Notes

Magnesium Complexes of Bis(phosphinimine)methane and -methanide Ligands

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*Summary: Mg complexes of bis(phosphoranimine)methane and -methanide ligands have been characterized. Reaction of $CH_2(Ph_2PNSiMe_3)_2$ with MeMgI and MeMgCl gave the crystalline products $CH_2(Ph_2PNSiMe_3)_2MgI_2$ (**1**) and $[HC(Ph_2PNSiMe_3)_2Mg(\mu\text{-}Cl)]_2$ (**2**), respectively. The related reaction of $LiCH(Ph_2PNSiMe_3)_2$ with MeMgI afforded $CH(Ph_2PNSiMe_3)_2MgI(THF)$ (**3**). Crystallographic data for **1**−**3** confirm a significant Mg−C interaction in complexes containing bis(phosphoranimine)methanide ligands.*

Main group derivatives of phosphinimine and phosphinimide ligands have drawn considerable attention in recent years. A wide variety of such derivatives have been characterized and reviewed by Dehnicke and coworkers.[1] More recently, we have used phosphinimide ligands to produce the novel linear cationic species $[(t\text{-}Bu_3PN)_2B]Cl$,[2] as well as in the formation of cationic Si, Ge, and Sn derivatives.[3] In related chemistry, employing a chelating bis-phosphinimine, Elsevier and co-workers have characterized a series of neutral and monoanionic complexes derived from $H_2C(R_2PNSiMe_3)_2$.[4−11] More recently, we have reported the first structure of a dilithiomethane derivative, $[Li_2C(Ph_2PNSiMe_3)_2]_4$.[12] This species[13] was also subsequently reported and exploited by Cavell and co-workers. The chemistry of Al-bis(phosphinimine)methanide and methanediide complexes, $HC(Ph_2PNSiMe_3)_2AlMe_2$ and $(Me_2Al)_2C(Ph_2PNSiMe_3)_2$,[14,15] as well as related Zn species has been described.[16] The research groups of Cavell[17,18] and Roesky[19] have demonstrated the structural diversity of Li, Na, and K salts of $[HC(Ph_2PNSiMe_3)_2]^-$. Only Li species showed evidence of M−C bonding interactions.[17,18] In this note, we describe related Mg complexes derived from reactions of methyl-Grignard reagents. Complexation of the neutral and monoanionic forms of the ligand is confirmed in $H_2C(Ph_2PNSiMe_3)_2MgI_2$, $[HC(Ph_2PNSiMe_3)_2Mg(\mu\text{-}Cl)]_2$, and $HC(Ph_2PNSiMe_3)_2MgI(THF)$. Structural data affirm significant Mg−C interactions are present in the anionic ligand complexes.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubbs' type solvent purification system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded in C_6D_6 at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance-300 and are referenced to external 85% H_3PO_4. Combustion analyses were done in-house employing a Perkin-Elmer CHN analyzer.

Synthesis of $CH_2(Ph_2PNSiMe_3)_2MgI_2$, 1. To a stirred solution of $CH_2(Ph_2PNSiMe_3)_2$ (0.112 g, 0.20 mmol) in benzene (15 mL) was added MeMgI (3.0 M) (0.067 mL, 0.20 mmol). The resulting solution was stirred overnight at room temperature. Colorless crystals were obtained from mixture solvents of toluene/THF/CH_2Cl_2. Yield: 0.060 g, 36%. Anal. Calcd (found) for $C_{31}H_{40}N_2P_2Si_2MgI_2$: C, 44.49 (45.01); H, 4.82 (5.25); N, 3.35 (3.59). $^{31}P\{^1H\}$ NMR: 25.2 (s). ^1H NMR: 7.60 (br, 8H, Ph),

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Table 1. Crystallographic Data

	1	**2**	**3**
formula	$C_{31}H_{40}I_2N_2P_2Si_2Mg$	$C_{31}H_{39}ClN_2P_2Si_2Mg$	$C_{70}H_{94}I_2Mg_2N_4O_2P_4Si_4$
fw	836.88	617.52	1562.15
a (Å)	17.463(10)	16.882(12)	18.331(9)
b (Å)	19.505(11)	17.616(13)	10.039(5)
c (Å)	11.444(7)	22.837(16)	44.48(2)
β (deg)			101.016(10)
cryst syst	orthorhombic	orthorhombic	monoclinic
V (Å^3)	3898(4)	6792(9)	8035(7)
space group	$Pna2(1)$	$P2_1/n$	$P2_1/n$
d(calc) g cm^{-1}	1.426	1.208	1.291
Z	4	8	4
abs coeff, μ, cm^{-1}	1.794	0.318	0.980
data collected	15 932	23 588	33 124
data $F_o^2 > 3\sigma(F_o^2)$	5535	4824	11 408
variables	361	352	793
R	0.0314	0.0815	0.0597
R_w	0.0547	0.1534	0.1299
GOF	0.816	1.184	1.030

6.92 (br, 12H, Ph), 2.01 (s, 1H, PCHP), 0.40 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: 131.9, 130.3, 128.1, 127.7, 29.3 (s, PCHP), 5.2 (s, $SiMe_3$).

Synthesis of $[HC(Ph_2PNSiMe_3)_2Mg(\mu\text{-}Cl)]_2$, 2. To a stirred solution of $CH_2(Ph_2PNSiMe_3)_2$ (0.112 g, 0.20 mmol) in benzene (15 mL) was added MeMgCl (3.0 M) (0.067 mL, 0.20 mmol). The resulting solution was stirred overnight at room temperature. The volatiles were removed under vacuum to give a white solid. Colorless crystals were obtained from mixture solvents of CH_2Cl_2/hexane. Yield: 0.065 g, 53%. Anal. Calcd (found) for $C_{31}H_{39}N_2P_2Si_2MgCl$: C, 60.29 (60.44); H, 6.37 (6.72); N, 4.54 (4.60). $^{31}P\{^1H\}$ NMR: 25.3 (s). ^1H NMR: 7.70 (br, 8H, Ph), 7.01 (br, 12H, Ph), 2.23 (br, s, 1H, PCHP), 0.39 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: 131.8, 129.9, 127.8, 127.5, 28.2 (s, PCHP), 4.7 (s, $SiMe_3$).

Synthesis of $CH(Ph_2PNSiMe_3)_2MgI(THF)$, 3. To a stirred solution of $LiCH(Ph_2PNSiMe_3)_2$ in toluene (15 mL), which was prepared in situ by a combination of $CH_2(Ph_2PNSiMe_3)_2$ (0.112 g, 0.20 mmol) with $LiN(SiMe_3)_2$ (0.034 g, 0.20 mmol) in toluene, was added MeMgI (3.0 M in Et_2O) (0.067 mL, 0.20 mmol). The resulting solution was stirred overnight at room temperature. Colorless crystals were obtained from the mixture of solvents toluene/THF/pentane. Yield: 0.076 g, 49%. Anal. Calcd (found) for $C_{35}H_{47}N_2P_2Si_2OMgI$: C, 53.82 (53.72); H, 6.07 (6.43); N, 3.59 (3.51). $^{31}P\{^1H\}$ NMR: 26.0 (s). ^1H NMR: 7.55 (br, 8H, Ph), 6.94 (br, 12H, Ph), 3.75 (m, 4H, THF), 2.02 (br, 1H, PCHP), 1.33 (m, 4H, THF), 0.53 (s, 9H, $SiMe_3$), 0.01 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: 135.5, 132.2, 130.9, 130.5, 69.2 (s, THF), 30.6 (s, PCHP), 25.8 (s, THF), 7.2 (s, $SiMe_3$), 4.9 (s, $SiMe_3$).

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45-50.0°$). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a Pentium computer.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[20] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. 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, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions 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. Additional details are provided in the Supporting Information.

Results and Discussion

The reaction of the bis(phosphoranimine)methane ligand $CH_2(Ph_2PNSiMe_3)_2$ with a stoichiometric amount of MeMgI led to the isolation of colorless crystals of a product **1** in 36% yield based on the ligand. Spectroscopic data showed no evidence of a methyl group, while crystallographic data confirmed the formulation of **1** as $CH_2(Ph_2PNSiMe_3)_2MgI_2$ (Figure 1). The geometry about Mg is the anticipated pseudo-tetrahedral, with Mg−N and Mg−I distances averaging 2.111(5) and 2.75(1) Å, respectively. The N−Mg−N bite angle of the chelating ligand is 106.06(18)°, while the I−Mg−I angle is 107.49(7)°.

The related reaction of $CH_2(Ph_2PNSiMe_3)_2$ with 1 equiv of MeMgCl resulted in the evolution of methane and also the formation of colorless crystals. Spectroscopic data of this product **2** confirmed the presence of the methine carbon and thus the bis(phosphoranimine)methanide ligand. X-ray data for **2** confirmed the formulation as $[HC(Ph_2PNSiMe_3)_2Mg(\mu\text{-}Cl)]_2$ (Figure 2). The geometry about Mg in **2** is distorted square pyramidal with one of the bridging chloride ions, the methine carbon, and the two nitrogen atoms comprising the basal plane. The second bridging chloride atom occupies the apical position. The geometry about the basal plane is

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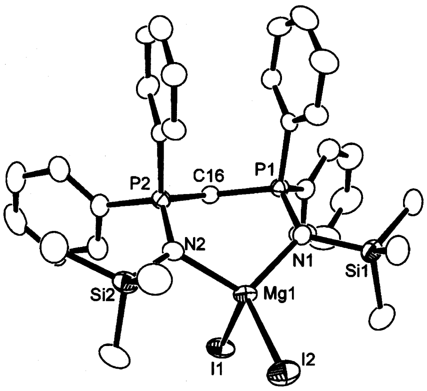

Figure 1. ORTEP drawing of **1**, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (deg): Mg(1)−N(1) 2.111(5), Mg(1)−N(2) 2.112(5), Mg(1)−I(2) 2.732(2), Mg(1)−I(1) 2.764(2), P(1)−N(1) 1.584(5), P(2)−N(2) 1.587(4), N(1)−Mg(1)−N(2) 106.06(18), N(1)−Mg(1)−I(2) 114.10(14), N(2)−Mg(1)−I(2) 114.81(13), N(1)−Mg(1)−I(1) 107.86(14), N(2)−Mg(1)−I(1) 106.06(14), I(2)−Mg(1)−I(1) 107.49(7), P(1)−N(1)−Si(1) 123.9(3), P(1)−N(1)−Mg(1) 116.3(2), SI(1)−N(1)−Mg(1) 118.1(2), P(2)−N(2)−Si(2) 125.4(3), P(2)−N(2)−Mg(1) 116.4(2), Si(2)−N(2)−Mg(1) 117.6(2), P(1)−C(16)−P(2) 121.2(3).

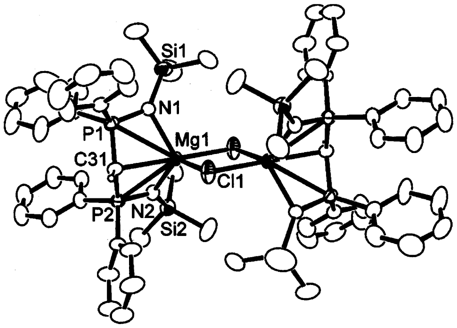

Figure 2. ORTEP drawing of **2**, 30% ellipsoids are shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Mg(1)−N(2) 2.104(7), Mg(1)−N(1) 2.163(7), Mg(1)−Cl(1) 2.427(3), Mg(1)−Cl(1) 2.440(3), Mg(1)−C(31) 2.460(8), P(1)−N(1) 1.610(7), N(2)−Mg(1)−N(1) 107.6(3), N(2)−Mg(1)−Cl(1) 129.5(2), N(1)−Mg(1)−Cl(1) 116.0(2), Cl(1)−Mg(1)−Cl(1) 86.88(11), N(2)−Mg(1)−C(31) 72.2(2), N(1)−Mg(1)-C(31) 71.6(2), Cl(1)−Mg(1)-C(31) 97.9(2), Cl(1)′−Mg(1)−C(31) 175.1(2), P(1)−N(1)−Si(1) 135.2(4), P(1)−N(1)−Mg(1) 95.9(3), Si(1)−N(1)−Mg(1) 128.8(4), P(2)−N(2)−Si(2) 133.1(4), P(2)−N(2)−Mg(1) 97.2(3), Si(2)−N(2)−Mg(1) 129.6(3), P(1)−C(31)−P(2) 126.1(4).

distorted. The two adjacent four-membered rings from the chelation of the bis(phosphoranimine)methanide give rise to N−Mg−C, N−Mg−Cl, N−Mg−N, and Cl−Mg−C angles of 72.2(2)°, 129.5(2)°, 107.6(3)°, and 175.1(2)°, respectively. The angles of these atoms with the apical Cl range from 71.6(2)° to 116.0(2)°. The Mg−N distances in **2** (2.104(7), 2.163(7) Å) are similar to those seen in **1**. As a result of the covalent Mg−C bonding, the Mg−C distance of 2.460(8) Å is dramatically shorter than the Mg−C approach of 3.168 Å seen in **1** as well as the average Li−C or Na−C distances of 2.65(10) and 2.992(4) Å in $[HC(Ph_2PNSiMe_3)_2M]_2$ (M = Li, Na).[17] It is noteworthy that the presence of the formal Mg−C bond also results in a significant shortening of the Mg−P distance from 3.153(3) Å in **1** to 2.813(3) Å in **2**.

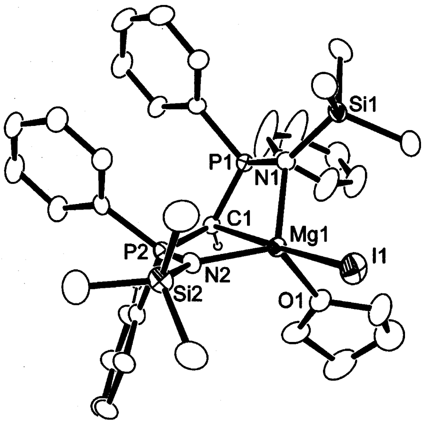

Figure 3. ORTEP drawing of one of the two molecules of **3** in the asymmetric unit, 30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Distances (Å) angles (deg): Mg(1)−O(1) 2.090(5), Mg(1)−N(2) 2.099(5), Mg(1)−N(1) 2.121(5), Mg(1)−C(1) 2.573(6), Mg(1)−I(1) 2.779(2), Mg(2)−N(4) 2.088(5), Mg(2)−O(2) 2.096(5), Mg(2)−N(3) 2.099(5), Mg(2)−C(36) 2.638(6), Mg(2)−I(2) 2.763(2), N(1)−P(1) 1.606(5), N(2)−P(2) 1.609(5), N(3)−P(3) 1.617(5), N(3)−Si(3) 1.732(5), N(4)−P(4) 1.617(5), O(1)−Mg(1)−N(2) 122.6(2), O(1)−Mg(1)−N(1) 112.1(2), N(2)−Mg(1)−N(1) 109.8(2), O(1)−Mg(1)−C(1) 88.48(19), N(2)−Mg(1)−C(1) 70.60(19), N(1)−Mg(1)−C(1) 70.51(19), O(1)−Mg(1)−I(1) 94.02(15), N(2)−Mg(1)−I(1) 108.44(15), N(1)−Mg(1)−I(1) 107.88(15), C(1)−Mg(1)−I(1) 177.42(16), N(4)−Mg(2)−O(2) 118.2(2), N(4)−Mg(2)−N(3) 112.9(2), O(2)−Mg(2)−N(3) 113.5(2), N(4)−Mg(2)−C(36) 70.01(19), O(2)−Mg(2)−C(36) 90.8(2), N(3)−Mg(2)−C(36) 69.55(19), N(4)−Mg(2)−I(2) 107.90(15), O(2)−Mg(2)−I(2) 92.73(15), N(3)−Mg(2)−I(2) 109.22(15), C(36)−Mg(2)−I(2) 176.43(17), P(1)−N(1)−Si(1) 131.7(3), P(1)−N(1)−Mg(1) 99.1(2), Si(1)−N(1)−Mg(1) 127.7(3), P(2)−N(2)−Si(2) 131.6(3), P(2)−N(2)−Mg(1) 99.8(2), Si(2)−N(2)−Mg(1) 128.4(3), P(3)−N(3)−Si(3) 132.1(3), P(3)−N(3)−Mg(2) 101.1(3), Si(3)−N(3)−Mg(2) 126.2(3), P(4)−N(4)−Si(4) 129.2(3), P(4)−N(4)−Mg(2) 100.8(2), Si(4)−N(4)−Mg(2) 128.0(3).

The contrasting nature of the products from iodo- and chloro-Grignard reagents may arise from methyl/iodide redistribution. This view is consistent with the observation of a relatively low yield of **1** based on the ligand. Attempts to isolate any methyl-containing Mg-bis(phosphoranimine)methanide product were unsuccessful. However, reaction of $LiCH(Ph_2PNSiMe_3)_2$ with MeMgI in THF afforded another Mg-bis(phosphoranimine)methanide product, **3**. Crystallographic characterization of this species revealed it to be the monometallic species $CH(Ph_2PNSiMe_3)_2MgI(THF)$ (Figure 3). The formation of **3** infers the elimination of MeLi. An apparently similar elimination of MeLi was previously reported for the reaction of *t*-Bu_3PNLi and $MeAlCl_2$.[21]

As observed for **2**, the geometry about Mg in **3** is best described as a distorted square-based pyramid with the THF oxygen atom occupying the pseudo-axial position. The chelating ligand geometry in **3** is similar to that seen in **2**, with the C−Mg−I angles averaging 176.9(5)° in the two crystallographically independent molecules in the asymmetric unit. The Mg−C distances in **3** of 2.573(6) and 2.638(6) Å are slightly longer than that seen in **2**, presumably reflecting the *trans* influence of I versus Cl. The relatively close approach of Mg to the

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(21) Ong, C. M.; McKarns, P.; Stephan, D. W. *Organometallics* **1999**, *18*, 4197−4204.

central C atom in both **2** and **3** stands in contrast to the Na−C or K−C distances seen in $CH(Ph_2PNSiMe_3)_2M(THF)_2$ (M = Na 3.749(7) Å; K 4.145(2) Å).[18] Close approach of the central C to Mg requires a pseudo-boat conformation of the MgN_2P_2C ring. The coordination of this ligand to Mg is similar to that see in the related Ir complex.[11] Although one might anticipate that such a geometry is generally energetically unfavorable, this must be balanced against the greater Lewis acidity of the Mg(II) center. It is noteworthy that in analogous Cr(II) complexes the cocrystallization of structural isomers infers that the energy difference between pseudo-boat and pseudo-chair conformations is small.[22]

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Wei, P.; Stephan, D. W. *Organometallics* **2002**, *21*, 1308−1310.