co-workers, but the utilisation of NHC sidearms promises to be a far more versatile approach, especially towards heterobimetallic Pd_3M systems.[158]

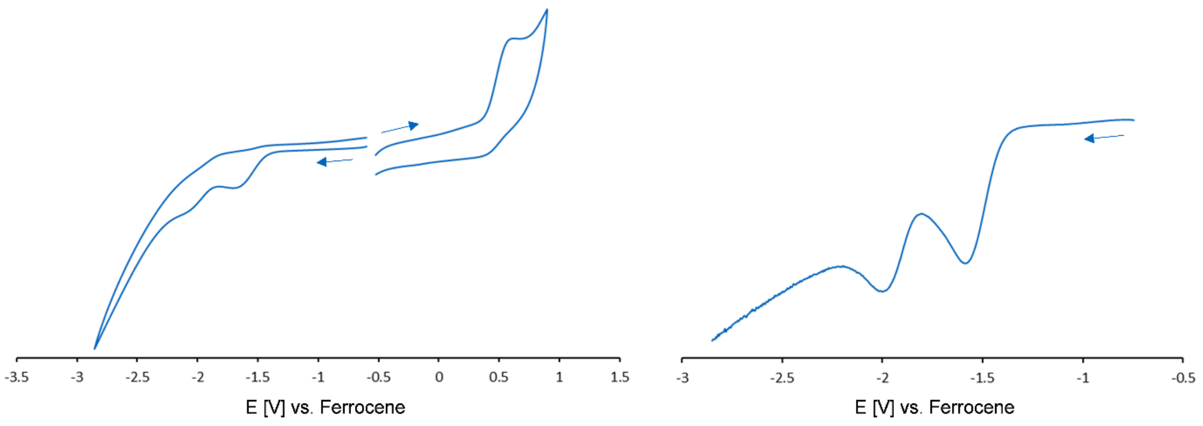


Figure 12: Cyclic voltammogram (left) and square wave voltammogram (right) of ***[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]*** *in CH_2Cl_2. Both measured at a scan rate of 100 mV s^{-1}. The current is arbitrary and and data are scaled for a better comparison.*

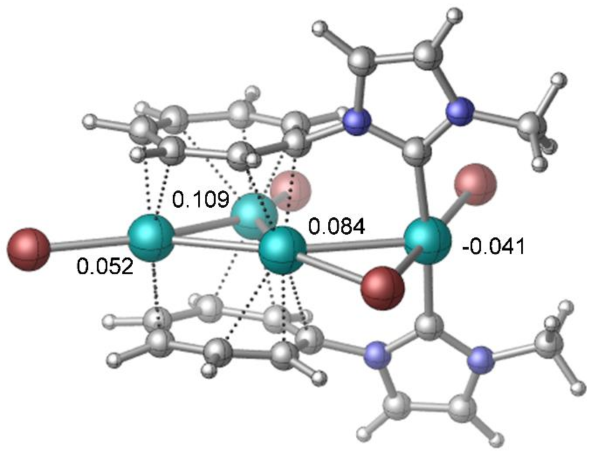


Figure 13: DFT-optimised structure of ***[$Pd_4Br_4(C_7H_6$-NHC-Me$)_2$]*** *with NBO charges of the Pd atoms.*

4. Conclusion and Outlook

The results in this thesis provide both important clarifications and revisions of older research and promising developments of novel strategies in the fields of cluster and carbene chemistry. As for the first point, the elucidation of the structure of halotropylium halides and their dynamic equilibrium with dihalocycloheptatrienes in solution is the basis for a correct mechanistic understanding of their reactivity. This will serve as important knowledge for the optimisation of their applications and correct their unfounded representation as 7,7-dihalocycloheptatrienes in the literature (see chapter 4.5). Another re-evaluation of older research led to the identification of $[C_3Ph_3]_2[Pd_6Cl_8(C_3Ph_3)_2]$ as the product of a protocol from 1964 which makes it the first isolated organometallic Pd cluster compound (see chapter 4.7). This also points out a route for the rational synthesis of Pd halide clusters in the future and shows the potential use of C_3Ph_3 ligands from the ring-opening of triphenylcyclopropenium ions as capping ligands in cluster chemistry.

On the basis of former research on the reactivity of Pd-CHT complexes towards N-nucleophiles, the structure of the resulting imidazolium- and pyridinium-substituted η^3-cycloheptatrienide Pd complexes was determined and a diverse structural chemistry could be established around them. Exchange of halide ligands for non-coordinating anions proved a valuable tool to open up access to dimeric derivatives with advantageous properties: For one, they feature a greatly enhanced solubility which is essential for further synthetic utilisation. Additionally, Pd-Pd interactions were observed in several of the dimeric structures which makes them useful precursors for Pd clusters. Their behaviour in solution turned out to be highly complex, involving dynamic equilibria between different regioisomers of the allyl bond, between different conformers of the substituent (only in the case of the imidazolium derivatives) and even between different Pd_nX_m core structures. Although detailed insights could be obtained into the first two areas by means of DFT calculations, there is no complete picture of the equilibria between different Pd halide core structures yet. For instance, the co-existence of the dimeric and tetrameric complex of one derivative (see chapter 4.2) could be a more common feature, not only for other imidazolium- and pyridinium-substituted η^3-cycloheptatrienide Pd complexes, but also for Pd chemistry in general. This structural aspect certainly needs further investigation as it could have major consequences for the understanding of structure-property relations in Pd chemistry.

The class of imidazolium- and pyridinium-substituted η^3-cycloheptatrienide Pd complexes was successfully employed in the synthesis of substituted trinuclear Pd sandwich cluster complexes. In the course of this research, the electronic structure of the $[Pd_3X_3(C_7H_7)_2]^-$ fragment could be clarified by electrochemical and computational methods, which will allow a more accurate interpretation of their chemical behaviour in the future. In the evaluation of different synthetic pathways, particularly the dimeric motifs with Pd-Pd interactions proved to be ideal precursors, because two of the target three Pd atoms are 1) already aligned closely together and 2) already each bound to a cycloheptatrienide ligand, so the term “pre-cluster” was introduced for such an arrangement. This strategy made a large variety of substitution patterns on the sandwiching ligands available and therefore grants access to a versatile class of bifunctional organometallic complexes combining the Murahashi cluster motif with an imidazolium or pyridinium sidearm. Especially the imidazolium sidearm was shown to bear great promise for further developments. Although attempts to employ an in-situ-generated free NHC next to the cluster in CO_2 activation were unsuccessful, it could be demonstrated that a metalation of the NHC sidearm is possible. Expanding the scope of metals on the sidearms should now be the primary interest for future research as heterobimetallic Pd_3M clusters could be highly interesting bifunctional catalysts or potential single-source precursors for Pd alloys.

Besides the synthesis of functionalised Murahashi complexes, imidazolium-substituted η^3-cycloheptatrienide Pd complexes also serve as suitable precursors for mixed carbocyclic/N-heterocyclic carbene complexes as demonstrated in chapter 4.3. The unprecedented CHT/NHC-ligand was built up in an exclusive on-site synthesis utilising several of the different binding modes of which cycloheptatriene-based ligand systems are capable. The full characterisation indicated an electronic interaction between the two cyclic carbene moieties, so the combination of them in a single ligand could give rise to cooperative effects. In this sense, first reactivity studies revealed a surprising behaviour of the CHT/NHC-Pd complex towards elemental iodine, so the influence of the combined carbene motif is certainly an interesting topic for further investigations.

5. References

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Appendix

A1. Contributions to the Publications

Table A1: Overview of the contributions of Ph. D. candidate C. Jandl to the individual publications (all as first author).

Publication	Reference	Contributions
Structure and Dynamics of Imidazolium- and Pyridinium-substituted η^3-Cycloheptatrienide-Pd Complexes[1]	C. Jandl, K. Öfele, F. E. Kühn, W. A. Herrmann, A. Pöthig, *Organometallics* **2014**, *33*, 6398–6407.	Compound synthesis and characterisation, computational chemistry, major part of X-ray crystallography, manuscript preparation, preparation of supporting material
A Pd_4Br_4 Macrocycle trapped by Cocrystallization from a Highly Dynamic Equilibrium of η^3-Cycloheptatrienide Complexes	C. Jandl, S. Stegbauer, A. Pöthig, *Acta Crystallogr., Sect. C* **2016**, *72*, 509–513.	Major part of compound synthesis and characterisation, supervision of co-author S. Stegbauer, X-ray crystallography, manuscript preparation
A Hybrid Carbocyclic/N-heterocyclic Carbene Ligand[1]	C. Jandl, A. Pöthig, *Chem. Commun.* **2017**, *53*, 2098–2101.	Compound synthesis and characterisation, computational chemistry, X-ray crystallography, manuscript preparation, preparation of supporting material
Rational Synthesis and Electronic Structure of Functionalized Trinuclear Pd Metal Sheet Sandwich Complexes[1]	C. Jandl, J. R. Pankhurst, J. B. Love, A. Pöthig, *Organometallics* **2017**, *36*, 2772–2783.	Compound synthesis and characterisation (except electrochemistry), computational chemistry, X-ray crystallography, manuscript preparation (except electrochemistry), preparation of supporting material (except electrochemistry)
The Ambivalent Nature of Halogenated Tropone Derivatives: Dihalocycloheptatriene versus Halotropylium Halide	C. Jandl, D. C. Mayer, A. Pöthig, *Eur. J. Org. Chem.* **2017**, 4255–4259.	Major part of compound synthesis and characterisation, supervision of co-author D. C. Mayer, computational chemistry, X-ray crystallography, manuscript preparation, preparation of supporting material
A Halide-free Pyridinium-substituted η^3-Cycloheptatrienide-Pd Complex	C. Jandl, S. Stegbauer, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 754–759.	Equal parts of compound synthesis and characterisation, supervision of co-author S. Stegbauer, X-ray crystallography, manuscript preparation

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[1] Parts of the results in these publications have already served for examination purposes in: C. Jandl, Master´s Thesis, Technische Universität München, **2013**. (Reference [131])

Continuation of Table A1.

Publication	**Reference**	**Contributions**
A Pd Halide Cluster from 1964: Pd_6Cl_8 Capped by Ring-Opened C_3Ph_3 Ligands from Oxidative Addition of Cyclopropenium Ions	C. Jandl, K. Öfele, A. Pöthig, *Organometallics*, **2017**, *36*, 4348–4350.	Equal part of synthesis, major part of characterisation, X-ray crystallography, manuscript preparation, preparation of supporting material
Hydroxytropylium Chloride: First Crystal Structure of an Unfunctionalized Hydroxytropylium Ion	C. Jandl, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 810–813.	Compound synthesis and crystallisation, X-ray crystallography, manuscript preparation
Dimerization of a Mixed-Carbene Pd^{II} Dibromide Complex by Elemental Iodine	C. Jandl, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 1131–1136.	Compound synthesis and characterisation, X-ray crystallography, manuscript preparation

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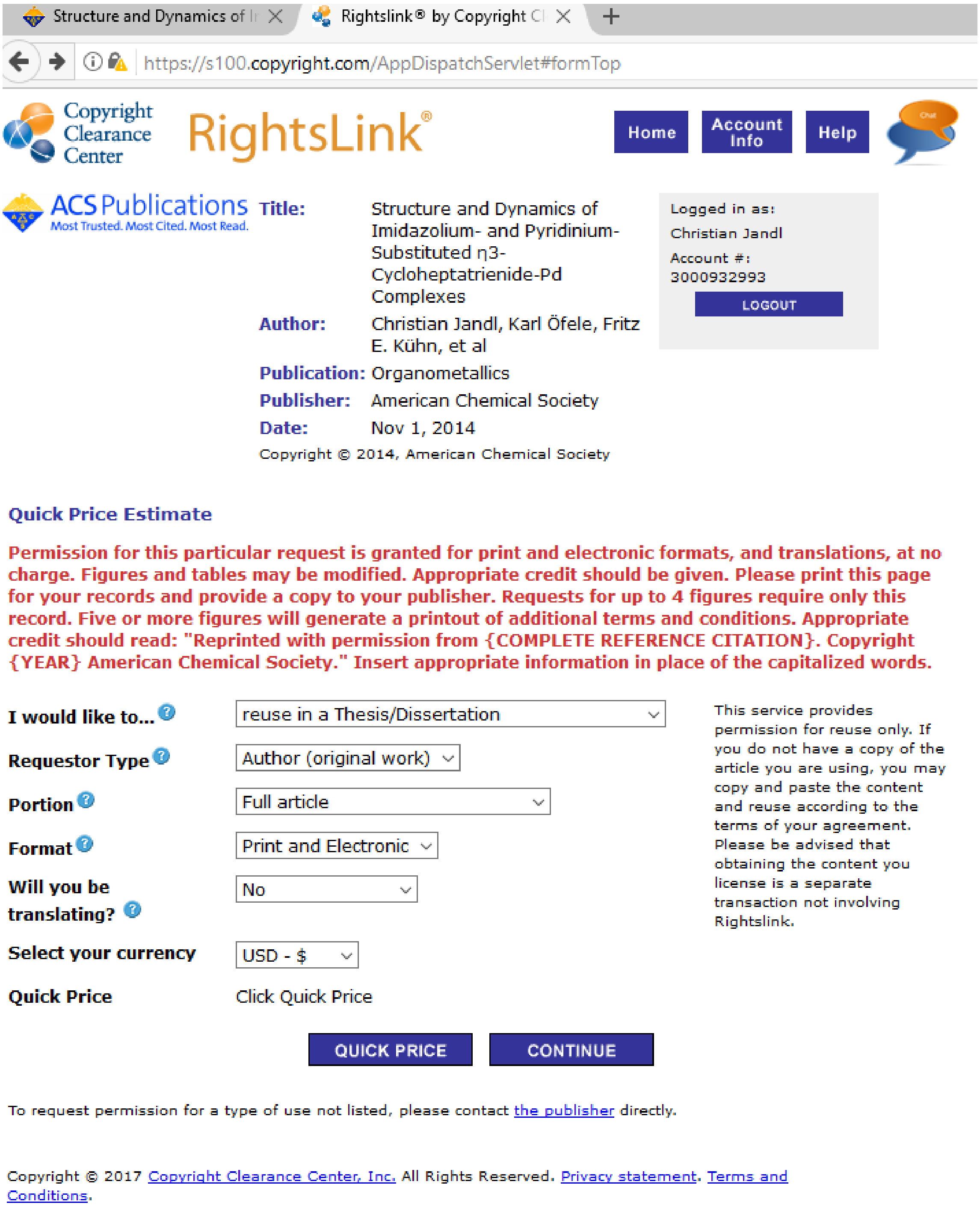
Structure and Dynamics of Imidazolium- and Pyridinium-substituted η^3-Cycloheptatrienide-Pd Complexes



Title:	Structure and Dynamics of Imidazolium- and Pyridinium-Substituted η3-Cycloheptatrienide-Pd Complexes
Author:	Christian Jandl, Karl Öfele, Fritz E. Kühn, et al
Publication:	Organometallics
Publisher:	American Chemical Society
Date:	Nov 1, 2014

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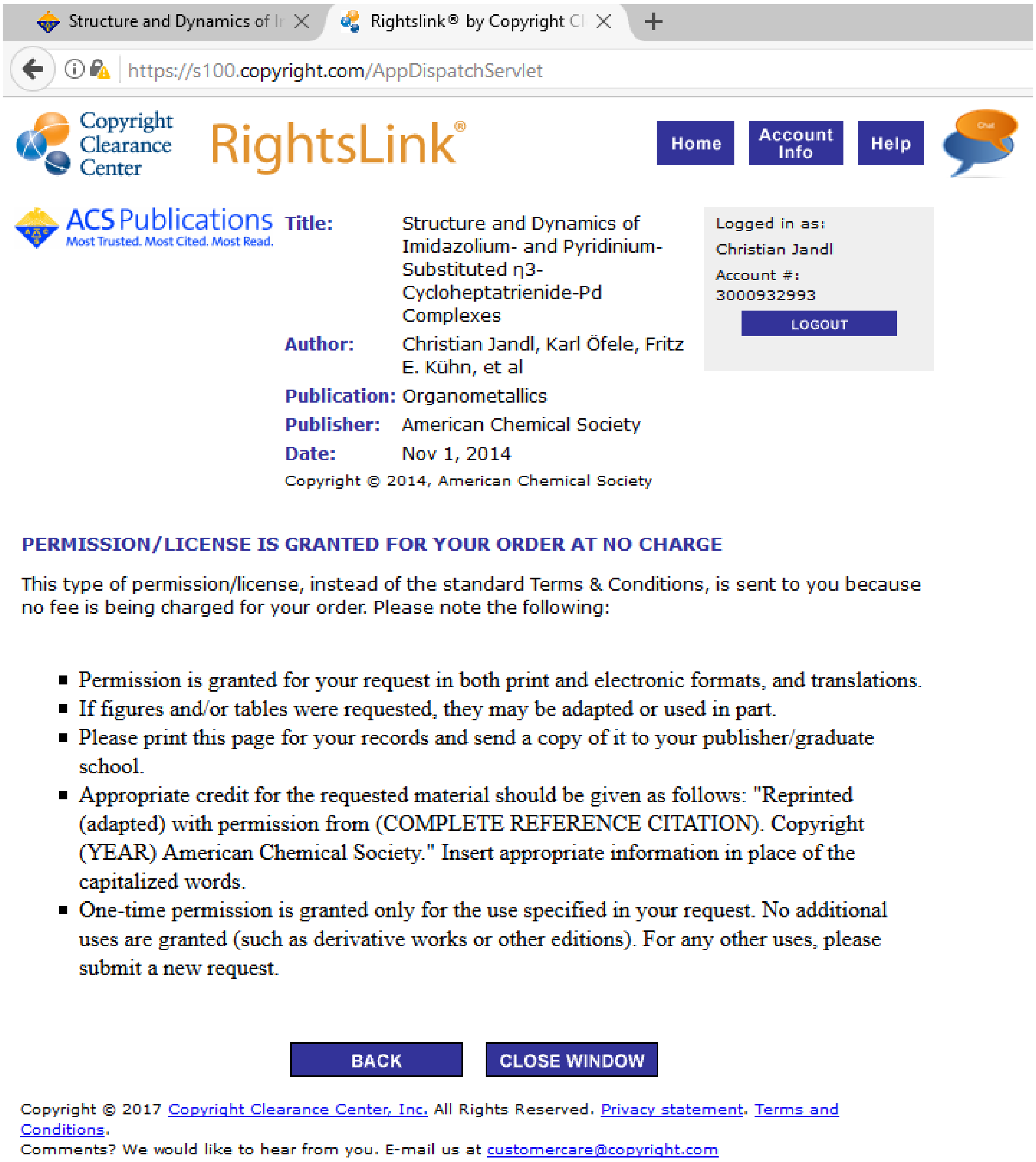

Title: Structure and Dynamics of Imidazolium- and Pyridinium-Substituted η3-Cycloheptatrienide-Pd Complexes

Author: Christian Jandl, Karl Öfele, Fritz E. Kühn, et al

Publication: Organometallics

Publisher: American Chemical Society

Date: Nov 1, 2014

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A Pd_4Br_4 macrocycle trapped by cocrystallization from a highly dynamic equilibrium of η^3-cycloheptatrienide complexes

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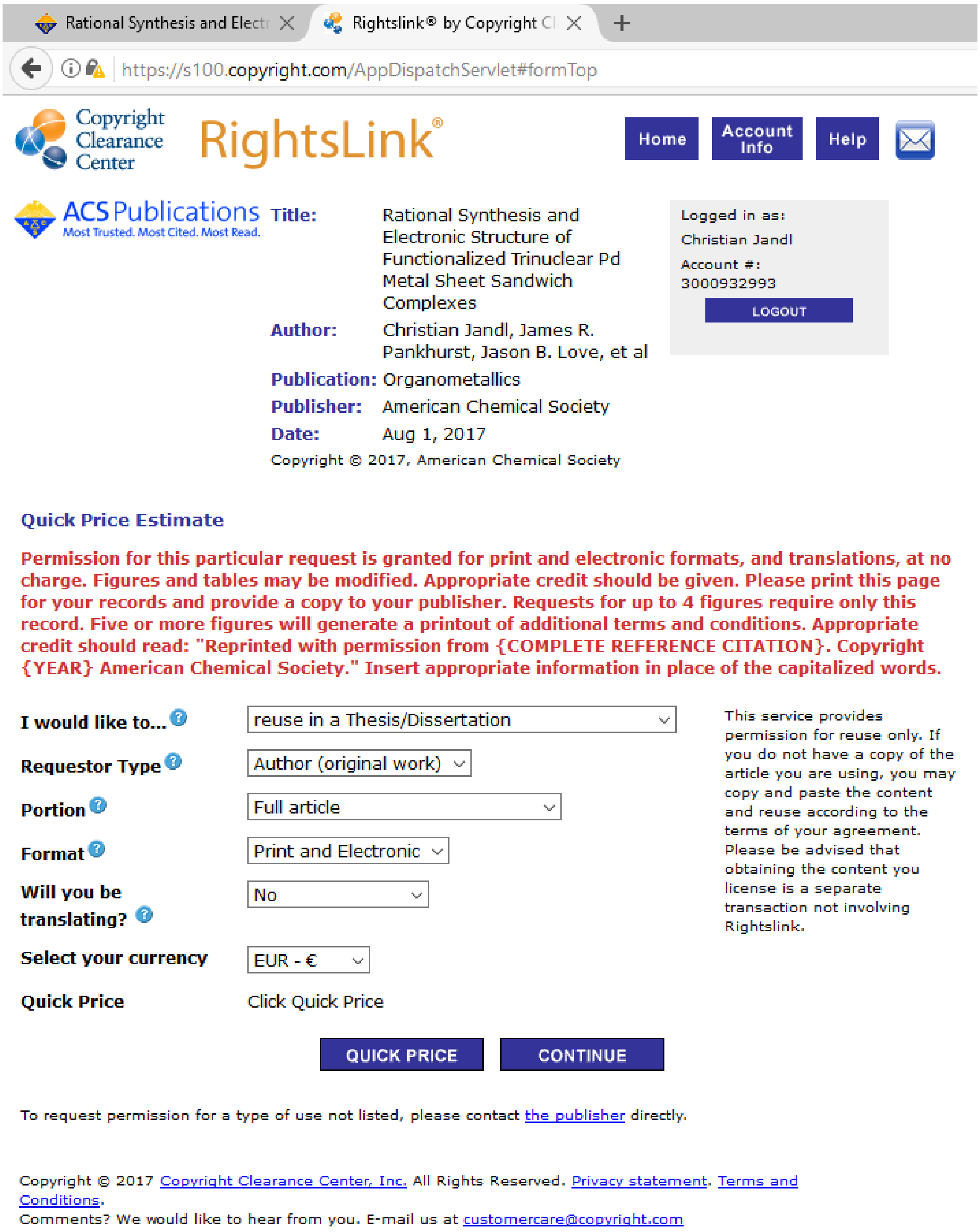

Title: Rational Synthesis and Electronic Structure of Functionalized Trinuclear Pd Metal Sheet Sandwich Complexes

Author: Christian Jandl, James R. Pankhurst, Jason B. Love, et al

Publication: Organometallics

Publisher: American Chemical Society

Date: Aug 1, 2017

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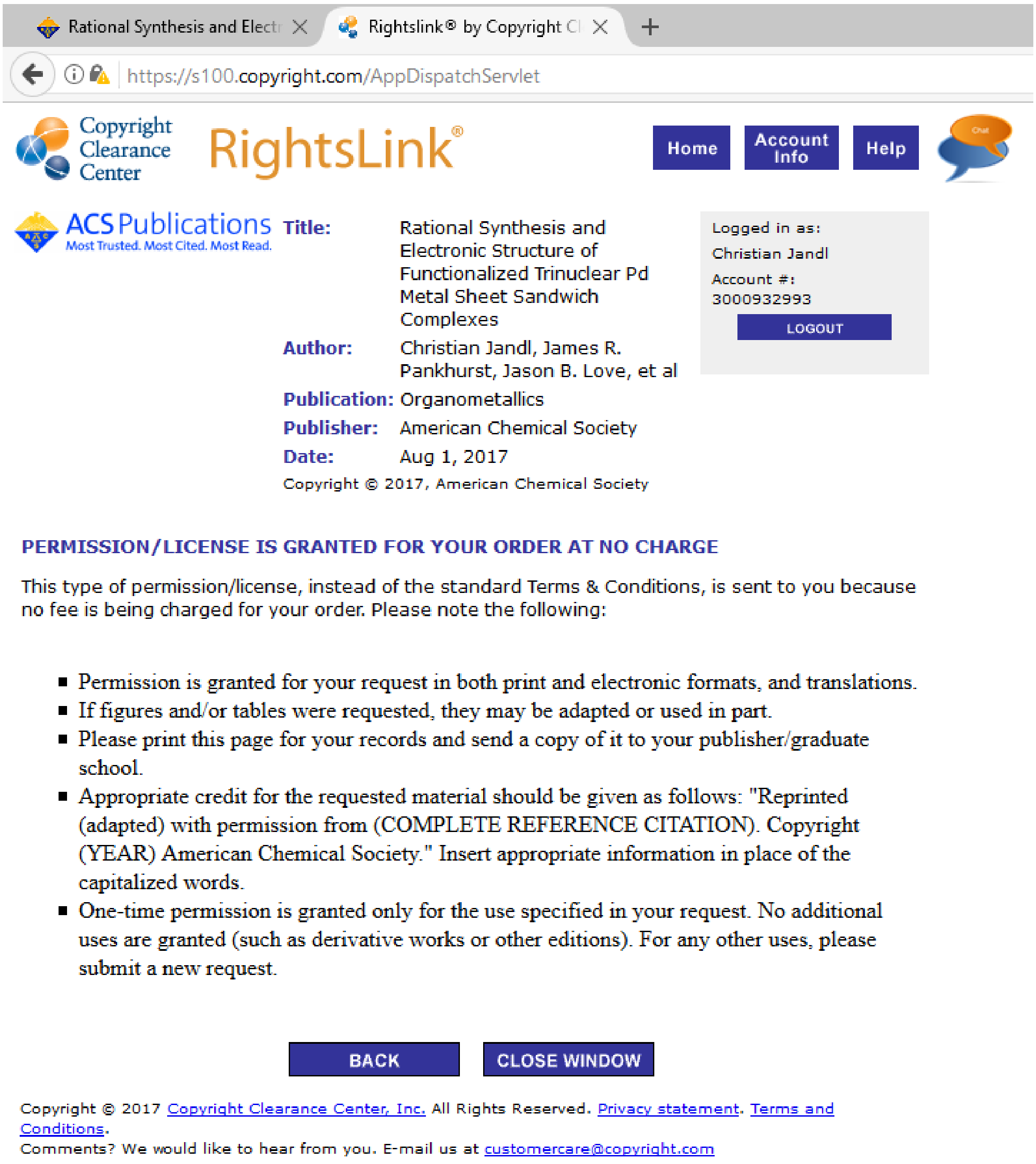

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The Ambivalent Nature of Halogenated Tropone Derivatives: Dihalocycloheptatriene vs. Halotropylium Halide

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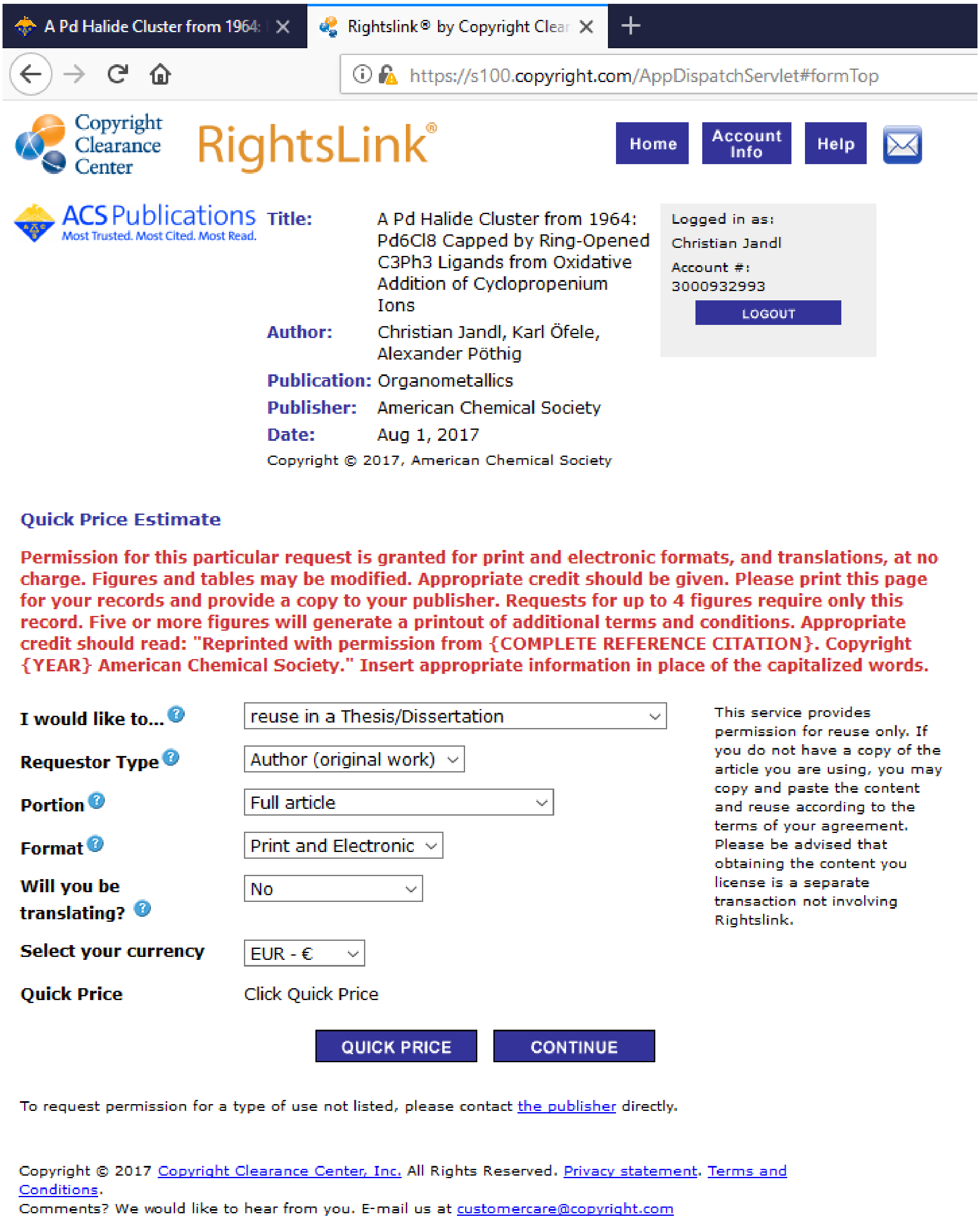

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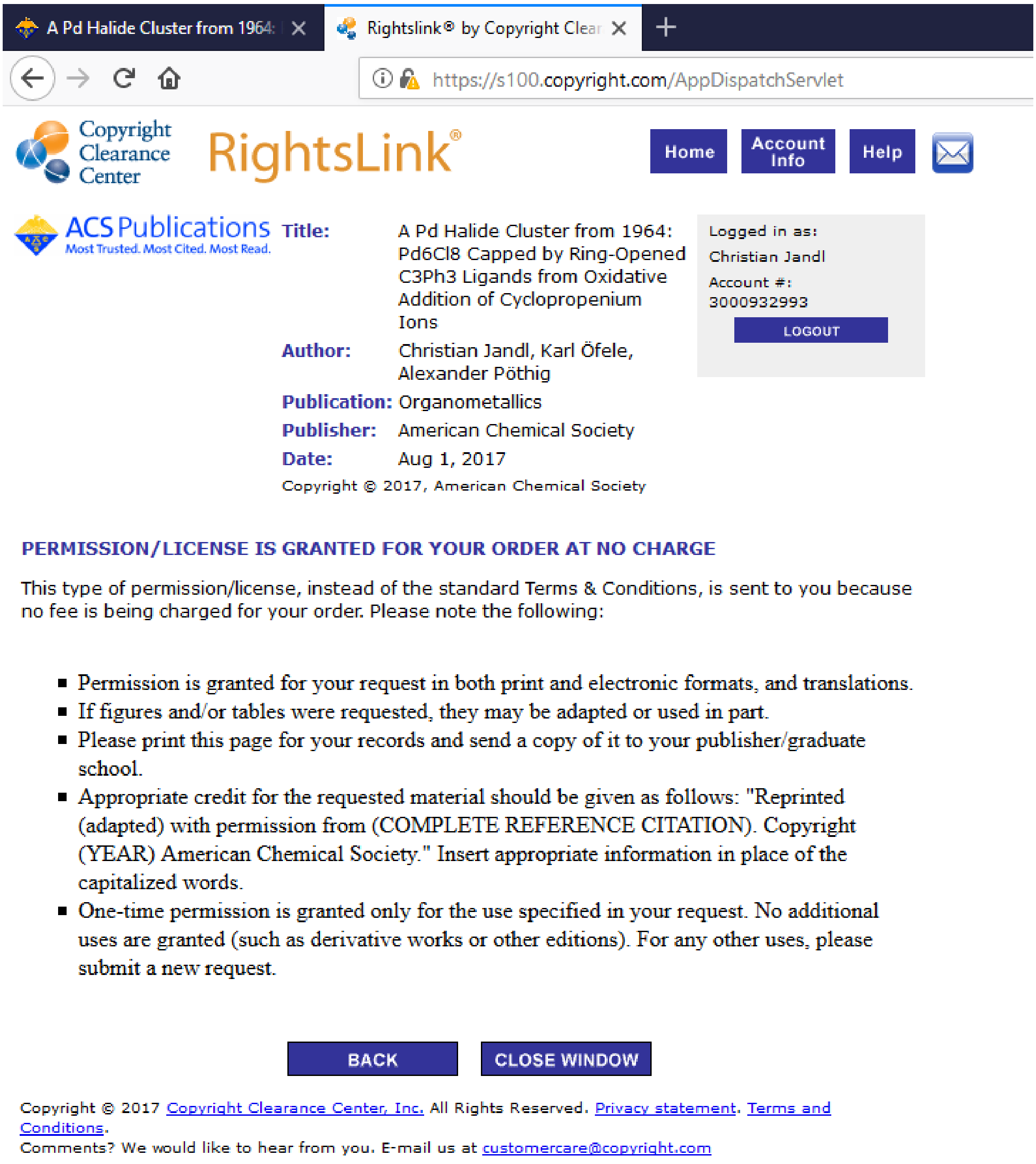

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Structure and Dynamics of Imidazolium- and Pyridinium-substituted η^3-Cycloheptatrienide-Pd Complexes

Christian Jandl, Karl Öfele, Fritz E. Kühn, Wolfgang A. Herrmann, and Alexander Pöthig*

Organometallics **2014**, *33*, 6398−6407

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

Direct Link: DOI 10.1021/om500738d

A Pd_4Br_4 macrocycle trapped by cocrystallization from a highly dynamic equilibrium of η^3-cycloheptatrienide complexes

C. Jandl, S. Stegbauer and A. Pöthig*

Acta Crystallogr., Sect. C **2016**, *72*, 509−513

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Direct Link: DOI 10.1107/S2053229616008275

A hybrid carbocyclic/N-heterocyclic carbene ligand

Christian Jandl and Alexander Pöthig*

Chem. Commun. **2017**, *53*, 2098−2101

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Rational Synthesis and Electronic Structure of Functionalized Trinuclear Pd Metal Sheet Sandwich Complexes

Christian Jandl,[†] James R. Pankhurst,[‡] Jason B. Love,[‡] and Alexander Pöthig*[,†]

Organometallics, **2017**, *36*, 2772–2783

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Direct Link: DOI 10.1021/acs.organomet.7b00276

The Ambivalent Nature of Halogenated Tropone Derivatives: Dihalocycloheptatriene vs. Halotropylium Halide

Christian Jandl,[a] David C. Mayer,[a] and Alexander Pöthig*[a]

Eur. J. Org. Chem. **2017**, 4255–4259

[a] Catalysis Research Center & Department of Chemistry, Technische Universität München, Ernst-Otto-Fischer-Str. 1, 85747 Garching b. München, Germany

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A halide-free pyridinium-substituted η^3-cycloheptatrienide–Pd complex

C. Jandl, S. Stegbauer and A. Pöthig*

Acta Crystallogr., Sect. C **2017**, *73*, 754–759

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A Pd Halide Cluster from 1964: Pd_6Cl_8 Capped by Ring-Opened C_3Ph_3 Ligands from Oxidative Addition of Cyclopropenium Ions

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Organometallics, **2017**, *36,* 4348–4350

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Hydroxytropylium chloride: the first crystal structure of an unfunctionalized hydroxytropylium ion

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Acta Crystallogr., Sect. C **2017**, *73*, 810–813

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Dimerization of a Mixed-Carbene Pd^{II} Dibromide Complex by Elemental Iodine

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Acta Crystallogr., Sect. C **2017**, *73*, 1131–1136

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Direct Link: DOI 10.1107/S2053229617016412

A4. Supporting Information on Unpublished Results

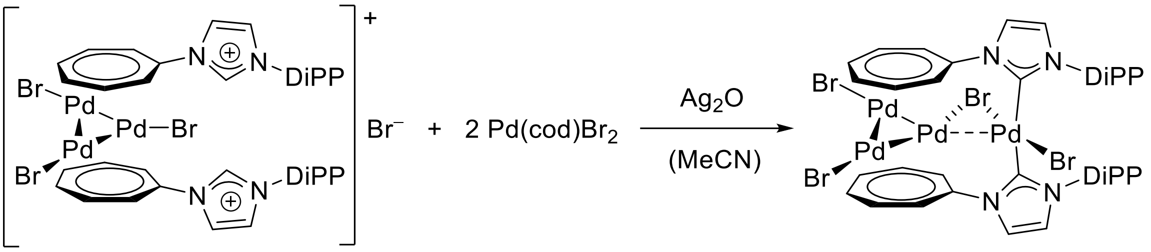
A4.1 Materials and Methods

All reactions were performed under Argon (99.996%, *Westfalen*) using standard Schlenk techniques or in a glove box (labmaster 130, *MBraun*). Dry solvents were obtained from an MB-SPS (*MBraun*) and stored over molecular sieves. Chemicals were purchased from commercial suppliers as *ABCR, Sigma Aldrich, Merck, AppliChem* and *Fluka* and used without further purification. Dibromo(cycloocta-1,5-diene)palladium(II) was synthesised according to literature procedures.[A1] **IV-3d-Br** was synthesised according to the method described in chapter 4.4 (reference: *Organometallics* **2017**, *36*, 2772–2783).

NMR spectra were recorded on a *Bruker* AVIII 400US spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C) and chemical shifts are referenced to the solvent residual signals with respect to tetramethylsilane; ^{13}C-spectra are proton-decoupled. Processing and analysis were performed with the MestReNova software package (Version 8.1.4, *Mestrelab Research*). ^{1}H-NMR data are reported as follows: chemical shift in ppm (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, virt. = virtual, br. = broad, n. r. = not resolved), coupling constant in Hz, integral, assignment). 2D-NMR spectra (COSY) were used to confirm the peak assignment. Elemental analyses were performed by the microanalytical laboratory of the Technische Universität München. ESI mass spectra were recorded on a Q-TOF micro (*micromass*) with the samples prepared as solution in acetonitrile, and *m*/*z* is reported in atomic units per elementary charge.

Electrochemical measurements were made using an Autolab ECO Chemie PGSTAT potentiostat and the data processed using GPES Manager Version 4.9. The supporting electrolyte, $[^{n}Bu_4N][PF_6]$, was purchased from Sigma Aldrich, recrystallized from ethanol three times and dried for two days at 100 °C under reduced pressure. CH_2Cl_2 was nitrogen-purged and dried by passing through vacuum atmosphere drying towers and then stored over molecular sieves. Experiments were undertaken in degassed solvent under a flow of N_2. The solution employed was 2 mM of the analyte in 12 cm^3 of the solvent, with 0.1 M $[^{n}Bu_4N][PF_6]$ as the supporting electrolyte. Cyclic voltammograms were recorded for a quiescent solution at variable scan rates. Square-wave voltammograms were recorded using a frequency of 10 Hz, a step potential of 5 mV and an amplitude of 20 mV, giving a scan rate of 100 mV s^{-1}. For these experiments, the working electrode was a glassy-carbon disc (d = 3 mm), the counter-electrode was a Pt-gauze, and a Ag-wire was used as a quasi-reference electrode. The voltammograms were calibrated against the ferrocenium/ferrocene redox couple (Fc^+/Fc = 0 V).

A4.2 Synthesis



$C_{44}H_{52}Br_4N_4Pd_3$
1275.80 g/mol

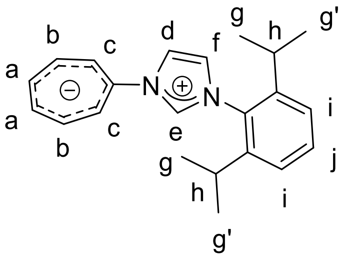
$C_8H_{12}Br_2Pd$
374.41 g/mol

$C_{44}H_{50}Br_4N_4Pd_4$
1380.21 g/mol

150 mg (0.118 mmol, 1 eq.) of **IV-3d-Br**, 48.4 mg (0.129 mg, 1.1 eq.) of Pd(cod)Br_2 and 163 mg (0.705 mmol, 6 eq.) of Ag_2O were dissolved/suspended in 8 mL of acetonitrile and stirred for 3d under exclusion of light. The reaction mixture was filtered through Celite® and the filtrate evaporated in vacuo. After two steps of fractioned precipitation (DCM/hexane and THF/Et_2O), 88 mg (0.0638 mmol, 54%) of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** were obtained as a shiny brown solid.

^{1}H-NMR (400 MHz, CD_3CN, 298 K): δ (ppm) = 7.98 (d, ^3J = 2.0 Hz, 2H, H-d), 7.33 (t, ^3J = 7.8 Hz, 2H, H-j), 7.23 (d, ^3J = 2.0 Hz, 2H, H-f), 7.05 (d, ^3J = 7.8 Hz, 4H, H-i), 5.13 (d, ^3J = 8.3 Hz, 4H, H-c), 4.98-5.09 (m, 8H, H-a H-b), 2.48 (septet, ^3J = 6.8 Hz, 4H, H-h), 0.88-0.92 (m, 24H, H-g, H-g')

^{13}C-NMR (100 MHz, CD_2Cl_2, 298 K): δ (ppm) = 170.62 (carbene-C), 146.67, 133.92, 130.46, 126.61, 125.47, 124.18, 98.54, 78.75, 78.70, 70.27, 28.83, 26.75, 23.05



Elemental Analysis (%): Calcd.: C, 38.29; H, 3.65; N, 4.06. Found: C, 38.37; H, 3.72; N, 4.00

ESI-MS (m/z): 926.57 (M-2Pd-3Br)$^+$,1298.70 (M-Br)$^+$

A4.3 NMR Spectra

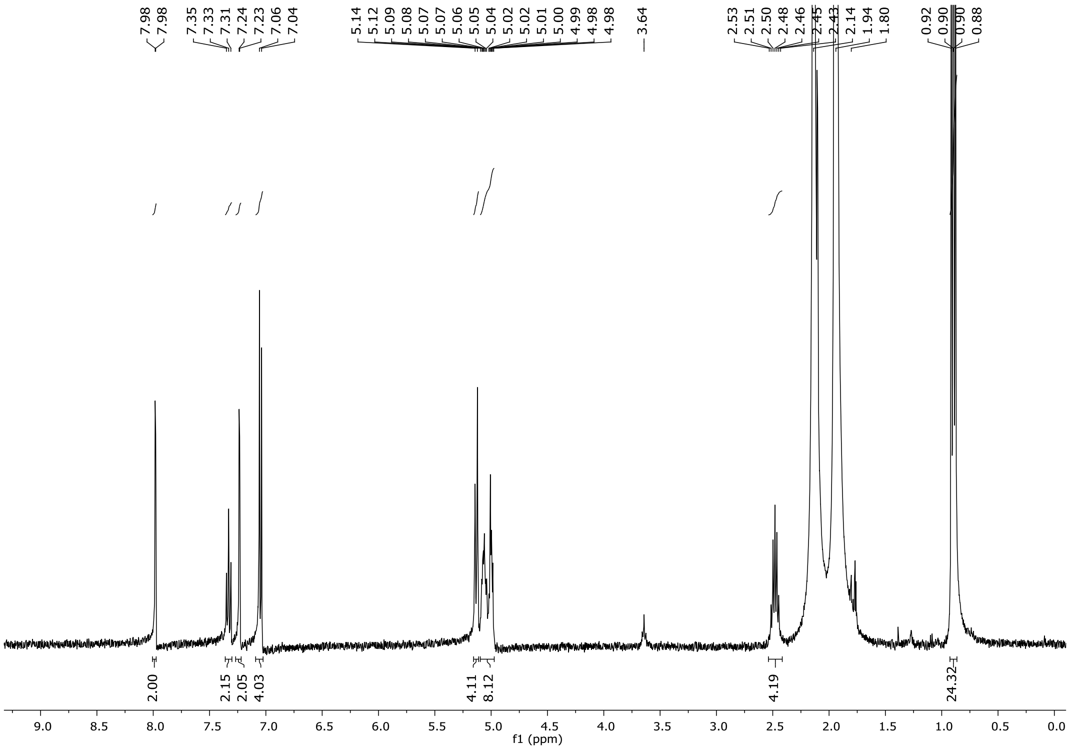


Figure A1: ^{1}H NMR spectrum of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** in deuterated acetonitrile. Solvent residual signal at 1.94 ppm, water at 2.14 ppm, residual THF at 3.64 ppm and 1.80 ppm.

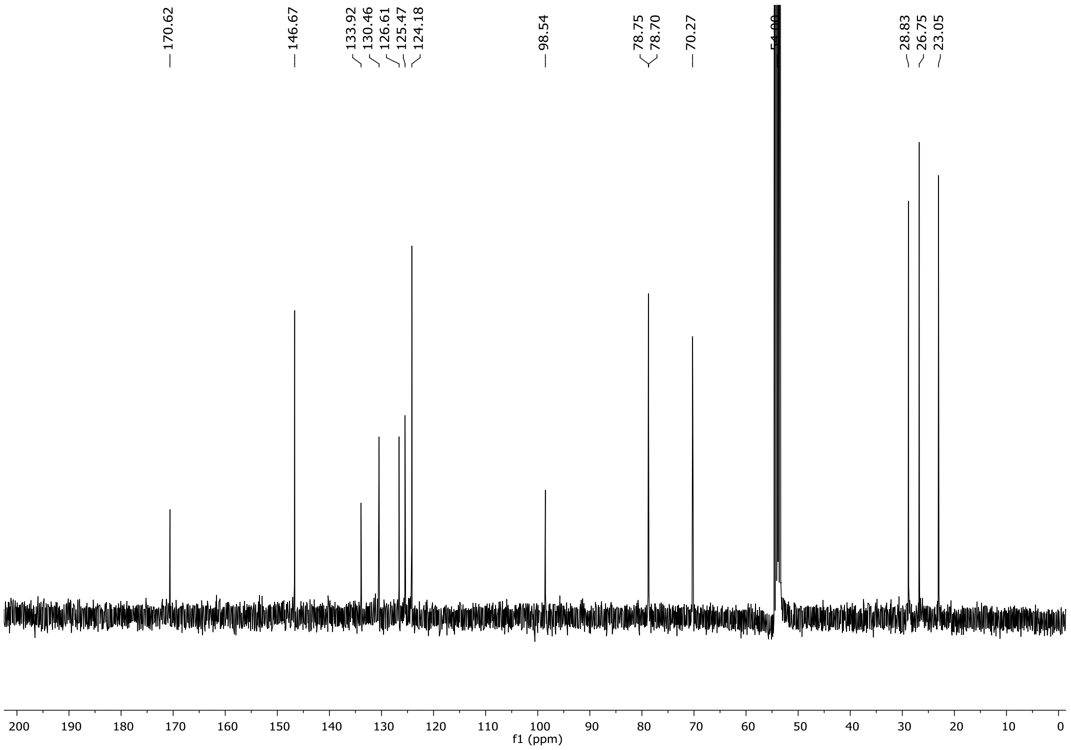


Figure A2: ^{13}C NMR spectrum of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** in deuterated dichloromethane. Solvent signal at 54.00 ppm.

A4.4 Electrochemical Data

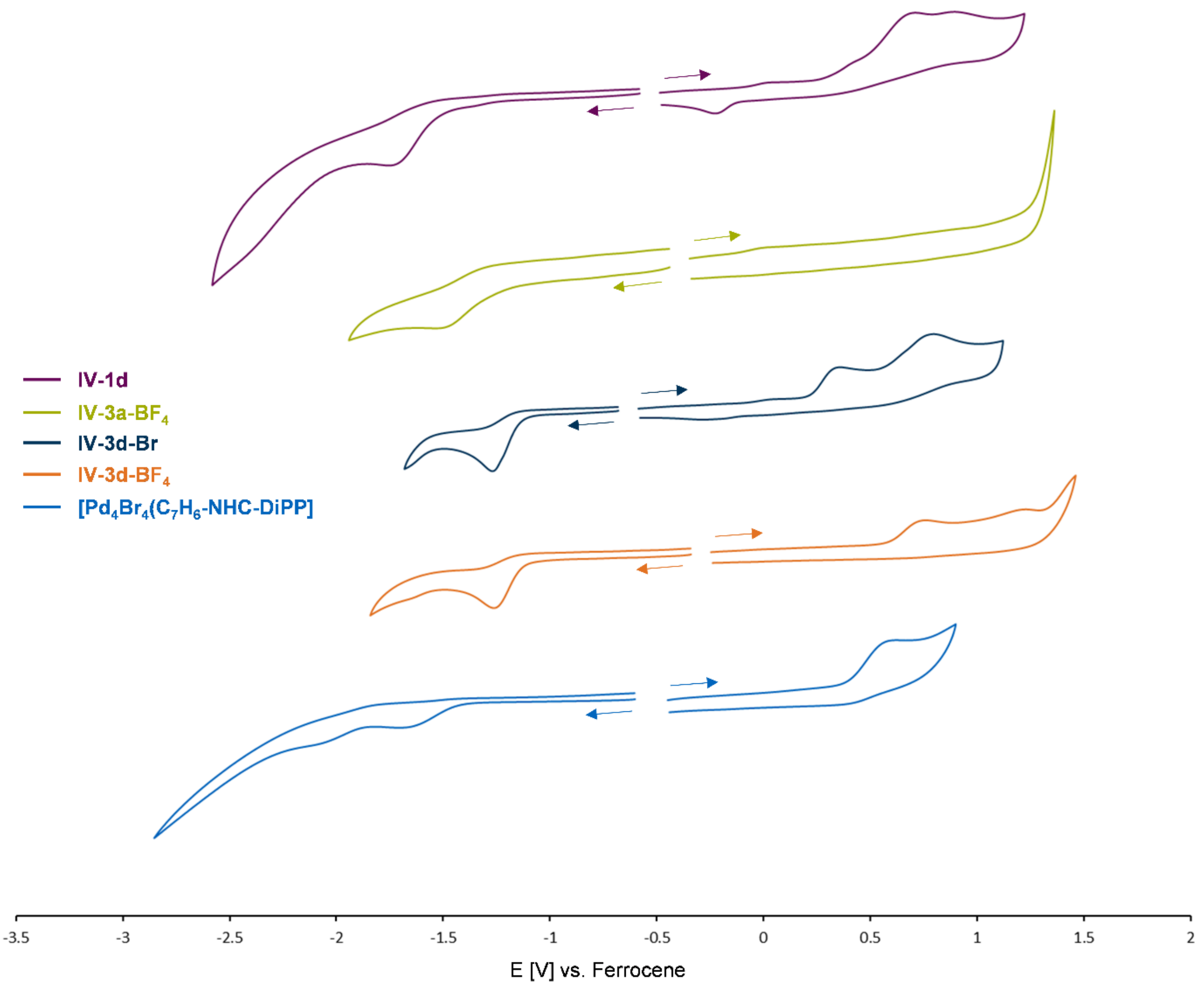


Figure A3: Cyclic voltammogram of **[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP)$_2$]** in comparison to the data for related trinuclear and mononuclear Pd complexes described in chapter 4.4 and the relevant section in the Appendix (reference: *Organometallics* **2017**, *36*, 2772–2783). Scan rate 100 mV s^{-1}. The current is arbitrary and voltammograms are scaled for a better comparison.

Table A2: Summary of electrochemical data for **[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP)$_2$]** in comparison to the data for related trinuclear and mononuclear Pd complexes described in chapter 4.4 and the relevant section in the Appendix (reference: *Organometallics* **2017**, *36*, 2772–2783).

Compound, Temperature	**CV**		**SWV**
	E_p^c [V] Red.	E_p^a [V] Ox.	E_p^c [V] Red.
[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP], 293 K	ca. –2.2, –1.70	0.61	–2.01, –1.60
IV-1d, 293 K	–1.76	0.71	
IV-3a-BF$_4$, 293 K	–1.53	–	
IV-3d-Br, 293 K	–1.31	0.32, 0.79	
IV-3d-BF$_4$, 293 K	–1.26	0.75	–1.22
IV-3d-BF$_4$, 273 K			–1.45, –1.21
IV-3d-BF$_4$, 263 K			–1.45, –1.22
IV-3d-BF$_4$, 253 K			–1.53, –1.27

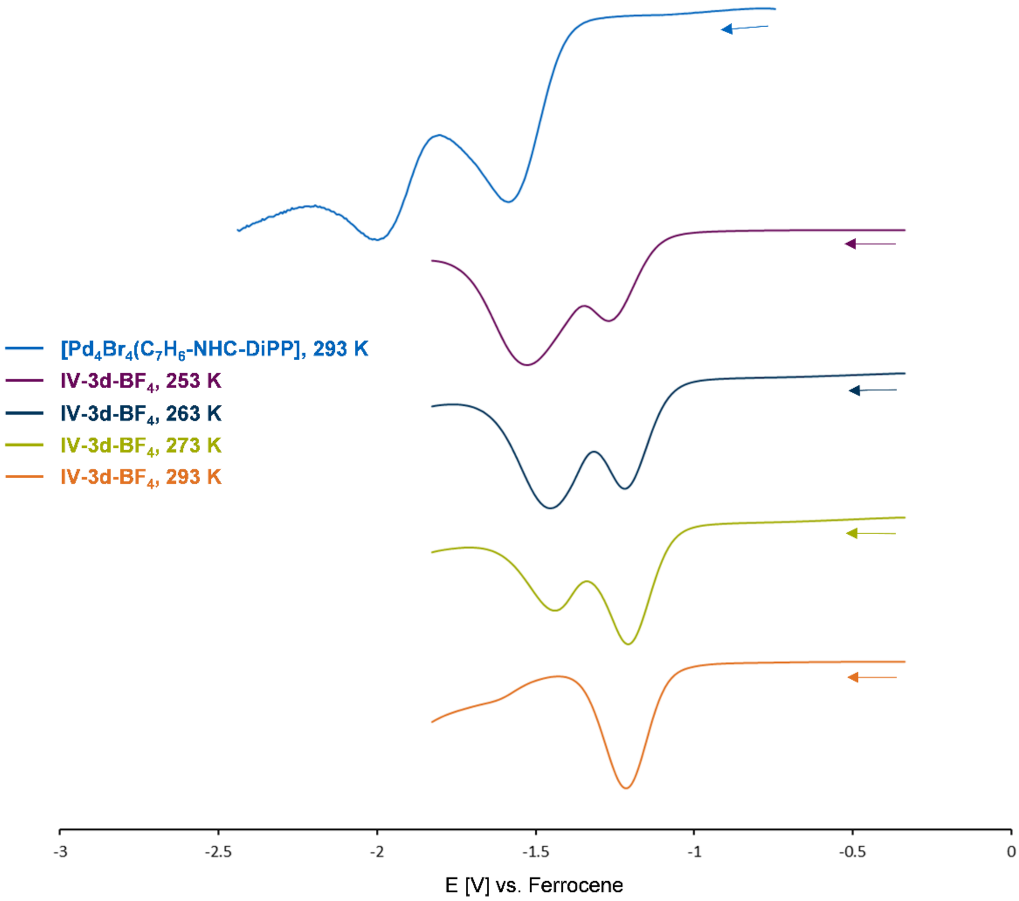


Figure A4: Square wave voltammogram of **[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP)$_2$]** in comparison to low temperature data for **IV-3d-BF$_4$** described in the Appendix section to chapter 4.4 (reference: *Organometallics* **2017**, *36*, 2772–2783). Scan rate 100 mV s^{-1}. The current is arbitrary and different voltammograms are scaled for a better comparison.

The cyclic voltammogram of **[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP)$_2$]** is shown in Figure A3 together with electrochemical data for related compounds already described in chapter 4.4 and the respective section in the Appendix. It features one irreversible oxidation wave at 0.61 V, which is assigned to the DiPP-substituent in analogy to the oxidation waves of the other DiPP-containing compounds. In contrast to the other compounds, **[Pd$_4$Br$_4$(C$_7$H$_6$-NHC-DiPP)$_2$]** exhibits two irreversible reduction waves, the more negative one of which is unfortunately only poorly resolved. Better data were obtained using square wave voltammetry (see Figure A4), which shows two distinct reductions at –2.01 V and –1.60 V, thus indicating two different charge densities of Pd in the complex. The higher intensity of the reduction at –1.60 V already indicates that it belongs to the Pd$_3$ cluster, even though it appears a little more cathodic than the other Pd$_3$ cluster complexes in Figure A3. This could be due to the change from an imidazolium- to an NHC-substituent, which is less electron withdrawing and therefore leads to a higher electron-density on the seven-membered rings and a correspondingly increased electron-donation to the metal cluster. It is also interesting to compare the data to the variable temperature SWV of **IV-3d-BF$_4$** (see Figure A4), where an additional reduction wave at –1.53 V was observed at low temperatures, which was assigned to a conformational change (see Appendix to chapter 4.4). As this agrees well with the potential at which the first reduction wave of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** is observed, this conformational change can be attributed to both substituents being located on the same side of the sandwich cluster as is naturally required by the additional Pd centre in **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]**. It also corroborates the assignment of this less cathodic reduction to the Pd_3 cluster. The more cathodic reduction at a potential of –2.01 V then belongs to the Pd(II) ion bound on the NHC sidearms. Same as for the cluster moiety of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]**, this is more cathodic than observed in the isolated Pd(II) complex **IV-1d**. The relation between the two reduction waves agrees well with both the Pd_3 cluster and Pd(II) maintaining their formal oxidation states from the precursor compounds. Moreover, the less cathodic reduction of the cluster as compared to Pd(II) confirms the interpretation from chapter 4.4 that the Pd_3 cluster has a more positive charge density and therefore a more positive formal oxidation state than Pd(II).

A4.5 Computational Details

A4.5.1 Methods

All quantum chemical calculations were performed using the Gaussian09 software package.[A2] The density functional ωB97X-D[A3], the methods NBO[A4], MK[A5], HLY[A6] and the basis set TZVP[A7] were employed as implemented in this software. The basis sets def2-TZVP[A8] with a corresponding ECP[A9] and def2-TZVPD[A10] were obtained from EMSL Basis Set Exchange[A11,A12].

All DFT calculations were performed in the gas phase using the ωB97X-D functional. As the starting point for the geometry optimisation, the molecular structure from the crystal structure of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** was used and the DiPP groups were simplified as methyl groups. All calculations were performed with a triple-zeta basis set (TZVP for first and second row elements, def2-TZVPD for higher non-metals, def2-TZVP (with ECP) for metals). Calculations of vibrational frequencies were used to confirm that the geometries represent minima on the potential energy surface. Calculations of atom charges were performed on gas-phase optimized structures. NBO charges are based on natural population analysis,[A4] ESP-derived charges were calculated using the method by Kolman (“MK”)[A5] with UFF radii as implemented in Gaussian09 and the method by Yang (“HLY”)[A6] with Gaussian09 standard atomic densities. Pictures of computationally obtained structures were created with CYLview.[A13]

A4.5.2 Results

Table A3: Calculated NBO and ESP-derived charges for Pd and Pd-bound atoms of **[$Pd_4Br_4(C_7H_6$-NHC-Me$)_2$]** (atom numbering scheme based on the crystal structure of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]**.

Atom	**NBO**	**MK**	**HLY**
Pd1	0.084	0.109	0.018
Pd2	0.052	-0.008	-0.076
Pd3	0.109	0.020	-0.017
Pd4	-0.041	0.222	-0.118
Br1	-0.284	-0.348	-0.294
Br2	-0.489	-0.499	-0.483
Br3	-0.484	-0.476	-0.461
Br4	-0.352	-0.355	-0.327
C1	-0.244	-0.242	-0.186
C2	-0.208	-0.013	-0.146
C3	-0.219	-0.086	-0.011
C4	-0.161	-0.056	-0.084
C5	-0.244	-0.094	-0.165
C6	-0.188	-0.144	-0.019
C7	0.094	0.275	0.373
C8	0.360	-0.177	0.154
C23	-0.243	-0.157	-0.294
C24	-0.221	-0.096	0.065
C25	-0.205	-0.046	-0.203
C26	-0.210	-0.076	0.065
C27	-0.225	0.024	-0.114
C28	-0.219	-0.219	-0.199
C29	0.140	0.171	0.311
C30	0.319	-0.250	-0.060

A4.5.3 Discussion

To supplement the electrochemical results, DFT calculations were undertaken in the same way as for chapter 4.4 (see corresponding section in the Appendix). As **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** itself turned out to be too large a molecule to finish the calculations within a reasonable amount of time, the simplified model **[$Pd_4Br_4(C_7H_6$-NHC-Me$)_2$]** with methyl instead of DiPP groups was used (see Table A3 for the results). The NBO charges of the cluster Pd atoms and the C atoms of the seven-membered rings are in the same order of magnitude as for the cluster model compounds in the former DFT study. Only the separation into one more negative and two more positive Pd atoms can no longer be seen clearly. The Pd atom on the NHC sidearms has a significantly more negative NBO charge than the atoms in the cluster, which agrees very well with the formal oxidation state of +2.666 for the Pd_3 cluster atoms in comparison to +2 for the Pd atom on the sidearms. In comparison to the reference compounds from the former study, the sidearm-Pd is even more electron-rich than expected for Pd(II), which might be attributed to the strongly donating NHC ligands.

Using ESP-based charge concepts, the results were inconsistent: One concept (HLY) agrees with the NBO results, whereas the other (MK) suggests exactly the opposite (see Table A3). As the latter also yields unreasonably high negative charges for the carbene-C atoms, which would be expected to be electron-deficient, it cannot be seen as a reliable method. Similar issues of the ESP-based concepts had already been noticed in the former DFT study, so NBO seems to be the preferable method for this type of coordination compounds. Altogether, the NBO results as well as the electrochemical data for **[$Pd_4Br_4(C_7H_6$-NHC-Me/DiPP$)_2$]** confirm the interpretation of the electronic structure of Murahashi complexes from chapter 4.4. Only the aspect of the cluster having a tendency towards mixed valence behaviour could not be clearly observed in **[$Pd_4Br_4(C_7H_6$-NHC-Me$)_2$]**. However, the different valence of the cluster in comparison to the Pd(II) on the sidearms is apparent. Together with the crystallographic data, this allows the conclusion that the terminology of an extended Murahashi cluster is a fitting expression as the additional Pd atom interacts with the Pd_3 cluster, but does not become part of it and retains its original formal oxidation state. Such a behaviour can also be expected when expanding the scope of this type of complexes towards heterobimetallic Pd_3M systems.

A4.5.4 Data

[$Pd_4Br_4(C_7H_6$-NHC-Me$)_2$]

- Optimised geometry (xyz) [Å]:

C	-2.662008	-3.519705	-2.637872
C	-1.353921	-3.200708	-2.623654
C	-2.404143	-1.859819	-1.158369
C	1.089490	-2.269560	-0.947837
C	0.026059	-1.469326	-1.477259
C	2.486227	-2.101977	-1.123128
C	0.119936	-0.253067	-2.221977
C	3.164890	-1.097373	-1.865447
C	1.270892	0.406138	-2.676683
C	2.628677	0.052674	-2.451886
C	-2.591099	1.027603	1.674722
C	0.320408	0.225481	2.502168
C	-0.134436	1.396372	1.858513
C	1.625494	-0.285323	2.573640
C	-3.238645	2.744494	2.972344
C	-1.896626	2.790202	2.898240
C	0.605028	2.365067	1.157674
C	2.846896	0.346785	2.198039
C	3.011205	1.517138	1.422197
C	2.004440	2.397155	0.917536
H	-3.200578	-4.256282	-3.207374
H	-0.519852	-3.586646	-3.181903
H	0.781221	-3.238174	-0.569780
H	3.102220	-2.925797	-0.785374
H	-0.827175	0.131687	-2.583442
H	4.226772	-1.257111	-2.003212
H	1.101377	1.203790	-3.388822
H	-0.420113	-0.277827	3.109967
H	3.350849	0.723121	-2.901848
H	1.736810	-1.176909	3.177294
H	-3.937005	3.380783	3.486539
H	0.057445	3.252982	0.864146
H	3.741157	-0.041579	2.668681
H	-1.181629	3.460799	3.340013
H	4.028706	1.878789	1.337688
H	2.367207	3.326793	0.497045
Br	-1.754883	-2.303181	1.799702
Br	-3.532267	1.068653	-1.352674
Br	5.420573	-1.109429	0.639760
Br	0.417143	3.566537	-1.975692
N	-3.289443	-2.680412	-1.736737
N	-1.214108	-2.177839	-1.699514
N	-3.641920	1.653980	2.228161
N	-1.511773	1.724815	2.100030
Pd	-2.589478	-0.479300	0.289484
Pd	0.313884	-0.901515	0.609581
Pd	3.016391	-0.367330	0.189844
Pd	1.043493	1.413238	-0.788240
C	-5.028469	1.296701	1.982405
H	-5.627447	1.590108	2.842914
H	-5.387145	1.791968	1.081014
H	-5.095729	0.220189	1.845514
C	-4.703818	-2.698049	-1.406827
H	-5.052325	-1.670924	-1.314183
H	-5.247292	-3.194286	-2.208267
H	-4.862796	-3.229183	-0.468593

- N_imag: 0
- E_HF [Hartree]: -11879.4950924

A4.6 Crystallographic Details

A4.6.1 General

Data were collected on a single-crystal X-ray diffractometer equipped with a CMOS detector (APEX III, *κ*-CMOS), an IMS microsource and a Helios optic using the APEX III software package.[A14] All measurements used MoK_α radiation (λ = 0.71073 Å).The crystals were fixed on the top of a kapton micro sampler with perfluorinated ether, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[A15] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[A15] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL-2014 in conjunction with SHELXLE.[A16,A17] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso}(H) = 1.5 \cdot U_{eq}(C)$. Methylene, aromatic and other H atoms were placed in calculated positions and refined using a riding model, with C–H distances of 0.99 Å, 0.95 Å and 1.00 Å, respectively, and $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL weighting scheme.[A17] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[A18] A split layer refinement was used to treat with disordered anion/solvent molecules and additional SIMU, DELU and SAME restraints were employed to ensure convergence within chemically reasonable and physically meaningful limits. Images were created with Mercury.[A19]

A4.6.2 Compound ***[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]***

Special Details

Crystals were grown by slow diffusion of diethyl ether into a solution in acetonitrile. Diffractometer operator C. Jandl, scanspeed 60 s per frame, dx 70 mm, 1330 frames measured in 5 data sets, phi-scans with delta_phi = 0.5, omega-scans with delta_omega = 0.5, shutterless mode.

Crystal data

$C_{44}H_{50}Br_4N_4Pd_4$	
M_r = 1380.08	D_x = 2.036 Mg m^{-3}
Orthorhombic, *Pbca*	Melting point: ? K
Hall symbol: -P 2ac 2ab	Mo *Kα* radiation, λ = 0.71073 Å
a = 17.9519 (9) Å	Cell parameters from 9963 reflections
b = 14.2652 (7) Å	θ = 2.3–26.4°
c = 35.1541 (18) Å	μ = 5.16 mm^{-1}
V = 9002.5 (8) Å^3	*T* = 100 K
Z = 8	Fragment, dark red-black
F(000) = 5328	0.26 × 0.16 × 0.13 mm

Data collection

Bruker Photon CMOS diffractometer	8545 independent reflections
Radiation source: IMS microsource	7724 reflections with $I > 2\sigma(I)$
Helios optic monochromator	R_{int} = 0.024
Detector resolution: 16 pixels mm^{-1}	θ_{max} = 25.7°, θ_{min} = 2.2°
phi– and *ω*–rotation scans	*h* = −20 21
Absorption correction: multi-scan *SADABS* 2016/2, Bruker	*k* = −16 17
T_{min} = 0.589, T_{max} = 0.745	*l* = −42 38
75525 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.066$	$W = 1/[\Sigma^2(FO^2) + (0.0215P)^2 + 43.6229P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
8545 reflections	$\Delta\rho_{max} = 1.62$ e Å^{-3}
626 parameters	$\Delta\rho_{max} = 1.62$ e Å^{-3}
444 restraints	Extinction correction: none
0 constraints	Extinction coefficient: -
Primary atom site location: intrinsic phasing	

A4.6.3 Reaction Intermediate

Special Details:

For crystal growth, the reaction from chapter A4.2 was performed in dichloromethane and after a reaction time of 1 day, a sample was taken, filtered, and slowly evaporated.
Diffractometer operator C. Jandl, scanspeed 120 s per frame, dx 45 mm, 642 frames measured in 5 data sets, phi-scans with delta_phi = 0.5, omega-scans with delta_omega = 0.5, shutterless mode.

Crystal data

$C_{88}H_{102}Br_{10}N_8Pd_8 \cdot 4(CH_2Cl_2)$	
$M_r = 3261.69$	$D_x = 2.002$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: ? K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 16.9164$ (15) Å	Cell parameters from 6525 reflections
$b = 15.4535$ (14) Å	$\theta = 2.4$–$24.4°$
$c = 21.3539$ (18) Å	$\mu = 5.23$ mm^{-1}
$\beta = 104.252$ (2)°	$T = 100$ K
$V = 5410.5$ (8) Å^3	Fragment, red
$Z = 2$	0.11 × 0.10 × 0.06 mm
$F(000) = 3144$	

Data collection

Bruker Photon CMOS diffractometer	9198 independent reflections
Radiation source: IMS microsource	5261 reflections with $I > 2\sigma(I)$
Helios optic monochromator	$R_{\text{int}} = 0.205$
Detector resolution: 16 pixels mm^{-1}	$\theta_{\text{max}} = 24.7°$, $\theta_{\text{min}} = 2.2°$
phi– and ω–rotation scans	$h = -19$ 19
Absorption correction: multi-scan *SADABS* 2016/2, Bruker	$k = -18$ 18
$T_{\text{min}} = 0.503$, $T_{\text{max}} = 0.745$	$l = -25$ 25
65317 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.104$	W = $1/[\Sigma^2(F\text{O}^2) + (0.0327P)^2 + 10.8977P]$ WHERE $P = (F\text{O}^2 + 2F\text{C}^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\text{max}} = 0.001$
9198 reflections	$\Delta\rho_{\text{max}} = 1.34$ e Å^{-3}
576 parameters	$\Delta\rho_{\text{min}} = -0.87$ e Å^{-3}
0 restraints	Extinction correction: none
0 constraints	Extinction coefficient: -
Primary atom site location: intrinsic phasing	

A4.6.4 Results and Discussion

The crystal structure of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** (see Figure A5) confirms the conversion of the imidazolium sidearms to NHCs and the additional Pd atom bound between the two NHCs. The geometry of the trinuclar Pd cluster and the sandwiching ligands is analogous to the imidazolium- and pyridinium-functionalised derivatives described in chapter 4.4. The additional Pd(II) centre features the typical square planar coordination environment with two NHC and two bromide ligands. It shows some distortion, indicated by the τ_δ value of 0.101.[A20,A21] The Pd—C_{NHC} bonds of Pd4—C8 = 2.023(4) Å and Pd4—C30 = 2.011(4) Å are elongated by ca. 0.05 Å in comparison to the NHC ligands connected to different cycloheptatriene-based systems described in chapter 4.3. The degree of distortion of the Pd—C_{NHC} bond differs significantly between the considerably distorted upper (Θ_{NHC} = 168.13°) and almost undistorted lower (Θ_{NHC} = 176.77°) NHC in Figure A5.[A22]

The bond from the cluster to the external Pd (Pd1—Pd4 = 2.8184(9) Å) is longer than the Pd—Pd bonds within the Pd_3 cluster (average: 2.766 Å) and oriented almost in linear continuation of the Pd1—Pd2 bond (Pd2—Pd1—Pd4 = 173.01(2)°). The bromide ion Br1 adopts a bridging mode between Pd1 and Pd4 with a considerably longer bond to Pd1 (2.6997(10) Å) than to Pd4 (2.4468(5) Å). The Pd1—Br1 bond is also longer than the Pd—Br bonds of the other cluster atoms and the Pd—Br bond lengths observed in chapter 4.4. This is probably due to the already distorted square planar environment of Pd4, which does not tolerate a further distortion by moving the bromide towards Pd1. On the other hand, the equatorial bonds of the Pd_3 cluster are rather flexible as observed in chapter 4.4.

The bonds between the cycloheptatrienide- and NHC-moieties are directed out of the cycloheptatrienide planes by angles of centroid(C1>C7)—C7—N1 = 162.01° and centroid(C23>C29)—C29—N3 = 156.00°. This is certainly energetically unfavourable as the examples from chapter 4.4 all feature in-plane bonds to the substituents, but it is necessary in order to allow sufficient space between the NHCs to accommodate the additional Pd centre. The lower NHC in Figure A5 is almost perpendicular to the cycloheptatrienide moiety (87.70° between the mean planes), while the upper one is rotated to some degree (72.90° between the mean planes). This leads to a tilting angle of 16.40° between the mean planes of the NHC-groups. All these parameters indicate that there is significant strain associated with the extension of the Pd_3 cluster. Nevertheless, the structure proves the viability of introducing an additional metal atom in an interacting position with the Pd_3 cluster via the NHC sidearms, which can now be expanded to further metals.

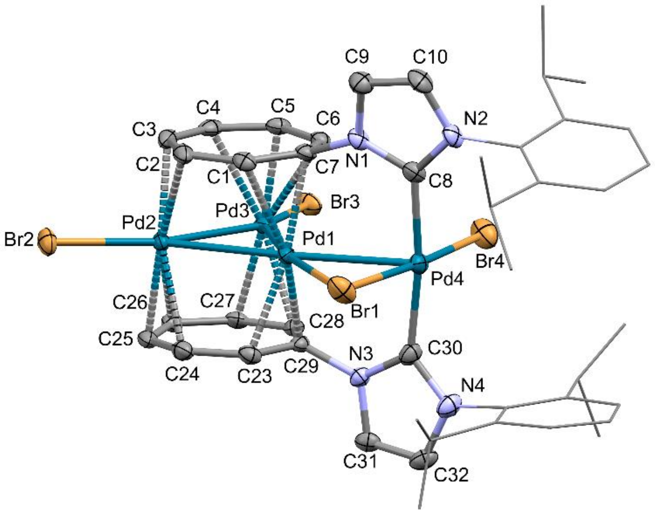


Figure A5: Molecular structure of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** in the solid state with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity and DiPP-substituents are simplified as wireframes. Selected distances [Å] and angles [°]: Pd1—Pd2 2.7657(9), Pd2—Pd3 2.7900(5), Pd1—Pd3 2.7432(9), Pd1—Pd4 2.8184(9), Pd1—Br1 2.6997(10), Pd2—Br2 2.5424(6), Pd3—Br3 2.5685(6), Pd4—Br4 2.4209(7), Pd4—Br1 2.4468(5), Pd1—C1 2.310(4), Pd1—C7 2.195(4), Pd2—C2 2.214(4), Pd2—C3 2.164(4), Pd3—C4 2.360(4), Pd3—C5 2.146(4), Pd3—C6 2.631(4), Pd1—C23 2.224(4), Pd1—C29 2.183(4), Pd2—C24 2.367(4), Pd2—C25 2.162(4), Pd2—C26 2.580(4), Pd3—C27 2.150(4), Pd3—C28 2.231(4), Pd4—C8 2.023(4), Pd4—C30 2.011(4), Pd2—Pd1—Pd4 173.01(2), Pd3—Pd1—Pd4 112.18(2), Pd2—Pd1—Br1 134.40(2), Pd3—Pd1—Br1 164.33(2), Br1—Pd4—Br4 173.32(4), Pd1—Pd4—Br4 112.13(3), Pd1—Pd4—C8 87.90(11), Pd1—Pd4—C30 84.72(11), C8—Pd4—C30 172.23(16), C1—C7—N1—C8 125.4(4), C23—C29—N3—C30 -92.8(5).

In the intermediate from the reaction leading to **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** (see Figure A6), only half the imidazolium-groups have been deprotonated and bind Pd(II). The retained imidazolium-groups are involed in hydrogen bonds to bromide ligands. The geometric parameters of the sandwich cluster moieties are mostly similar to the examples discussed before (see chapter 4.4). As the only exception, the C atom on which the NHC is bound has considerably longer distances to the adjacent Pd atoms than any other C atom (Pd1—C7 = 2.838(9) Å, Pd2—C7 = 2.671(8) Å), so it contributes less to the bonding of the sandwiching ligands. The NHC sidearm coordinates to a $PdBr_2$-group originating from the precursor Pd(cod)Br_2 and the fourth valence of the Pd(II) ion is filled by an equatorial bromide of another Murahashi complex, which thus adopts a μ^2-binding mode. In this way, two Murahashi complexes are connected to an organometallic macrocycle. The additional Pd has a square planar coordination environment with minor distortions (τ_δ = 0.077) as expected for Pd(II).[A20,A21] The carbene bond length Pd4—C8 = 1.963(9) Å matches with NHC ligands connected to different cycloheptatriene-based systems described in chapter 4.3, but it also features a significant distortion of the carbene-metal bond (Θ_{NHC} = 169.41°), the major part of which is an out-of-plane displacement. The fact that an intermediate was found in which one imidazolium-group is not deprotonated, while the other is already bound to Pd as an NHC shows that – as is to be expected – the deprotonation by silver(I) oxide is the rate-determining step and the transmetalation step is very fast in comparison. However, it cannot be decided yet, if this intermediate is even a productive intermediate leading to the desired product or an unproductive one which leads to side-products. It is possible that, once formed, the macrocycle is too stable, so that the deprotonation of the remaining imidazolium sidearm does not allow a coordination to the Pd(II) on the other NHC, so instead it reacts with Pd(cod)Br_2 and potentially another Murahashi complex to form the next macrocycle, which then continues towards polymerisation.

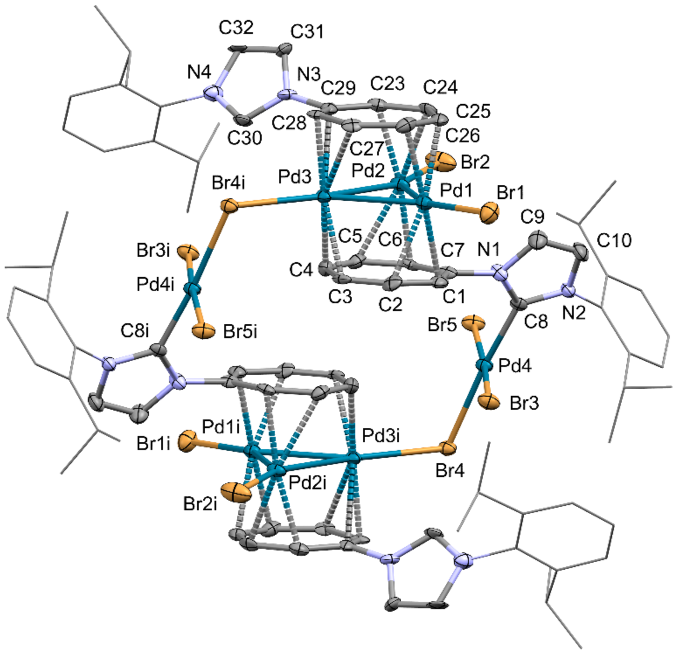


Figure A6: Molecular structure of the intermediate from the synthesis of **[$Pd_4Br_4(C_7H_6$-NHC-DiPP$)_2$]** in the solid state with ellipsoids at the 50% probability level. Hydrogen atoms and co-crystallised solvent molecules are omitted for clarity and DiPP-substituents are simplified as wireframes. Selected distances [Å] and angles [°]: Pd1—Pd2 2.7872(11), Pd2—Pd3 2.7558(11), Pd1—Pd3 2.7363(10), Pd1—Br1 2.5475(13), Pd2—Br2 2.5217(13), Pd3—Br4i 2.6078(12), Pd4—Br3 2.4355(13), Pd4—Br4 2.5205(12), Pd4—Br5 2.4204(13), Pd1—C1 2.219(9), Pd1—C2 2.256(10), Pd1—C7 2.838(9), Pd2—C5 2.331(10), Pd2—C6 2.165(8), Pd2—C7 2.671(8), Pd3—C3 2.231(9), Pd3—C4 2.171(9), Pd1—C25 2.238(10), Pd1—C26 2.183(8), Pd2—C23 2.158(8), Pd2—C24 2.244(9), Pd3—C27 2.458(9), Pd3—C28 2.169(9), Pd3—C29 2.477(10), Pd4—C8 1.963(9), Pd1—Pd3—Br4i 143.12(4), Pd2—Pd3—Br4i 155.62(4), Pd4—Br4—Pd3i 109.35(4), Br4—Pd4—C8 175.1(3), Br3—Pd4—Br4 90.55(4), Br5—Pd4—Br4 91.81(4), C1—C7—N1—C8 122.5(10), C28—C29—N3—C30 -58.3(11), N1—C8—Pd4—Br3 -62.2(7), Br3—Pd4—Br4—Pd3i 71.76(5). Symmetry code to create equivalent atoms: (i) –x + 1, –y + 1, –z + 1.

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Full List of Publications

1) **C. Jandl**, K. Öfele, F. E. Kühn, W. A. Herrmann, A. Pöthig, *Organometallics* **2014**, *33*, 6398–6407. DOI: 10.1021/om500738d (Structure and Dynamics of Imidazolium- and Pyridinium-Substituted η^3-Cycloheptatrienide-Pd Complexes).

2) D. T. Weiss, S. Haslinger, **C. Jandl**, A. Pöthig, M. Cokoja, F. E. Kühn, *Inorg. Chem.* **2015***,* *54*, 415–417. DOI: 10.1021/ic502838x (Application of Open Chain Tetraimidazolium Salts as Precursors for the Synthesis of Silver Tetra(NHC) Complexes).

3) R. Zhong, A. Pöthig, D. C. Mayer, **C. Jandl**, P. J. Altmann, W. A. Herrmann, F. E. Kühn, *Organometallics* **2015**, *34*, 2573–2579. DOI: 10.1021/om5012402 (Spectroscopic and Structural Properties of Bridge-Functionalized Dinuclear Coinage-Metal (Cu, Ag, and Au) NHC Complexes: A Comparative Study).

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6) P. J. Altmann, **C. Jandl**, A. Pöthig, *Dalton Trans.* **2015**, *44*, 1278–11281. DOI: 10.1039/c5dt01775k (Introducing a pyrazole/imidazole based hybrid cyclophane: a hydrogen bond sensor and binucleating ligand precursor).

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10) B. S. Soller, Q. Sun, S. Salzinger, **C. Jandl**, A. Pöthig, B. Rieger, *Macromolecules* **2016**, *49*, 1582–1589. DOI: 10.1021/acs.macromol.5b01937 (Ligand Induced Steric Crowding in Rare Earth Metal-Mediated Group Transfer Polymerization of Vinylphosphonates: Does Enthalpy Matter?).

11) P. J. Altmann, D. T. Weiss, **C. Jandl**, F. E. Kühn, *Chem. Asian J.* **2016**, *11*, 1597–1605. DOI: 10.1002/asia.201600198 (Exploring Coordination Modes: Late Transition Metal Complexes with a Methylene-bridged Macrocyclic Tetra-NHC Ligand)

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26) **C. Jandl**, S. Stegbauer, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 754–759. DOI: 10.1107/S2053229617012244 (A halide-free pyridinium-substituted η^3-cycloheptatrienide-Pd complex)

27) **C. Jandl**, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 810–813. DOI: 10.1107/S2053229617013183 (Hydroxytropylium chloride: The first crystal structure of an unfunctionalized hydroxytropylium ion)

28) **C. Jandl**, A. Pöthig, *Acta Crystallogr., Sect. C* **2017**, *73*, 1131–1136. DOI: 10.1107/S2053229617016412 (Dimerization of a mixed-carbene Pd^{II} dibromide complex by elemental iodine)

Curriculum Vitae

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