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Tricyclohexylphosphine Derivatives of Bis(2,6-difluorophenoxide)cadmium: A Solution and Solid-State NMR Study

Donald J. Darensbourg,* Jacob R. Wildeson,
Jason C. Yarbrough, and Robert E. Taylor

Department of Chemistry, Texas A&M University,
P.O. Box 30012, College Station, Texas 77842

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Introduction

Recently, we have been interested in exploring the solution and solid-state structural chemistry associated with phosphine derivatives of bisphenoxide complexes of zinc and cadmium. The initial impetus for investigating this chemistry was based on our use of bisphenoxides of zinc as catalysts for the polymerization of CO_2 and cyclohexene oxide to provide poly(cyclohexenylene carbonate).[1,2] In the meantime, it has become apparent that the coordination chemistry of the group 12 metals, zinc and cadmium, is intrinsically worthy of detailed study.[3−6] It is of particular interest to compare and contrast the coordination chemistry of these metals since cadmium, because of its NMR-active nuclei (^{113}Cd and ^{111}Cd), is routinely used as a structural probe of zinc in enzymes and proteins.[7,8]

Previous investigations have illustrated significant differences in the coordination chemistry of the bisphenoxides of zinc and cadmium, with the latter metal derivatives being structurally more diverse. For example, $Zn(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2L_2$ (L = tetrahydrofuran (THF) or propylene carbonate) complexes are distorted tetrahedral in the solid-state, whereas their cadmium analogues are square planar.[2−4,9] Pertinent to a discussion of phosphine derivatives, the larger size of cadmium accounts for the observation that although phosphine complexes of $Zn(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ and $Zn(O\text{-}2,6\text{-}Ph_2C_6H_3)_2$ are trigonal planar in structure for basic phosphine ligands spanning a range of steric requirements,[5,10] cadmium analogues afford both trigonal planar monophosphine complexes for the sterically encumbering PCy_3 ligand and tetrahedral bisphosphine complexes for smaller phosphines such as PMe_3.[6] Our most recent efforts in this area have noted that bisphenoxides with small substituents in the 2,6-positions, such as halogens, provide dimeric metal species that have the capacity for binding only one tricyclohexylphosphine ligand, that is, $[M(O\text{-}2,6\text{-}F_2C_6H_3)_2(\mu\text{-}O\text{-}2,6\text{-}F_2C_6H_3)PCy_3]_2$ (M = Zn or Cd) (**1**).[11] Although the dimeric zinc derivative is unreactive toward added PCy_3, its cadmium analogue (**1**) readily adds a second equivalent of PCy_3 to afford the monomeric complex, $Cd(O\text{-}2,6\text{-}F_2C_6H_3)_2(PCy_3)_2$ (**2**). Herein, we wish to report the isolation and solid-state structure of **2**, along with its solution and solid-state ^{113}Cd and ^{31}P NMR spectra.

Experimental Section

Methods and Materials. Unless otherwise specified, all syntheses and manipulations were carried out on a double manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. Glassware was flamed out thoroughly prior to use. Solvents were freshly distilled from sodium benzophenone before use. Tricyclohexylphosphine and 2,6-difluorophenol were purchased from Aldrich Chemical Co. and were sublimed and stored in a glovebox prior to use. $Cd[N(SiMe_3)_2]_2$ was prepared according to published literature,[12] stored in the glovebox, and used immediately after removal from the box. Infrared spectra were recorded on a Mattson 6081 spectrometer with DTGS and mercury cadmium telluride (MCT) detectors. All isotopically labeled solvents for NMR experiments were purchased from Cambridge Isotope Laboratories. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-200E, Unity +300 MHz, and VXR 300 MHz superconducting high-resolution spectrometers. ^{19}F and ^{31}P data were acquired on a Unity +300 MHz superconducting NMR spectrometer operating at 282 and 121 MHz, respectively. All ^{19}F NMR data are referenced to 10% $CFCl_3$ and 1% $CClH_2CClF_2$ in acetone-d_6, whereas all ^{31}P NMR data are referenced to H_3PO_4 (85% in D_2O). Solution-state ^{113}Cd spectra were recorded on a Varian XL-400 superconducting high-resolution spectrometer operating at 88 MHz using an external 0.1 M $Cd(ClO_4)_2/D_2O$ reference. Elemental analyses were carried out by Galbraith Laboratories Inc.

Note! Cadmium compounds and their wastes are extremely toxic and must be handled carefully. Cadmium waste products should be stored in a separate, clearly marked container.

Synthesis of Cadmium(2,6-difluorophenoxide)$_2$(PCy$_3$)$_2$, (2). A 10-mL THF solution of 2,6-difluorophenol (0.120 g, 0.92 mmol) and PCy_3 (0.260 g, 0.92 mmol) was added concurrently to a 5-mL THF solution of $Cd[N(SiMe_3)_2]_2$ (0.20 g, 0.46 mmol), leading to a clear solution that was stirred at room temperature for 2 h. The solution was then concentrated to approximately 5 mL and placed in a freezer at −20 °C. Colorless block crystals formed after several days. The supernate was transferred off by cannula, and the crystals were dried under vacuum to yield 0.183 g of product (76%). Anal. Calcd for $C_{48}H_{72}O_2F_4P_2Cd$: C, 61.89; H, 7.81. Found: C, 60.50; H, 7.16. The disagreement between calculated and observed C/H analysis is due to the presence of a slight impurity of the dimeric monophosphine derivative. ^{1}H NMR (C_6D_6): δ 0.97−2.25 (m, 66H, PC_6H_{11}), 6.18 (m, 2H, 4-H), 6.73 (t, 4H, [3,5-H]). ^{13}C {H} NMR (C_5D_5N): δ 27.26−32.65 (PC_6H_{11}), 108.86 (t, [4-C_6H_3]), 111.94 (m, [3,5-C_6H_3]), 148.16 (t, J_{C-F} = 15.6 Hz, [ipso-C_6H_3]), 157.83 (dd, J_{C-F1} = 235.45 Hz, J_{C-F2} = 11.07 Hz, [2,6-C_6H_3]). ^{19}F {H} NMR(C_6D_6): δ −134.74.

Solid-State ^{113}Cd NMR. The solid-state NMR spectra were acquired utilizing a Bruker MSL 300 superconducting spectrometer with a magnet operating at 7.05 T (Larmor frequency of 66.546 MHz for ^{113}Cd). The samples were ground and packed into zirconium oxide rotors with Kel-F end caps for use in a 7-mm magic-angle spinning probe from Bruker. Spinning speeds were regulated by a Bruker spin-rate controller. All chemical shifts and tensor elements are referenced to an external sample of 0.1 M $Cd(ClO_4)_2$ in D_2O solution at 25 °C with positive shifts denoting movement of resonances to lower shielding.

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10.1021/ic010104q CCC: $20.00

Table 1. Crystallographic Data for **2**

empirical formula	$C_{48}H_{72}F_4O_2P_2Cd$
fw	931.4
cryst syst	monoclinic
space group	$C2/c$
V, Å^3	4509.4(7)
Z	4
a, Å	28.232(3)
b, Å	10.1021(9)
c, Å	20.5468(8)
β, deg	129.6890(10)
T, K	110(2)
d(calcd), g/cm^3	1.372
abs coeff, mm^{-1}	0.609
R, %^{a}	7.37
R_w, %^{a}	17.51

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

$Cd(NO_3)_2 \cdot 4H_2O$ was used as a secondary standard relative to the cadmium perchlorate solution in D_2O to account for the cross-polarization with proton decoupling. The recycle delay used was 15 s with a 1H $\pi/2$ pulse width of 5.25 μs and a contact time of 15 ms for all samples. Principle elements of the shielding tensor were extracted utilizing the WINFIT software package from Bruker Instruments running on an Adosea Pentium personal computer.

X-ray Crystallography. A Bausch and Lomb 10× microscope was used to identify a suitable colorless crystal of **2** from a representative sample of crystals of the same habit. The representative crystal was coated in a cryogenic protectant (i.e., mineral oil and apezeon grease) and was then fixed to a glass fiber, which in turn was fashioned to a copper mounting pin. The mounted crystals were then placed in a cold nitrogen stream (Oxford) maintained at 110 K on a Bruker SMART 1000 three circle goniometer.

Crystal data and details of data collection for the complexes are provided in Table 1. The X-ray data were collected on a Bruker CCD diffractometer and 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.[13]

The structure was solved by direct methods. **2** crystallizes with disorder with respect to the phenolic ligands. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded R(F) and wR(F^2) values at convergence, as indicated in Table 1. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed 1.2 or 1.5× the value of the attached atom. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography, Vol. C.

For the title compound, data reduction, SAINTPLUS (Bruker);[14] program(s) used to solve the structure, SHELXS-86 (Sheldrick);[15] program(s) used to refine the structure, SHELXL-97 (Sheldrick);[16] program(s) used for molecular graphics, SHELXTL version 5.0 (Bruker);[17] software used to prepare material for publication, SHELXTL version 5.0 (Bruker).[17]

Results and Discussion

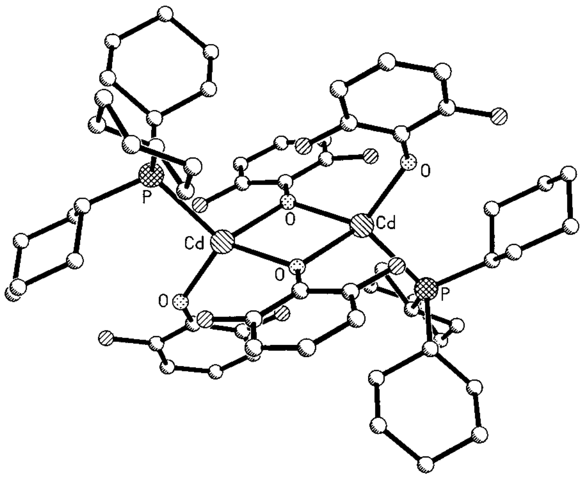
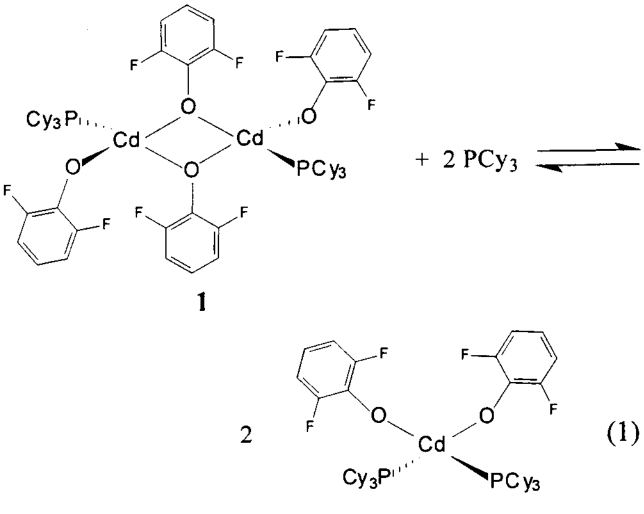


Figure 1. Ball-and-stick representation of **1**.

The reaction of $Cd[N(SiMe_3)_2]_2$ with 2 equiv of 2,6-difluorophenol in the presence of 1 equiv of PCy_3 has been shown to provide the dimer **1**.[11] **1** has been structurally characterized in the solid state by X-ray crystallography (ball-and-stick representation shown in Figure 1) and by cross-polarization/magic-angle spinning(CP/MAS) ^{113}Cd NMR spectroscopy. During the characterization of **1** in solution via ^{113}Cd and ^{31}P NMR spectroscopy, it was noted that spectra of the complex were very dependent on the presence of slight excesses of PCy_3, with a concomitant dependence on temperature in these instances. That is, ^{31}P and ^{113}Cd NMR spectra of **1** in a THF solution with less than 0.1 equiv of PCy_3 revealed the presence of two metal species in solution, both exhibiting ^{113}Cd$-^{31}$P coupling at low temperature. After 6 equiv of PCy_3 was added to **1**, the ^{31}P NMR spectrum at ambient temperature displayed two broad signals at ~30 and ~10 ppm, which correspond roughly to the positions of **1** and free PCy_3, respectively. Similarly, the ^{113}Cd NMR spectrum exhibited two broad resonances centered at ~220 and ~360 ppm at ambient temperature. As the temperature was lowered to −80 °C, both spectra were simplified, the ^{31}P NMR to a resonance at 22.4 ppm ($J_{^{111}Cd-P} = 1590$ Hz and $J_{^{113}Cd-P} = 1665$ Hz) and the ^{113}Cd NMR to a triplet at 395.1 ppm ($J_{^{113}Cd-P} = 1678$ Hz), see Figure 2. This behavior was ascribed to the equilibrium reaction depicted in eq 1, which is shifted to the right upon lowering the temperature.



1

2

(1)

We have synthesized **2** directly in an isolated yield of 76% by the reaction of $Cd[N(SiMe_3)_2]_2$ with 2 equiv each of 2,6-

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(13) *SMART 1000 CCD*; Bruker Analytical X-ray Systems: Madison, WI, 1999.

(14) *SAINT-Plus*, version 6.02; Bruker: Madison, WI, 1999.

(15) Sheldrick, G. *SHELXS-86*: *Program for Crystal Structure Solution*; Institut fur Anorganische Chemie der Universitat: Gottingen, Germany, 1986.

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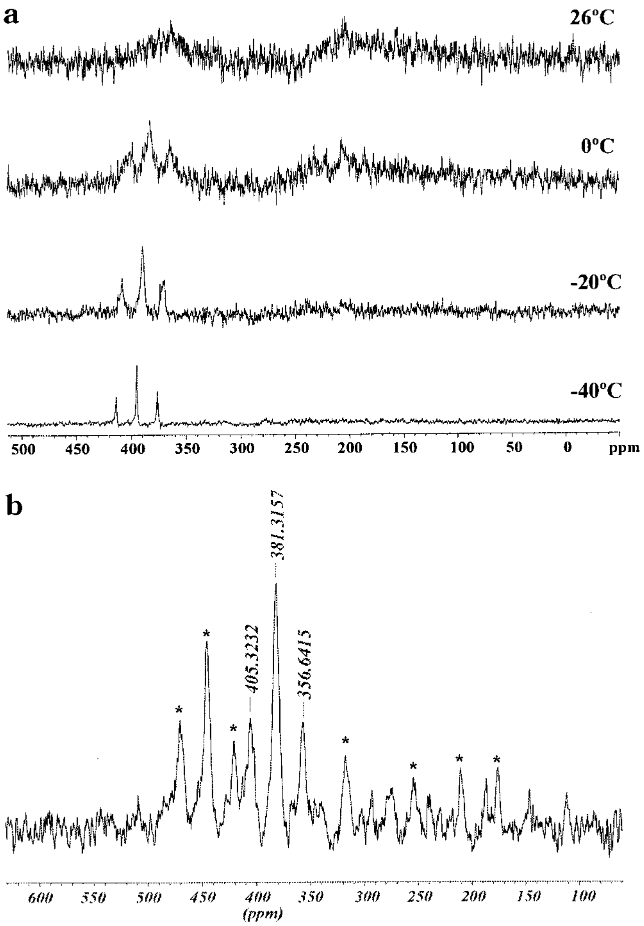

Figure 2. (a) Temperature-dependent ^{113}Cd NMR spectra of **1** in the presence of 6 equiv of PCy_3 in THF solution. (b) CP/MAS solid-state ^{113}Cd NMR spectrum of **2**. Peaks marked by asterisks are spinning sidebands.

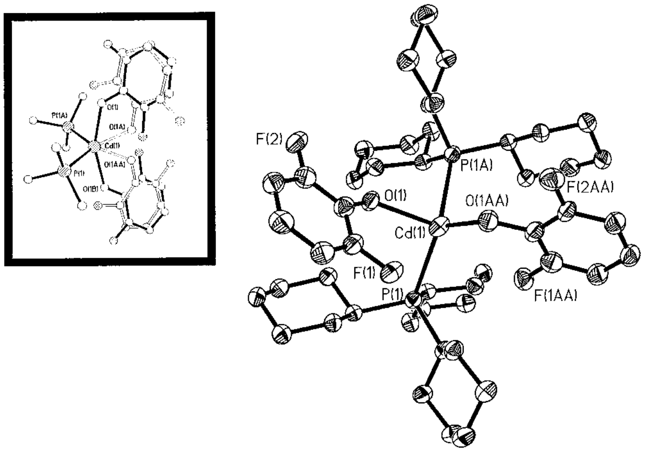

Figure 3. Thermal ellipsoid representation of **2**. Disorder observed in phenoxide ligands illustrated in ball-and-stick drawing in insert.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **2**^{a,b}

Cd(1)−O(1)	2.249(7)
Cd(1)−P(1)	2.6484(14)
O(1)−C(1)	1.329(11)
O(1)−Cd(1)−O(1AA)	108.3(3)
O(1)−Cd(1)−P(1)	99.60(19)
P(1)−Cd(1)−P(1A)	119.79(6)
O(1)−Cd(1)−P(1A)	91.3(2)
O1AA-Cd(1)−P(1A)	103.7(2)
Cd(1)−O(1)−C(1)	133.0(6)

[a] Estimated standard derivatives are given in parentheses. [b] Symmetry-generated atoms designated as (*n*A).

Figure 4. Space-filling model of **2**.

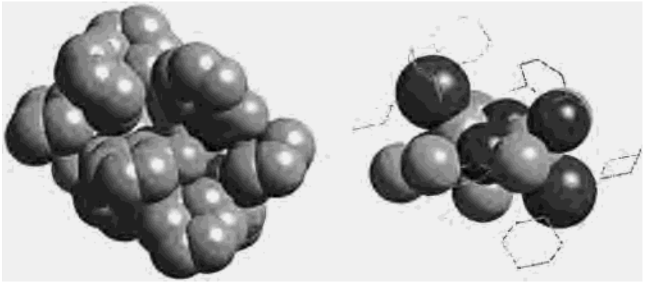

Figure 5. Space-filling model of **1**.

difluorophenol and PCy_3 in THF solution. X-ray quality crystals of **2** were obtained after the reaction solution was concentrated and subsequently cooled to −20 °C. **2** crystallizes as a distorted tetrahedron that is disordered in the unit cell with regard to the phenoxide ligands. Figure 3 contains a thermal ellipsoid representation of **2**, along with a partial atomic numbering scheme. Table 2 contains a selected listing of bond distances and bond angles. The Cd−P distance of 2.6484(14) Å observed in the bistricyclohexylphosphine derivative (**2**) is, as expected, longer than that found in the trigonal monoPCy_3 complex containing sterically bulky phenoxides, $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2\text{-}PCy_3$,[6] and the dimer **1**,[11] where Cd−P distances of 2.5274(12) and 2.5426(10) Å were observed, respectively. Similarly, the Cd−O distance of 2.249(7) Å noted in **2** is somewhat longer to that seen for the Cd−O (terminal phenoxide) bond length in **1** of 2.124(2) Å. The shortest Cd···F nonbonding distance in **2** was determined to be that involving Cd(1)···F(1) of 3.043 Å.

The CP/MAS solid-state ^{113}Cd NMR spectrum of **1** has previously been reported to consist of a doublet with an isotropic shift of 252.6 ppm with $J_{^{113}Cd-P} = 2297$ Hz.[11] Correspondingly, the ^{113}Cd NMR spectrum of **1** in THF solution is consistent with the solid-state spectrum, exhibiting a doublet with a chemical shift of 232.2 ppm with $J_{^{113}Cd-P} = 2480$ Hz at −80 °C. Similarly, the solution ^{113}Cd NMR spectrum of **2** in THF at −40 °C ($\delta = 395.1$ ppm and $J_{^{113}Cd-P} = 1678$ Hz, see Figure 2) correlates with that obtained in the solid state. That is, the solid-state ^{113}Cd NMR spectrum of **2** displays a triplet ($J_{^{113}Cd-P} = 1653$ Hz) with an isotropic shift (σ_{iso}) of 381.5 ppm (see insert in Figure 3). Hence, the solid-state ^{113}Cd NMR observations on **1** and **2** confirm that the facile equilibrium process noted in solution can be ascribed to the reaction depicted in eq 1. Furthermore, the ^{31}P NMR spectra in solution ($\delta = 22.4$ at -80 °C) and in the solid state ($\sigma_{\text{iso}} = 21.3$ ppm) of **2** are consistent with this affirmation.[18]

Interestingly, as would be anticipated on the basis of the ambient temperature ^{113}Cd NMR spectrum illustrated in Figure 2, after a pure sample of **2** was dissolved in THF, the ^{113}Cd NMR spectrum revealed that the principal species in solution at ambient temperature is **1**, with **2** being favored as the temperature is lowered. Indeed, the equilibrium is completely shifted in the direction of **2** at -80 °C. This in turn requires the enthalpy and entropy changes associated with eq 1 to be of the same sign, most likely both being negative. By way of contrast, because of the steric requirements of two very bulky PCy_3 ligands and the greater propensity of cadmium vs zinc for phosphine ligands, the zinc analogue complex of **1** is observed in the presence of excess PCy_3 to be stable relative to the bisphosphine monometallic complex. Certainly, this steric crowding in the latter complex is amply demonstrated in the space-filling model of **2** (see Figure 4). Furthermore, upon close scrutiny of the space-filling model of **1**, it would appear that the mechanism for formation of **2** from **1** and PCy_3 must be dissociative in nature, for there is little space for an attack at the metal center of PCy_3 at the intact dimer (see Figure 5).

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Supporting Information Available: Complete details in CIF format of the X-ray diffraction study of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Because the solution state ^{113}Cd and ^{31}P NMR spectra of **1** and its monomer THF adduct, $Cd(O\text{-}2,6\text{-}F_2C_6H_3)_2(PCy_3)(THF)$, may be similar, we cannot completely rule out that the chemical species involved in the equilibrium described in eq 1 are not the monomeric THF adduct and the bisphosphine complex. Studies in progress on the chloro analogue of **1**, where Cd···F spin−spin coupling cannot obscure the ^{113}Cd−^{111}Cd coupling (90−120 Hz) normally seen in dimeric phenoxide complexes, should definitely resolve this issue.