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Structure and Reactivity of a Methyl Zinc **Bis(iminophosphorano)methanide Chelate Complex**

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Summary: Reaction of dimethyl zinc with bis-{trimethylsilyliminodi(phenyl)phosphorano}methane, $H_2C(Ph_2P=NSiMe_3)_2$ (1), in toluene gave the alkyl zinc complex $[ZnMe\{HC(Ph_2P=NSiMe_3)_2 + \kappa^2 N, N\}]$ (2) via elimination of methane. The crystal structure of the complex confirms its monomeric nature and the bidentate coordination of the bis(iminophosphorano)methanide ligand to the zinc. AdNCO ($A\hat{d} = \hat{a}damantyl$) reacted smoothly with 2 via a nucleophilic addition forming a new C-C bond in the novel tripodal alkyl zinc complex, $[ZnMe{HC{C(O)N(Ad)}(Ph_2P=NSiMe_3)_2-\kappa^3N,N,N'}], 3.$ The methine carbon atom resonances (δ 28.4 for **2** and 52.9 for 3) were observed as triplets due to the coupling to two equivalent phosphorus atoms. The crystal structure of $\hat{\boldsymbol{3}}$ shows a propeller type arrangement with the three nitrogen atoms of the monoanionic tridentate ligand bound to zinc.

Organozinc compounds are widely used synthetic reagents which offer valuable alternatives to the analogous magnesium and lithium species in terms of both reactivity and selectivity.¹⁻⁶ Recently, zinc-based complexes, particularly the aryloxide^{7–9} and β -diimine^{10,11} complexes, have been recognized as important catalysts for copolymerization of carbon dioxide and epoxides to polycarbonates. Other transition metal and main group complexes of β -diimine ligand systems have also been used for catalytic processes.^{10–15} Of relevance herein is

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that the less familiar bis(iminophosphorano)methanide ligands (II) are isovalent-electronic to carbon-based β -diimine ligands (I).



In this context we extended our study of bis(iminophosphorano)methane ligands¹⁶⁻¹⁹ to zinc, a posttransition metal, because there is a fairly extensive chemistry of monoanionic bis(iminophosphorano)methane ligands with group 9 and 10 transition metals.^{20–28} Recently we described novel group 4 carbene complexes with related ligand systems.^{17–19} Herein we report the reaction of the prototypical ligand with ZnMe₂ which leads to a novel complex stabilized by bis(iminophosphorano)methanide chelation.

The complex [ZnMe{HC(Ph₂P=NSiMe₃)₂- $\kappa^2 N, N$ }], **2**, was obtained as a colorless air-sensitive crystalline solid in good yield upon the addition of 1 equiv of dimethyl zinc to a toluene solution of H₂C(Ph₂P=NSiMe₃)₂, 1,²⁹ (eq 1) under an argon atmosphere at room temperature.³⁰ Methane is eliminated.

Complex 2 showed strong absorptions at 1259 and 1244 cm⁻¹, which can be ascribed to the P=N stretch.

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The ³¹P NMR spectrum of the final reaction mixture showed that quantitative conversion of ligand **1** to product **2** had occurred. The spectrum consisted of one sharp singlet, indicating two equivalent phosphorus atoms with a chemical shift of 26.2 ppm, shifted downfield by 34.4 ppm vs the free ligand. The ¹³C{¹H} APT spectrum of **2** gave a negative triplet signal at 28.4 ppm (¹*J*_{PC} \approx 120.6 Hz) for the ligand backbone methanide unit, coupled to two equivalent phosphorus nuclei.

The molecular structure of [ZnMe{HC(Ph₂P=NSiMe₃)₂- $\kappa^2 N, N$], **2**, determined by X-ray crystallography³¹ is illustrated (Figure 1). The ORTEP³² diagram shows the atom-labeling scheme. Selected bond lengths and bond angles are given in the caption. The core structure consists of a six-membered metallacyclic ring with Zn, N(1), P(1), C(1), P(2), and N(2) atoms adopting a distorted boat conformation. Complex 2 is monomeric in which the two phosphinimine units of the ligand chelate to a monomethylated Zn to form a tricoordinated distorted trigonal planar geometry $\{N(1)-Zn-N(2) =$ 99.4(1), N(1)-Zn-C(2) = 128.9(2), C(2)-Zn-N(2) =129.8(2)°}about the metal center. The sum of the angles around zinc is 358.1(2)°; thus the zinc environment is nearly planar. This tricoordinate environment for zinc is rare, but not unknown;³³⁻³⁵ zinc is usually found in a four-coordinate environment.

Complex **2** did not react with a nitrile (AdCN) or with isonitriles (Ar'NC) even under reflux conditions in

(30) Preparation of $[ZnMe{HC(Ph_2P=NSiMe_3)_2-\kappa^2N, N]$, 2 All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox. To a toluene (5 mL) solution of $H_2C(Ph_2P=NSiMe_3)_2$ (0.20 g, 0.36 mm0) was added ZnMe₂ (1.0 M solution in heptane, 0.36 mL, 0.36 mmol) with stirring at room temperature. Immediate evolution of gas was observed. The reaction mixture was stirred at room temperature for 1 day. Colorless crystals were obtained upon concentration of the solution to half of the original volume and allowing the flask to stand at -15°C for 3 days. The product was isolated by filtration and dried under vacuum. Yield: 0.145 g, 63.5%. IR data (Nujol mull): 1589w, 1482m, 1436s, 1311w, 1259s, 1244s, 1160s, 1111s, 1069m, 1000m, 927s, 834s, 803s, 745s, 729s, 711s, 695s, 651s, 615m, 593s, 547s, 516s. ¹H NMR $\rm [C_6D_6):~\delta~7.65~(m,~phenyl),~7.00~(m,~phenyl),~1.92~(t,~P-CH-P,~^2J_{HP}=4.5~Hz),~0.17~(s,~CH_3-Zn),~0.11~(s,~CH_3Si~methyl).^{-13}C~\{^1H\}~NMR$ (C₆D₆): Some phenyl resonances are second-order multiplets: δ 138.0 (m), 131.7 (m), 130.3 (s), 128.1 (m). Other resonances are: δ 28.4 (t, Si₂Zn: C, 60.22; H, 6.63; N, 4.39. Found: C, 59.99; H, 6.62; N, 4.37.

(31) Crystal data for [ZnMe{HC(Ph₂P=NSiMe₃)_{2⁻κ²</sup>N,N], **2** : Triclinic, $P\overline{1}$ (No. 2), a = 10.8871(3) Å, b = 11.3994(4) Å, c = 15.6589(6) Å, $\alpha = 81.555(3)^\circ$, $\beta = 87.067(2)^\circ$, $\gamma = 62.480(2)^\circ$, V = 1704.5(1) Å³, Z = 2. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R1 = 0.0484 and 0.0513, (wR2 = 0.1142 and 0.1179) for 4149 reflections with $F_0^{-2} \ge 2\sigma(F_0^{-2})$ and all data, respectively.}

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Figure 1. ORTEP³² view of $[ZnMe{HC(Ph_2P=NSiMe_3)_2-\kappa^2N,N]}$, **2**, showing the atom-labeling scheme. Hydrogen atoms are shown only on the methine and zinc methyl centers. Only ipso phenyl carbon atoms are shown. The remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic distances [Å] and angles [deg] are Zn–N(1) = 2.083(3), Zn–N(2) = 2.042(3), Zn–C(2) = 1.958(4), N(1)–P(1) = 1.585(3), P(1)–C(1) = 1.728(4), P(2)–C(1) = 1.739(4), P(2)–N(2) = 1.600(3), N(1)–Zn–N(2) = 99.4(1), C(2)–Zn–N(1) = 128.9(2), C(2)–Zn–N(2) = 129.8(2), P(1)–C(1)–P(2) = 120.1(2), N(1)–P(1)–C(1) = 106.8(2), Zn···C(1) = 2.527(4).

toluene for 3 days, but did undergo addition reactions with heteroallenes such as carbodiimides, isocyanates, etc. Thus, adamantyl isocyanate reacted smoothly to yield the novel four-coordinated derivative [ZnMe{HC-{ $C(O)N(Ad)}(Ph_2P=NSiMe_3)_2-\kappa^3N,N,N'$ }] (3) (eq 2) con-



taining a tripodal ligand,³⁶ by means of nucleophilic addition of the methanide carbon to the adamantyl carbon to form a new C–C bond. The reaction emphasizes the inertness of the methyl substituent on the zinc which we surmise is due to steric protection of this unit by the bulky ligand environment provided by the SiMe₃ and Ad groups.³³ Previous heteroallene insertion reac-

⁽³⁶⁾ Preparation of [ZnMe{HC{C(O)N(Ad)}(Ph₂P=NSiMe₃)₂-κ³N, N, N''], **3** (also in the argon drybox). To a toluene (5 mL) solution of $[ZnMe{HC(Ph_2P=NSiMe_3)_2-\kappa^2 N, N], 2 (0.20 g, 0.31 mmol), was added$ AdNCO (0.056 g, 0.31 mmol) and the mixture was stirred at room temperature for a day. Concentration of the solution to half of the original volume and allowing the flask to stand at -15 °C for 2 days gave colorless crystals which were isolated by filtration and dried under vacuum. Yield: 0.16 g, 62.6%. IR data (Ňujol mull): 1611s, 1603s, 1587m, 1484w, 1438s, 1297s, 1247s, 1179s, 1166s, 1148s, 1125m, 1107s, 994w, 950w, 913m, 840s, 794w, 783w, 760m, 749m, 742m, 712s, 694s, 656m, 595m, 541m, 511s. ¹H NMR (C₆D₆): δ 8.03 (m, phenyl), $P_{A}^{(3)}$ (3.1) (3.1) (3.1) (3.1) (3.1) (3.1) (3.1) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3.2) (3. phenyl resonances are second-order multiplets: δ 132.6 (m), 132.3 (m), 131.9 (s), 131.0 (s), 127.9 (s). Other resonances are: δ 162.1 (t, CO, $^{2}J_{PC} = 3.8$ Hz), 56.1 (s, C-Ad), 52.9 (t, P-CH-P, $^{1}J_{PC} = 44.6$ Hz), 43.0 (s, CH₂-Ad), 37.6 (s, CH₂-Ad), 30.9 (s, CH-Ad), 4.4 (s, CH₃Si), -1.0 (s, CH₃-Zn). ³¹P{¹H} MMR (C₆D₆): δ 21.8 (s). Anal. Calcd for C43H57N3OP2Si2Zn·C7H8: C, 66.17; H, 7.22; N, 4.63. Found: C, 66.14; H, 7.27; N, 4.66.

Communications

tions^{37,38} of zinc alkyl amido complexes inserted into the Zn–N bond yielding dimeric and oligomeric bridged complexes;² thus the reaction exhibited by **2** is unique. The reaction of isocyanate with **2** is also different from the reactions of isocyanates with β -ketoimines and β -dicarbonyls; in these cases the methine hydrogen atom was replaced and an amine was formed.^{39–41}

Complex 3 was isolated as a colorless crystalline solid sensitive to air and moisture. The Infrared spectrum showed strong absorptions at 1611, 1603 cm⁻¹ and at 1297 cm⁻¹ due to the C=O and P=N stretching vibrations. Only a single peak was observed in the phosphorus NMR spectrum, indicating that the phosphorus atoms are equivalent. The ¹³C{¹H} APT spectrum for the CH of the P-C-P frame consisted of a negative triplet (${}^{1}J_{PC} \approx 44.6$ Hz) at 52.9 ppm, (downfield shift of 24.5 ppm with respect to **2**). The monomeric molecular structure of $[ZnMe{HC{C(0)N(Ad)}(Ph_2P=NSiMe_3)_2-\kappa^3N_{-}]$ N, N'], **3**,⁴² confirmed by X-ray crystallography is illustrated in an ORTEP³² plot (Figure 2). The metal is subtended by a methyl group and three nitrogens, one from the isocyanate adduct and the other two are the previously chelated phosphinimine centers. The basic framework consists of three six-membered rings fused at two opposite apexes to form a propeller. The nonbonding distance across the chelate ring in 3 (i.e., Zn to C(1), 3.009(2) Å, is longer than this separation in complex 2 (2.527(4) Å); thus the addition of the AdNCO opens the structure. There is no interaction between the zinc and the carbonyl group of the AdNCO, which in any case faces away from the metal. In 3, the zinc center is located in a trigonally distorted tetrahedral geometry, a shape similar to that observed previously for the η^3 bis(pyrazolyl)hydroborato complexes of zinc.^{34,43} The newly added nitrogen, N(3), has a slightly shorter bond to Zn than the chelated imine bonds, Zn-N(1) and Zn-N(2), indicating that the negative charge is more localized on N(3). The range of observed Zn-N distances is within that observed for Zn-amide complexes.^{44,45} The zinc methyl distances in 2 and 3 are in the range observed for other terminal zinc alkyl complexes.⁴⁶

The bond distances within the ligand framework in **2** and **3** are considerably altered in comparison with the related values in free bis(iminophosphorane) ligands;^{22,47} the P=N bond distances are slightly elongated and the



Figure 2. ORTEP³² view of [ZnMe{HC{C(O)N(Ad)}(Ph₂-P=NSiMe₃)_{2⁻ κ^{3} N,N,N"}], **3**, showing the atom-labeling scheme. For clarity all hydrogen atoms (except for those on the methine center and the zinc methyl center) and all phenyl group carbon atoms (except the *ipso* carbon) have been removed. Remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic distances [Å] and angles [deg] are Zn-N(1) = 2.132(2), Zn-N(2) = 2.191(2), Zn-N(3) = 2.050(2), Zn-C(3) = 1.998(2), N(1)-P(1) = 1.576(2), P(1)-C(1) = 1.827(2), P(2)-C(1) = 1.817(2), P(2)-N(2) = 1.573(2), N(1)-Zn-N(3) = 94.53(7), P(1)-C(1)-P(2) = 119.9(1), N(1)-P(1)-C(1) = 110.9(1).}

P-C-P bond angles $(120.1(2)^{\circ} \text{ in } 2 \text{ and } 119.9(1)^{\circ} \text{ in } 3)$ are expanded compared to the corresponding values in, for example, CH₃CH{Ph₂P=N(Tol)}₂ $(112.39(19^{\circ})^{22}$ and H₂C{Cy₂P=NSiMe₃}₂ $(117.41(12)^{\circ}).^{47}$ The endocyclic P-C bond distances are shorter in complex 2 than comparable bonds in the free ligands, although they are essentially unchanged in complex 3. These factors suggest that there is a delocalization of π electron density within the six-membered ZnN₂P₂C ring in 2which is not applicable in 3.

The alkyl zinc complex **2** of the bis(iminophosphorano)methanide ligand is the first example of a group 12 complex of the bis(iminophosphorano)methane ligand system. The complex contains a rare example of a threecoordinated zinc center. Nucleophilic addition to the carbon center of an isocyanate gave a novel tripodal four-coordinated zinc complex. Reactivity studies are presently being pursued.

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