



Taming a silyldiium cation and its reactivity towards sodium phosphoethynolate†

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A dicationic bis(NHC)-stabilised silyldiium complex, $[\text{bis}(\text{NHC})\text{-SiPh}_2]^{2+}$ (7^{2+}) ($\text{bis}(\text{NHC}) = [\text{CH}_2(\text{NC}_3\text{H}_2\text{NDipp})_2]$, $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$), was synthesised for the first time. It reacts with sodium phosphoethynolate (NaOCP) as a source of monoanionic phosphorus to give the P-insertion product $[\text{bis}(\text{NHC})\text{-PSiPh}_2]^+$ (8^+). The latter comprises a seven-membered heterocycle containing a Si–P moiety which can easily be desilylated when exposed to dichlorophosphanes as exemplified by the synthesis of the diphosphanide cations $[\text{bis}(\text{NHC})\text{-PPCy}]^+$ (9^+) and $[\text{bis}(\text{NHC})\text{-PPPh}]^+$ (10^+).

Since the first synthesis of a stable imidazol-2-ylidene in 1991,¹ N-heterocyclic carbenes (NHCs) have been employed for the stabilisation of various main group elements in unusual electronic states,² among them silicon and phosphorus.³ Commonly, the ligand is introduced in its deprotonated form, as “free” NHC, often followed by reduction reactions. However, in some cases, the use of a “free” NHC leads to side reactions, like for example the reduction of P^{III} centres to P^{I} , and is therefore not applicable.^{4,5} Other strategies have been developed to overcome this limit, such as adduct formation with silyl moieties and subsequent desilylation of the NHC. This approach has been used, *inter alia*, by Weigand *et al.* to access imidazoliumyl substituted phosphines by reacting the NHC-silyl adducts $1[\text{OTf}]$ and $2[\text{OTf}]$ with PCl_3 liberating Me_3SiCl (Fig. 1).^{5,6} The same group has also described the imidazoliumyl-functionalised diphosphorus cations 3^+ and 6^+ , which are depicted in Fig. 1.^{7,8} A related synthetic approach to obtain carbene-phosphinidene transition metal complexes was used by Tamm and co-workers who introduced the IPr-PSiMe_3 adduct ($\text{IPr} = 1,3\text{-bis}(\text{Dipp})\text{imidazol-2-ylidene}$, $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) as a silylated ligand precursor.⁹

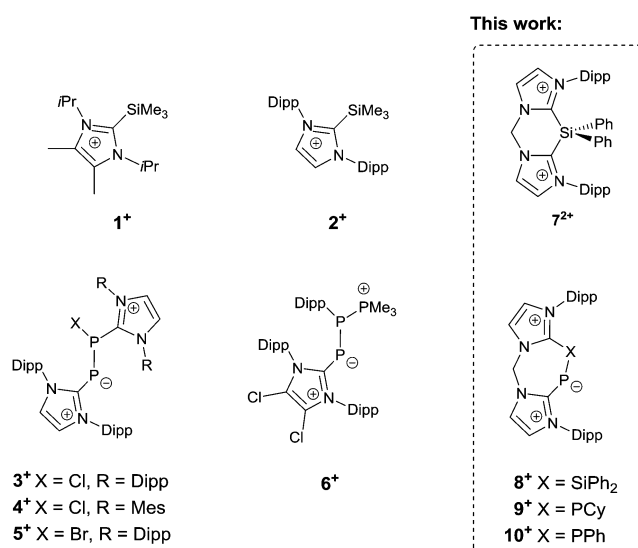


Fig. 1 Selected known cationic imidazoliumyl-stabilised silicon and phosphorus compounds and the new compounds 7^{2+} , 8^+ , 9^+ , and 10^+ .

In this case, the silicon moiety is also introduced as a leaving group and removed in the course of the synthetic route. Accordingly, the solvolysis of IPr-PSiMe_3 afforded IPr-PH , which had been prepared originally by transferring parent phosphinidene ($:\text{PH}$) from a silylene to IPr .¹⁰ The same species can also be obtained by reacting sodium phosphoethynolate (NaOCP) with the imidazolium salt $[\text{IPr-H}][\text{Cl}]$.¹¹ Compared to other synthetic routes, the use of NaOCP as monoanionic phosphorus transfer reagent is advantageous by means of atom economy as only one equivalent of CO and the corresponding Na salt are generated in a salt metathesis reaction as by-products. By taking advantage of this approach some novel species were synthesised, among them the NHC-phosphinidene adducts IPr-PEPh_3 (E = Ge, Sn).¹²

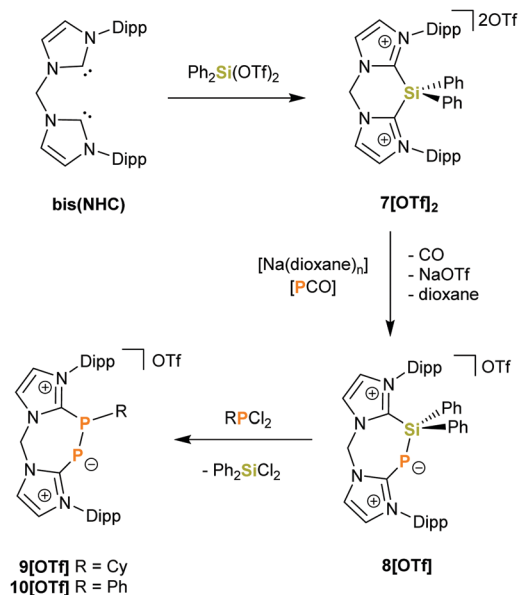
Herein we report the synthesis of the novel bis(NHC)-silyldiium salt $7[\text{OTf}]_2$ ($\text{bis}(\text{NHC}) = [\text{CH}_2(\text{NC}_3\text{H}_2\text{NDipp})_2]$) and its reactivity towards NaOCP which affords the cyclic bis(NHC)-PSiPh₂

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Scheme 1 Synthetic route to compounds $7[\text{OTf}]_2$, $8[\text{OTf}]$, $9[\text{OTf}]$ and $10[\text{OTf}]$. (Dipp = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$; Cy = Cyclohexyl).

adduct $8[\text{OTf}]$. The latter can be employed as a precursor for unprecedented seven-membered heterocycles by subsequent desilylation with dichlorophosphanes. This is illustrated by the reaction of $8[\text{OTf}]$ with RPhCl_2 (R = Cy, Ph), which gives rise to the phosphinidene-phosphanide cations 9^+ and 10^+ .

The reaction of $\text{Ph}_2\text{Si}(\text{OTf})_2$ with an equimolar amount of bis(NHC) in diethyl ether afforded the desired salt $7[\text{OTf}]_2$ in 84% yields (Scheme 1). The observed resonance in the ^{29}Si NMR spectrum in CD_3CN at $\delta = -36.7$ ppm lies within the range reported for four-coordinate Si^{IV} centres.¹³ Indeed, X-ray structural analysis of single crystals grown in concentrated acetonitrile solutions showed no close contact between the triflate anions and the central Si atom (Fig. 2). Moreover, the C–N bond lengths in the N–C–N moieties of the imidazoliumyl rings (average $d(\text{C–N}) = 1.35$ Å) express strong C–N double-bond character and thus suggest that the positive

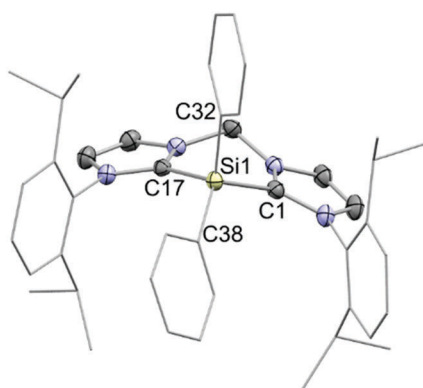


Fig. 2 Molecular structure of the cation 7^{2+} in $7[\text{OTf}]_2 \cdot 2(\text{CH}_3\text{CN})$, (thermal ellipsoids are given at 50% probability; H atoms are omitted for clarity); selected experimental bond lengths (Å) and angles ($^\circ$): C1–Si1 1.9033(15), C17–Si1 1.8919(15), Si1–C32 1.8535(16), Si1–C38 1.8471(15), C17–Si1–C1 94.8(6), C32–Si1–C1 110.69(6), C38–Si1–C32 113.82(7).

charges are delocalized over the imidazoliumyl substituents. These C–N distances are comparable to those reported for the imidazolium salt $[\text{IPr–H}]\text{Cl}$.¹⁴ In order to investigate the desilylation of 7^{2+} we exposed $7[\text{OTf}]_2$ to PhPCL_2 in $o\text{-C}_6\text{H}_4\text{F}_2$ at 55 °C for three days. As expected this afforded the salt $[\text{bis}(\text{NHC})(\text{PPh})][\text{OTf}]_2$ (Scheme S1, ESI^+) whose synthesis we have described previously from bis(NHC) and PhPCL_2 .¹⁵ This desilylation complies with reported reactions of NHC-silyl adducts with halogenated phosphanes that have been used in the literature to access different carbene-stabilised phosphorus compounds,^{5,6} and, in this regard, the “ SiPh_2 ” moiety in 7^{2+} only serves as a leaving group.

Nevertheless expecting the silicon centre to be electrophilic and thus, to allow for unprecedented synthetic pathways, we probed the reactivity of the system towards the nucleophilic phosphoethynolate anion. While literature compound IPr–PSiMe_3 was synthesized using a different approach,⁹ IPr–PEPh_3 (E = Ge, Sn),¹² IPr–PH ¹¹ and an amino(phosphanylidene phosphorene)-stabilised germylene¹⁶ were obtained by using NaOCP as P^- transfer reagent after CO loss at elevated temperatures. Interestingly, when mixing $7[\text{OTf}]_2$ with $[\text{Na}(\text{dioxane})]_n[\text{PCO}]$ (molar ratio 1:1) in CH_2Cl_2 at ambient temperature an immediate colour-change from ochre to red occurred, together with gas evolution (CO). Full conversion to $8[\text{OTf}]$ (Scheme 1) was evidenced by the rise of one singlet resonance with a characteristic high-field shift of $\delta = -161.0$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum which is in the same range as for related carbene-stabilised phosphinidene adducts.^{9,12,17} Both ^1H and ^{13}C NMR spectra reflect the presence of two chemically inequivalent imidazoliumyl moieties and confirm that decarbonylation has occurred in the course of the reaction. Compared to the starting material $7[\text{OTf}]_2$, the ^{29}Si NMR spectrum of $8[\text{OTf}]$ shows a low-field shifted doublet resonance at $\delta = -16.1$ ppm ($J_{\text{SiP}} = 85$ Hz). Unlike the above-mentioned literature reactions, the formation of $8[\text{OTf}]$ (including CO elimination) proceeds rapidly at ambient temperature and the product could be isolated in good yields (85%). No further reaction with excess NaOCP was observed, even upon addition of up to one more molar equivalent of NaOCP .

Finally, the connectivity of 8^+ was confirmed by a single crystal X-ray structure determination and evidences this rare example of a seven-membered ring that contains a Si–P moiety (Fig. 3). The $\text{C}_{\text{NHC}}\text{–P}$ bond length (1.770(2) Å) compares well to those in similar NHC-phosphinidene adducts^{9,12} whereas the P–Si distance ($d(\text{P–Si}) = 2.1987(7)$ Å) in 8^+ is slightly contracted compared to IPr–PSiMe_3 . This could be explained by the cationic charge in 8^+ which makes the Si centre more electrophilic or due to ring strain. In fact, the arrangement of the atoms in a seven-membered ring leads to a distortion of the ligand backbone with respect to 7^{2+} , as visualized by comparison of the tilt angle α between the two planes defined by the imidazoliumyl rings (compare Fig. 2 and 3). While α amounts to 31.4° for 7^{2+} , α adds up to 55.3° for 8^+ . Furthermore, the P-insertion leads to different bonding situations in the N–C–N moieties of the two imidazoliumyl-rings. The C–N bond lengths in the Si-bonded ring (average $d(\text{C–N}) = 1.35$ Å) are well comparable to those in 7^{2+} , whereas the C–N distances in the P-bonded ring are somewhat elongated (average $d(\text{C–N}) = 1.37$ Å). This possibly reflects contributions of the canonical structures 8b^+ and 8c^+ to the ground state (Fig. 4). \ddagger The distinct ^{13}C NMR shifts



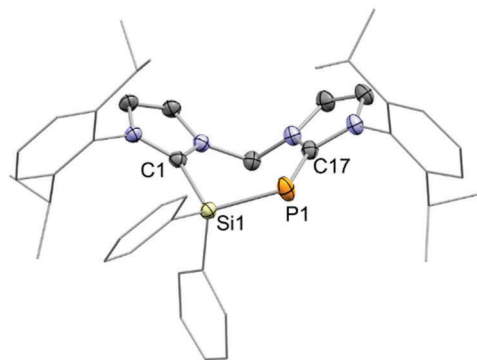


Fig. 3 Molecular structure of the cation **8⁺** in **8[OTf]·(CH₃CN)**, (thermal ellipsoids are given at 50% probability; H atoms are omitted for clarity); selected experimental bond lengths (Å) and angles (°): Si1–P1 2.1987(7), C1–Si1 1.913(2), C17–P1 1.770(2), C1–Si1–P1 111.55(7), C17–P1–Si1 105.98(7).

of $C_{\text{NHC-P}}$ ($\delta = 170.8$ ppm, $^1J_{\text{CP}} = 102.1$ Hz) and $C_{\text{NHC-Si}}$ ($\delta = 151.8$ ppm) also mirror these differences.

In order to investigate whether the reaction of **7²⁺** with NaOCP is a particular case, we synthesised the related non-cyclic NHC-silyl cation $[\text{IPr-SiPh}_3]^+$ from an equimolar mixture of Ph_3SiOTf and IPr in diethyl ether. The product precipitated from the reaction mixture in form of colourless microcrystals and was characterised by heteronuclear NMR spectroscopy and high-resolution mass spectrometry indicating that the Si atom is tetracoordinate in solution. Subsequently, mixing equimolar amounts of $[\text{IPrSiPh}_3]\text{OTf}$ and NaOCP in THF led to formation of the rearrangement product $\text{IPr}=\text{C}=\text{P}-\text{O}-\text{SiPh}_3$ (Scheme S2, ESI[†]) which was obtained previously by Grützmacher and co-workers from *in situ* generated $\text{Ph}_3\text{Si-PCO}$ and IPr.¹² This finding underlines the unique properties of **7²⁺**, which are most likely due to the arrangement in a cyclic system and the presence of a second positive charge. Furthermore, compared to IPr the higher steric bulk of the bis(NHC) might influence the spatial approach of the PCO^- nucleophile. Additionally, Tamm *et al.* reported on the dissociation equilibrium of $[(\text{NHC})\text{SiMe}_3]\text{OTf}$ (forming NHC + Me_3SiOTf) which could occur for $[\text{IPrSiPh}_3]\text{OTf}$, as well.¹⁸ Owing to the chelating nature of the bis(NHC) ligand the respective equilibrium is most likely completely in favour of the dicationic adduct in the case of **7[OTf]₂**.

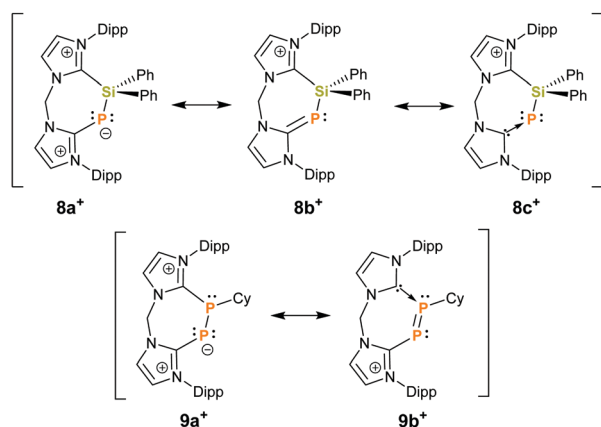


Fig. 4 Selected resonance structures for **8⁺** (top) and **9⁺** (bottom).

Formally, cation **8⁺** can be considered as a silylated chelate ligand consisting of a NHC and NHC-phosphinidene donor site. Therefore, we investigated the reaction of **8⁺** with dichlorophosphanes RPCl_2 ($\text{R} = \text{Cy}, \text{Ph}$) at ambient temperature in order to elucidate whether this compound can be desilylated. Indeed, this led to fast and quantitative conversion of **8⁺** to **9⁺** ($\text{R} = \text{Cy}$) and **10⁺** ($\text{R} = \text{Ph}$), respectively (Scheme 1), as evidenced by the rise of two new doublet resonances in the respective $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The signals with $\delta = -66.5$ ppm and -97.5 ppm (**10⁺**: $\delta = -65.0$ ppm, -102.4 ppm) can be assigned to the three-coordinate P atom and to the di-coordinate phosphinidenyl moiety, respectively. These values are in excellent agreement with those reported for the related species **6⁺** ($\delta = -62.1, -108.1$ ppm),⁸ but differ somewhat from what was observed for **4⁺** ($\delta = 138.0, -22.1$ ppm)¹⁹ and **5⁺** ($\delta = 145.4, -7.6$ ppm)²⁰ which might be due to the presence of halogen atoms in the structures of **4⁺** and **5⁺** (Fig. 1). Additionally, the observed coupling constants (**9⁺**: $|^1J_{\text{PP}}| = 453.5$ Hz and **10⁺**: $|^1J_{\text{PP}}| = 478.8$ Hz) are much larger than those accounted for comparable systems with P–P single bonds, where $|^1J_{\text{PP}}|$ ranges between 235 Hz and 391 Hz.^{7,8,19–21} This could be attributed to the arrangement of the P_2 -unit in a rigid cyclic system, considering that $^1J_{\text{PP}}$ is strongly influenced by internal rotation around the P–P bond.²² In fact, the values of $^1J_{\text{PP}}$ come close to such that were reported for diphosphenes of the type $[(\text{NHC})\text{P}=\text{PR}]^{x+}$ ($\text{R} = \text{Aryl}, \text{NHC}'$ and $x = 1, 2$) which range between 543 Hz and 578 Hz.^{8,19,23} In this regard, the observed $^1J_{\text{PP}}$ might be an indication for partial P–P double-bond character, arising from contributions of resonance structure **9b⁺** to the ground state (Fig. 4). However, the ^{31}P chemical shifts for $[(\text{NHC})\text{P}=\text{PR}]^{x+}$ were observed at substantially lower fields ($\delta(^{31}\text{P}) = 398$ to 452 ppm) compared to **9⁺** and **10⁺** what indicates that the double-bond character is not very pronounced.^{8,19,23} In the ^{13}C NMR spectrum of **9[OTf]** two doublet of doublet resonances with $\delta = 169.2$ ppm ($^1J_{\text{CP}} = 145.2$ Hz, $^2J_{\text{CP}} = 10.6$ Hz) and 151.5 ppm ($^1J_{\text{CP}} = 76.2$ Hz, $^2J_{\text{CP}} = 7.4$ Hz) assignable to the N_2C -carbon atoms evidence the presence of two chemically inequivalent imidazoliumyl moieties. Furthermore, a doublet resonance at $\delta = 45.1$ ppm with a considerably smaller coupling constant ($^1J_{\text{CP}} = 22.5$ Hz) is observed for the cyclohexyl-carbon that is attached to one phosphorus atom.

An X-ray structure analysis confirmed the replacement of the SiPh_2 fragment by the respective PR moieties in the molecular structures of **9⁺** and **10⁺** (Fig. 5 and Fig. S23, ESI[†]). As observed for cation **8⁺**, the arrangement in a seven-membered ring leads to distortion of the bis(NHC) backbone. The tilt angles α between the two planes defined by the imidazoliumyl rings amount to 57.1° for **9⁺** and 70.4° for **10⁺** and are hence even larger than α in the structure of **8⁺** (compare Fig. 3, 5 and Fig. S23, ESI[†]). The P–P distances of $2.1527(10)$ Å (**9⁺**) and $2.1561(18)$ Å (**10⁺**) are very close to the one reported for the related cation **6⁺** ($d(\text{P}–\text{P}) = 2.151(1)$ Å),⁸ but somewhat elongated in comparison to **4⁺** ($d(\text{P}–\text{P}) = 2.1067(10)$ Å)¹⁹ and **5⁺** ($d(\text{P}–\text{P}) = 2.096(2)$ Å)²⁰ what may be due to the presence of phosphorus-bonded halogen atoms in the structures of **4⁺** and **5⁺**. Furthermore, because of the chelating nature of the bis(NHC) ligand the torsion angles ϕ defined by $C_{\text{NHC}}-\text{P}2-\text{P}1-C_{\text{NHC}}$



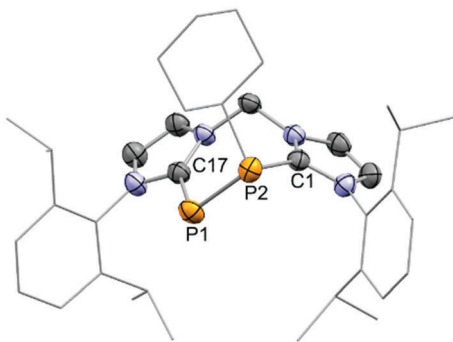


Fig. 5 Molecular structure of the cation 9^+ in $[9OTf] \cdot (CH_2Cl_2) \cdot (C_7H_8)$, (thermal ellipsoids are given at 50% probability; H atoms are omitted for clarity); selected experimental bond lengths (Å) and angles (°); P1–P2 2.1527(10), P1–P17 1.791(2), P2–C1 1.831(2), C17–P1–P2 105.42(9), C1–P2–P1 99.33(8).

($\Phi(9^+) = -52^\circ$ and $\Phi(10^+) = -46^\circ$) differ strongly from the corresponding Φ in the solid state structures of 4^+ ($\Phi = 156^\circ$)¹⁹ and 5^+ ($\Phi_1 = 161^\circ$ and $\Phi_2 = 177^\circ$, two crystallographically independent molecules).²⁰ Compared to the P–P distances in cationic NHC-stabilised diphosphenes where $d(P-P)$ ranges between 2.038(1) Å and 2.083(2) Å^{8,19,23} the P–P bond lengths in 9^+ and 10^+ are elongated illustrating mostly P–P single bond character. It is worth mentioning that the desilylation of 8^+ with dichlorophosphanes represents a viable procedure for a modular approach to synthesise novel cyclic compounds that assemble different main group heteroatoms in a seven-membered ring.

In summary, we have presented the synthesis of the first bis(NHC)-stabilised silyldiium salt $7[OTf]_2$, and shown that the particular properties of this system induce a different reactivity towards sodium phosphoethynolate than observed for the related NHC-silyl adduct $[IPr-SiPh_3][OTf]$. The selective P-insertion reaction into one of the NHC–Si bonds in 7^{2+} afforded cation 8^+ , which was subsequently desilylated with $RPCL_2$ (R = Cy, Ph) to give the diphosphanide cations 9^+ and 10^+ . In this way, the utility of $8[OTf]$ as a precursor for unprecedented seven-membered heterocyclic P–X compounds was demonstrated and is subject of further research in our laboratories.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ A comprehensive discussion on the bonding features of NHC-element adducts can be found in the literature.²⁴

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