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Synthesis and Reactivity of Bidentate *N*-Heterocyclic Carbene-Phosphinidene Supported Si(IV) Dicationic Complexes

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Herein, we report the synthesis and isolation of Si(IV) dications stabilized by a bidentate *N*-heterocyclic carbene-phosphinidene (NHCP). Treatment of the bis(NHCP) with Si(IV) bis(triflate) R₂Si(OTf)₂ (with R=H, Ph) resulted in the instant formation of Si(IV) dicationic complexes [2a] and [2b] featuring a tetraoor-

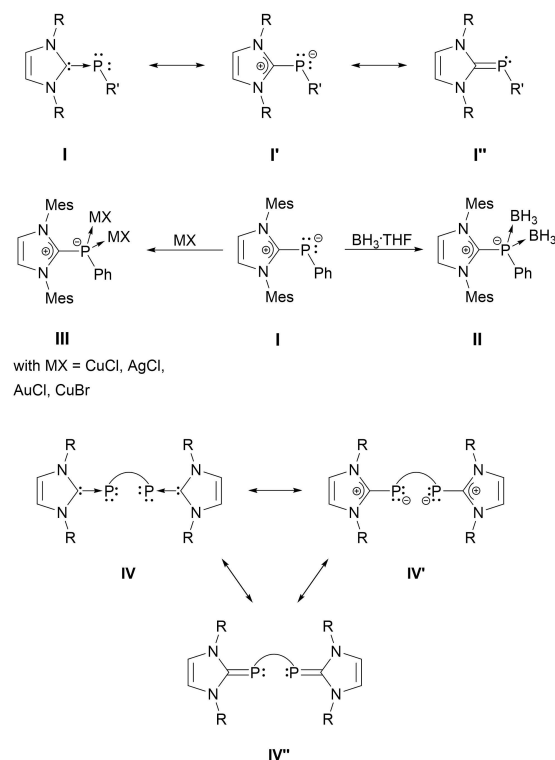
inated silicon centre. The dications show expected high Lewis acidity. The bis(NHCP)-stabilized parent silyl dication 2a (SiH₂²⁺) presents the first isolable example of a parent SiH₂ dication. In addition, dication [2a] is able to react with diphenylketene by insertion into the Si–P bond.

Introduction

Development of ligand systems for stabilization of reactive intermediates is of paramount importance in organometallic chemistry. The prototypical *N*-heterocyclic carbenes (NHCs), discovered by Arduengo in 1991, offer strong σ-donor as well as π-acceptor properties. Those characteristics qualify them as efficient ligands in stabilization of electron-deficient, ambiphilic and paramagnetic species, and thus they are widely utilized for isolation of low-valent/low oxidation state main group species.^[1–7] From the perspective of silicon chemistry, pivotal work in the stabilization of halosilanes and highly reactive halosilylenes by NHCs opened the way towards the synthesis of numerous novel organosilicon compounds with unusual electronic properties and bonding situations.^[8–12]

Related classes of compounds, e.g. the *N*-heterocyclic imines (NHIs) and their heavier analogues *N*-heterocyclic carbene-phosphinidenes (NHCPs), are also gradually finding their way into main group chemistry.^[13–14] NHCPs have already been discovered in 1997 by Arduengo *et al.*,^[15–17] nevertheless, only in the last few years they attracted attention, as their potential as ligands in main group and transition metal

chemistry has been exemplified.^[14–16,18–23] NHCPs are inversely polarized phosphalkenes with the mesomeric structures I, I', and I'', out of which I and I' exhibit two electron pairs at the phosphorus atom. This was demonstrated by the reaction with BH₃·THF forming the bis(borane) adduct II or treatment with metal halides (e.g. CuCl, AgCl, AuCl, CuBr) forming the bis(group 11 metal) complexes III (Scheme 1).^[15,24]



Scheme 1. Canonical forms of monodentate and bidentate *N*-heterocyclic carbene-phosphinidenes I and IV and reactivity towards borane and group 11 metal halides forming bisadducts II and III (with Mes = 2,4,6-trimethylphenyl).

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Recently, the first two examples of bis(*N*-heterocyclic carbene-phosphinidene) (bis(NHCP)) ligands have been reported.^[25–26] Their coordination capabilities have been demonstrated by formation of stable Ge(II), Sn(II), and transition metal halide (CuCl, ZnI₂, FeCl₂) complexes. According to the resonance structures of bis(NHCP)s (Scheme 1, IV–IV'), they additionally appear to be an ideal ligand for stabilization of di- or polycationic main group complexes. For instance, free silicon(IV) dications (R₂Si²⁺) are only known in the gas phase, however, not in condensed phase.^[27–28] To be able to isolate an uncommon Si(IV) dication, stabilization *via* neutral Lewis bases is necessary. Up to date, NHC ligands with their σ-donor properties emerged to be suitable.

The groups of Filippou and Driess succeeded in the isolation of the four-coordinated dicationic Si(IV) complexes **V** and **VI** both using NHCs for stabilization (Figure 1).^[29–30] NHC stabilization was also used in the isolation of dication **VII**, recently published by the Inoue group.^[31] Additionally, in 2020 the group of Driess reported several examples of five-coordinated Si(II) dications **VIII** stabilized by a terpyridine ligand system, adding to the sparse examples of isolated Si(IV) dications.^[32] To the best of our knowledge, however, an isolable example of a dicationic complex containing the parent [SiH₂]²⁺ moiety has not been reported. Additionally, the use of NHCPs for stabilization of silicon compounds is unexplored. In this work we present the expansion of the NHCP chemistry towards the stabilization of tetra-valent silicon compounds and present the first examples of bis(NHCP)-stabilized Si(IV) dications **[2a]** and **[2b]** and their reactivity.

Results and Discussion

Treatment of the recently published ferrocene bridged bis(NHCP) **1** with bis(triflate)silanes (R₂Si(OTf)₂, R = H, Ph) in

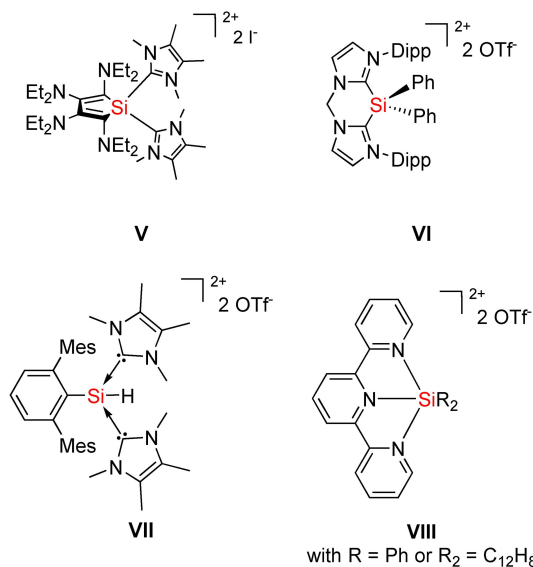
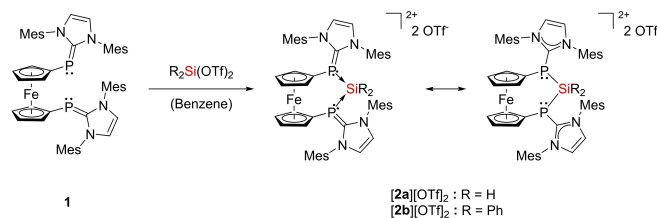


Figure 1. Selected examples of Si(IV) dicationic complexes from the literature.

benzene at room temperature resulted in the instant formation and precipitation of complexes **[2a]**[OTf]₂ and **[2b]**[OTf]₂ in 70% and 88% yield respectively (Scheme 2).^[26] Both complexes dissolve well in acetonitrile and 1,2-difluorobenzene. The products were characterized by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis. The ³¹P NMR signals in CD₃CN are shifted upfield in comparison to the free bis(NHCP) (−56.98 ppm^[26]) with a shift of −96.68 ppm for the parent silyl dication **[2a]** and −66.01 ppm for the phenyl-substituted silyl dication **[2b]** (Table 1). In comparison to the reported bis(NHCP)-stabilized stannylumidenes (³¹P δ = −30.56 to −59.76 ppm), the ³¹P NMR signals are upfield shifted.^[26] The recorded ²⁹Si NMR spectra of **[2a]**[OTf]₂ and **[2b]**[OTf]₂ show the respective triplet signals at −44.09 ppm (¹J_{P,Si} = 24.8 Hz) and −10.74 ppm (¹J_{P,Si} = 65.7 Hz), whereby the coupling constants are in the range of ¹J_{P,Si} Si–P couplings (256–16 Hz).^[33] In comparison, the fourfold coordinated Si(IV) dications **V**, **VI** and **VII** (²⁹Si δ = −29.2, −36.7, and −63.4 ppm) resonate in a similar region.^[29–31]

Despite numerous attempts, **[2a]** could not be crystallized successfully. However, the bis(triflate) complex of dication **[2b]** could be crystallized from a concentrated fluorobenzene solution at −35 °C forming yellow needles suitable for single crystal X-ray diffraction (SC-XRD). The molecular structure of **[2b]**[OTf]₂, which crystallizes in P21/n space group, reveals a distorted tetrahedral coordinated Si(IV) center with elongated Si–P single bonds (2.3137(16) Å, 2.3128(16) Å) (Figure 2). The P–C_{Carbene} bond length of 1.849(4) Å and 1.851(4) Å are elongated in comparison to the free ligand (1.731(10) Å, 1.808(19) Å). Additionally, the C_{Carbene}–N bonds of 1.354 Å to 1.357 Å (free ligand: 1.372 to 1.377 Å) are shortened, speaking for predominant canonical forms **IV** and **IV'**. The positive charge is delocalized, hence stabilized in the NHC ring system. Analogue bond elongation/shortening has been reported in the bis(NHCP)-stabilized Sn(II) complex.^[26] The sum of bond angles around P1 and P2 are 319.76° and 320.96° respectively, accounting for a trigonal pyramidal coordination of the phosphorus atoms. Similarly to the free bis(NHCP) as well as the reported bis(NHCP)-supported stannylumidene complex, the mesityl substituents show a sandwich π–π stacking interaction



Scheme 2. Synthesis of bis(NHCP)-supported Si(IV) dications **[2a]** and **[2b]**.

Table 1. ³¹ P and ²⁹ Si NMR shifts of Si(IV) dications in CD ₃ CN.			
Silane	³¹ P [ppm]	²⁹ Si [ppm]	
[2a] [OTf] ₂	H ₂ Si(OTf) ₂	−96.24	−44.09 (t, ¹ J _{P,Si} = 24.8 Hz)
[2b] [OTf] ₂	Ph ₂ Si(OTf) ₂	−66.06	−10.74 (t, ¹ J _{P,Si} = 65.7 Hz)

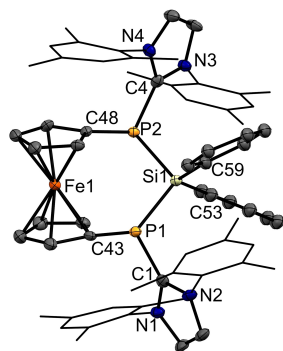


Figure 2. SC-XRD structure of **[2b]**. Translational ellipsoids are plotted at the 50% probability level. For reasons of clarity, hydrogens and triflate counter ions are omitted and mesityl groups are depicted in wireframe models. Selected bond lengths (Å) and angles (°): P1–Si1 2.3137(16), P2–Si1 2.3128(16), Si1–C53 1.807(19), Si1–C59 1.891(15), P1–C1 1.849(4), P2–C4 1.851(4), P1–C43 1.793(4), P2–C48 1.791(4), C1–N1 1.356(6), C1–N2 1.356(6), C4–N3 1.357(6), C4–N4 1.354(6), P1–Si1–P2 108.17(6), C53–Si1–C59 111.65.

with the Cp ring of the ferrocene visible in the SC-XRD structure.^[26] Furthermore, the molecular structure of dication **[2b]** displays a sandwich π – π stacking interaction between the second mesityl substituent and the Si-bonded phenyl rings.

Since ferrocene is highly redox active, the free ligand **1** and both complexes **[2a]**[OTf]₂ and **[2b]**[OTf]₂ were examined with cyclic voltammograms recorded in 0.1 M Bu₄NClO₄/THF and all potentials (V) were referenced against ferrocene/ferrocenium (Fch/Fch⁺) as internal standard (Figure S22–27). The free ligand **1** shows oxidation signals on a glassy carbon electrode at –0.63 V, –0.35 V, and 0.64 V vs. Fch/Fch⁺ while only the potential at –0.63 V vs. Fch/Fch⁺ shows a slight reversibility with a reduction potential of –1.20 V vs. Fch/Fch⁺ followed by a chemical reaction preventing reversibility (Figure S23). The dication **[2a]**[OTf]₂ shows an oxidation signal on a platinum electrode with a potential of 0.66 V vs. Fch/Fch⁺ with the reduction potential of 0.22 V vs. Fch/Fch⁺ and further reduction potentials at –0.84 V, –1.61 V, –2.33 V, and –2.61 V vs. Fch/Fch⁺ (Figure S24 and S25). All reduction potentials are irreversible. Dication **[2b]**[OTf]₂ shows an oxidation signal on a platinum electrode with a potential of 0.55 V vs. Fch/Fch⁺ with the reduction potential of 0.22 V vs. Fch/Fch⁺. A second oxidation potential at –0.42 V vs. Fch/Fch⁺ only occurs when the substrate is reduced to over –2.37 V vs. Fch/Fch⁺ (Figure S26 and S27). Further reduction potentials are at –0.71 V, –1.30 V, –2.15 V, and –2.64 V vs. Fch/Fch⁺. All reduction potentials are non-reversible.

In order to investigate the electronic structure and properties of compounds **[2a]** and **[2b]**, quantum chemical calculations at the B3PW91 level of theory were carried out (for details regarding the computational methods see Supporting Information). In **[2a]**, the five highest occupied molecular orbitals (*i.e.* HOMO–5 – HOMO) do not correspond to bonding interactions involving the NHCPs and the Si center, but rather to the d orbitals of iron, bonding interactions within the ferrocene backbone and π -systems of the mesityl substituents. HOMO–6 is dispersed over the entire NHC–P²–Si(H)₂–P¹–NHC fragment,

showing both phosphorus lone pairs, phosphorus silicon bonding interaction, as well as the π orbitals of the NHC moieties. The LUMO is also dispersed over the NHC–P²–Si(H)₂–P¹–NHC fragment, predominantly corresponding to the Si–H antibonding orbitals, and the π^* orbitals of the NHCs. To get a more intuitive picture regarding the bonding situation [bis(NHCP)–SiH₂]²⁺, natural bond orbital (NBO) analysis was carried out. Since **[2a]** is C₂ symmetrical, the interactions between the two NHCP moieties with SiH₂ as well as the internal interactions are identical, therefore only the NHCP¹ moiety will be discussed.

NBO analysis shows a Wiberg bond index (WBI) (Figure 3) of 0.91 between Si¹–P¹, which arises from a single almost non-polarized bond (Si(sp^{3.2}) 41.7%, P(sp^{5.7}) 58.3%), while P¹ retains a localized lone pair (Figure 4, top left). Second order perturbation theory analysis shows that this σ -type lone pair (*s* 51.4%, *p* 48.6%) with occupancy of 1.87 el. exhibits only minor donor-acceptor interactions (DAI) with $\sigma^*(\text{Si}^1\text{--H}^1)$ and $\sigma^*(\text{Si}^1\text{--H}^2)$ summing up to 3.8 kcal mol^{–1}. Additionally, the P¹ lone pair interacts with a $\sigma^*(\text{C}^1\text{--C}^2)$ orbital of the ferrocene moiety (DAI = 5.4 kcal mol^{–1}), $\sigma^*(\text{C}^1\text{--N}^1)$ (DAI = 3.2 kcal mol^{–1}) and $\pi^*(\text{C}^1\text{--N}^1)$

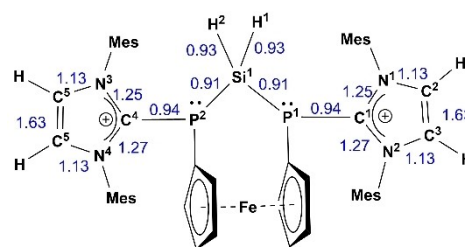


Figure 3. Lewis structure, atom labels (superscript), and Wiberg bond indices (WBI, numbers in blue) of **2a**.

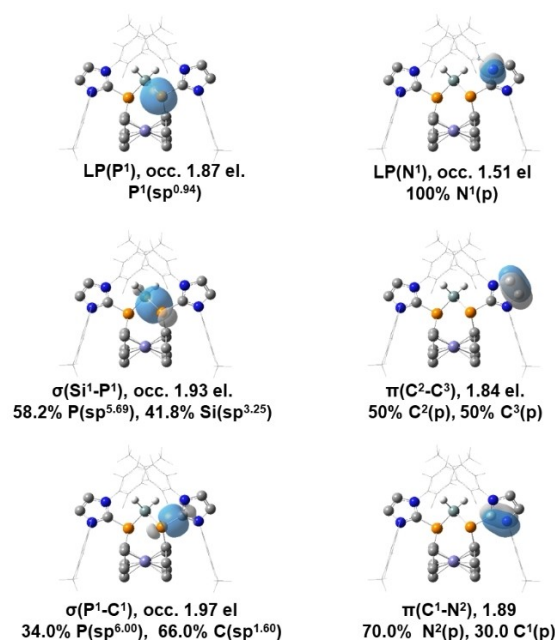


Figure 4. Selected NBOs of **2a**, their occupancy and composition.

(DAI = 11.2 kcal mol⁻¹). WBI between P¹ and C¹ of 0.94 indicates a single bond, stemming from a somewhat polarized $\sigma(\text{P}^1-\text{C}^1)$ (P(sp^{6.0}) 34.0%, C(sp^{1.6}) 66.0%). The bonding situation within the carbene moiety is typical –C¹ and N¹ form a double bond and N² possess a lone pair, which is strongly delocalized to $\pi^*(\text{C}^1-\text{N}^1)$ (DAI = 78.4 kcal mol⁻¹), resulting in N¹–C¹–N² 3-center-4-electron hyperbond, and to $\pi^*(\text{C}^2-\text{N}^2)$ (DAI = 34.2 kcal mol⁻¹). The corresponding natural localized molecular orbitals NLMOs are presented in Figure S28.

Inspection of the NPA charges of [2a] reveals that the +2 charge of the molecule is located mainly on the atoms, which constitute the NHCP moieties with $\Sigma q(\text{NHCP}^1, \text{NHCP}^2) = +2.18$ el. The SiH₂ moiety accommodates only +0.27 el. (+0.46 el. on Si and –0.10 el. on each hydrogen), while the ferrocene backbone is negatively charged with $\Sigma q(\text{Fc}) = -0.45$ el. The calculated ²⁹Si NMR chemical shifts of [2a] and [2b] $\delta = -49.8$ ppm and $\delta = -13.2$ ppm are in good agreement with the respective experimentally observed signals at –44.1 ppm and –10.7 ppm.

In order to quantify the Lewis acidity of the isolated dicationic complexes, the Gutmann Beckett method was applied.^[34–35] After addition of one equivalent triethylphosphine oxide to a 1,2-difluorobenzene solution of complexes [2a][OTf]₂ and [2b][OTf]₂, the difference in ³¹P NMR chemical shifts ($\Delta\delta$ ³¹P) between the free (³¹P $\delta = 47.37$ ppm) and the coordinated triethylphosphine oxide were measured. A larger difference in the shifts corresponds to a higher Lewis acidity. Adduct [2a][OTf]₂(OPEt₃) shows a chemical shift of 81.67 ppm and a $\Delta\delta$ ³¹P of 34.30 ppm accounting for high Lewis acidity. However, the complex [2a][OTf]₂(OPEt₃) is not stable and fully decomposes within 20 h, therefore it eluded further investigation. While dications VIII demonstrated lower $\Delta\delta$ ³¹P shifts (R = Ph: $\Delta\delta$ ³¹P 23.5 ppm, R = C₁₂H₈: $\Delta\delta$ ³¹P 28.6 ppm) compared with [2a][OTf]₂ and therefore lower Lewis acidity, aryl silylium ions are even more Lewis acidic with $\Delta\delta$ ³¹P of 39.2–44.9 ppm (Figure 5).^[32,36] Addition of triethylphosphine oxide to a 1,2-difluorobenzene solution of complex [2b][OTf]₂ yielded a $\Delta\delta$ ³¹P of 53.22 ppm and 5.14 ppm. As observed in other Si(IV) dications a coordination of two equivalents triethylphosphine oxide is possible and could account for the $\Delta\delta$ ³¹P of 5.14 ppm, while $\Delta\delta$ ³¹P of 53.22 ppm shows the shift of a single triethylphosphine oxide coordination.^[32] Since the tendency to form the bisadduct seems to be very high, the monoadduct is only visible when 0.5 eq OPET₃ are added. Calculations predicts the coordination of triethylphosphine to [2a] to be exergonic

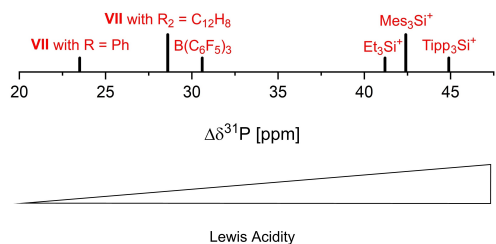
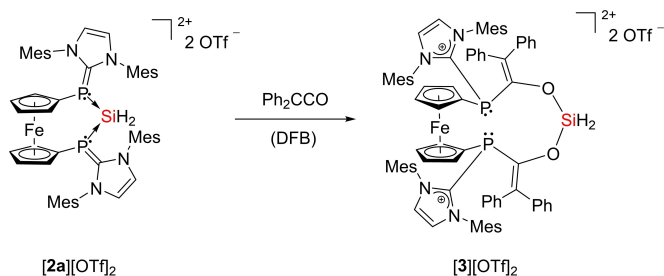


Figure 5. Lewis acidity assessment of different silyl cations and BCF via Gutmann Beckett method.

by 6.8 kcal mol⁻¹. The computational predictions of the Gutmann–Beckett method have been previously attempted, giving poor correlations between the experimental and calculated $\Delta\delta$ ³¹P values.^[37] In the case of [2a] the calculated $\Delta\delta$ ³¹P accounts for 20.4 ppm.

To investigate the thermal stability as well as the reactivity of [2a][OTf]₂ and [2b][OTf]₂, CD₃CN solutions were heated for several days. While [2a][OTf]₂ already shows very slow decomposition at 80 °C, [2b][OTf]₂ is stable at 80 °C but slowly starts to decompose at 100 °C. The ¹H NMR shows only signals of the imidazolium salt after heating overnight. The other decomposition products could not be identified. Both complexes are unreactive towards ethylene, acetylene, phenyl-, and diphenylacetylene in CD₃CN even at elevated temperature (heating up to 80 °C for 1–2 days). However, addition of excess diphenylketene to the dication [2a] in 1,2-difluorobenzene shows full conversion at 80 °C after 20 h, while [2b] is unreactive. Multinuclear NMR analysis as well as LIFDI-MS indicate the formation of the compound [3] (Scheme 3). The ³¹P NMR and the ²⁹Si NMR signal are downfield shifted in comparison to the starting material at –23.08 ppm and –53.81 ppm. Both signals do not show J(Si–P) indicating the Si–P bond cleavage via C–O insertion into the Si–P bonds. Additionally, LIFDI-MS measurement shows the mass for [2a + 2 eq Ph₂CCO]²⁺. Similar reactivity is observed by Appel as well as by Weber and coworkers.^[38–39] Treatment of PhP(SiMe₃)₂ with an equimolar amount of diphenylketene afforded the adduct Ph(Me₃Si)P–C(OSiMe₃)=CPh₂. The same reactivity was observed for [Fe]–P(SiMe₃)₂. According to the measured data and literature comparison, the structure of [3] was proposed.

To support the proposed structure, an optimized structure was calculated (Figure 6). DFT calculations show that [3] adopts a nearly ideal C₂ symmetry. The calculated ²⁹Si NMR and ³¹P NMR chemical shifts of the optimized geometry at –50.2 ppm and –31.2 ppm are in a good agreement with the experiment (–53.8 ppm and –23.1 ppm). Further theoretical considerations predict the reaction of [2a] with two equivalents of diphenylketene to form [3] to be exergonic by 57.7 kcal mol⁻¹.



Scheme 3. Reactivity of [2a][OTf]₂ towards diphenylketene in 1,2-difluorobenzene (DFB).

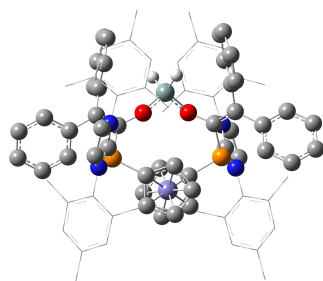


Figure 6. Optimized structure of [3].

Conclusion

In conclusion, we were able to isolate the first examples of bis(NHCP)-supported Si(IV) dications presenting an unique electronic nature. The dications [2a] and [2b] reveal high Lewis acidity being confirmed *via* Gutmann Beckett method. While the dications show high thermal stability in CD₃CN solution, [2a] readily reacts with diphenylketene at elevated temperature to yield a heterocyclic complex. These results further demonstrate the coordination abilities of bis(NHCP)s in main group chemistry and open the way for further investigations such as small molecule activation.

Experimental Section

Synthesis of [2a][OTf]₂ and [2b][OTf]₂: To a stirred solution of FcPIMes (1) (87 mg, 101.8 μmol, 1.0 eq) in benzene (1.5 mL) the silane (122.2 μmol, 1.2 eq) dissolved in benzene (0.5 mL) was added dropwise. The complex formed immediately as red oil. The solution was decanted and after washing the residue with benzene (2·2 mL), the product was dried under vacuum to yield an orange solid.

[2a][OTf]₂: ¹H NMR (400 MHz, CD₃CN, 300 K): δ[ppm] = 7.64 (s, 4H, NCH), 7.11 (s, 4H, C_{Mes}H), 7.07 (s, 4H, C_{Mes}H), 4.34 (s, 2H, C_{Cp}H), 4.29 (s, 2H, SiH), 4.19 (s, 2H, C_{Cp}H), 3.77 (s, 2H, C_{Cp}H), 3.72 (s, 2H, C_{Cp}H), 2.38 (s, 24H, *o*-C_{Mes}CH₃), 1.83 (s, 12H, *p*-C_{Mes}CH₃). ¹⁹F NMR (376 Hz, CD₃CN): δ[ppm] = -78.94. ²⁹Si-IG NMR (99 Hz, CD₃CN): δ[ppm] = -44.09 (t, ¹J_{SiP} = 24.8 Hz). ³¹P NMR (162 Hz, CD₃CN): δ[ppm] = -96.24.

[2b][OTf]₂: ¹H NMR (400 MHz, CD₃CN): δ[ppm] = 7.58 (t, ¹J_{H,H} = 7.3 Hz, 6H, C_{Ph}H), 7.32 (d, ¹J_{H,H} = 7.6 Hz, 4H, C_{Ph}H), 7.30 (s, 4H, NCH), 6.69 (s, 8H, C_{Mes}H), 4.28 (s, 4H, C_{Cp}H), 3.94 (s, 4H, C_{Cp}H), 2.28 (s, 12H, *p*-C_{Mes}CH₃), 1.52 (s, 24H, *o*-C_{Mes}CH₃). ¹⁹F NMR (376 Hz, CD₃CN): δ[ppm] = -78.88. ²⁹Si-IG NMR (79.51 Hz, CD₃CN): δ[ppm] = -10.74 (t, ¹J_{SiP} = 65.7 Hz). ³¹P NMR (162 Hz, CD₃CN): δ[ppm] = -66.06.

Synthesis of [3][OTf]₂: To a solution of [2a][OTf]₂ (38.0 mg, 32.12 μmol, 1.0 eq) in 1,2-difluorobenzene (0.4 mL) diphenylketene (62.4 mg, 321.20 μmol, 10.0 eq) was added. The solution was heated to 60 °C for 3 d to observe full conversion in the ³¹P NMR. The solvent was removed and the residue washed with benzene (4·1 mL) and pentane (2·1.5 mL) to yield the diphenylketene adduct [3][OTf]₂ as yellow powder (44.0 mg, 28.0 μmol, 87%). ¹H NMR (400 MHz, CD₃CN): δ[ppm] = 7.43 (m, 8H, C_{Ph}H), 7.35 (s, 4H, NCH), 7.24 (m, 8H, C_{Ph}H), 7.03 (s, 4H, C_{Mes}H), 6.90 (s, 4H, C_{Mes}H), 6.64 (dd, 4H, ¹J_{H,H} = 7.6 Hz, 2.0 Hz, C_{Ph}H), 4.57 (m, 2H, C_{Cp}H), 4.28 (m, 2H, C_{Cp}H), 3.90 (m, 2H, C_{Cp}H), 3.81 (s, 2H, SiH), 3.75 (m, 2H, C_{Cp}H), 2.36 (s,

12H, C_{Mes}CH₃), 1.65 (s, 12H, C_{Mes}CH₃), 1.52 (s, 12H, C_{Mes}CH₃). ¹⁹F NMR (376 Hz, CD₃CN): δ[ppm] = -79.04. ²⁹Si-INEPT NMR (99 Hz, CD₃CN): δ[ppm] = -53.81 (d, ¹J_{SiH} = 568.0 Hz). ³¹P NMR (162 Hz, CD₃CN, 300 K): δ[ppm] = -23.08.

Deposition Number 2203508 (for [2b][OTf]₂·3(C₆H₅F)) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Coordination chemistry · Main group elements · *N*-Heterocyclic carbene-phosphinidene · Si(IV) Dications · Silanes

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