Bis(phosphinimino)methanides as non-innocent ligand in zinc chemistry: synthesis and structures†

Sebastian Marks,[a] Tarun K. Panda[b] and Peter W. Roesky*[a]

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Reactions of the bis(phosphinimino)methane $\{CH_2(Ph_2PNSiMe_3)_2\}$ with the zinc dihalides $ZnCl_2$ and ZnI_2 afforded the corresponding bis(phosphinimino)methane complexes $[\{(Me_3SiNPPh_2)_2CH_2\}ZnCl_2]$ (**1**) and $[\{(Me_3SiNPPh_2)_2CH_2\}ZnI_2]$ (**2**). In contrast, treatment of $\{CH_2(Ph_2PNSiMe_3)_2\}$ with $ZnPh_2$ in toluene gave the bis(phosphinimino)methanide complex of $[\{(Me_3SiNPPh_2)_2CH\}ZnPh]$ (**3**). Further reaction of **3** with the heterocumulenes di(*p*-tolyl)carbodiimine and diphenyl ketene resulted *via* a nucleophilic addition of the methine carbon atom of the $\{CH(Ph_2PNSiMe_3)_2\}^-$ ligand to the heterocumulenes in a C–C bond formation. New tripodal phenyl zinc complexes of composition $[\{(Me_3SiNPPh_2)_2CH)(p\text{-Tol})N{=}C{-}N(p\text{-Tol})\}ZnPh]$ (**4**) and $[\{(Me_3SiNPPh_2)_2CH)(Ph_2C{=}C{-}O)\}ZnPh]$ (**5**) were obtained.

Introduction

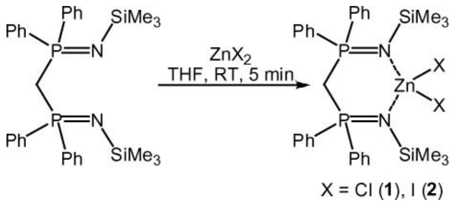
In the last 20 years, a number of reports were published dealing with the design and application of amido-metal chemistry of the s- and p-block elements and transition metals.[1-6] In transition metal chemistry this concept is today sometimes referred as "post-metallocene" chemistry.[7-9] Part of that research is dealing with ligands that contain P–N units such as phosphoraneiminate $(R_3PN)^-$,[10-14] phosphinimines (R_2PNR'),[15-19] diphosphanylamides $(R_2PNPR_2)^-$ [20-23] and iminophosphonamides $((R_2P(NR')_2)^-$.[24-28] These kinds of compounds were widely used as ligands in main-group and transition-metal chemistry. In this context, we and other groups were recently attracted by the bis(phosphinimino)methanides ($\{CH(PPh_2NR)_2\}^-$, R = Mes, $SiMe_3$) as very useful ligands in coordination chemistry.[29-32] In zinc chemistry the reaction of dimethyl zinc with the neutral ligand bis(phosphinimino)methane, $\{CH_2(Ph_2PNSiMe_3)_2\}$ was reported to give $[\{CH(Ph_2PNSiMe_3)_2\}ZnMe]$.[33] The zinc methyl compounds $[\{CH(Ph_2PNMes)_2\}ZnMe]$ and $[\{CH(Ph_2PNPh)(Ph_2PNMes)\}ZnMe]$ were obtained in a similar way starting from $\{CH_2(Ph_2PNMes)_2\}$ and $\{CH_2(Ph_2PNPh)(Ph_2PNMes)\}$, respectively.[34] Further reactions with alcohols resulted in the corresponding alkoxy derivatives. These compounds were used as initiators in ring-opening polymerization catalysis of *rac*-lactide.

Reaction of $[\{CH(Ph_2PNSiMe_3)_2\}ZnMe]$ with adamantyl isocyanate was reported to give a nucleophilic addition of the methanide carbon to the adamantyl carbon by forming a new C–C bond to yield the tetra-coordinated derivative $[\{HC\{C(O)N(Ad)\}(Ph_2PNSiMe_3)_2\}ZnMe]$.[33] Reaction of the dilithium salt $[Li_2\{C(PPh_2NSiMe_3)_2\}]_2$ with $ZnCl_2$ was studied by Westerhausen. It resulted in the trinuclear compound $[ClZn\{\mu\text{-}(Me_3Si)NP(Ph)_2\}_2C]_2Zn$.[35]

In this contribution we now report on the reaction of the neutral ligand bis(phosphinimino)methane, $\{CH_2(Ph_2PNSiMe_3)_2\}$ with the zinc halides $ZnCl_2$ and ZnI_2 first, followed by a report on the synthesis of $[\{(Me_3SiNPPh_2)_2CH\}ZnPh]$. Finally the reaction of latter compound with some heterocumulenes is discussed.

Results and discussion

Reaction of $\{CH_2(Ph_2PNSiMe_3)_2\}$ with the zinc dihalides $ZnCl_2$ and ZnI_2 in a 1 : 1 molar ratio in THF afforded the corresponding bis(phosphinimino)methane complexes $[\{(Me_3SiNPPh_2)_2CH_2\}ZnCl_2]$ (**1**) and $[\{(Me_3SiNPPh_2)_2CH_2\}ZnI_2]$ (**2**) as colorless crystals in good yields (Scheme 1). The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures were established by single-crystal X-ray diffraction.



Scheme 1

The NMR data of both complexes point towards a symmetric coordination of the ligand onto the zinc atom in solution. The signal of the P–CH_2–P protons in the ^{1}H NMR spectrum are split into a sharp triplet for both compounds. These signals (δ 4.20 (**1**) and 4.25 (**2**) ppm) are slightly low field shifted compared to the starting material (δ 3.42)[36] and to the bis(triphenylsiloxy) zinc complex $[\{CH_2(Ph_2PNC_6H_2Me_3\text{-}2,4,6)_2\}Zn(OSiPh_3)_2]$ (δ 3.91 ppm).[34] The phenyl region in the ^{1}H NMR spectra is as expected. Compounds **1** and **2** show sharp signals in the $^{31}P\{^1H\}$ NMR spectrum (δ 24.6 (**1**) and 23.4 (**2**) ppm), which significantly differ from

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[a] *Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstr., 15, Geb. 30.45, 76131, Karlsruhe, Germany. E-mail: roesky@kit.edu; Fax: (+49) 721-608-4854; Tel: (+49) 721-608-6117*
[b] *Department of Chemistry, Indian Institute of Technology Hyderabad, Yeddumailaram, 502205, Andhra Pradesh, India*

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the starting material (δ −5.9 ppm)[36] and [{$CH_2(Ph_2PNC_6H_2Me_3$-2,4,6$)_2$}$Zn(OSiPh_3)_2$] (δ −16.4 ppm).[34]

Compound **1** crystallizes in the triclinic space group $P\bar{1}$, having two independent molecules of **1** and three molecules of toluene in the asymmetric unit (Fig. 1). The bis(phosphinimino)methane coordinates as a bidentate ligand through the two imine nitrogen atoms onto the zinc atom forming a six-membered metallacycle (N1–P1–C1–P2–N2–Zn). Although there is no carbon–zinc contact, the metallacycle adopts a twist boat conformation presumably due to crystal packing. Thus, the zinc atom is four-fold coordinated by the bis(phosphinimino)methane ligand and the two chlorine atoms. The N–Zn–N bite angles of the ligands inside the bis(phosphinimino)methane moiety are smaller than in a regular tetrahedron (N1–Zn1–N2 104.86(10)° and N3–Zn2–N4 103.97(10)). The Zn–N bond distances are in the expected range of Zn1–N1 2.055(3) Å, Zn1–N2 2.061(3) Å, Zn2–N3 2.064(3) Å, Zn2–N4 2.046(2) Å (*e.g.* Zn1–N1 1.980(4) Å, and Zn1–N2 1.955(4) Å in *N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl).[37]

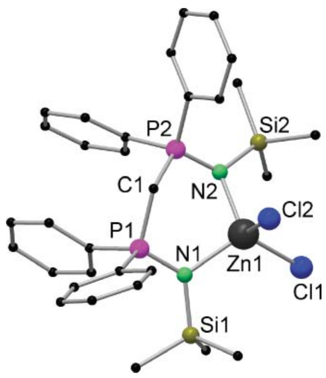


Fig. 1 Solid-state structure of **1** showing the atom labeling scheme, omitting hydrogen atoms. One of two independent molecules in the unit cell is shown. Selected bond lengths (Å) and angles (°): Zn1–N1 2.055(3), Zn1–N2 2.061(3), Zn1–Cl1 2.2370(11), Zn1–Cl2 2.3019(11), Zn2–N3 2.064(3), Zn2–N4 2.046(2), Zn2–Cl3 2.2375(11), Zn2–Cl4 2.2909(12); N1–Zn1–N2 104.86(10), N1–Zn1–Cl1 114.47(8), N1–Zn1–Cl2 106.38(8), N2–Zn1–Cl1 114.10(8), N2–Zn1–Cl2 107.45(8), Cl1–Zn1–Cl2 109.09(4), N3–Zn2–Cl3 113.74(7), N3–Zn2–Cl4 108.50(8), N3–Zn2–N4 103.97(10), N4–Zn2–Cl3 115.73(7), N4–Zn2–Cl4 106.04(8), Cl3–Zn2–Cl4 108.40(4).

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ having four molecules of compound **2** and eight molecules of THF in the unit cell (Fig. 2). As observed for compound **1** the bis(phosphinimino)methane coordinates as bidentate ligand with the two imine nitrogen atoms onto the zinc atom. The thus obtained six-membered metallacycle (N1–P1–C1–P2–N2–Zn) which shows no carbon–zinc contact adopts a twist boat conformation. The zinc atom is in the center of a distorted tetrahedral coordination polyhedron. The observed Zn–N bond distances are in the expected range of Zn–N1 2.061(5) Å and Zn–N2 2.033(6) Å.

In contrast to the reaction of {$CH_2(Ph_2PNSiMe_3)_2$} with the zinc halides, which resulted in bis(phosphinimino)methane adducts, treatment of {$CH_2(Ph_2PNSiMe_3)_2$} with $ZnPh_2$ in toluene gave a bis(phosphinimino)methanide complex of composition [{$(Me_3SiNPPh_2)_2CH$}ZnPh] (**3**) (Scheme 2). During the course of the reaction the bis(phosphinimino)methane ligand was deprotonated. The new complex has been characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction (Fig. 3). The room-temperature ^1H and $^{31}P\{H\}$ NMR spectra of compound **3** show a symmetrical pattern for the {$CH(Ph_2PNSiMe_3)_2$}$^-$ ligand. In the ^1H NMR spectrum a significant upfield shift for the P–C*H*–P resonance (δ 2.07 (**3**)) is observed compared to the neutral ligand (δ 3.42).[36] Compound **3** shows one signal in the $^{31}P\{^1H\}$ NMR spectrum (δ 27.1 (**3**) ppm), which is significantly downfield shifted compared to the starting material (δ −5.9 ppm).[36] On the other hand the analogue mesityl bis(phosphinimino)methanide complex [{$CH(Ph_2PNC_6H_2Me_3$-2,4,6$)_2$}$ZnN(SiMe_3)_2$] shows a signal in the $^{31}P\{^1H\}$ NMR spectrum in a comparable range (δ 33.1 ppm).[34]

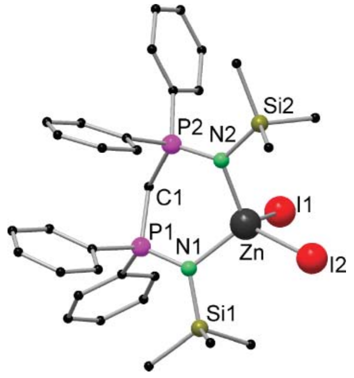
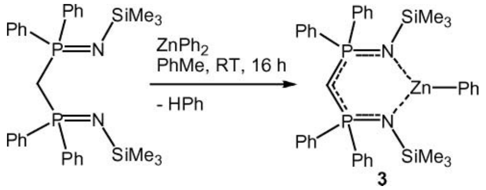


Fig. 2 Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (Å) and angles (°): Zn–N1 2.061(5), Zn–N2 2.033(6), Zn–I1 2.6675(10), Zn–I2 2.5891(9); N1–Zn–N2 107.9(2), N1–Zn–I1 107.7(2), N1–Zn–I2 112.5(2), N2–Zn–I1 105.47(15), N2–Zn–I2 115.30(14), I1–Zn–I2 107.52(3), P1–C1–P2 120.1(3).



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Scheme 2

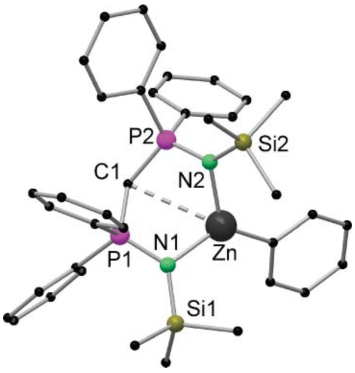
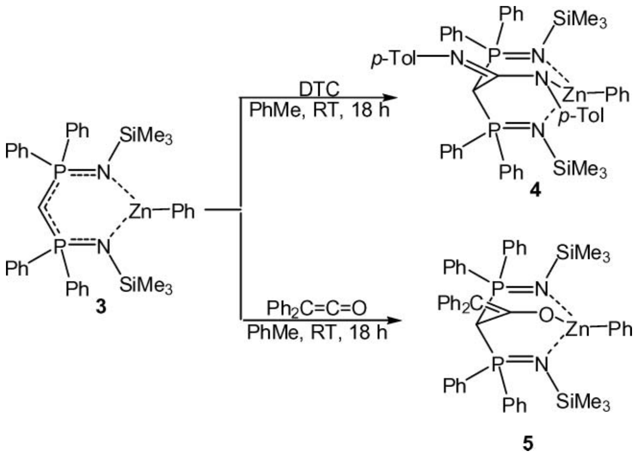


Fig. 3 Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (Å) and angles (°): Zn–C1 2.923(2), Zn–C2 1.965(2), Zn–N1 1.9853(13), Zn–N2 2.0298(14), C1–P1 1.728(2), C1–P2 1.716(2); N1–Zn–C2 129.48(8), N2–Zn–C2 125.97(8), N1–Zn1–N2 104.52(6), P1–C1–P2 124.90(9).

The solid-state structure of **3** was investigated by single-crystal X-ray diffraction. The data is in agreement with the NMR data obtained in solution. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ having four molecules in the unit cell. In the solid state, a pseudo-triangular coordination sphere about the zinc atom is defined by the two phosphinimine nitrogen atoms and the carbon atom of the phenyl group. The six-membered metallacycle formed by the bis(phosphinimino)methanide ligand and the zinc atom has a twist boat conformation showing Zn–N bond distances of Zn–N1 1.9853(13) Å and Zn–N2 2.0298(14) Å. A comparison of the Zn–C bond distances clearly indicates that the bonding of the zinc atom to the phenyl group (Zn–C2 1.965(2) Å) is much tighter than to the methanide carbon atom (Zn–C1 2.923(2) Å).

It is established that zinc alkyl compounds react with carbodiimides in an insertion reaction into the metal–carbon bond.[5,38,39] On the other hand the reaction of $[\{CH(Ph_2PNSiMe_3)_2\}ZnMe]$ with adamantyl isocyanate resulted in an insertion of the ligand backbone into the C=N bond.[33] Therefore we were interested to study the reactivity of compound **3** with the heterocumulenes di(*p*-tolyl)carbodiimine (DTC) and diphenyl ketene.

Reaction of compound **3** with DTC in toluene resulted at room temperature after workup in a yellow crystalline solid of composition $[\{(Me_3SiNPPh_2)_2CH\}(p\text{-Tol})N{=}C{-}N(p\text{-Tol})\}ZnPh]$ (**4**) (Scheme 3). Obviously there was no reaction of the phenyl group, but the methine carbon atom of the $\{CH(Ph_2PNSiMe_3)_2\}^-$ ligand underwent a nucleophilic addition to the carbodiimine instead, resulting in a C–C bond formation. As a result of this reaction a new kind of mono-anionic tripodal N-donor ligand was formed. The modification of the ligand is clearly seen in the NMR spectra. The signal of the CH group of the newly formed bridgehead of the ligand shows in the ^{1}H NMR spectrum a characteristic triplet (δ 4.40 ppm), which is about 2.3 ppm downfield shifted in comparison to compound **3** but is in the range of the P–CH$_2$–P group of compounds **1** and **2**. A similar tendency is observed in the $^{13}C\{^1H\}$ NMR spectra. The signal of the carbon bridgehead (δ 44.2 ppm) is about 15 ppm downfield shifted compared to compound **3**. For the methyl groups of the *p*-tolyl moiety two singlets are seen in the ^{1}H NMR (δ 2.13 ppm and 2.34 ppm) and in the $^{13}C\{^1H\}$ NMR spectrum (δ 19.8 ppm and 20.3 ppm) each. In the $^{31}P\{^1H\}$ NMR spectrum one signal was detected at δ 24.8 ppm, which is slightly shifted in comparison to compound **3**. In the EI-MS spectrum a molecular peak with low intensity was detected.



Scheme 3

The solid-state structure of compound **4** was established by single-crystal X-ray diffraction. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The solid-state structure of compound **4** (Fig. 4) is consistent with the NMR data obtained in solution. The zinc atom, which is four-fold coordinated by the three nitrogen atoms of the new tripodal ligand and the phenyl group, is in the center of a distorted tetrahedron. The bond distance of the zinc atom to the phenyl group (Zn–C2 2.010(3) Å) is in the range of the starting material group (Zn–C2 1.965(2) Å). The Zn–N bonds of the former bis(phosphinimino)methanide ligand (Zn–N1 2.107(2) Å and Zn–N2 2.126(2) Å) are about 0.1 Å longer than in compound **3**, whereas the newly formed Zn–N3 bond (2.070(2) Å) is slightly shorter. Due to the modification of the ligand the N1–Zn–N2 angle (93.72(9)°) is reduced about 11° in comparison to compound **3**. The newly formed C–C bond in the ligand backbone has the expected value of C1–C8 1.536(4) Å. As a result of the reduction of one of the two imine functions of the former DTC molecule the C–N bond distances vary significantly (C8–N3 1.361(3) Å and C8–N4 1.284(4) Å). The reduction also has an influence onto the bis(phosphinimino)methanide ligand moiety. In the bis(phosphinimino)methanide ligand a considerable delocalization of the negative charge throughout the ligand backbone is observed. This results in short endocyclic P–C bond distances, *e.g.* C1–P1 1.728(2) Å and C1–P2 1.716(2) Å (**3**). As a result of the addition reaction which led to compound **4**, the delocalization is removed, leading to elongated C–P bond lengths (C1–P1 1.853(3) Å and C1–P2 1.844(3) Å) and a reduced P1–C1–P2 bond angle of 114.89(15)° (124.90(9)° in **3**).

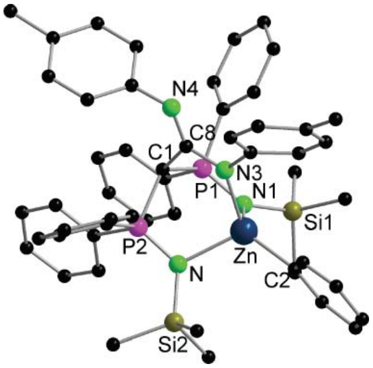


Fig. 4 Solid-state structure of **4** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (Å) and angles (°): Zn–C2 2.010(3), Zn–N1 2.107(2), Zn–N2 2.126(2), Zn–N3 2.070(2), C1–C8 1.536(4), C1–P1 1.853(3), C1–P2 1.844(3), N1–P1 1.582(2), N2–P2 1.574(2), C8–N3 1.361(3), C8–N4 1.284(4); C2–Zn–N1 126.63(12), C2–Zn–N2 116.47(10), C2–Zn–N3 117.37(11), N1–Zn–N2 93.72(9), N1–Zn–N3 96.64(9), N2–Zn–N3 100.69(9), P1–C1–P2 114.89(15), N1–P1–C1 111.12(12), N2–P2–C1 109.71(12), C1–C8–N3 111.9(2), C1–C8–N4 122.3(2), N3–C8–N4 125.8(2), C8–N3–Zn 120.50(2).

Next, we studied the reaction of compound **3** with another heteroallene to get a better insight into the reactivity of this compound. Treatment of compound **3** with diphenyl ketene[40] resulted in the nucleophilic addition of the methine carbon atom onto the carbonyl carbon atom of the diphenyl ketene molecule.

The obtained product [{($Me_3SiNPPh_2)_2CH)(Ph_2C{=}C{-}O$)}ZnPh] (**5**) was isolated as yellow crystalline solid (Scheme 3). During the course of reaction a new tripodal N,N′,O ligand was formed, in which the ketene was transformed into an enol. As observed in compound **4** the ^1H NMR signal of the bridgehead carbon group is about 1.5 ppm downfield shifted to δ 3.64 ppm in comparison to compound **3**. In contrast to compounds **1**, **2** and **4** this shift is less significant. The shift of signals of the phenyl region are less significant. More characteristic is the $^{13}C\{^1H\}$ NMR spectrum. A weak triplet is observed for the bridgehead carbon atom (δ 47.8 ppm). Other characteristic signals are seen at δ 114.9 ppm for the $Ph_2\mathit{C}$ carbon atom and at δ 160.0 ppm for the *C*–O group. In the $^{31}P\{^1H\}$ NMR the expected resonance was detected at δ 25.3 ppm. In the EI-MS spectrum a weak molecular peak was measured.

The solid-state structure of compound **5** was established by single-crystal X-ray diffraction (Fig. 5). Compound **5** crystallizes in the monoclinic space group $P2_1/c$ with four molecules of the complex and four molecules of THF in the unit cell. The solid-state structure is in agreement with the data obtained in solution. The zinc atom is distorted tetrahedral coordinated by the phenyl group and the two nitrogen atoms and the oxygen atom of the newly formed tripodal ligand. As a result of the ligand transformation, the Zn–N bond distances (Zn–N1 2.069(2) Å, Zn–N2 2.093(3) Å) are a bit longer than in the starting material **3** (Zn–N1 1.9853(13) Å and Zn–N2 2.0298(14) Å). The N1–Zn–N2 bite angle of 99.26(10)° is about 5° reduced in comparison to compound **3** (N1–Zn1–N2 104.52(6)°). The Zn–O bond distance (Zn–O1 2.024(2) Å) is in the expected range. An enolate type structure of the newly formed ligand is observed. The bond distances of O1–C38 1.314(4) Å and C38–C39 1.373(4) Å are in the range of other zinc enolate complexes, *e.g.* [BrZn{OC(=CH_2)Mes}(DMF)].[41]

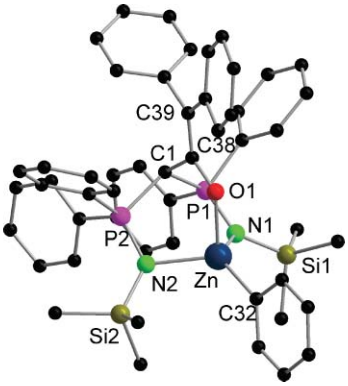


Fig. 5 Solid-state structure of **5** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths (Å) and angles (°): Zn–C32 1.985(3), Zn–N1 2.069(2), Zn–N2 2.093(3), Zn–O1 2.024(2), C1–P1 1.850(3), C1–P2 1.847(3), N1–P1 1.576(3), N2–P2 1.584(3), O1–C38 1.314(4), C38–C39 1.373(4); C32–Zn–N1 125.07(11), C32–Zn–N2 122.90(12), C32–Zn–O1 111.42(11), N1–Zn–N2 99.26(10), N1–Zn–O1 95.18(9), N2–Zn–O1 96.37(10), P1–C1–P2 114.4(2), C39–C38–O1 126.3(3), C1–C38–O1 113.4(3), C38–O1–Zn 122.6(2).

Conclusions

In bis(phosphinimino)methanide complexes of the main group and transition metals the ligand is usually not involved in any reactions and thus acts as innocent ligand.[42] In contrast, in zinc chemistry derivations of the bis(phosphinimino)methanide ligand are observed.[43] New kinds of compounds were obtained by a nucleophilic addition of the methine carbon atom of the $\{CH(Ph_2PNSiMe_3)_2\}^-$ ligand to heterocumulenes.

Experimental

General considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled MBraun glove box. THF was distilled under nitrogen from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored *in vacuo* over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich (99 atom% D). NMR spectra were recorded on Jeol JNM-LA 400 FT-NMR, a Bruker Avance 400 MHz NMR or a Bruker Avance II 300 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR), respectively. IR spectra were performed on a Bruker IFS 113v. Mass spectra were recorded at 70 eV on Varian Mat SM 11(Finnigan MAT 8200). Elemental analyses were carried out with an Elementar vario EL or EL III. {($Me_3SiNPPh_2)_2CH_2$}[36] and diphenylketene[40] were prepared according to literature procedures.

[{($Me_3SiNPPh_2)_2CH_2$}$ZnCl_2$] (1). $ZnCl_2$ (61 mg, 0.45 mmol) and [$CH_2(PPh_2NSiMe_3)_2$] (250 mg, 0.45 mmol) were dissolved in 10 ml of THF at room temperature. After 5 min a colorless precipitate was formed. The mixture was stirred for another 5 min and then heated to reflux to obtain a colorless crystalline solid. The product was collected by filtration, washed with 5 ml of *n*-pentane and dried in vacuum. Yield: 295 mg (95%). Single crystals suitable for X-ray analysis were obtained from hot toluene.

^1H NMR (C_6D_6, 400 MHz): δ 0.02 (s, 18 H, $SiMe_3$), 4.20 (t, 2 H, P–CH_2–P, $^2J_{H-P}$ = 13.3 Hz), 7.34–7.40 (m, 8 H, Ph), 7.45–7.50 (m, 4 H, Ph), 7.80–7.88 (m, 8 H, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, 161 MHz): δ 24.5 ppm. EI-MS (70 eV): *m*/*z* (%) = 658 ([*M* − HCl]$^+$, rel. int. 32), 569 ([$C_{28}H_{30}NP_2SiZnCl]^+$, 18), 543 ([$C_{30}H_{36}N_2P_2Si_2]^+$, 61), 471 ([$C_{28}H_{31}NP_2Si]^+$, 100), 456 ([$C_{27}H_{28}NP_2Si]^+$, 97). $C_{31}H_{40}Cl_2N_2P_2Si_2Zn\cdot 3/2C_7H_8$ (695.10 + 138.21): calc. C 59.82, H 6.30, N 3.36; found: C 59.26, H 6.68 N 3.74%.

[{($Me_3SiNPPh_2)_2CH_2$}ZnI_2] (2). ZnI_2 (142 mg, 0.45 mmol) and [$CH_2(PPh_2NSiMe_3)_2$] (250 mg, 0.45 mmol) were dissolved in 10 ml of THF at room temperature. After 5 min a colorless precipitate was formed. The mixture was stirred for another 5 min and then heated to reflux to obtain colorless needles suitable for X-ray analysis. The product was collected by filtration, washed with 5 ml of *n*-pentane and dried in vacuum. Yield: 361 mg (92%).

^1H NMR (d_8-THF, 400 MHz): δ 0.12 (s, 18 H, $SiMe_3$), 4.25 (t, 2 H, P–CH_2P), 7.36–7.41 (m, 8 H, Ph), 7.48–7.53 (m, 4 H, Ph), 7.84–7.89 (m, 8 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (d_8-THF, 161 MHz): δ 23.2 ppm. EI-MS (70 eV): *m*/*z* (%) = 748 ([*M* − HI]$^+$, rel. int.

73), 661 ($[C_{28}H_{30}NP_2SiZnI]^+$, 25), 543 ($[C_{30}H_{36}N_2P_2Si_2]^+$, 100), 471 ($[C_{28}H_{31}NP_2Si]^+$, 66), 456 ($[C_{27}H_{28}NP_2Si]^+$, 98). $C_{31}H_{40}I_2N_2P_2Si_2Zn$ (878.00): calc. C 42.41, H 4.59, N 3.19; found: C 42.41, H 4.64 N 3.01%.

[{(Me$_3$SiNPPh$_2$)$_2$CH}ZnPh] (3). $ZnPh_2$ (200 mg, 0.91 mmol) and $[CH_2(PPh_2NSiMe_3)_2]$ (510 mg, 0.91 mmol) were dissolved in 5 ml of toluene at room temperature. The mixture was stirred for 16 h. The volatiles were evaporated in vacuum to leave a foamy residue. Upon washing with *n*-pentane (5 ml) a pale yellow crystalline solid was formed and single crystals suitable for X-ray analysis could be obtained. Yield: 480 mg (76%).

^{1}H NMR (C_6D_6, 400 MHz): δ 0.15 (s, 18 H, $SiMe_3$), 2.07 (t, 1 H, P–CH–P), 6.95–7.01 (m, 12 H, *o*-, *p*-PPh), 7.28–7.32 (m, 1 H, Zn–*o*-Ph), 7.44–7.48 (m, 2 H, Zn–*p*-Ph), 7.61–7.67 (m, 8 H, *m*-PPh), 8.13–8.15 (m, 2 H, Zn–*m*-Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 3.8 (t, $SiMe_3$), 29.2 (t, P–CH–P), 126.5 (Zn–*o*-Ph), 127.6 (Zn–*p*-Ph), 128.1 (m, *o*-PPh), 130.5 (*p*-PPh), 131.7 (m, *m*-PPh), 137.5 (dd, *i*-PPh), 139.5 (Zn–*m*-Ph), 154.9 (Zn–*i*-Ph) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 161 MHz): δ 27.1 ppm. IR (cm^{-1}): 3048 (m), 2946 (m), 1433 (m), 1267 (s), 1241 (m), 1178 (w), 1102 (m), 1060 (m), 956 (w), 828 (s), 741 (s), 693 (s), 497 (s). EI-MS (70 eV): m/z (%) = 698 ($[M]^+$, 35), 621 ($[M - Ph]^+$, 80), 558 ($[CH(PPh_2NSiMe_3)_2]^+$, 88), 543 ($[CH(PPh_2NSiMe_3)_2 - Me]^+$, 100), 455 ($[CH(PPh_2)(PPh_2NSiMe_2)]^+$, 48). $C_{37}H_{44}N_2P_2Si_2Zn$ (700.29): calc. C 63.46, H 6.33, N 4.00; found: C 62.77, H 6.27, N 3.70%.

[{(Me$_3$SiNPPh$_2$)$_2$CH(*p*-tol)N=C–N(*p*-tol)}ZnPh] (4). A solution of [{(Me$_3$SiNPPh$_2$)$_2$CH}ZnPh] (200 mg, 0.28 mmol) in 5 ml of toluene was added to a stirred suspension of di(*p*-tolyl)carbodiimine (65 mg, 0.28 mmol) in 5 ml of toluene at ambient temperature. After 5 min the suspension became a pale yellow solution. Stirring was continued for 2 h. The reaction mixture was then filtered and concentrated. Pale yellow single crystals suitable for X-ray analysis could be obtained from hot toluene. Yield: 120 mg (46%).

^{1}H NMR (d_8-THF, 300 MHz): δ –0.16 (s, 18 H, $SiMe_3$), 2.13 (s, 3 H, $N_{amide}PhMe$), 2.34 (s, 3 H, $N_{imine}PhMe$), 4.40 (t, 1 H, P–CH–P, $^2J_{H-P}$ = 9.9 Hz), 6.55 (m, br, 2 H, Ph), 6.93 (m, 4 H) 7.09–7.58 (m, 23 H, Ph), 8.02 (m, 4 H, Ph) ppm. ^{13}C{^{1}H} NMR (d_8-THF, 75 MHz): δ 3.3 (t, $SiMe_3$), 19.8 (N_{amide}PhMe), 20.3 (N_{imie}PhMe), 44.2 (t, P–C–P, $^1J_{C-P}$ = 66.9 Hz), 121.6 (Ph), 124.2 (Ph), 125.4 (Ph), 126.4 (Ph), 127.8–128.7 (m, Ph), 132.2–133.5 (m, Ph), 141.2 (Ph), 147.3 (Ph), 158.2 (N=C–N) ppm. ^{31}P{^{1}H} NMR (d_8-THF, 121 MHz): δ 24.8 ppm. EI-MS (70 eV): m/z (%) = 922 ($[M]^+$, 2), 876 ($[M - 3Me]^+$, 2), 843 ($[M - Ph]^+$, 3), 698 ($[M - DTC]^+$, 54), 621 ($[M - DTC - Ph]^+$, 91), 558 ($[CH_2(PPh_2NSiMe_3)_2]^+$, 75), 543 ($[CH_2(PPh_2NSiMe_3)_2\text{-}Me]^+$, 95), 455 ($[CH_2(PPh_2)(PPh_2NSiMe_2)]^+$, 66), 222 ($[DTC]^+$, 93). $C_{52}H_{58}N_4P_2Si_2Zn$ (922.57): calc. C 67.70, H 6.34, N 6.07; found: C 68.08, H 6.17 N 5.96%.

[{(Me$_3$SiNPPh$_2$)$_2$CH(Ph$_2$C=C–O)}ZnPh] (5). A solution of [{(Me$_3$SiNPPh$_2$)$_2$CH}ZnPh] (200 mg, 0.28 mmol) in 5 ml of toluene was added to a stirred solution of $Ph_2C=C=O$ (39 mg, 0.2 mmol) in 1 ml of toluene at ambient temperature. The yellow solution is stirred for 4 h. The reaction mixture was filtered and the solvent removed in vacuum. Pale yellow single crystals suitable for X-ray analysis could be obtained from hot THF. Yield: 120 mg (46%).

^{1}H NMR (d_8-THF, 300 MHz): δ –0.17 (s, 18 H, $SiMe_3$), 3.64 (t, 1 H, P–CH–P, $^2J_{H-P}$ = 8.9 Hz), 6.91 (t, 2 H, Ph), 7.03–7.34 (m, 23 H, Ph), 7.44–7.49 (m, 2 H, Ph), 7.82–7.95 (m, 6 H, Ph), 8.17–8.20 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR (d_8-THF, 75 MHz): δ 4.1 (t, $SiMe_3$), 47.8 (t, P–C–P, $^1J_{C-P}$ = 66.9 Hz), 114.9 (t, CPh_2), 123.1 (Ph), 125.8 (Ph), 126.6 (Ph), 127.5 (Ph), 128.1–129.5 (m, Ph), 132.8–135.0 (m, Ph), 141.0 (Ph), 143.7 (Ph), 145.6 (Ph), 154.1 (Ph), 160.0 (t, C–O) ppm. ^{31}P{^{1}H} NMR (d_8-THF, 121 MHz): δ 25.3 ppm. EI-MS (70 eV): m/z (%) = 892 ($[M]^+$, 6), 647 ($[M - DPK - C_4H_4]^+$, 100), 621 ($[M - DPK - Ph]^+$, 51), 558 ($[CH_2(PPh_2NSiMe_3)_2]^+$, 92), 543 ($[CH_2(PPh_2NSiMe_3)_2 - Me]^+$, 100), 455 ($[CH_2(PPh_2)(PPh_2NSiMe_2)]^+$, 100), 193 ($[DPK]^+$, 88). $C_{51}H_{54}N_2OP_2Si_2Zn$ (894.52): calc. C 68.48, H 6.08, N 3.13; found C 67.84, H 6.23, N 2.74%.

X-Ray crystallographic studies of 1–5

A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS 2 or Stoe IPDS 2T. Subsequent computations were carried out on an Intel Pentium Core2Duo PC.

All structures were solved by the Patterson method (SHELXS-97).[44] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[44] Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon atoms to which they are bonded. The hydrogen atom contributions of compounds **1–5** were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Crystal data for 1. $2(C_{31}H_{40}Cl_2N_2P_2Si_2Zn)\cdot 3(C_7H_8)$, M = 1666.48, triclinic, space group $P\bar{1}$, a = 12.585(3), b = 16.613(3), c = 21.407(4) Å, α = 84.54(3), β = 82.55(3), γ = 76.71(3)°, V = 4309.3(15) Å^3, T = 200(2) K, Z = 2, μ(Mo-Kα) = 0.854 mm^{-1}, 42069 reflections measured, 22790 independent reflections (R_{int} = 0.0636). The final R_1 values were 0.0589 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1075 (all data).

Crystal data for 2. $C_{31}H_{40}I_2N_2P_2Si_2Zn\cdot 2(C_4H_8O)$, M = 1022.15, monoclinic, space group $P2_1/n$, a = 11.523(2), b = 22.951(5), c = 16.995(3) Å, β = 91.95(3)°, V = 4491.9(16) Å^3, T = 203(2) K, Z = 4, μ(Mo-Kα) = 2.079 mm^{-1}, 8149 reflections measured, 8149 independent reflections. The final R_1 values were 0.0462 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1135 (all data). The goodness of fit on F^2 was 0.899.

Crystal data for 3. $C_{37}H_{44}N_2P_2Si_2Zn$, M = 700.23, monoclinic, space group $P2_1/n$, a = 10.286(2), b = 16.726(3), c = 22.270(5) Å, β = 101.73(3)°, V = 3751.1(13) Å^3, T = 203(2) K, Z = 4, μ(Mo-Kα) = 0.831 mm^{-1}, 30061 reflections measured, 8939 independent reflections (R_{int} = 0.0616). The final R_1 values were 0.0333 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0918 (all data).

Crystal data for 4. $C_{52}H_{58}N_4P_2Si_2Zn$, $M = 922.55$, monoclinic, space group $P2_1/c$, $a = 11.032(2)$, $b = 19.711(4)$, $c = 22.993(5)$ Å, $\beta = 101.71(3)°$, $V = 4895.9(17)$ Å^3, $T = 200(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.655 mm^{-1}, 37500 reflections measured, 10377 independent reflections ($R_{int} = 0.0725$). The final R_1 values were 0.0510 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1043 (all data).

Crystal data for 5. $C_{51}H_{54}N_2OP_2Si_2Zn\cdot C_4H_8O$, $M = 966.56$, monoclinic, space group $P2_1/c$, $a = 10.987(2)$, $b = 21.913(4)$, $c = 21.031(4)$ Å, $\beta = 98.72(3)°$, $V = 5005(2)$ Å^3, $T = 203(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.645 mm^{-1}, 49953 reflections measured, 10625 independent reflections ($R_{int} = 0.1287$). The final R_1 values were 0.0600 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1661 (all data).

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