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Phosphine Adducts of Monomeric Zinc(bis-phenoxides): Solution and Solid-State Structures of (2,6-Di-*tert*-butylphenoxide)ZnL Complexes (L = $PMePh_2$ and PCy_3)

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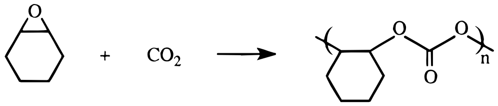
Recently, we have demonstrated that monomeric Zn(II) phenoxides which possess sterically encumbering substituents in the 2- and 6-positions of the phenolate ligands along with two ether donors, typified by (2,6-di-*tert*-butylphenoxide)$_2$Zn^{II}(THF)$_2$, are the most active catalysts known for the copolymerization of cyclohexene oxide and carbon dioxide (eq 1).[1] Solution ^{1}H NMR studies have revealed that the ether ligands are quite labile at ambient temperature,[2,3] being completely dissociated for some phenoxide derivatives. In a closely related investigation we have determined the thermodynamic binding parameters for the interactions of various oxygen and sulfur bases with cadmium pyrazolylborate derivatives which have been shown to be excellent models for the initiation step in the copolymerization of epoxides with CO_2.[4,5] These studies have demonstrated that THF binds more strongly to the cadmium center than do the epoxides, propylene oxide and cyclohexene oxide. Qualitative observations on the binding of these oxygen bases to the zinc (2,6-R$_2$-phenoxide)$_2$ derivatives exhibit similar trends.[3,6] In an effort to further probe the binding of various bases to the zinc metal center in these metal phenoxide species, we have taken advantage of the rich steric and electronic diversity of phosphine ligands to synthesize a group of novel zinc bis-phenoxide phosphine complexes.



(1)

Phosphine derivatives of the group 12 metals (and of zinc in particular) are rare. Much of the work has centered on ^{31}P NMR solution studies of phosphine interactions with zinc halides.[7] McAuliffe and co-workers have reported the structure of [Zn(PEt$_3$)I$_2$]$_2$ in which the geometry about zinc is tetrahedral with iodide in both terminal and bridging positions.[8] Examples of crystallographically characterized zinc chalcogenates are limited to the structures of Zn(S-2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_2$(Ph$_2$PMe)[9] and (Et$_2$NCS$_2$)$_2$Zn(PMe$_3$).[10] In this communication, the structures of two novel zinc phenoxide−phosphine complexes will be presented along with their solution behavior.

The monomeric zinc complexes (2,6-di-*tert*-butylphenoxide)-ZnL, where L = PMePh$_2$ (**1**) and PCy$_3$ (**2**), have been synthesized by the addition of 2 equiv of 2,6-di-*tert*-butylphenol to Zn[N(SiMe$_3$)$_2$]$_2$ in a toluene solution under an argon atmosphere followed by the addition of the appropriate phosphine ligand. Subsequently, the reaction mixture was stirred for 1 h at ambient temperature, during which time the solution remained clear and colorless. X-ray quality crystals of **1** were obtained through slow diffusion of hexane into a concentrated toluene solution of the complex over several days at −20 °C. On the other hand, crystals of **2** emerged directly from a concentrated toluene solution of the reaction mixture maintained at −20 °C overnight. Both complexes were characterized by elemental analysis, and ^{31}P and ^{1}H NMR spectroscopies.[11] Care must be taken to handle the samples in the absence of moist air to avoid hydrolysis of the phenoxide ligands and/or oxidation of the phosphines.[12]

The solid-state structures of complexes **1** and **2** were determined by X-ray crystallographic analysis.[13,14] A 50% thermal ellipsoid drawing of complex **1** is provided in Figure 1, where the zinc center displays near trigonal planar geometry. That is, the zinc atom lies only 0.009(2) Å out of the plane defined by the phosphorus and two oxygen donor groups, and the phenoxide ligands are fairly symmetrically displaced about the Zn−P vector with the O(2)−Zn−P bond angle being only 7° less than the O(1)−Zn−P angle. The average Zn−O bond distance of 1.854[4] Å found in **1** is slightly shorter than that observed in the distorted tetrahedral complexes (2,4,6-tri-*tert*-butylphenoxide)$_2$Zn(THF)$_2$ (1.887[7] Å)[2] and (2,6-di-*tert*-butylphenoxide)$_2$Zn(THF)$_2$ (1.876[5] Å).[3,15] On the contrary, the O(1)−Zn−O(2) bond angle of 111.7(2)° is considerably more acute than the corresponding S−Zn−S angle of 138.2(1)° determined in its thiolate analogue, Zn(S-2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_2$(Ph$_2$PMe).[9] The Zn−P bond distance in

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[6] Nevertheless, the binding of these various oxygen donor bases is dependent upon the nature of the substituents on the phenoxide ligands.

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[11] Anal. Found (calcd) for **1**: C, 72.85 (70.10); H, 8.14 (8.15). ^{1}H NMR (C$_6$D$_6$, 298 K): δ 6.8−7.2 (m, 13 H, P(C$_6$*H*$_5$)$_2$, OC$_6$*H*$_3$), 1.62 (s, 18 H, C(C*H*$_3$)$_3$), 1.25 (d, $^2J_{P,H}$ = 6.8 Hz, 3 H, PC*H*$_3$). ^{31}P NMR (C$_6$D$_6$, 298 K): δ −19.9 (s, *P*Ph$_2$Me). ^{13}C NMR (C$_6$D$_6$, 298 K): δ 35.9 (P*C*H$_3$), 129.4−132.9 (d, P*C*$_6$H$_5$), 31.9, 34.2, 165.6 (2,6-[(*C*H$_3$)$_3$*C*]$_2$*C*$_6$H$_3$)., Anal. Found (calcd) for **2**: C, 73.10 (71.60); H, 9.90 (9.88). ^{1}H NMR (C$_6$D$_6$, 298 K): δ 0.8−2 (m, 33 H, PC$_6$*H*$_{11}$), 1.77 (s, 18 H, C(C*H*$_3$)$_3$), 6.81 (t, 2H, *p*-C$_6$*H*$_3$), 7.35 (d, 4H, *m*-C$_6$*H*$_3$). ^{31}P NMR (C$_6$D$_6$, 298 K): δ 7.97 (s, *P*Cy$_3$). ^{13}C NMR (C$_6$D$_6$, 298 K): δ 27.6−32.0 (P*C*$_6$H$_{11}$), 32.5, 165.2 (2,6-[(*C*H$_3$)$_3$C]$_2$*C*$_6$H$_3$).

[12] Goel[7a] has suggested that zinc complexes actually catalyze aerobic oxidation of phosphines.

[13] Crystal data for **1**: C$_{55}$H$_{71}$O$_2$PZn, M_w = 860.46, monoclinic, $P2_1/c$, a = 10.76(2) Å, b = 37.078(7) Å, c = 12.866(3) Å, α = 90°, β = 106.57(3)°, γ = 90°, T = 293(2) K, Z = 4, V = 4921(2) Å^3, 7789 reflections with $I > 2\sigma(I)$ used, R = 0.0739, R_w = 0.1856.

[14] Crystal data for **2**: C$_{60}$H$_{91}$O$_2$PZn, M_w = 940.67, triclinic, $P\bar{1}$, a = 10.984(2) Å, b = 14.297(2) Å, c = 18.800(2) Å, α = 71.978(9)°, β = 78.081(11)°, γ = 85.012(11)°, T = 293(2) K, Z = 2, V = 2746.2(6) Å^3, 10 088 reflections with $I > 2\sigma(I)$, R = 0.0886, R_w = 0.2087.

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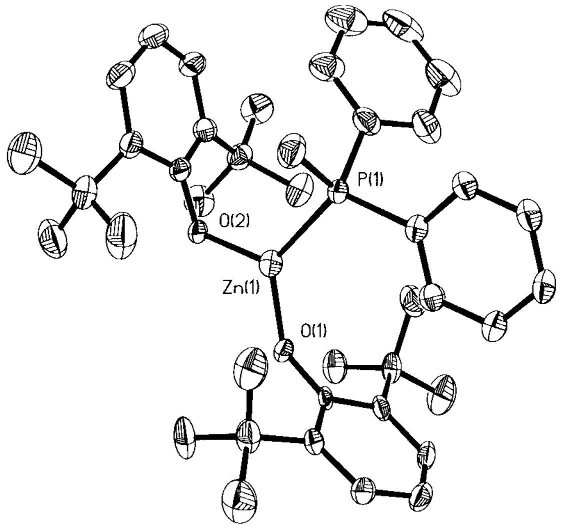

Figure 1. 50% thermal ellipsoid drawing of complex **1** with partial atomic numbering scheme. Selected bond lengths and angles: Zn−O(1) = 1.844(4) Å, Zn−O(2) = 1.864(4) Å, O(1)−Zn−P = 127.80(13)°, O(2)−Zn−P = 120.49(13)°.

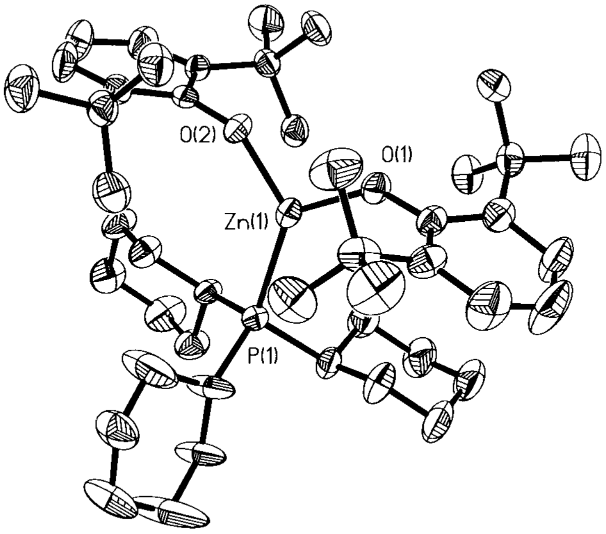

Figure 2. 50% ellipsoid drawing of complex **2** with partial atomic numbering scheme. Selected bond lengths and angles: Zn−O(1) = 1.869(4) Å, Zn−O(2) = 1.875(4) Å, O(1)−Zn−P = 129.50(14)°, O(2)−Zn−P = 126.89(14)°.

1 of 2.375(2) Å is shorter than that observed (2.413(4) Å) in the analogous thiolate derivative.

Complex **2** (Figure 2), which contains the sterically encumbering PCy_3 ligand (cone angle = 170°),[16] retains the trigonal planar geometry about the zinc center as exhibited in complex **1**. However, in this instance the deviation of zinc from the plane defined by the donor atoms of the phosphine and phenoxide ligands is greater, at 0.070(2) Å. The average Zn−O bond length of 1.872[4] Å and the O(1)−Zn−O(2) bond angle of 103.2 (2)° in **2** are slightly longer and more acute, respectively, than the corresponding parameters in **1**. The Zn−P bond distance at 2.433(2) Å is *longer* in **2** than the analogous distance in **1**. This observation is counterintuitive when one considers the relative basicities of tricyclohexylphosphine versus methyldiphenylphosphine.[17] Presumably, all of the above comparative structural parameters in complexes **1** and **2** can be readily explained by the sizable difference in the steric requirements of the two phosphine ligands (cone angle of PPh_2Me = 136°).

Because the ether ligands in the $Zn(O\text{-}2,6\text{-}R_2C_6H_3)_2(ether)_2$ derivatives have been shown by ^1H NMR to be quite labile and to varying extents dissociated from the zinc center in noninteracting solvents,[2,3] it was of interest to examine the phosphine derivatives prepared herein for ligand binding and reactivity in solution. ^{31}P NMR measurements carried out on complexes **1** and **2** in deuterated toluene solution over the temperature range 25 to −90 °C indicated the phosphine ligands to be bound to zinc at ambient temperature. That is, the ^{31}P resonances observed to be shifted downfield and upfield, respectively, from that of the free phosphines for complex **1** (−19.9 ppm) and complex **2** (7.9 ppm) were found to be essentially temperature independent.[18] Furthermore, upon addition of 1 equiv of the corresponding free phosphine to toluene solutions of **1** or **2** at ambient temperature, the ^{31}P signals assigned to complexes **1** and **2** were unshifted and unbroadened. Consistent with this observation, the free phosphine's ^{31}P resonance was unperturbed. Hence, there is no further binding of these phosphines to the trigonal planar zinc center, nor is there any rapid exchange of free and bound phosphines.[19] However, upon addition of 1 equiv of the small (cone angle = 118°), less basic phosphine ligand PMe_3 to complex **2**, facile ligand substitution of PCy_3 occurs with concomitant formation of the zinc-bound PMe_3 species (−50.9 ppm).[20] Hence, as may be anticipated, steric influences play a determining role in phosphine ligand binding to these sterically hindered zinc centers. Indeed with the addition of another 1 equiv of PMe_3 to the solution above, a bis-phosphine complex appears to form at low temperatures.

In conclusion, we have reported on the synthesis and characterization of monomeric, bis-phenoxide complexes of zinc containing phosphine ligands. It was further shown that the rates of bound versus free phosphine exchange in these derivatives is slow compared to the chemical shift difference between the two ^{31}P resonances which range from 200 to 700 Hz. On the other hand, on the time scale of minutes, the phosphine exchange process occcurs readily, with the less sterically demanding phosphine ligands being favored thermodynamically, e.g., PMe_3 preferentially binds over PCy_3. Future studies designed to quantitatively define the binding of a variety of oxygen, sulfur, and phosphorus donors to bis-phenoxide derivatives of both zinc and cadmium are underway.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1** and **2** are available on the Internet only. Access information is given on any current masthead page.

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(18) The ^{31}P resonances for the free ligands appear at −27.7 and 10.0 ppm in deuterated toluene for PPh_2Me and PCy_3, respectively.

(19) On the basis of the chemical shift differences in Hz between the bound and free phosphine ligands, the exchange rates for the two phosphorus sites must be considerably slower than 700 and 200 s^{-1} at 298 K for complexes **1** and **2**, respectively.

(20) The ^{31}P resonance for free PMe_3 in deuterated toluene was observed at −62.3 ppm.