P/Si Ligands

Synthesis and Coordination Behavior of a New Hybrid Bidentate Ligand with Phosphine and Silylene Donors

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Dedicated to Professor Wolfgang Kaim on the occasion of his 70th birthday

Abstract: This work describes the synthesis and coordination behavior of a new mixed-donor ligand PhC(NRBu)SiC₄H₄PPh₂ (1) containing both silylene and phosphine donor sites. Ligand 1 was synthesized from a reaction of ortho-lithiated diphenylphosphino benzene (LiC₄H₄PPh₂) with chloro-silylene (PhC(NRBu)SiCl). Treatment of 1 with Se and GeCl₂ resulted in SiIV compounds 2 and 3 by selective oxidation of the silylene donor. This strong α-donor ligand induces dissociation of CuCl and PhBCl₂, leading to formation of ionic complexes 4 and 5 respectively. The reaction of 1 with ZnCl₂ and AlCl₃ resulted in the formation of chelate complexes 6 and 7, respectively, while treatment with EtAlCl₂ and GaCl₃ forms monodentate complexes 8 and 9. X-ray analysis of 4 showed that the copper is in the spiro center of the two five-membered rings. Moreover, the copper chloride has not been oxidized but dissociates to Cu⁺ and [CuCl₄]²⁻. All the compounds are well characterized by mass spectrometry, elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction studies.

Introduction

The structure, reactivity and catalytic activities of the main group and transition metal complexes are strongly related to the steric and electronic factors of the coordinating ligand. Over the last few decades, highly reactive compounds with low-valent silicon, phosphorus and other main-group elements have been isolated and structurally characterized.[1–4] These compounds have attracted significant attention due to their exciting electronic structures, small molecules activating capability at ambient conditions and catalytic properties in organic transformations.[5,6] Most of these novel achievements were due to the suitable design and synthesis of ligands which stabilize species with low-valent elements. N-heterocyclic carbene ligands (NHCs),[7] cyclic alkyl(amino) carbene (CAACs)[8] and N-heterocyclic silylenes (NHsSis)[9] are the most successful and commonly used ligand systems to stabilize compounds with low valent elements.

Silylenes have been effectively used as stabilizing ligands in low valent main-group elements, transition metals and for the metal free activation of robust bonds in small molecules. Few examples that illustrate the possibility to form new silylene ligands bearing an additional coordination site were published in 2016 by S. Khan et al. They have used silylene phosphine based bidentate ligand and showed the coordination of silylene with gold.[10] Very recently, Stalke et al. synthesized a side-arm functionalized silylene ligand and their transition metal complexes.[11] In 2014, Driess et al. reported silylene coordinated mono- and dinuclear copper(I) complexes.[12] The same group has synthesized mixed silylene-carbene chelate ligands to stabilize transition metal. Furthermore they have studied the catalytic activity of A (Scheme 1).[13] Scheschkewitz et al. have shown the synthesis of ketenyl-ligated metal-silylene complexes of group 6 (B).[14] Li and co-workers recently have synthesized bis(silylene)-based SiC₄H₄Si pincer ligand and studied its coordination chemistry with Fe[5] under Ar and N₂.[15] Tilley and others have reported chemical and catalytic properties of silylene coordinated transition metal complexes.[16] In 2011, Kato et al. published the synthesis of a stable and isolable tricoordinate silicon(II) hydride (C), stabilized by a phosphine ligand.[17] The same research group has also delivered silylene based complexes to stabilize transition metal and a highly electron rich carbon(0).[18] Driess and co-workers have successfully used bis(silylene) to stabilize zero valent silicon and germanium, respectively (D).[19] Very recently, the same group reported homocoupling of CO and isocyanide, mediated by a bis(silylene) ligand (E).[20]
Recent studies indicated that catalytic efficiencies of various catalytic reactions can be increased by silylene ligands due to their stronger 
$s$-donation ability along with cooperative effects of the divalent silicon atoms in the process of catalysis. In many cases, it was found that silylenes function as powerful 
$s$-donor ligands surpassing the activities of analogous phosphine- and NHC-based metal complexes.\(^\text{[2]}\)

Mixed donor ligand systems allow fine tuning of the steric and electronic properties at the metal center by choosing appropriate donor atoms. Such a fine tuning can have a significant impact on the chemoselectivity of organic substrates. Our group has longstanding interest in the synthesis and reactivity of silylenes and phosphinidenes. In 2017, we reported the synthesis of CAAC anchored silylene-phosphinidene.\(^\text{[3]}\) In the subsequent studies, we found that the reaction of silylene-phosphinidene with chalcogens resulted in the selective formation of silicon bonded chalcogen phosphinidenes.\(^\text{[4]}\) Silylenes were found to be strong 
$s$-donor ligands compared to phosphiridines. We envisioned the synthesis of a mixed donor ligand system with phosphane and silylene donors to study its electronic properties and coordination behavior. The present work is an extension of our effort to study the reactivity of such mixed donor ligand with transition metals as well as main group elements. Herein, we present the synthesis of a novel hybrid phosphate-silylene ligand (1) and its coordination properties with various transition metals and main group elements.

Results and Discussion

In 2010, our group reported a high yielding method for the synthesis of $N,N$-di(tert-butyl)amidinato chlorosilylene.\(^\text{[5]}\) It is a versatile reagent, used in the synthesis of diverse silylene-based ligands with different spacer lengths, specific structural and electronic features. We envisioned the use of chlorosilylene precursor for the synthesis of phosphate-silylene ligand system. \textit{ortho}-lithiated diphenylphosphane and $N,N$-di(tert-butyl)amidinato chlorosilylene were treated in toluene (−78 °C to room temperature) and resulted in a purple solution. The solution was filtered and concentrated to 10 mL and stored at −30 °C in a freezer for crystallization. Colorless crystals of compound 1 were obtained after 24 hours (Scheme 2).

\[\begin{align*}
\text{Scheme 1. Reported silylene-}, \text{bis(silylene)-, diphenylphosphine-}, \text{and phosphinidene-based ligand systems.}
\end{align*}\]

\[\begin{align*}
\text{Scheme 2. Synthesis of phosphate-silylene ligand (1).}
\end{align*}\]

\[\begin{align*}
\text{Figure 1. Crystal structure of PhC(NBu)\_2SiC\_6H\_4PPh\_2 (1). The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.8595(13); Si1–N2 1.8452(16); P1–C21 1.8384(17); P1–C22 1.8384(17); P1–C28 1.7833(18); N1–Si1–C16 100.02(6); Si1–N1–Si1–C16 100.02(6).}
\end{align*}\]
An equimolar reaction of 1 with elemental selenium in toluene at room temperature resulted in the selective oxidation of silylene donor to form 2. The $^{31}$P NMR spectrum of 2 shows a single NMR resonance at $-12.3$ ppm (Figure S6). The structure of 2 was confirmed by single-crystal X-ray diffraction. Compound 2 crystallizes in the monoclinic space group $C2/c$ as well, with one molecule of 2 and two solvent molecules of THF in the asymmetric unit. Selenium binds exclusively with silicon, at $2.1330(5)$ Å bond length. The greater distance between selenium and phosphorus atoms, about $5.6$ Å, as well as the orientation of the phosphine moiety strongly invalidate the hypothesis of additional bonding (Figure 2).

Surprisingly, the reaction of 1 with GeCl$_2$ did not yield a germanium complex but resulted in the oxidation of silylene moiety to yield the dichlorinated compound 3 (Scheme 3). The $^{31}$P NMR of 3 shows single NMR resonance at $12.2$ ppm (Figure S10) which shows a downfield shift of $23.4$ ppm, when compared with ligand 1. The formation of compound 3 was further confirmed by single crystal X-ray diffraction studies, which crystallizes in the monoclinic space group $P2_1/n$ without any additional solvent molecules in the asymmetric unit. The penta-coordinated silicon features a distorted environment comparable to a transition state between trigonal bipyramidal and square pyramidal, due to the rigid structure of the amidinate (Figure 3).

The reaction of 1 with CuCl in toluene at room temperature leads to the dissociation of CuCl resulting in the formation of the diamagnetic complex $[L_2Cu][CuCl_2]$ (Scheme 4). We use several analysis methods to determine the magnetic state of compound 4: a dismutation of Cu$^I$ in Cu$^0$ and Cu$^II$ would be assessed paramagnetic, whereas simple dissociation of Cu$^I$ would remain diamagnetic. $^1$H and $^{13}$C NMR measurements are measurable in the standard chemical shift range. Moreover, a toluene solution of 4 is found EPR silent, which is also in agreement with SQUID analysis results, invalidating the hypothesis of the formation of paramagnetic species.

The $^31$P NMR of compound 4 shows single resonance at $8.7$ ppm (Figure S14) which exhibits downfield shift of $2.5$ ppm when compared with ligand 1. Single crystals of 4 were obtained by storing a concentrated toluene solution at...
–30°C for 2 days in a freezer. Compound 4 crystallizes in space group P with two units of [L2Cu][CuCl6] and nine toluene molecules. The crystal structure reveals that the copper is in the spiro center of the two five-membered rings (Figure 4). The central copper atom is featuring a distorted tetrahedral geometry, possibly due to the steric arrangement of the phosphine phosphorus and the tert-buty1 groups. Comparison with already reported Cu–X bond lengths (X = P, Si, Cl; see the Supporting Information) also suggests that compound 4 is diamagnetic and that copper chloride is not oxidized, but rather dissociates to Cu+ and [CuCl4]−. The Si1–Cu1 and Si2–Cu1 distances are 2.264 and 2.273 Å, which is comparable to other Si–Cu distances in copper(I) complexes.26 Additionally, the [CuCl6]− unit features two short Cu–Cl bonds of 2.099 and 2.104 Å. This distance is closer to the one of copper monochloride than average distances for Cu+–Cl about 2.3 Å (see the Supporting Information). It is not entirely excluded that Cu+ remains unoxidized but the presented analysis overall strongly suggests that the obtained complex 4 is diamagnetic.

The reaction of 1 with ZnCl2 leads to the formation of a chelate complex L2ZnCl2 (L = PhC(NBu)2SiC6H4PPh2; 5) where the ligand exhibits chelating mode of coordination. The 31P NMR of 5 shows a single resonance at −26.7 ppm (Figure S17) which exhibits a upfield shift of 15.5 ppm in comparison with the ligand 1. Crystals suitable for single-crystal X-ray analysis are obtained from THF solution after two weeks in the freezer at −30°C. Compound 5 crystallizes in the monoclinic space group P21/c, presenting one single molecule of 5 in the asymmetric unit. In this complex, both phosphine and silylene moieties are participating in metal coordination (Figure 5). The Zn1–Si1 bond is somewhat shorter than the Zn1–P1 bond, indicative of a preference for the silylene moiety. The slight distortion of the tetrahedral geometry around the Zn atom is due to the P1–Zn1–Si1 angle of about 85°, shortened to adapt to the backbone rigid structure.

![Figure 4. Crystal structure of one formula unit of [L2Cu][CuCl6]− (4). The anisotropic displacement parameters are depicted at the 50% probability level. Pheny1 groups, 1Bu groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Cu1 2.2637(16); Si2–Cu2 2.2728(16); P1–Cu1 2.2982(15); P2–Cu1 2.2807(16); Si1–N1 1.867(4); Si1–N2 1.838(5); Si2–N3 1.837(4); Si2–N4 1.841(5); S11–C16 1.883(5); P1–C21 1.832(5); P2–C54 1.840(5); S11–Cu1–S12 135.4(5); S11–Cu1–P1 111.0(9); S12–Cu1–P2 87.3(4); S11–Cu1–P1 87.6(8); S22–Cu1–P1 110.1(2); N1–Si1–C16 103.9(2); N1–Si1–N2 70.0(2).](image_url)

![Figure 5. Molecular structure of PhC(NBu)2SiZnCl2C6H4PPh2 (5). The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.3947(8); Zn1–P1 2.4812(8); Zn1–C1 2.2661(7); Zn1–C2 2.2463(10); S11–N1 1.8231(19); S11–N2 1.820(2); S11–C16 1.879(2); P1–C12 1.838(2); P1–C22 1.821(2); P1–C28 1.821(2); S11–Cu1–P1 85.41(2); Zn1–C1–C2 104.7(8); Zn1–P1–C22 115.0(9); Zn1–P1–C28 120.1(5); Zn1–Si1–C16 106.1(7); N1–Si1–N2 71.88(9); Zn1–Si1–N1 132.52(7); Zn1–Si1–N2 125.27(6).](image_url)

Both the complexes 4 and 5 are crystalline solids, soluble in common organic solvents, and stable at room temperature under inert atmosphere. Melting points of complexes 4 and 5 were found to be 280 and 270°C, respectively. Similar to the formation of the copper complex 4, ligand 1 reacted with PhBCl3 in toluene at −78°C. This leads to a quite unusual dissociation of PhBCl3 into the product [LPBPhCl]+[PhBCl4]− (6; Scheme 5) as confirmed by single-crystal X-ray diffraction. Crystals were obtained after two weeks at room temperature in toluene. Compound 6 crystallizes in the triclinic centrosymmetric space group P-1, with no residual solvent molecule in the asymmetric unit. Interestingly, the ligand chelates the small boron atom with both coordinating moieties. The boron center is almost perfectly tetrahedral, and its coordination to the ligand induces a distortion on the phosphine moiety instead of modifying the tetrahedral geometry on the boron atom (Figure 6). This suggests that the small size of the boron atom enables it to fit inside of the chelating moiety, however through a shrinking of the host pocket. All bonds to boron are indeed shorter than with any other guest atom of the present study (see Table 1 for a detailed comparison). Surprised by the ability of ligand 1 in the dissociation of CuCl and PhBCl3, we investigated the reaction with Al salts for the formation of ionic aluminium compounds.

The reaction of 1 with AlCl3 in diethyl ether at −78°C resulted in the formation of compound 7. Crystals are grown from CH3Cl at 0°C. Compound 7 crystallizes in the monoclinic space group P21/c with one molecule of 7 and one molecule
of CH$_3$Cl$_2$ in the asymmetric unit. The aluminium atom is in a distorted tetrahedral environment: all Cl-Al-Cl angles are about 109°, but the Si-Al-Cl2 angle is remarkably smaller (98.77(3)°), probably to allow an additional weaker interaction between Al and the pending phosphine group (Figure 7). Single-crystal X-ray analysis also reveals that the Al atom is bounded to the silylene moiety while the phosphorus donor atom is “only” oriented towards the metal. This shows as expected that silylene is a stronger σ-donor ligand compared to the P atom of phosphine.

In the same spirit, the reaction of 1 with EtAlCl$_2$ and GaCl$_3$ in diethylether resulted in the formation of compounds 8 and 9. Compound 8 crystallizes in the orthorhombic space group $P2_1 2_1 2_1$ with one molecule of 8 in the asymmetric unit. The AlIII is placed in a tetrahedral environment, with an deviation comparable to 7 (one angle is 95.53(5)° and the others are about 109°) to leave some space for the phosphino group oriented towards the aluminium atom. The distance between Al and P atoms is shorter than in 7 (3.36 and 3.59 Å respectively), which is probably due to the additional flexibility given by the ethyl moiety in comparison with the halide (Figure 8).

Single-crystal X-ray analysis reveals that compounds 7 and 9 are isostructural. Indeed, the gallium atom is also exhibiting a

**Table 1. Comparison of selected distances and bond angles for 1–9.**

| X   | X–Si [Å]       | Si–N [Å]      | X–P [Å]       | Distance X from SiPCC plane | Si–X–P [°] | N–Si–X [°] | N–Si–C16/C49 [°] | N1–Si–N2 [°] |
|-----|----------------|---------------|---------------|----------------------------|------------|------------|-------------------|------------|
| 1   | 1.8589(13)     | –             | –             | 100.02(6)                  | 69.28(6)   | 99.99(7)   |                   |            |
| 2   | 1.8698(13)     | –             | –             | 116.19(3)                  | 116.50(4)  |            |                   |            |
| 3   | 1.8249(9)      | 0.751(2)      | 0.3184(19)    | 140.05(11)                 | 69.42(9)   | 97.41(10)  |                   |            |
| 4   | 1.8571(4)      | 0.506(4)      | 0.3184(19)    | 128.60(17)                 | 101.2(2)   | 70.0(2)    |                   |            |
| 5   | 1.841(5)       | 0.495(4)      | 0.3184(19)    | 111.09(6)                  | 113.11(15) | 70.5(2)    |                   |            |
| 6   | 1.8231(19)     | 0.4105(19)    | 0.3184(19)    | 111.07(6)                  | 140.41(17) | 71.88(9)   |                   |            |
| 7   | 1.8202(2)      | 0.4105(19)    | 0.3184(19)    | 85.41(2)                   | 125.27(6)  | 70.59(9)   |                   |            |
| 8   | 1.8149(12)     | 0.3587(14)    | 0.3184(19)    | 95.33(10)                  | 125.06(9)  | 73.09(8)   |                   |            |
| 9   | 1.8263(12)     | 0.3587(14)    | 0.3184(19)    | 123.11(8)                  | 117.77(9)  | 73.09(8)   |                   |            |
tetrahedral coordination environment, with similar angle values. A deviation from perfectly tetrahedral geometry is again observed (the av. angle value from the sum of all angles is 109° but the angle values range from 100 to 118°) and attributed to the structural adaptation at the metal center in order to acknowledge the preferred orientation of the phosphorus towards the aluminum atom. The distances between the two atoms is similar to those of compounds 7 and 8, about 3.56 Å.

The ligand 1 coordinates through the silylene moiety in monodentate fashion in compounds 8 and 9 with a noticeable orientation of the phosphane moiety towards Al and Ga, respectively. Thus, considering complexes 2, 4, 5, 7–9, the newly designed hybrid phosphane-silylene ligand shows different coordination behavior depending on the metal center. Probably due to the higher Lewis acidity of aluminum, the lattice energy for the formation of the $\left[\text{AlCl}_2\right]^{-}$ $\left[\text{AlCl}_3\right]^+$ salt in 7 (or 8 or 9) is not high enough. Selected bond lengths and angles for all compounds 1–9 are reported in Table 1. Overall trends for bond and angle variations can be summarized as the following. While the oxidation of the silylene results in a shrinking of the Si–N bonds from 1 (mean 1.86 Å) to 2 (mean 1.82 Å), the chlorination cancels the equivalence of the two Si–N bonds in 3 (1.832 and 1.937 Å) influencing the C1–N bonds (1.353(3) and 1.315(3) Å in 3 compared to both 1.336(4) Å in 1). The attached phosphane moiety is displaced, as observable in the N–Si–C16 bond angle (100.02(6)° and 99.99(7)° in 1 and 140.05(11)° and 97.41(10)° in 3). Interestingly, in complexes 4, 5, and 6, both the phosphane and silylene moieties are efficiently coordinating the host atom. This is the only complex featuring a transition metal coordinated to two ligands without any additional halide coordination. The copper center has a highly distorted tetrahedral environment (from 88 to 135°). In contrast to all other complexes 5–9, the Si–N bond lengths (1.838(5) to 1.867(4) Å) are not significantly shortened compared to the bonds in 1 (mean 1.86 Å). For both Si atoms there is one shorter bond (mean 1.84 Å compared to mean 1.86 Å) coming along with a larger Cu–Si–N angle (mean 128° compared to 139°). Also the N–Si–C (mean 102°) and the N–Si–N (mean 70°) bond angles in 4 are closest to the values in 1 (100° and 69°, respectively), while 5–9 have larger values (104.60(13)° in 8 to 117.77(9)° in 6, and 71.43(12)° in 8 to 73.09(8)° in 6). Only in 6 the X–P distance is shorter than the X–Si bond. It is also the structure with the largest distance of X from the SiPCC plane although the B atom has smallest atomic radius. In the complexes 7–9, no bonding with the phosphorus atom is observed, but the phosphane moiety is oriented towards the host atom, as a hint of potential weak interaction. The two aluminium complexes 7 and 8 do not exhibit noticeable differences, although the distance between the non-bonding Al and P decreases about 0.23 Å (3.5920(7) Å, 3.3587(14) Å). A similar value of 3.5640(6) Å in 9 (isomorphous to 7) between Ga and P is observable (Figure 9).
Conclusions
In summary, we have synthesized a new hybrid bidentate phosphorus-silylene ligand and studied its coordination behavior with transition metal and main group precursors. Reaction of 1 with Se and GeCl₄ resulted in selective oxidation of silylene moiety to form complexes 2 and 3, respectively. The strong σ-donating ligand 1 on reaction with CuCl and PhBCl₂ results in dissociation leading to the formation of compounds 4 and 6, respectively where the ligand displays a chelating mode of coordination. In complex 5, the phosphine moiety also participates in bonding.

The ligand 1 then offers a different coordination environment for the LAI₂Cl₇, BeAlI₃, and GeCl₄ complexes: while the host atom is bonded to the silicon, the phosphine moiety is obviously preferably oriented towards it as well, which indicates that the two atoms are interacting together. Thus, the overall reactivity of the newly developed ligand 1 confirms that silylene is a strong σ-donating ligand compared to phosphine. All compounds were fully characterized by single-crystal X-ray studies and various spectroscopic studies.

Experimental Section
All manipulations were carried out under a dry argon or nitrogen atmosphere using Schlenk line and glovebox techniques. Tetrahydrofuran, tolune and hexane were dried by refluxing with sodium/potassium under N₂ prior to use. The NMR (1H, 31P and 77Ge) spectra were recorded on Bruker Avance II 500 MHz spectrometer. Melting points of compounds were measured in sealed glass tube using the Büchi-540 instrument. Elemental analyses were performed by the Analytisches Labor des Instituts für Organische Chemie der Universität Göttingen. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. Heteroleptic chlorosilylene LSiCl (L = PhCH(N(Bu))₂) was prepared according to the literature.[25]

Synthesis of [PhC(N(Bu))₂SiC(Ph)₃Ph] (1): LSiCl (0.295 g, 1.0 mmol) and Ph₅PC(HEt₂)Li (0.268 g, 1.0 mmol) were placed in a 100 mL round bottom flask. Toluene (30 mL) was added under stirring at room temperature. The reaction mixture was stirred for 1 day. After filtration, the filtrate was concentrated to 5 mL under vacuum and stored at –30 °C in a freezer. After one week, yellow colored crystals were obtained and collected by filtration (0.49 g, 40 %). Mp: 280 °C; 1H NMR (CD₂Cl₂, 202 MHz, 298 K): δ = 1.05 (s, 18 H, Bu), 1.18 (s, 18 H, Bu), 6.73–6.78 (m, s, 4H, Ph), 6.85–7.09 (m, 22 H, Ph), 7.20–7.22 (m, 2H, Ph), 7.34–7.39 (m, 2H, Ph), 7.51–7.55 (m, 2H, Ph), 7.98–8.10 ppm (m, 6H, Ph); 31P{1H} NMR (CD₂Cl₂, 202 MHz, 298 K): δ = 15.55, 21.34, 29.14, 31.00, 31.86, 32.92, 54.42, 56.05, 65.88, 125.61, 128.43, 128.46, 129.27, 129.34, 130.14, 131.34, 131.37, 131.40, 131.91, 132.44, 132.53, 133.38 ppm; 13C{1H} NMR (99 MHz, 298 K, CD₂Cl₂): δ = 18.52 ppm (δ sp3 = 410 Hz); elemental analysis calcd (%) for C₄₉H₃₈N₄P₂Si: MW = 951.19: C 66.88, H 6.46, N 4.73; found: C 67.14, H 6.58, N 4.85.

Synthesis of [PhC(N(Bu))₂C₅H₄P(Ph)₃] (4): Ligand 1 (0.52 g, 1.0 mmol) and CuCl (0.99 g, 1.0 mmol) were placed in a 100 mL round bottom flask. Toluene (30 mL) was added under stirring at room temperature. The reaction mixture was stirred for 1 day. After filtration, the filtrate was concentrated to 5 mL under vacuum and stored at –30 °C in a freezer. After one week, yellow colored crystals were obtained and collected by filtration (0.49 g, 40 %). Mp: 280 °C; 1H NMR (CD₂Cl₂, 298 K): δ = 1.05 (s, 18 H, Bu), 1.18 (s, 18 H, Bu), 6.73–6.78 (m, s, 4H, Ph), 6.85–7.09 (m, 22 H, Ph), 7.20–7.22 (m, 2H, Ph), 7.34–7.39 (m, 2H, Ph), 7.51–7.55 (m, 2H, Ph), 7.98–8.10 ppm (m, 6H, Ph); 31P{1H} NMR (CD₂Cl₂, 298 K): δ = 15.55, 21.34, 29.14, 31.00, 31.86, 32.92, 54.42, 56.05, 65.88, 125.61, 128.43, 128.46, 129.27, 129.34, 130.14, 131.34, 131.37, 131.40, 131.91, 132.44, 132.53, 133.38 ppm; 13C{1H} NMR (99 MHz, 298 K, CD₂Cl₂): δ = 18.52 ppm (δ sp3 = 410 Hz); elemental analysis calcd (%) for C₄₉H₃₈N₄P₂Si: MW = 951.19: C 66.88, H 6.46, N 4.73; found: C 67.14, H 6.58, N 4.85.

Synthesis of [PhC(N(Bu))₂C₅H₄P(Ph)₃]ZnCl₂ (5): Ligand 1 (0.52 g, 1.0 mmol) and ZnCl₂ (0.99 g, 1.0 mmol) were placed in a 100 mL round bottom flask. Toluene (30 mL) was added under stirring at room temperature. The reaction mixture was stirred overnight. After solvent evaporation the white precipitate was washed with hexane two times and dissolved in distilled methylene chloride and concentrated to 5 mL under vacuum and stored at –30 °C in a freezer. After two weeks, colorless crystals were obtained and collected by filtration (0.49 g, 60 %). Mp: 270 °C; 1H NMR (CD₂Cl₂, 298 K): δ = 1.19 (s, 18 H, Bu), 7.05–7.28 (m, 3H, Ph), 7.38–7.45 (m, 2H, Ph), 7.52–7.62 (m, 10H, Ph), 7.78–7.82 (m, 1H, Ph), 8.95 ppm (brs, 3H, Ph); 13C{1H} NMR (CD₂Cl₂, 298 K): δ = 12.67, 31.28, 55.39, 125.78, 128.70, 129.27, 129.51, 130.84, 131.86, 134.71, 134.82, 136.50 ppm; 31P{1H} NMR (202 MHz, 298 K, CD₂Cl₂): δ = –26.77 ppm; 13C{31P} NMR (99 MHz, 298 K, CD₂Cl₂): δ = 31.57 ppm (δ sp3 = 840 Hz); elemental analysis calcd (%) for C₄₉H₃₈N₄P₂Zn₂: MW = 1365.11: C 63.03, H 5.68, N 4.26; found: C 63.09, H 5.71, N 4.54.

Synthesis of [PhC(N(Bu))₂C₅H₄P(Ph)₃]PbCl₂ (6): Ligand 1 (0.52 g, 1.0 mmol) was placed in a 100 mL round bottom flask and dissolved
solved in 50 mL toluene. PhBCl₂ (0.130 mL, 1 mmol) was added under stirring at −78 °C. The reaction mixture was stirred overnight. After filtration, the filtrate was concentrated to 5 mL under vacuum and stored at room temperature. After two weeks, colorless crystals were obtained and collected by filtration, (0.58 g, 70%), Mp: 185 °C; ¹H NMR (CDCl₃, 298 K): δ = 1.00 (s, 18H, tBu), 1.24 (bs, 3H, Ph), 3.76 (s, 8H, Ph), 7.18–7.24 ppm (m, 12H, Ph), 7.29–7.34 ppm (m, 3H, Ph), 7.42–7.45 ppm (m, 3H, Ph), 7.53–7.55 ppm (m, 5H, Ph), 7.57–7.60 ppm (m, 5H, Ph); ¹³C(¹H) NMR (CDCl₃, 298 K): δ = 12.30 ppm.

Crystallographic details: The datasets were collected on an Incoatec Mo/Ag Microsource⁵⁰ (1, 3, 7–8) and on a Bruker TKS-Mo rotating anode (2, 4–6) with mirror optics and an APEX II detector with a 8° goniometer. The data were integrated with SAINT.³¹ A multi-scan absorption correction and a 3Δ⁰ correction (1–3, 5–9) was applied using SADABS.²⁴ For 4 the multi-scan absorption correction was applied using TWINABS.³¹ The structures were solved by SHELXT³¹ and refined on F² using SHELXL in the graphical user interface ShelX.³¹ Full crystallographic data is available in the Supporting Information. Deposition numbers 1994257 (1); 1994258 (2), 1994259 (3), 1994260 (4), 1994261 (5), 1994262 (6) 1994263 (7) 1994264 (8) and 1994265 (9) contain 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 Interests
The authors declare no conflict of interests.

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