Solution ^{31}P and ^{113}Cd NMR Studies of Phosphine Adducts of Monomeric Cadmium (Bisphenoxide) Complexes and the Solid-State Structures of (2,6-Di-*tert*-butylphenoxide)$_2$Cd(PCy$_3$) and (2,6-Di-*tert*-butylphenoxide)$_2$Cd(PMe$_3$)$_2$[†]

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Monomeric phosphine derivatives of cadmium phenoxides, (phenoxide)$_2$CdL$_n$, where the phenoxide ligands contain sterically demanding substituents in the 2,6-positions (2,6-di-*tert*-butylphenoxide and 2,6-diphenylphenoxide) are described. These derivatives were synthesized from the reaction of Cd[N(SiMe$_3$)$_2$]$_2$ and the corresponding phenol followed by the addition of the phosphine. For the large PCy$_3$ ligand (Tolman's cone angle $(\theta) = 170°$) $n = 1$, whereas for the smaller Me$_3$P ($\theta = 118°$) and *n*-Bu$_3$P ($\theta = 132°$) ligands both mono- and bis(phosphine) derivatives ($n = 1$ and 2) were prepared. The (2,6-di-*tert*-butylphenoxide)$_2$Cd(PCy$_3$) and (2,6-di-*tert*-butylphenoxide)$_2$Cd(PMe$_3$)$_2$ were characterized in the solid-state by X-ray crystallography. The structure of the monophosphine adduct of PCy$_3$ consists of a near trigonal planar geometry about the cadmium center, where the average P−Cd−O angle of 131.4° is larger than the O−Cd−O angle of 96.72° with a Cd−P bond length of 2.5247(12) Å. On the other hand, the bis(phosphine) adduct, Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PMe$_3$)$_2$ is a distorted tetrahedral structure with O−Cd−O and P−Cd−P bond angles of 116.7(6)° and 104.3(2)°, respectively. The average Cd−P bond length in this derivative was determined to be 2.737[5] Å. The monotricyclohexylphosphine derivatives of these cadmium bisphenoxides were shown by ^{31}P NMR spectroscopy not to be undergoing facile exchange with free phosphine in solution at ambient temperature. On the contrary, the corresponding Me$_3$P and *n*-Bu$_3$P analogues readily undergo self-exchange with free phosphine in solution via a rapid equilibrium between monophosphine adduct plus free phosphine and the bis(phosphine) adduct. The ^{113}Cd chemical shifts in the CdO$_2$P moieties shift downfield and the ^{113}Cd−^{31}P coupling constants decrease by about 900 Hz upon binding an additional phosphine ligand.

Introduction

Our keen interest in monomeric zinc bis(phenoxide) complexes is based on the observations that these derivatives are effective catalysts for the homopolymerization of epoxides to polyethers or copolymerization of CO$_2$ and epoxides to polycarbonates.[1,2] These zinc complexes, typified by (2,6-diphenylphenoxide)$_2$Zn(THF)$_2$ (where THF is tetrahydrofuran), are rendered monomeric by virtue of the steric requirements of the bulky phenoxide ligands employed in these studies.[3] Relevant to the copolymerization of CO$_2$ and epoxides catalyzed by zinc bis(phenoxide) derivatives is the simultaneous production of polyether linkages, a process which is diminished in importance in the presence of added tricyclohexylphosphine.[4] This phenomenon appears to be the consequence of PCy$_3$ occupying one of the coordination sites of zinc. Indeed, the trigonal planar adduct, (2,6-di-*tert*-butylphenoxide)$_2$Zn·PCy$_3$, has been isolated and characterized crystallographically.[5] Furthermore, PCy$_3$ has been shown by ^{31}P NMR to be bound to the zinc center under the conditions of catalysis. The sparsity of coordination chemistry of zinc with phosphine ligands has led us to focus some of our attention on this subject. Herein, we wish to extend these investigations to include the coordination chemistry of the cadmium analogues, for these not only can exhibit more diverse structural features, but can be probed by both ^{31}P and ^{113}Cd NMR spectroscopies.[6] ^{113}Cd and ^{111}Cd are nuclei with relatively high sensitivity for use as NMR probes, spanning a chemical shift range of more than 1000 ppm. Indeed, because of this feature ^{113}Cd NMR probes have been extensively employed in the study of cadmium-substituted zinc enzymes and/or proteins.[7−12]

Pertinent to these studies cadmium(II) phosphine complexes were first synthesized nearly 60 years ago.[13] Since that time, many investigations have been undertaken utilizing ^{31}P and ^{113}Cd solution and solid-state NMR and X-ray crystallog-

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[†] Dedicated to Professor Dirk Walthers on the occasion of his 60th birthday.

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raphy.[14−23] Most of these studies involved cadmium(II) phosphine complexes with various anions including halides, nitrate, carboxylates, thiocyanates, and perchlorate. Dakternieks observed that in these systems, phosphine exchange and anion exchange occurred in solution and that several different molecular species ranging from monomeric to symmetrical and unsymmetrical dimeric complexes could exist depending upon the number of equivalents of trialkyl phosphine (one or two) used.[24] It was also determined by Dakternieks and co-workers that in systems where the ligands are labile, lattice and solvation effects are the predominant factors in determining which complex crystallized from solution.[25] Therefore, what is observed in solution is not necessarily the same as that observed in the solid state. Similar phosphine and anionic ligand lability has been reported by many different research groups.[26−28] By way of contrast the phenoxide ligands in the complexes reported upon within were not observed to be labile in solution in the absence of protic reagents.

Experimental Section

Methods and Materials. All syntheses and manipulations were carried out on a double-manifold Schlenk line or in a glovebox under argon. Glassware was flamed out thoroughly before use. Toluene, hexane, and benzene were freshly distilled from sodium benzophenone and dichloromethane was distilled from P_2O_5 prior to their use. Trimethylphosphine was purchased from Strem and stored in a Schlenk tube under an atmosphere of argon. Tricyclohexylphosphine was purchased from Aldrich and was stored in a glovebox. Tri-*n*-butylphosphine (>90% purity) was purchased from Aldrich packaged as a sure-seal container and was stored under an argon atmosphere. All phosphines were used without further purification. The phenols, 2,6-di-*tert*-butylphenol and 2,6-diphenylphenol, were purchased from Aldrich. $Cd[N(SiMe_3)_2]_2$ was synthesized and distilled according to the literature procedure.[29] This material is extremely moisture sensitive and, as such, was stored in a glovebox and used immediately after removal from the box. ^{31}P NMR data were acquired on Varian XL200 and Unity+ 300 MHz superconducting NMR spectrometers operating at 81 and 121 MHz, respectively. Both instruments are equipped with variable-temperature control modules. All ^{31}P NMR data are referenced to H_3PO_4 (85% in D_2O). ^{113}Cd NMR spectra were recorded on a Varian XL-400E superconducting high-resolution spectrometer operating at 88 MHz using an external 0.1 M $Cd(ClO_4)_2/D_2O$ reference. ^{1}H and ^{13}C NMR spectra were acquired on Varian XL200E, Unity+ 300 MHz, and VXR 300 MHz superconducting NMR spectrometers. The operating frequencies for ^{13}C experiments were 50.29 and 75.41 MHz for the 200 and 300 MHz instruments, respectively. Infrared spectra were recorded on a Mattson 6021 FT-IR spectrometer with DTGS and mercury cadmium telluride (MCT) detectors.

Synthesis of $Cd(O\text{-}2,6\text{-di-}^{t}BuC_6H_3)_2(PCy_3)$ (1). Cd-bishexamethyl-disilylamide (0.20 g, 0.46 mmol) was dissolved in 5 mL of toluene, and 2,6-di-^{t}Buphenol (0.19 g, 0.92 mmol) dissolved in 5 mL of toluene was cannulated onto the Cd-bishexamethyl-disilylamide solution resulting in some solid formation. Addition of tricyclohexylphosphine (PCy_3) (0.13 g, 0.46 mmol) to the solution obtained above provided initially a clear yellow solution, which within a few minutes formed a precipitate. Evacuation of the solvent produced a pale yellow powder in 91% yield. Anal. Calcd for $CdC_{46}H_{75}O_2P$: C, 68.76; H, 9.41. Found: C, 65.67; H, 9.30. ^{1}H NMR (298 K C_6D_6 solvent) δ 7.38 (d, 2H, *m*-aryl), δ 6.79 (t, 1H, *p*-aryl), δ 0.9−1.9 (m, 33H, $P(C_6H_{11})_3$), δ 1.77 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (298 K C_6D_6 solvent) δ 31.6, 30.4, 28.0, 26.9 ($P(C_6H_{11})_3$), δ 167.8, 139.6, 125.3, 115.2, 35.9, 31.2 ($2,6\text{-}O[(CH_3)C]_2C_6H_3$). ^{31}P NMR (298 K C_6D_6 solvent) δ 31.3 $^{1}J_{113Cd-31P} = 2274$ Hz. ^{113}Cd NMR (298 K C_6D_6 solvent) δ 240 (d) $^{1}J_{113Cd-31P} = 2279$ Hz. There was no change in ^{31}P NMR spectrum signal for complex **1** upon the addition of a second equivalent of PCy_3.

Synthesis of $Cd(O\text{-}2,6\text{-Diphenyl }C_6H_3)_2(PCy_3)$ (2). An analogous procedure for the synthesis of complex **2** as employed in the preparation of complex **1** was followed, except that 2,6-diphenylphenol (0.23 g, 0.92 mmol) was used in place of 2,6-di-^{t}Buphenol and benzene was used as solvent. Complex **2** remained in solution and upon evacuation of the solvent a yellow oil was obtained. Three washings with 5 mL of hexanes produced a white powder in 78% yield. ^{1}H NMR (298 K C_6D_6 solvent) δ 7.80 (br), 7.38 (br), 7.19 (t), 7.09 (d), 6.80 (br) (13H, $2,6\text{-}O(C_6H_5)_2C_6H_3$), δ 0.8−1.9 (m, 33H, $P(C_6H_{11})_3$). ^{13}C NMR (298 K C_6D_6 solvent) δ 31.5, 29.9, 27.3, 25.7 ($P(C_6H_{11})_3$), δ 162.4, 143.6, 131.1, 130.3, 129.6, 129.1, 126.2, 115.2 ($2,6\text{-}O[C_6H_5]_2C_6H_3$). ^{31}P NMR (298 K C_6D_6 solvent) δ29.8 $^{1}J_{113Cd-31P} = 2156$ Hz. ^{113}Cd δ 288 (d) $^{1}J_{113Cd-31P} = 2163$ Hz. There was no change in the ^{31}P NMR signal for complex **2** upon the addition of a second equivalent of PCy_3.

Synthesis of $Cd(O\text{-}2,6\text{-Di-}^{t}BuC_6H_3)_2(PnBu_3)_{1,2}$ (3),(4). The preparation of the bis(phenoxide) cadmium derivative was identical to that described in the synthesis of complex **1**. Addition of tri-*n*-butylphosphine ($P(^{n}Bu)_3$) (115 mL, 0.46 mmol) resulted in a bright yellow, clear solution. Evacuation of toluene solvent produced a yellow powder in 63% yield. For **4**, an extra equivalent of $P(^{n}Bu)_3$ was added directly to the NMR tube prior to ^{31}P and ^{113}Cd NMR spectral analysis. ^{1}H NMR complex **3** (298 K C_6D_6 solvent) δ 7.38 (d, 2H, *m*-aryl), δ 6.79 (t, 1H, *p*-aryl), δ 1.73 (s, 9H, $C(CH_3)_3$), δ 1.18 (m), 1.11 (m), 0.88 (m), 0.73 (t) (27H, $P(C_4H_9)_3$). ^{13}C NMR complex **3** (298 K C_6D_6 solvent) δ 25.9 (s), 24.2 (d), 21.8 (d), 13.8 (s), ($P(C_4H_9)_3$), δ 168.1, 138.3, 125.2, 114.7, 35.9, 31.9 ($2,6\text{-}O[(CH_3)_3C)]_2C_6H_3$). ^{31}P and ^{113}Cd NMR data are listed in Table 3.

Synthesis of $Cd(O\text{-}2,6\text{-Diphenyl }C_6H_3)_2(PnBu_3)_{1,2}$ (5),(6). The preparation of the bis(phenoxide) cadmium derivative was identical to that described in the synthesis of complex **1**. One equiv of tri-*n*-butylphosphine (115 mL, 0.46 mmol) was added via syringe to the above solution. Evacuation of the benzene solvent produced a waxy, yellow solid. The same procedure was followed with 2 equiv of $P(^{n}Bu)_3$ resulting in another waxy, yellow solid of complex **6**. ^{1}H NMR complex **5** (298 K C_6D_6 solvent) δ 1.21 (m), 1.13 (m), 0.88 (m), 0.73 (t) (27H, $P(C_4H_9)_3$), δ 7.80 (br), 7.38 (br), 7.19 (br), 7.09 (br), 6.80 (br) (13H, $2,6\text{-}O\ (C_6H_5)_2C_6H_3$). ^{13}C NMR complex **5** (298 K C_6D_6 solvent) δ 25.9 (s), 24.4 (d), 21.7 (d), 13.8 (s), ($P(C_4H_9)_3$), δ 161.9, 144.3, 131.2, 130.3, 129.9, 129.1, 126.2, 114.2 ($2,6\text{-}O[C_6H_5]_2C_6H_3$). ^{31}P and ^{113}Cd NMR data are listed in Table 3.

Synthesis of $Cd(O\text{-}2,6\text{-Di-}^{t}BuC_6H_3)_2(PMe_3)_{1,2}$ (7),(8). The preparation of the bis(phenoxide) cadmium derivative was identical to that described in the synthesis of complex **1**. Addition of trimethylphosphine (PMe_3) (42.9 mL, 0.46 mmol) and subsequent evacuation of solvent resulted in a yellow powder in 90% yield. An extra equivalent of PMe_3 was added directly to the NMR tube containing **7** prior to ^{31}P and ^{113}Cd NMR spectral analysis to provide spectra of complex **8**. ^{1}H NMR complex **7** (298 K C_6D_6 solvent) δ 0.63 (s, 9H, $P(CH_3)_3$), δ 1.71 (s, 9H, $C(CH_3)_3$), δ 7.38 (d, 2H, *m*-aryl), δ 6.78 (t, 1H, *p*-aryl). ^{13}C NMR complex **7** (298 K C_6D_6 solvent) δ 13.6 (d, $P(CH_3)_3$) δ 168.1, 138.3, 125.2, 114.7, 35.9, 31.9 ($2,6\text{-}O[(CH_3)_3C)]_2C_6H_3$). ^{31}P and ^{113}Cd NMR data are listed in Table 3.

Synthesis of $Cd(O\text{-}2,6\text{-Diphenyl }C_6H_3)_2(PMe_3)_{1,2}$ (9),(10). The preparation of the bis(phenoxide) cadmium derivative was identical to

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Table 1. Crystallographic Data and Data Collection Parameters for Complexes **1** and **8**

	1	**8**
formula	$C_{46}H_{75}CdO_2P{\cdot}C_7H_8$	$C_{34}H_{60}CdO_2P_2{\cdot}C_7H_8$
fw	895.56	767.29
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$C222_1$
a, Å	10.8553(9)	11.002(2)
b, Å	18.832(2)	22.452(5)
c, Å	23.952(2)	17.572(4)
V, Å^3	4896.4(7)	4340.4(15)
Z	4	4
d (calcd), g/cm^3	1.215	1.174
abs coeff, mm^{-1}	0.516	4.939
goodness of fit on F^2	0.989	1.061
λ, Å	0.710 73	1.541 78
T, K	193(2)	173(2)
R,[a] %	5.54	5.67
R_w,[b] %	12.21	13.55

[a] $R = \sum||F_o| - |F_c||/\sum F_o$. [b] $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/(\sum w(F_o^2)^2]\}^{1/2}$.

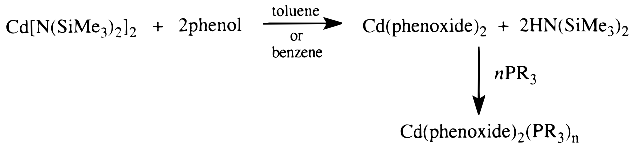
that described in the synthesis of complex **1**. Addition of 1 equiv of PMe_3 (42.9 mL, 0.46 mmol) to the above solution and subsequent evacuation of benzene solvent resulted in a yellow waxy solid. The same procedure using 2 equiv of PMe_3 also produced a yellow waxy solid, complex **10**. ^{1}H NMR complex **9** (298 K CD_2Cl_2 solvent) δ 0.58 (s, 9H, $P(CH_3)_3$), δ 6.78 (t, 1H, *p*-aryl), δ 7.13 (d, 2H, *m*-aryl), δ 7.21 (m, 6H, *m*/*p*-aryl), δ 7.98 (d, 4H, *o*-aryl). ^{13}C NMR complex **9** (298 K CD_2Cl_2 solvent) δ 13.2 (d, $P(CH_3)_3$), δ 115.1 (s), δ 125.8 (s), δ 128.6 (s), δ 129.9 (s), δ 130.2 (s), δ 131.3 (s), δ 142.2 (s), δ 165.1 (s) (2,6-O-$[C_6H_5]_2C_6H_3$). ^{31}P and ^{113}Cd NMR data are listed in Table 3.

X-ray Crystallography. Single crystals of complex **1** were obtained from a concentrated solution of **1** in toluene at −20 °C. The X-ray data collection covered more than a hemisphere of reciprocal space by a combination of three sets of exposures; each exposure set had a different φ angle for the crystal orientation and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.9 cm. Crystal decay was monitored by repeating the data collection for 50 initial frames at the end of the data set and analyzing the duplicate reflections; crystal decay was negligible. The space group was determined based on systematic absences and intensity statistics.[30] The structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined with anisotropic displacement parameters. The H-atoms attached to the N and O atoms were located from a difference map, and were refined using a riding model. All H atoms attached to C atoms were placed in ideal positions and refined using a riding model with aromatic C−H = 0.96 Å, methyl C−H = 0.98 Å, and with fixed isotropic displacement parameters equal to 1.2 (1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they were attached. The methyl groups were allowed to rotate about their local 3-fold axis during refinement.

For complex **1**, data collection: SMART;[31] cell refinement: SAINT (Siemens[32]); data reduction: SAINT (Siemens[31]); program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick[30]); program(s) used to refine structures: *SHELXTL-Plus* (Sheldrick, 1996); molecular graphics: *SHELXTL-Plus* (Sheldrick[30]); software to prepare material for publication: *SHELXTL-Plus* (Sheldrick[30]).

Crystal data and details of the data collections are provided in Table 1. A colorless block crystal of **8** was mounted on a glass fiber with epoxy cement at room temperature and cooled to 163 K in a N_2 stream. Preliminary examination and data collection were performed on a Rigaku AFC5 X-ray diffractometer (Cu K$\alpha\lambda$ = 1.54178 Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections. ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for 8.0° = 2θ = 120°. Three control reflections collected for every 97 reflections showed no significant trends. Lorentz and polarization corrections were applied as was a semiempirical absorption correction to each. Structures were solved by direct methods [*SHELXS*, *SHELXTL-Plus* program package]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded R, $R_w(F^2)$, and S values at convergence. Hydrogen atoms were placed at idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.

Scheme 1



phenol = 2,6-*di*-^{t}Buphenol 2,6-*di*-Phphenol

R	n	Compound	Compound
Cy	1	**1**	**2**
n-Bu	1	**3**	**5**
n-Bu	2	**4**	**6**
Me	1	**7**	**9**
Me	2	**8**	**10**

Results and Discussion

Preparations. The synthesis of monomeric mono- or bis(phosphine) derivatives of cadmium phenoxides, where the phenoxides contain sterically demanding substituents in the 2,6-positions, is relatively straightforward. Typically, 2 equiv of the phenol dissolved in toluene or benzene is cannulated onto a solution of $Cd[N(SiMe_3)_2]_2$ in the respective hydrocarbon, and the solution is stirred for 1 h at ambient temperature. To the resultant bright yellow, clear solution is added 1 or 2 equiv of the desired phosphine by microliter syringe, or as a hydrocarbon solution in the case of solid phosphines. The solution was stirred for an additional 30 min at ambient temperature, and the solvent was removed under vacuum to provide a solid product. Scheme 1 summarizes the synthetic methodology along with the specific derivatives reported upon herein.

Molecular Structures. X-ray quality crystals of complexes **1** and **8**, $Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(PCy_3)$ and $Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(PMe_3)_2$, respectively, were obtained from toluene at −20 °C, and their solid-state structures were determined by X-ray crystallographic analysis. Figure 1 contains a thermal ellipsoid drawing of complex **1**, along with a partial atomic numbering scheme. A molecule of toluene was found in the crystal lattice. The structure of complex **1**, like its zinc analogue, consists of a nearly planar arrangement of cadmium along with the three ligands' binding atoms (two oxygens and phosphorus). This is apparent from the sum of the angles O(2)−Cd(1)−O(1), O(1)−Cd(1)−P(1), and O(2)−Cd(1)−P(1) which is 359.52°. Selected bond lengths and bond angles are provided in Table 2. The average Cd−O bond length of 2.089[3] Å is 0.22 Å longer than that found in the zinc analogue which is consistent with the difference in the radii of cadmium and zinc.[5,33] On the other hand, the Cd−P distance of 2.5247(12) Å is shorter than expected on the basis of the corresponding Zn−P bond length of 2.433(2) Å.[5]

Like complex **1**, complex **8** crystallized with a toluene molecule in its crystal lattice. A thermal ellipsoid drawing of **8** is depicted in Figure 2, along with a partial atomic numbering

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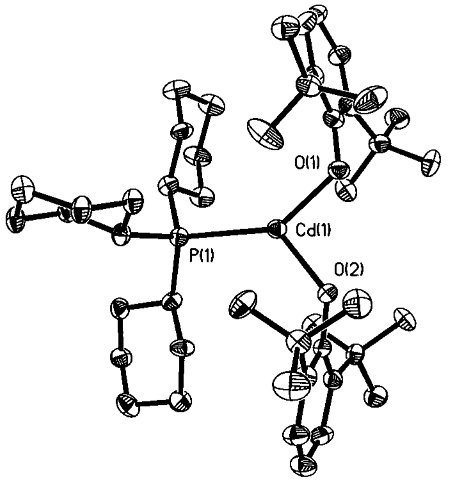

Figure 1. Thermal ellipsoid representation of Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$$\cdot$PCy$_3$, complex **1**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes **1** and **8**[a,b]

Complex **1**: Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PCy$_3$)			
Cd(1)−O(1)	2.092(3)	Cd(1)−O(2)	2.086(3)
Cd(1)−P(1)	2.5274(12)	O(1)−C(1)	1.340(5)
O(2)−C(15)	1.332(5)		
O(2)−Cd(1)−O(1)	96.72(11)	O(2)−Cd(1)−P(1)	125.62(9)
O(1)−Cd(1)−P(1)	137.18(8)	C(1)−O(1)−Cd(1)	128.7(3)
C(15)−O(2)−Cd(1)	135.9(3)		
Complex **8**: Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PMe$_3$)$_2$[c]			
Cd(1)−O(1)	2.043[10]	Cd(1)−P(1)	2.737[5]
O(1)−C(1)	1.353[18]		
O(1)−Cd(1)−O(1A)	116.7(6)	P(1)−Cd(1)−P(1A)	104.3(2)
O(1)−Cd(1)−P(1)	123.9(4)	O(1′)−Cd(1)−P(1′)	97.2(5)
C(1)−O(1)−Cd(1)	128.3(13)	C(1′)−O(1′)−Cd(1)	135.3(14)

[a] Estimated standard deviations given in parentheses. [b] Symmetry-generated atoms designated by (XA). [c] Atoms labeled with primes are the other interpenetrating set of tetrahedrally arranged ligands about the cadmium center.

scheme. The solid-state structure of **8** consisted of two interpenetrating [CdO$_2$P$_2$] distorted tetrahedra 50% disordered about a common cadmium center. The structural parameters were quite similar and selected values are contained in Table 2. The average Cd−O bond length was found to be 2.043[10] Å and the average Cd−P bond length observed was 2.737[5] Å, with the latter being considerably longer than that determined for complex **1**. The O−Cd−O bond angle of 116.7(6) is less obtuse than that found in other tetrahedral cadmium phenoxide. As in the zinc analogue the O−Cd−P bond angles varied widely from 97.2(5)° to 123.9(4)°. Note that the structure of **8** greatly contrasts that of its THF adduct counterpart, Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(THF)$_2$, which is square planar.[6,34] This observation is supportive of the assertion that the latter structure is the result of a linear cadmium bis(phenoxide) species with weak THF interactions.[34] PMe$_3$ is expected to be a much stronger base than THF, leading to a tetrahedral structure. In the two cadmium structures the toluene solvate is almost perpendicular to the phenyl ring of the aryloxide, i.e., there is no π-stacking between the two aromatic systems.

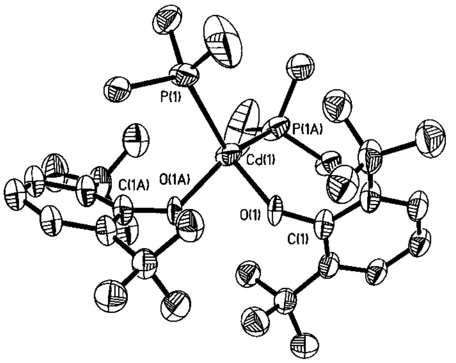

Figure 2. Thermal ellipsoid representation of Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$$\cdot$2PMe$_3$, complex **8**.

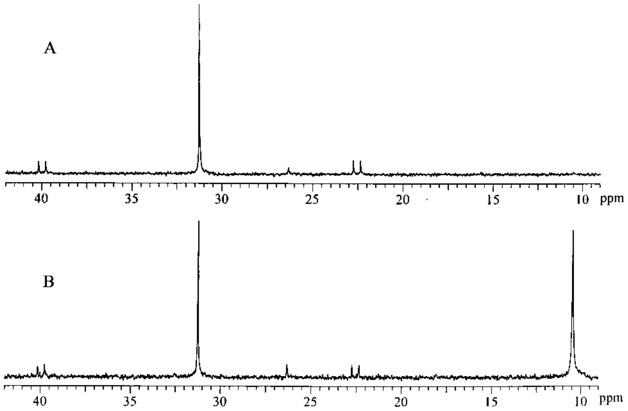

Figure 3. ^{31}P NMR spectra of complex **1**. (A) in C$_6$D$_6$. (B) In C$_6$D$_6$ with 1 equiv of added PCy$_3$.

NMR Spectroscopy. The ^{31}P NMR spectra of Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$ in C$_6$D$_6$ in the presence of 1 and 2 equiv of the sterically demanding phosphine, PCy$_3$ (cone angle (θ) = 170°),[35] are illustrated in Figure 3. There is a large downfield shift in the ^{31}P resonance of the bound vs free PCy$_3$ ligand, from 10.6 ppm for free to 31.3 ppm for bound. The ^{113}Cd−^{31}P coupling constant is also quite large at 2274 Hz. In contrast, in the zinc analogue the chemical shift for the bound PCy$_3$ ligand exhibits a much smaller *upfield* shift from that of free PCy$_3$ at 7.74 ppm.[4,5] Note that as was noted for the zinc derivative, the ^{31}P resonance in complex **1** does not shift upon addition of a second equivalent of PCy$_3$. Concomitantly, there is no change in the ^{113}Cd−^{31}P coupling constant. As depicted in Figure 3, upon addition of the second equivalent of PCy$_3$ an equally intense resonance is seen at 10.6 ppm which corresponds to that of free PCy$_3$. Similar observations were noted for analogous experiments carried out with the Cd(O-2,6-Ph$_2$C$_6$H$_3$)$_2$ complex (**2**), where the bound PCy$_3$ signal appeared at 29.8 ppm with a slightly smaller $J_{113\text{Cd}-31\text{P}}$ value of 2156 Hz. Attendantly, the ^{113}Cd NMR spectra of complexes **1** and **2** at 298 K in the presence of 1 equiv of PCy$_3$ both show well-defined doublets centered at 240 and 288 ppm, respectively, with coupling constants of the same magnitude as observed in the ^{31}P NMR spectra. As expected, there was no change in the ^{113}Cd NMR spectra upon addition of a second equivalent of PCy$_3$. On the other hand, the addition of 2 equiv of a small phosphine ligand (e.g., PMe$_3$) to Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$ or Cd(O-2,6-Ph$_2$C$_6$H$_3$)$_2$ results in a triplet in the ^{113}Cd NMR spectra (vide infra).

Hence, these NMR data indicate that the cadmium centers of these bulky phenoxide derivatives are incapable of binding two large phosphine ligands. Indeed, the X-ray structures of both M(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PCy$_3$) (M = Zn or Cd) derivatives indicate that the metal center is congested and can only accommodate the addition of a small fourth ligand (see Figure 4 for a space-filling model). Furthermore, the cadmium−

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(34) Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *J. Am. Chem. Soc.* **1990**, *112*, 6724.

(35) Colton, R.; Dakternieks, D. *Aust. J. Chem.* **1980**, *33*, 955.

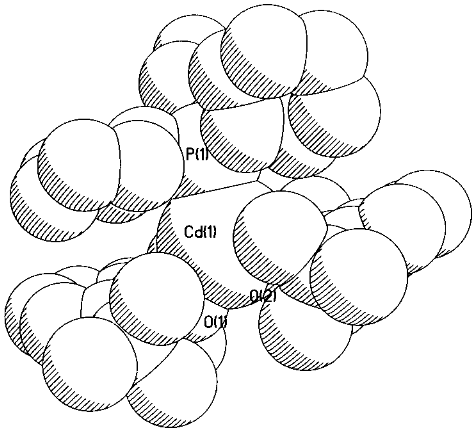

Figure 4. Space-filling model of complex **1**.

phosphine interaction is quite strong such as to make phosphine exchange via the required dissociative mechanism in this instance highly unfavorable. On the contrary, the zinc derivative was shown to undergo a facile exchange process with PMe_3, presumably by an associative mechanism.

Proceeding to the less sterically hindered phosphines, PMe_3 ($\theta = 118°$) and P^nBu_3 ($\theta = 132°$), the possibility exists for binding two phosphines at the cadmium center. In these instances a route exists for facile ligand exchange between the monophosphine derivative and free phosphine in solution via an associative process (eq 1). That is, rapid phosphine exchange can occur by way of a bis(phosphine) species which itself undergoes rapid phosphine dissociation. This is indeed what is noted when slightly more than 1 equiv of *n*-Bu_3P is added to a methylene chloride solution of Cd(O-2,6-$Ph_2C_6H_3)_2$.

$$\mathrm{Cd(phenoxide)_2(PR_3)} \overset{\mathrm{PR_3}}{\rightleftharpoons} \mathrm{Cd(phenoxide)_2(PR_3)_2} \qquad (1)$$

Figure 5 displays the ^{31}P NMR spectra of complex **5** in the presence of 1.05 equiv of *n*-Bu_3P as a function of temperature. Notably, there is a significant downfield shift of ~27 ppm of the ^{31}P chemical shift upon *n*-Bu_3P binding to cadmium in complex **5**. Furthermore, the ^{31}P resonance is broad with poorly resolved $^{113}Cd-P$ and $^{111}Cd-P$ coupling at ambient temperature. Upon lowering the temperature the phosphorus signal shifts further downfield and sharpens with the simultaneous appearance of a weak sharp signal due to the bis(phosphine) derivative (**6**) at ~ −15 ppm (vide infra). On the other hand, as indicated in the spectral overlay in Figure 5, Cd(O-2,6-$Ph_2C_6H_3)_2$ in the presence of a deficiency of *n*-Bu_3P exhibits a sharp ^{31}P resonance at −1.80 ppm at ambient temperature with $^{113}Cd-^{31}P$ and $^{111}Cd-^{31}P$ coupling constants of 2325 and 2222 Hz, respectively. There was only a small, upfield ^{31}P chemical shift upon lowering the temperature to −80 °C. Similar observations were noted for the bis-$^tBu_2$phenoxide cadmium mono-$^nBu_3P$ analogue, where the ^{31}P resonance occurred at −3.20 ppm at −80 °C with a $^{113}Cd-^{31}P$ coupling constant of 2434 Hz (see Table 3). The ^{113}Cd NMR spectrum of complex **5** (Figure 6) consists of a doublet centered at 325 ppm at −80 °C with a $J_{113Cd-31P}$ value of 2490 Hz, whereas the corresponding parameters in the 2,6-$^tBu_2$phenoxide analog (complex **3**) are 276 ppm and $J_{113Cd-31P} = 2434$ Hz.

The ^{31}P and ^{113}Cd NMR spectra of the monotrimethylphosphine derivative of Cd(O-2,6-$^tBu_2C_6H_3)_2$, complex **7**, are closely akin to those observed for its *n*-Bu_3P analogue. That is, the ^{31}P spectrum exhibits a single ^{31}P resonance significantly shifted downfield from that of free PMe_3 (−61.9 ppm in CH_2Cl_2) at −35.9 ppm. The ^{31}P signal remains sharp and undergoes only a small downfield chemical shift as the temperature is incremently lowered to −80 °C, where the value is −34.3 ppm (Table 3). The $^{113}Cd-^{31}P$ coupling constant increases slightly over this temperature range from 2325 to 2533 Hz. As expected, the ^{113}Cd NMR spectrum consists of a doublet at ambient temperature with a δ value of 247 ppm, which shifts downfield to 267 ppm upon lowering the temperature to −80 °C.

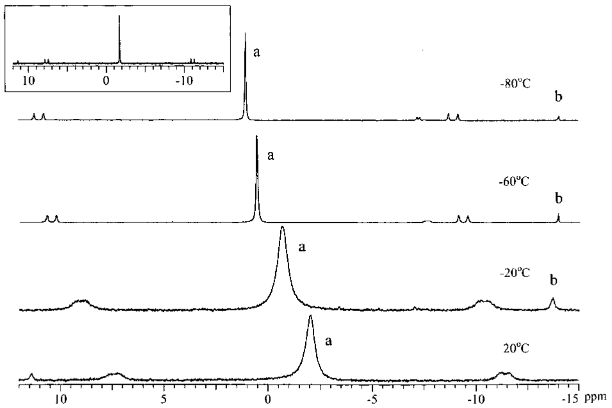

Figure 5. Temperature-dependent ^{31}P NMR spectra of Cd(O-2,6-$Ph_2C_6H_3)_2$·P^nBu_3 in the present of a slight amount of excess P^nBu_3. (a) ^{31}P resonance for mono-*n*-Bu_3P adduct. (b) ^{31}P resonance for bis-*n*-Bu_3P adduct. Overlay represents a ^{31}P NMR spectra of Cd(O-2,6-$Ph_2C_6H_3)_2$ in the presence of <1 equiv of *n*-Bu_3P at ambient temperature.

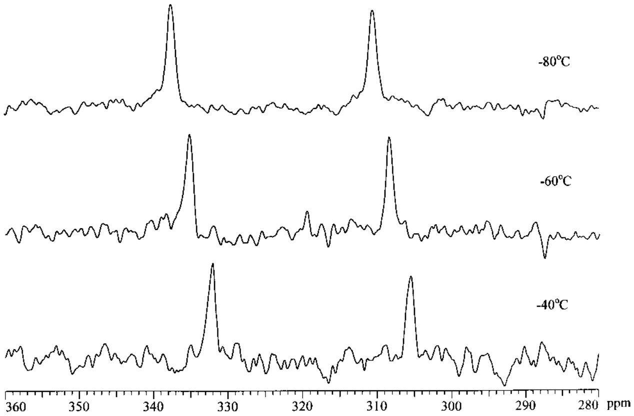

Figure 6. Temperature-dependent ^{113}Cd NMR spectra of Cd(O-2,6-$Ph_2C_6H_3)_2$·P^nBu_3.

Unlike what was observed for the voluminous PCy_3 ligand, notable changes in both the ^{31}P and ^{113}Cd NMR spectra from the corresponding spectra of the monophosphine derivatives occurred upon the addition of 2 equiv of the sterically less-encumbered phosphines, PMe_3 and P^nBu_3, to the cadmium bis(phenoxide) derivatives. Figures 7 and 8 illustrate representative ^{31}P and ^{113}Cd NMR spectra of these bis(phosphine) species, namely those of complex **6**, Cd(O-2,6-$Ph_2C_6H_3)_2(P^nBu_3)_2$ (see Table 4). As is readily apparent in Figure 7, at 0 °C the ^{31}P resonance of complex **6** is broad, with unresolved $^{113}Cd-^{31}P$ coupling. The ^1J(Cd−P) is not completely resolved until the temperature is lowered to −40 °C, at which time the ^{31}P resonance sharpens. Only a small upfield shift (~1 ppm) in the ^{31}P chemical shift is noted upon further lowering of the temperature to −80 °C. The ^{31}P resonance appeared at −14.7 ppm with a $J_{113Cd-31P}$ value of 1582 Hz. The ^{113}Cd NMR spectrum of complex **6** as depicted in Figure 8 consists of a 1:2:1 triplet centered at 392 ppm at −20 °C. This triplet became

Table 3. ^{31}P and ^{113}Cd NMR Data for Cd(2,6-di-^{t}Buphenoxide)$_2$L$_n$ Complexes in CD_2Cl_2 Solution[a]

L	n	T (°C)	^{31}P (ppm)	^{113}Cd (ppm)	^{31}P NMR[d] $^1J(^{113}\mathrm{Cd}-^{31}\mathrm{P})$[b]	^{113}Cd NMR $^1J(^{113}\mathrm{Cd}-^{31}\mathrm{P})$[b]
P(^{n}Bu)$_3$ complex **3**	1	20	−4.6 (br)	*c*	*c*	*c*
		0	−4.2 (br)	*c*	*c*	*c*
		−20	−4.4 (br)	262 (d)	*c*	2372
		−40	−3.5 (br)	267 (d)	*c*	2464
		−60	−3.3 (br)	273 (d)	*c*	2437
		−80	−3.2 (br)	276 (d)	2417	2434
P(^{n}Bu)$_3$ complex **4**	2	20	−10.3 (s)	*c*	*c*	*c*
		0	−10.3 (s)	*c*	*c*	*c*
		−20	−10.3 (s)	*c*	1628	*c*
		−40	−10.3 (s)	277 (br)	1638	*c*
		−60	−10.3 (s)	284 (t)	1648	1598
		−80	−10.3 (s)	290 (t)	1658	1604
P(Me)$_3$ complex **7**	1	20	−35.9 (s)	247 (d)	2325	2337
		0	−35.7 (s)	253 (d)	2356	2479
		−20	−35.4 (s)	258 (d)	2390	2459
		−40	−34.9 (s)	262 (d)	2452	2512
		−60	−34.6 (s)	263 (d)	2499	2542
		−80	−34.3 (s)	267 (d)	2533	2575
P(Me)$_3$ complex **8**	2	20	−40.6 (br)	*c*	*c*	*c*
		0	−40.2 (br)	*c*	*c*	*c*
		−20	−39.8 (s)	*c*	*c*	*c*
		−40	−39.4 (s)	*c*	1561	*c*
		−60	−39.1 (s)	352 (t)	1573	1602
		−80	−38.8 (s)	356 (t)	1583	1631

[a] 121.43 MHz ^{31}P{^{1}H} NMR data with chemical shifts (in ppm) relative to external 85% H_3PO_4 reference. 88.71 MHz ^{113}Cd{^{1}H} NMR data with chemical shifts (in ppm) relative to external 0.1 M $Cd(ClO_4)_2$ reference, (br), broad; (s), singlet; (d), doublet; (t), triplet. [b] Coupling constants are in Hz. [c] The spectrum is too noisy to determine chemical shifts or coupling constants. [d] In all ^{31}P NMR spectra, ^{113}Cd−^{31}P and ^{111}Cd−^{31}P coupling were seen. The larger J value was assigned to $^1J_{^{113}\mathrm{Cd}-^{31}\mathrm{P}}$.[35]

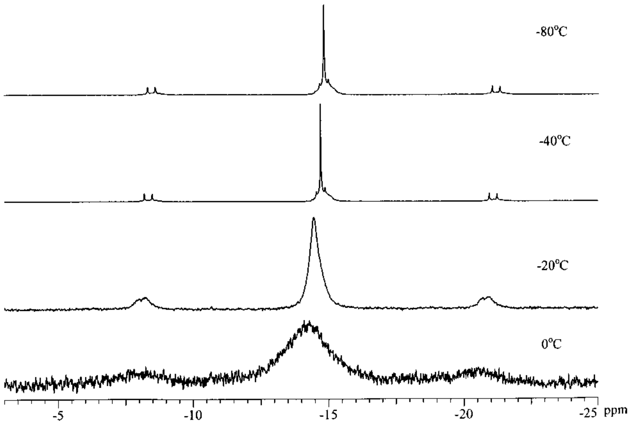

Figure 7. Temperature-dependent ^{31}P NMR spectra of Cd(O-2,6-$Ph_2C_6H_3)_2$·2P^{n}Bu$_3$.

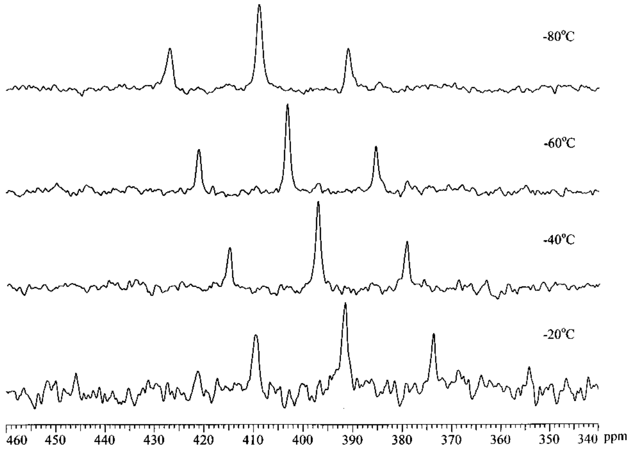

Figure 8. Temperature-dependent ^{113}Cd NMR spectra of Cd(O-2,6-$Ph_2C_6H_3)_2$·2P^{n}Bu$_3$.

more resolved and shifted downfield to 409 ppm as the temperature was lowered to −80 °C.

A comparison of the data in Tables 3 and 4 for the mono- and bis(phosphine) derivatives of Cd(O-2,6-$Ph_2C_6H_3)_2$ reveals that the ^{31}P resonance shifts upfield (toward that for *free* P^{n}Bu$_3$) proceeding from the mono- to bis(phosphine) adducts (i.e., from 1.0 ppm to −14.0 ppm at −80 °C) with a corresponding decrease in the ^1J(Cd−P) values by about 900 Hz. This upfield shift and decreased coupling constant upon binding a second phosphine ligand is expected as the coordination number of the cadmium center is increased from three to four. The broadness of the signals and the unresolved coupling in both the ^{31}P and ^{113}Cd NMR spectra at higher temperatures (between −20 and 20 °C) is indicative of rapid phosphine exchange via eq 1 (vide supra). However, in the presence of 2 equiv of phosphine the equilibrium, as defined in eq 1, lies far to the right (in favor of the bis(phosphine) derivative) because the ^{31}P NMR chemical shift is not significantly changed as the temperature is lowered. Concomitantly, the ^{113}Cd NMR spectra exhibit a well-defined triplet as the temperature is lowered with little shifting of the ^{113}Cd resonance.

The ^{31}P NMR chemical shifts and J(Cd−P) parameters listed in Table 3 for complex **4**, Cd(O-2,6-^{t}Bu$_2C_6H_3)_2$(P^{n}Bu$_3)_2$, suggest that the P^{n}Bu$_3$ ligands bind more strongly to the cadmium center in this instance than in complex **6**, Cd(O-2,6-$Ph_2C_6H_3)_2$(P^{n}Bu$_3)_2$. That is, the ^{31}P signal is shifted less upfield at −10.3 ppm at ambient temperature and does not change position as the temperature is lowered. This appears to be contradictory to the assumption that the more electron withdrawing phenyl substituents in complex **6** should result in the cadmium binding the phosphine ligands more strongly. Hence, this phenomenon is again ascribed to steric effects being less significant in the case of the symmetrical *tert*-butyl substituents. On the other hand, this steric argument should be of less importance for the more compact PMe_3 ligand. Indeed, from the data in Tables 3 and 4 only modest differences in chemical shifts and ^1J(Cd−P) values were observed in the corresponding complexes **8** and **10**.

Table 4. ^{31}P and ^{113}Cd NMR Data for Cd(2,6-di-phenylphenoxide)$_2$L$_n$ Complexes in CD_2Cl_2 Solution[a]

L	*n*	*T* (°C)	^{31}P (ppm)	^{113}Cd (ppm)	^{31}P NMR[d] $^1J(^{113}\mathrm{Cd}-^{31}\mathrm{P})$[b]	^{113}Cd NMR $^1J(^{113}\mathrm{Cd}-^{31}\mathrm{P})$[b]
P(^{n}Bu)$_3$ complex **5**	1	20	−2.1 (s)	*c*	*c*	*c*
		0	−1.4 (s)	*c*	*c*	*c*
		−20	−0.7 (s)	317 (d)	*c*	2396
		−40	−0.0 (s)	319 (d)	2430	2448
		−60	0.5 (s)	322 (d)	2457	2468
		−80	1.0 (s)	325 (d)	2476	2491
P(^{n}Bu)$_3$ complex **6**	2	20	*c*	*c*	*c*	*c*
		0	−13.9 (br)	384 (br)	*c*	*c*
		−20	−14.3 (s)	392 (t)	1572	1584
		−40	−14.4 (s)	397 (t)	1579	1585
		−60	−14.6 (s)	403 (t)	1581	1586
		−80	−14.7 (s)	409 (t)	1582	1594
P(Me)$_3$[e] complex **9**	1	–	–	–	–	–
P(Me)$_3$ complex **10**	2	20	−39.6 (br)	*c*	*c*	*c*
		0	−38.9 (br)	*c*	*c*	*c*
		−20	−38.7 (br)	*c*	*c*	*c*
		−40	−38.5 (s)	*c*	*c*	*c*
		−60	−37.9 (s)	393 (t)	1552	1568
		−80	−37.4 (s)	394 (t)	1560	1584

[a] 121.43 MHz ^{31}P{^{1}H} NMR data with chemical shifts (in ppm) relative to external 85% H_3PO_4 reference. 88.71 MHz ^{113}Cd{^{1}H} NMR data with chemical shifts (in ppm) relative to external 0.1 M Cd(ClO$_4$)$_2$ reference, (br), broad; (s), singlet; (d), doublet; (t), triplet. [b] Coupling constants are in Hz. [c] The spectrum is too noisy to determine peaks or coupling constants. [d] In all ^{31}P NMR spectra, ^{113}Cd−^{31}P and ^{111}Cd−^{31}P coupling were seen. The larger *J* value was assigned to $^1J_{^{113}\mathrm{Cd}-^{31}\mathrm{P}}$.[35] [e] The ^{31}P and ^{113}Cd NMR data for this compound are discussed within the text due to their complexity.

Conclusions

We described the synthesis of monomeric phosphine derivatives of cadmium bis(phenoxides), along with their solution and solid-state structures. In general these cadmium derivatives mimic their zinc analogues, where the large basic phosphine Cy$_3$P forms a mono-adduct and the sterically less-demanding basic phosphines, Me$_3$P and *n*-Bu$_3$P, form both mono- and bis(phosphine) derivatives. Interestingly, upon replacing the weakly coordinating bases (THF, tetrahydrothiophene, and propylene carbonate) in the (2,6-di-*tert*-butylphenoxide)$_2$Cd(base)$_2$ derivatives (which have been structurally characterized to be square-planar[6,34]) with PMe$_3$ results in the formation of a distorted tetrahedral structure. As might be anticipated, the Cd−P bond in Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PCy$_3$) was found to be stronger than the corresponding Zn−P bond in Zn(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PCy$_3$) as indicated by a Cd−P bond distance of 2.5247(12) Å which is only 0.09 Å longer than the Zn−P bond length. This is consistent with our previous findings of a thermodynamic preference of 2.5 times for PCy$_3$ binding to cadmium vs zinc in competition studies.[4]

Although the ionic radius of cadmium(II) in four-coordinate derivatives is 0.18 Å longer than the similar value in zinc(II) derivatives, there is no tendency for the Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(PCy$_3$) to undergo a facile exchange process with free PCy$_3$ via a four-coordinate intermediate. On the other hand, the smaller phosphine ligands, PMe$_3$ and *n*-Bu$_3$P in Cd bis(phenoxide)L derivatives (L = PMe$_3$ and *n*-Bu$_3$P) readily undergo rapid self-exchange in solution by way of a Cd(bisphenoxide)L$_2$ species. That is, phosphine exchange on Cd(OAr)$_2$L via an associative mechanism is fast, whereas exchange via a dissociative process is quite slow on the NMR time scale investigated.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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