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Crystalline phosphino(silyl)carbenes that readily form transition metal complexes†‡

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Phosphino(silyl)carbenes are known for their ineptitude to form transition metal complexes. We describe the synthesis of phosphino(silyl)carbenes bearing N-heterocyclic imine groups and show that these isolable, crystalline carbenes readily form stable copper(I) and gold(I) complexes. The solid-state structures of the free carbenes and their transition metal complexes are reported.

Since the first isolation of stable carbenes by Bertrand and co-workers in 1988 (Fig. 1a, **I**),^{1,2} and by Arduengo and co-workers in 1991 (1,3-diadamantylimidazolin-2-ylidene),³ the class of isolable singlet carbenes vastly expanded, covering a wide range of substitution patterns.^{4–6} Great efforts have been made to understand how their reactivity and donor properties can be tailored, particularly for the use as ligands in transition metal catalysis.^{5,7} The stability of phosphino(silyl)carbenes (*e.g.* **I** and **II**) is attributed to the mesomeric push-pull effect of the substituents at the carbene carbon atom. Due to the efficient π -donation from the phosphino group to the carbene carbon atom, phosphino(silyl)carbenes are best described as vinyl ylides (Fig. 1b, **B**) with modest contributions from the phosphaacetylene (**C**) and heterocumulene (**D**) electronic structures.⁸ **C** and **D** represent the negative hyperconjugation of the carbene lone pair into σ^* orbitals centered at phosphorus and silicon, leading to a widening of the carbene bond angle. This structural hallmark results in significant energy requirement to form a bent carbene structure for metal complexation, which in turn leads to rather low metal–carbon bond energies.⁹ Therefore, apart from complexes with group 13 element chlorides ECl_3 ($E = Al, Ga, In$),¹⁰

direct complexation of phosphino(silyl)carbenes to metals has not yet been reported.¹¹

One strategy towards more bent acyclic phosphinocarbenes and thus improved ligand properties was to replace the pull-type silyl group with a spectator-type alkyl or aryl substituent.¹² Unfortunately, phosphino(alkyl)carbenes turned out to be unstable at ambient conditions owing to low barrier rearrangement reactions. The first formation of transition metal complexes with isolable phosphinocarbenes was reported by Bertrand and co-workers in 2002, who showed that the phosphino(aryl)carbene **V** binds to rhodium(I) complexes in either η^1 or η^2 coordination mode along the P–C bond.^{13,14} Yet, phosphinocarbene complexes remain rare, although persistent phosphinocarbenes with various substitution patterns have been prepared,⁵ including the more recent phosphino(boryl)carbene **III** and the phosphino(auro)carbene **IV**.^{15,16}



Fig. 1 (a) Selected examples of phosphinocarbenes and the phosphino-carbene presented in this work. Dipp = 2,6-diisopropylphenyl. (b) Possible electronic structures of phosphino(silyl)carbenes ([Si] = silyl group).

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We herein report an alternative approach to form more stable phosphinocarbene complexes by modifying the phosphino group with N-heterocyclic imine (NHI) substituents. NHI groups are significantly stronger π donors than amino groups and have found broad application for the stabilization of low-valent main group and metallic species.¹⁷ We previously showed that NHI groups are extremely effective in increasing the electron donor ability of phosphines.¹⁸ From these results, we reasoned that NHI-substituted phosphino(silyl)carbenes should exhibit enhanced π -donation from the phosphino group to the carbene center and reduced back-bonding of the carbene lone pair, resulting in an overall increased vinyl ylide character (**B**).

Phosphino(silyl)carbenes **3a,b** were prepared based on the established route: Reaction of the phosphonium chloride salts **1a,b**¹⁹ with lithio-(trimethylsilyl)diazomethane gave the diazomethane derivatives **2a,b**, which were used directly for the next step. Irradiation of the orange solutions of **2a,b** in *n*-hexane with UV light at 365 nm or with sunlight led to the formation of carbenes **3a,b** as yellow crystalline material (Scheme 1).

Phosphino(silyl)carbenes **3a,b** are stable at ambient conditions. § The ³¹P NMR signals of **3a,b** (**3a**: -7.3 ppm, **3b**: 19.9 ppm) are deshielded compared to phosphinocarbenes **I** (-40 ppm),¹ **II** (-26.7 ppm),²⁰ **III** (-36.7 ppm),¹⁵ **IVa,b** (**a**: -17.1 ppm, **b**: -20.7 ppm),¹⁶ and **V** (-22.2 ppm).¹³ The ¹³C NMR resonance of the carbene carbon atom (**3a**: 75.1 ppm, **3b**: 77.4 ppm) is shifted to lower frequencies compared to **I** (142.8 ppm),¹ but is in the range of **II** (77.6 ppm).²⁰ An exceptional feature of **3a,b** are the small ¹J_{PC} coupling constants (**3a**: 49 Hz, **3b**: 47 Hz) compared to the other phosphinocarbenes **I** (159 Hz),¹ **II** (153 Hz),²⁰ **III** (209 Hz),¹⁵ **IVa,b** (**a**: 79 Hz, **b**: 77 Hz)¹⁶ and **V** (271 Hz).¹³ A similar trend has been observed for amino(phosphino)carbenes of type R₂PCN(iPr)₂, showing that the ¹J_{PC} coupling constants are significantly smaller for R = N(iPr)₂ (23 Hz) than for R = Ph (102 Hz).²¹

Crystals obtained in the synthesis of **3a,b** were suitable for X-ray diffraction (XRD) studies (Fig. 2). The solid-state structures of **3a** and **3b** reveal planar central SiCPN₂ units flanked by the bulky *tert*-butyl groups of the NHI substituents. The P atoms in both compounds are in perfectly planar environments (sums of angles: 360°). The P-C bond lengths (**3a**: 1.582 Å, **3b**: 1.589 Å) are elongated compared to those of **II** (1.532 Å)²⁰ and **V** (1.544 Å),¹³ consistent with a reduced contribution of electronic structure C, however, they are shorter than the P-C bond in methylenephosphonium ion (iPr₂N)₂P = C(SiMe₃)₂⁺ (1.620 Å).²²



Fig. 2 Solid-state structures of **3a** (left) and **3b** (right). Hydrogen atoms are omitted and *tert*-butyl groups are shown in wireframe for clarity. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles [°]: **3a**: C1–Si 1.786(2), C1–P 1.582(2), P–N1 1.596(2), P–N2 1.593(2), Si–C1–P 131.75(12), C2–N1–P 147.9(2), C3–N2–P 133.18(14). **3b**: C1–Si 1.781(2), C1–P 1.589(2), P–N1 1.594(2), P–N2 1.6146(14), Si–C1–P 134.84(12), C2–N1–P 138.87(13), C3–N2–P 121.43(12).

Most strikingly, the carbene bond angles in **3a** (132°) and **3b** (135°) are significantly smaller than those of phosphinocarbenes **II** (153°),²⁰ **IVb** (145°),¹⁶ **V** (162°),¹³ and (iPr₂N)₂P–C–Mes (149°, Mes = 2,4,6-trimethylphenyl).¹² With respect to their suitability as ligands in transition metal complexes, the bent structure of phosphino(silyl)carbenes **3a,b** is beneficial because complexation is associated with less conformational energy penalty.⁹ Preliminary DFT calculations on **3a,b** and the model phosphino(silyl)carbene (Me₂N)₂PCSiMe₃ (**3c**) show that substitution of the amino groups with the NHI substituents leads to higher energies of the HOMO which corresponds to the carbene lone pair (**3a**: -4.216 eV, **3b**: -4.035 eV, **3c**: -5.143 eV) and of the π^* -type acceptor orbitals (**3a**: 1.012 eV, **3b**: 1.077 eV, **3c**: 0.222 eV), indicating that **3a,b** are better σ donors and weaker π acceptors than **3c** (for details see ESI†).

The new carbene **3a** readily reacts with AuCl(tht) (tht = tetrahydrothiophene) to give complex **4** as a colorless solid in 97% yield (Scheme 2a). Treatment of carbene **3b** with one equivalent of CuOtBu in THF or benzene resulted in the formation of a white solid that is insoluble in common



Scheme 1 Synthesis of phosphino(silyl)carbenes **3a,b**.



Scheme 2 (a) Synthesis of gold(i) complex **4**. (b) Synthesis of copper(i) complexes **5**, **6** and **7**.



solvents. We suspect that complex **5** forms an intermolecular coordination polymer in the solid state (Scheme 2b), which was corroborated by the reaction of **5** with another equivalent of CuOtBu, leading to the bimetallic copper complex **6** in quantitative yield. Note that copper(I) alkoxide complexes of N-heterocyclic carbenes (NHCs) are well-established precursors for copper hydride complexes²³ and are thus active catalysts for semihydrogenations,^{24,25} hydroalkoxylations,²⁶ and hydroborations.²⁴ The η^1 coordination mode of the carbenes in **4** and **6** is indicated by their ³¹P NMR chemical shifts (**4**: 70.0 ppm, **6**: 80.8 ppm), which appear in the range of methylenephosphonium salts²⁷ and trigonal NHI-substituted phosphonium ions.²⁸ Moreover, similar deshielding of the ³¹P NMR resonance upon η^1 coordination has been observed for phosphino(aryl)carbene **V** in complex [Rh(**V**)(nbd)Cl] (100.8 ppm; nbd = norbornadiene).¹⁴ As expected, the ¹³C NMR signal of the carbene carbon atoms are shifted to lower frequencies upon complexation (**4**: 57.8 ppm, **6**: 53.1 ppm). However, the ¹J_{PC} coupling constants (**4**: 89 Hz, **6**: 57 Hz) are larger than those of the free carbenes, which is in contrast to complex [Rh(**V**)(nbd)Cl] (rhodium complex: ¹J_{PC} = 2 Hz, free **V**: ¹J_{PC} = 271 Hz).¹⁴

XRD quality crystals of **4** and **6** (Fig. 3, top) were obtained by cooling a saturated THF solution to -40 °C and by cooling a hot benzene solution to 21 °C, respectively. Due to the low solubility of **5** in THF, recrystallization was attempted in 1,2-difluorobenzene, leading to the formation of few crystals of complex **7**, which were suitable for an XRD study (Fig. 3, bottom). Complex **7** presumably results from a C-H activation of 1,2-difluorobenzene at complex **5** but could not be characterized spectroscopically due to lack of substance.

Selected geometrical parameters of **4**, **6** and **7** are summarized in Table 1. The carbene-metal bond distances are comparable to those of NHC complexes (e.g. (ItBu)AuCl: 2.018 Å²⁹ and (ItBu)-CuOtBu: 1.876 Å,³⁰ ItBu = 1,3-di-*tert*-butylimidazolin-2-yliden).³¹ In **4**, **6** and **7** as well as the free carbenes **3a,b** the P-N1-C2 angles are larger than the P-N2-C3 angles, which can be explained by the high steric demand of the SiMe₃ group. The phosphorus-

Table 1 Selected bond lengths [Å] and angles [°] of **4**, **6** and **7**

Entry	4	6	7
C1-Si	1.828(7)	1.820(3)	1.813(4)
C1-P	1.624(7)	1.610(3)	1.605(5)
C1-M	2.024(7)	1.887(3)	1.907(4)
Si-C1-M	114.1(4)	109.9(2)	111.1(2)
M-C1-P	116.1(4)	116.1(2)	113.8(2)
P-C1-Si	129.1(4)	133.8(2)	134.6(3)
P-N1-C2	144.4(5)	135.0(2)	137.8(2)
P-N2-C3	128.7(5)	125.9(2)	126.3(3)
∑C1(Si,M,P)	359.3	359.8	359.5
∑P(C,N,N)	360.0	360.0	360.0

carbon bonds are slightly elongated in **4**, **6** and **7** compared to those of the free carbenes (**3a**: 1.582 Å, **3b**: 1.589 Å). In the metal complexes, both the carbene and the phosphorus atoms adopt a trigonal planar environment. It is noteworthy that all P-C-Si bond angles (**4**: 129.1°, **5**: 133.8°, **7**: 134.6°) are very similar to those of the free carbenes, suggesting that the conformational change of **3a,b** upon metal complexation is indeed negligible. For comparison, the P-C-C bond angle of **III** (162.1°) is reduced by 43° in [Rh(**III**)(nbd)Cl] (119.0°).¹⁴

Cavallo and co-workers established the % buried volume (% V_{bur}) model for the quantification of the steric impact of ancillary ligands.³² The value of **3a** (50.1%) is higher than that of ItBu (39.3%)³³ and sDipp (1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) (47.4%),³⁴ based on the geometry of the carbene-AuCl complexes. The calculated steric map (see ESI†) indicates that the high value is mainly caused by the bulky NHI substituent flanking the metal atom. This structural feature explains why attempts to synthesize nonlinear complexes by reacting **3a** with [(BiPr)PdBr₂]₂ (BiPr = 1,3-diisopropylbenzimidazolin-2-ylidene) or [(PEt₃)PtCl₂]₂ were not successful.

In conclusion, the synthesis of two room-temperature stable, crystalline phosphino(silyl)carbenes **3a,b** supported by bulky NHI substituents is reported. In contrast to other phosphino-carbenes, **3a,b** directly form stable η^1 complexes with Cu^I and Au^I metal ions. Due to the strong π donor properties of the NHI groups, the free carbenes exhibit unusually small carbene bond angles which is advantageous for the formation of transition metal complexes. Thus, the use of NHI substituents could also improve the ligand properties of other carbenes.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

§ After storage of solid **3a,b** under an argon atmosphere for more than one year, no decomposition was observed according to ¹H and ³¹P NMR spectroscopy.



Fig. 3 Solid-state structures of **4** (top left), **6** (top right) and **7** (bottom). Hydrogen atoms are omitted and *tert*-butyl groups are shown in wire-frame for clarity. Ellipsoids are drawn at 50% probability.



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