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Taming a silyldiium cation and its reactivity towards sodium phosphaethynolate[†]

André Hermannsdorfer, a Douglas W. Stephan 💿 b and Matthias Driess 💿 * a

A dicationic bis(NHC)-stabilised silyldiium complex, $[bis(NHC)-SiPh_2]^{2+}$ (7²⁺) (bis(NHC) = $[CH_2(NC_3H_2NDipp)_2]$, Dipp = 2,6-ⁱPr_2C_6H_3), was synthesised for the first time. It reacts with sodium phosphaethynolate (NaOCP) as a source of monoanionic phosphorus to give the P-insertion product $[bis(NHC)-PSiPh_2]^+$ (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 $[bis(NHC)-PPCy]^+$ (9⁺) and $[bis(NHC)-PPPh]^+$ (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 silvl moieties and subsequent desilvlation 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[OTf] and 2[OTf] with PCl₃ liberating Me₃SiCl (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-phosphinidyne transition metal complexes was used by Tamm and co-workers who introduced the IPr-PSiMe₃ adduct (IPr = 1,3-bis-(Dipp)imidazol-2ylidene, Dipp = 2.6^{-1} Pr₂C₆H₃) as a silvlated 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–PSiMe₃ afforded IPr–PH, which had been prepared originally by transferring parent phosphinidene (:PH) from a silylene to IPr.¹⁰ The same species can also be obtained by reacting sodium phosphaethynolate (NaOCP) with the imidazolium salt [IPr–H][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–PEPh₃ (E = Ge, Sn).¹²

Herein we report the synthesis of the novel bis(NHC)silyldiium salt 7[OTf]₂ ($bis(NHC) = [CH_2(NC_3H_2NDipp)_2]$) and its reactivity towards NaOCP which affords the cyclic bis(NHC)-PSiPh₂

^a Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany. E-mail: matthias.driess@tu-berlin.de

^b Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5S 3H6, Canada

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Scheme 1 Synthetic route to compounds 7[OTf]₂, 8[OTf], 9[OTf] and **10**[OTf]. (Dipp = $2,6^{-i}Pr_2C_6H_3$; Cy = Cyclohexyl).

adduct 8[OTf]. The latter can be employed as a precursor for unprecedented seven-membered heterocycles by subsequent desilvlation with dichlorophosphanes. This is illustrated by the reaction of 8[OTf] with RPCl₂ (R = Cy, Ph), which gives rise to the phosphinidene-phosphanide cations 9^+ and 10^+ .

The reaction of Ph₂Si(OTf)₂ with an equimolar amount of bis(NHC) in diethyl ether afforded the desired salt $7[OTf]_2$ in 84% yields (Scheme 1). The observed resonance in the ²⁹Si NMR spectrum in CD₃CN 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(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 $7[OTf]_2$ ·2(CH₃CN), (thermal ellipsoids are given at 50% probability; H atoms are omitted for clarity); selected experimental bond lengths (Å) and angles (°); 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 [IPr-H]Cl.¹⁴ In order to investigate the desilvlation of 7^{2+} we exposed 7[OTf]₂ to PhPCl₂ in o-C₆H₄F₂ at 55 °C for three days. As expected this afforded the salt [bis(NHC)(PPh)][OTf]2 (Scheme S1, ESI[†]) whose synthesis we have described previously from bis(NHC) and PhPCl2.15 This desilylation complies with reported reactions of NHC-silvl 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 "SiPh₂" 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 phosphaethynolate anion. While literature compound IPr-PSiMe₃ was synthesized using a different approach,⁹ IPr-PEPh₃ (E = Ge, Sn),¹² IPr-PH¹¹ 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[OTf]₂ with [Na(dioxane), PCO] (molar ratio 1:1) in CH₂Cl₂ at ambient temperature an immediate colour-change from ocher to red occurred, together with gas evolution (CO). Full conversion to 8[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 ${}^{31}P_{1}^{1}H_{1}^{1}$ NMR spectrum which is in the same range as for related carbenestabilised phosphinidene adducts.^{9,12,17} Both ¹H and ¹³C 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[OTf]₂, the ²⁹Si NMR spectrum of 8[OTf] shows a low-field shifted doublet resonance at $\delta = -16.1$ ppm (¹ $J_{\text{SiP}} = 85$ Hz). Unlike the abovementioned literature reactions, the formation of 8[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 C_{NHC}-P bond length (1.770(2) Å) compares well to those in similar NHC-phosphinidene adducts9,12 whereas the P-Si distance (d(P-Si) = 2.1987(7) Å) in 8⁺ is slightly contracted compared to IPr-PSiMe₃. 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 7²⁺, 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 imdazoliumyl-rings. The C-N bond lengths in the Si-bonded ring (average d(C-N) = 1.35 Å) are well comparable to those in 7²⁺, whereas the C-N distances in the P-bonded ring are somewhat elongated (average d(C-N) = 1.37 Å). This possibly reflects contributions of the canonical structures 8b⁺ and 8c⁺ to the ground state (Fig. 4).[‡] The distinct ¹³C 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 $C_{\text{NHC-P}}$ (δ = 170.8 ppm, ${}^{1}J_{\text{CP}}$ = 102.1 Hz) and $C_{\text{NHC-Si}}$ (δ = 151.8 ppm) also mirror these differences.

In order to investigate whether the reaction of 7^{2+} with NaOCP is a particular case, we synthesised the related non-cyclic NHC-silyl cation [IPr-SiPh₃]⁺ from an equimolar mixture of Ph₃SiOTf and IPr in diethyl ether. The product precipated 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 [IPrSiPh₃]OTf and NaOCP in THF led to formation of the rearrangement product IPr=C=P-O-SiPh₃ (Scheme S2, ESI⁺) which was obtained previously by Grützmacher and co-workers from in situ generated Ph₃Si-PCO and IPr.¹² This finding underlines the unique properties of 7^{2+} , 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 [(NHC)SiMe₃]OTf (forming NHC + Me₃SiOTf) which could occur for [IPrSiPh₃]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 silvlated chelate ligand consisting of a NHC and NHC-phosphinidene donor site. Therefore, we investigated the reaction of 8⁺ with dichlorophosphanes $RPCl_2$ (R = Cy, Ph) at ambient temperature in order to elucidate whether this compound can be desilylated. Indeed, this led to fast and quantitative conversion of $\mathbf{8}^+$ to $\mathbf{9}^+$ (R = Cy) and 10^+ (R = Ph), respectively (Scheme 1), as evidenced by the rise of two new doublet resonances in the respective ${}^{31}P{}^{1}H{}$ NMR spectra. The signals with $\delta = -66.5$ ppm and -97.5 ppm $(10^+: \delta = -65.0 \text{ ppm}, -102.4 \text{ ppm})$ can be assigned to the threecoordinate 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^+ (δ = 138.0, -22.1 ppm¹⁹ and 5⁺ (δ = 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 $(9^+: |^{1}J_{PP}| = 453.5 \text{ Hz and } 10^+: |^{1}J_{PP}| = 478.8 \text{ Hz})$ are much larger than those accounted for comparable systems with P-P single bonds, where $|^{1}J_{PP}|$ ranges between 235 Hz and 391 Hz.^{7,8,19–21} This could be attributed to the arrangement of the P₂-unit in a rigid cyclic system, considering that ${}^{1}J_{PP}$ is strongly influenced by internal rotation around the P-P bond.²² In fact, the values of ${}^{1}J_{PP}$ come close to such that were reported for diphosphenes of the type $[(NHC)P = PR]^{x+}$ (R = Aryl, NHC' and x = 1, 2) which range between 543 Hz and 578 Hz.^{8,19,23} In this regard, the observed ¹J_{PP} might be an indication for partial P-P doublebond character, arising from contributions of resonance structure **9b**⁺ to the ground state (Fig. 4). However, the ³¹P chemical shifts for $[(NHC)P = PR]^{x+}$ were observed at substantially lower fields (δ (³¹P) = 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 ¹³C NMR spectrum of 9[OTf] two doublet of doublet resonances with $\delta = 169.2$ ppm (${}^{1}J_{CP} =$ 145.2 Hz, ${}^{2}J_{CP}$ = 10.6 Hz) and 151.5 ppm (${}^{1}J_{CP}$ = 76.2 Hz, ${}^{2}J_{CP}$ = 7.4 Hz) assignable to the N₂C-carbon atoms evidence the presence of two chemically inequivalent imidazoliumyl moieties. Furthermore, a doublet resonance at δ = 45.1 ppm with a considerably smaller coupling constant (${}^{1}J_{CP}$ = 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 SiPh₂ 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*(P–P) = 2.151(1) Å), ⁸ but somewhat elongated in comparison to **4**⁺ (*d*(P–P) = 2.1067(10) Å)¹⁹ and **5**⁺ (*d*(P–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_{NHC}–P2–P1–C_{NHC}

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Fig. 5 Molecular structure of the cation **9**⁺ in **9[OTfl**·(CH₂Cl₂)·(C₇H₈), (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 phosphaethynolate than observed for the related NHC-silyl adduct [IPr–SiPh₃][OTf]. The selective P-insertion reaction into one of the NHC–Si bonds in 7^{2+} afforded cation **8**⁺, which was subsequently desilylated with RPCl₂ (R = Cy, Ph) to give the diphosphanide cations **9**⁺ and **10**⁺. In this way, the utility of **8**[OTf] as a precursor for unprecedented sevenmembered 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

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

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