Inorg. Chem. **1998,** *37,* 1099−1104

Heterocubane Phosphoraniminato Complexes of Cadmium

Klaus Harms, Jan Merle, Cäcilia Maichle-Mössmer,† Werner Massa, and Matthias Krieger*

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse,
D-35032 Marburg, Germany

Received August 14, 1997

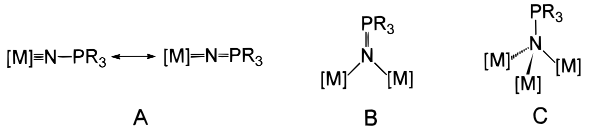
Phosphoraniminato complexes of cadmium $[CdX(NPEt_3)]_4$ {X = Cl (**1**), Br (**2**), I (**3**), $[CdI(NPMe_3)]_4$ (**4**)} are formed by the reaction of cadmium dihalides with silylated phosphoranimines Me_3SiNPR_3 (R = Me, Et) in the presence of a fluoride source, e.g. NaF, at elevated temperatures. High yields can be achieved when R = Et and X is a heavy halogen. The exocyclic bromo function in complex **2** can be replaced by reaction with organolithium reagents to give organocadmium compounds $[CdMe(NPEt_3)]_4$ (**5**) and $[Cd(C_2SiMe_3)(NPEt_3)]_4$ (**6**) in excellent yields. Complexes **1**−**6** consist of a $[Cd_4N_4]$ heterocubane core in which the cadmium atoms are linked by μ_3-N bridges of the phosphoraniminato ligand with the cubane angles being close to 90°. The crystal structure of an unsymmetrical cubane $[Cd_4I_4(OSiMe_3)(NPEt_3)_3]$ (**7**) is reported, in which one of the phosphoraniminato moieties has been replaced by a silyloxy function. All complexes are colorless oxygen- and moisture-sensitive crystalline materials, the heterocubane structure of which has been shown by crystal structure determinations and is consistent with spectroscopic findings, including IR, NMR, and mass spectra.

Introduction

The negatively charged phosphoraniminato ligand (NPR_3^-) is isoelectronic with, *inter alia*, $OSiR_3^-$ groups and neutral phosphorane oxides OPR_3. But unlike these, the (NPR_3^-) ligand is capable of a rich coordination chemistry comprising terminal (type A), μ_2-bridging (type B), or μ_3-bridging (type C) bonding modes, Chart 1.

Two factors affect which bonding mode is chosen.[1] First, the nature of the organic substituents at the phosphorus atom and secondly, the oxidation number (ON) of the metal complexed by (NPR_3^-). Electron-rich transition metals of the 3d series with ON = II have been shown to form tetrameric complexes with heterocubane structure (type C) if R is a sterically nondemanding alkyl group.[2] On the other hand, in (NPR_3^-) complexes of electron-poor 4d-metals in their highest oxidation states {e.g. Zr(IV),[3] Nb(V),[4] Mo(VI)[5]} both terminal (A) and μ_2-bridging (B) modes of the ligand have recently been described.

Chart 1. Bonding Modes of the Phosphoraniminato Ligand



$[Cd_4O_4]$ heterocubanes including Cd alkoxides,[6] phenolates,[7] or hydroxide[8] are well-known, but structural information on cadmium heterocubanes with nonmetal moieties other than oxygen is scarce.[9] In particular, crystal structures of complexes with a $[Cd_4N_4]$ core have, to our knowledge, not yet been reported. Formation of organometallic derivatives $[MR'(NPR_3)]_4$ (M = Zn, Cd; R = R′ = Me, Et) by reaction of the metal dialkyls with $HNPR_3$ has been reported by Schmidbaur and Jonas.[10] The tetrameric nature of the compounds was derived from molecular mass determinations and powder diffraction, which we can confirm. Except for these early attempts, we know of no reports of cadmium phosphoraniminor phosphoraniminato complexes. In connection with our current studies of phosphoraniminato complexes of electron-

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* Author to whom correspondence should be adressed. E-mail: krieger@ps1515.chemie.uni-marburg.de.

† Institut für Anorganische Chemie der Universität Tübingen, D-72076 Tübingen, Germany.

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S0020-1669(97)01036-7 CCC: $15.00

rich 3d metals, we considered it of interest to attempt the synthesis of halogeno cubanes of 4d metals and organometallic derivatization thereof.

Experimental Section

General Procedures. All manipulations were performed in flame-dried glassware under an argon (4.8 grade) atmosphere using Schlenk techniques. Solvents were dried and distilled under argon prior to use according to standard techniques. Commercially available $CdCl_2$ and $CdBr_2$ were dried by refluxing with the corresponding thionyl halide (Fluka) for 8 h, filtration and evacuation at high vacuum. CdI_2 was heated to 140 °C at high vacuum for 4 h prior to use. Silylated phosphoranimines Me_3SiNPR_3 were prepared according to literature procedures by Staudinger reactions of the corresponding PR_3 with Me_3SiN_3 (Merck).[11] MeLi (Merck) and bis(trimethylsilyl)ethyne (Aldrich) were used as received.

Physical Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer (using the deuterated solvent as internal lock, δ relative to TMS), ^{31}P on a Bruker AM 400 (85% H_3PO_4 as external standard), and ^{29}Si on a Bruker AMX 500 (TMS as external standard). Chemical shifts are reported in parts per million, positive chemical shifts lying downfield of the standard. IR spectra were recorded as Nujol mulls on a Bruker IFS-88 FT, using CsI and polyethylene plates. Assignment of IR bands was made on the basis of comparative literature data.[1−5,10,12] Mass spectra were recorded on either Varian MAT CH 7 or Varian MAT 711 by electron impact at 70 eV.

X-ray Crystallography. Crystal, data collection, and refinement parameters are given in Table 2. A colorless block-shaped crystal of **1** and yellowish equant crystals of **2** and **7** were mounted on an Enraf-Nonius CAD4 diffractometer; a colorless needle of **3** was mounted on a STOE IPDS area detector, and a colorless block-shaped crystal of **4** was mounted on a Siemens P4 diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda = 71.073$ pm) was used throughout. Data reduction included Lorentz and polarization corrections. The structures were solved by direct and difference Fourier methods using SHELXS-96[13] and SIR92[14] packages. Refinement to convergence was carried out by the least-squares method minimizing $\sum w(F_o - F_c)^2$ for all observed reflections using SHELXL-93, SHELXL-96, and SHELXL-97 programs.[15] In all complexes, ethyl groups of the ($NPEt_3^-$) ligands are disordered, as are the (trimethylsilyl)ethynyl ligands in complex **7**. The hydrogen atoms were placed at calculated positions with isotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters.

[CdCl(NPEt₃)]₄ (1). A mixture of 5.51 g of $CdCl_2$ (30.0 mmol), 3.57 g of NaF (85.0 mmol), and 13.5 mL of $Me_3SiNPEt_3$ (61.4 mmol) was heated at 210 °C for 4 h. Excess *N*-(trimethylsilyl)triethylphosphoranimine was then condensed from the mixture. The remaining white solid residue was extracted three times with 25 mL portions of CH_2Cl_2, using an ultrasonic bath. Evaporation of the solvent to dryness and washing the remaining material with 15 mL of CH_3CN gave 5.40 g of **1** (4.8 mmol, 64% yield). **1** is easily soluble in CH_2Cl_2 and THF and sparingly soluble in benzene and toluene. Crystals suitable for X-ray diffraction were grown by cooling a saturated CH_2Cl_2 solution to 4 °C. Anal. Calcd for $C_{24}H_{60}N_4P_4Cl_4Cd_4$ (1120.11 g/mol): C, 25.74; H, 5.40; N, 5.00. Found: C, 25.74; H, 5.35: N, 5.05. ^1H NMR (CD_2Cl_2): δ 1.09 (dt, $J = 7.8$, 16.2 Hz, 3H, ($C\underline{H}_3CH_2)_3P$), 2.04 (dq, $J = 7.8$, 11.9 Hz, 2H, ($CH_3C\underline{H}_2)_3P$). ^{13}C NMR (CD_2Cl_2): δ 7.35 (d, $^2J_{P-C} = 4.4$ Hz, ($\underline{C}H_3CH_2)_3P$), 23.22 (d, $^1J_{P-C} = 59.3$ Hz, ($CH_3\underline{C}H_2)_3P$). ^{31}P NMR (CD_2Cl_2): δ 44.4 (Et_3PN). IR (cm^{-1}): 1270 w, 1048 vs, 985 m, 775 m, 764 m, 723 mw, 483 s, 289 w. MS (*m/z*): 1091, 527, 281, 246, 134, 132, 105, 104, 76.

[CdBr(NPEt₃)]₄ (2). Synthesized by the same procedure as for **1**, using the following amounts: 4.10 g of $CdBr_2$ (15.1 mmol), 6.30 g of NaF (150 mmol), 20 mL of $Me_3SiNPEt_3$ (90.4 mmol), 220 °C. Yield: 3.67 g (2.8 mmol, 75%). Recrystallization from toluene afforded large colorless blocks of **2**·$2C_7H_8$. Anal. Calcd for $C_{24}H_{60}N_4P_4Br_4Cd_4$ (1297.92 g/mol): C, 22.21; H, 4.66; N, 4.32. Found: C, 22.30; H, 4.85: N, 4.25. ^1H NMR (CD_2Cl_2): δ 1.10 (dt, $J = 7.7$, 16.4 Hz, 3H, ($C\underline{H}_3CH_2)_3P$), 2.04 (dq, $J = 7.6$, 12.0 Hz, 2H, ($CH_3C\underline{H}_2)_3P$). ^{13}C NMR (CD_2Cl_2): δ 7.62 (d, $^2J_{P-C} = 4.1$ Hz, ($\underline{C}H_3CH_2)_3P$), 23.33 (d, $^1J_{P-C} = 59.5$ Hz, ($CH_3\underline{C}H_2)_3P$). ^{31}P NMR (CD_2Cl_2): δ 44.4 (Et_3PN). IR (cm^{-1}): 1270 m, 1047 vs, 986 m, 775 s, 741 m, 722 mw, 483 s, 206 w. MS (*m/z*): 1269 ($M^+ - Et$), 894, 133, 132, 104, 76.

[CdI(NPEt₃)]₄ (3) and [Cd₄I₄(OSiMe₃)(NPEt₃)₃] (7). Compound **3** was synthesized by the same procedure as for **1**, using the following amounts: 3.24 g of CdI_2 (8.9 mmol), 2.10 g of NaF (50.0 mmol), 35.0 mL of $Me_3SiNPEt_3$ (158.1 mmol). Yield: 2.7 g (1.8 mmol, 82%). Recrystallization from toluene gave large colorless blocks of **3**·$3C_7H_8$. Anal. Calcd for $C_{24}H_{60}N_4P_4I_4Cd_4$ (1485.92 g/mol): C, 19.40; H, 4.07; N, 3.77. Found: C, 19.72; H, 4.12: N, 3.57. ^1H NMR (CD_2Cl_2): δ 1.10 (dt, $J = 7.7$, 16.4 Hz, 3H, ($C\underline{H}_3CH_2)_3P$), 1.84 (dq, $J = 7.7$, 11.8 Hz, 2H, ($CH_3C\underline{H}_2)_3P$). ^{13}C NMR (CD_2Cl_2): δ 8.10 (d, $^2J_{P-C} = 4.2$ Hz, ($\underline{C}H_3CH_2)_3P$), 23.47 (d, $^1J_{P-C} = 59.2$ Hz, ($CH_3\underline{C}H_2)_3P$). ^{31}P NMR (CD_2Cl_2): δ 44.3 (Et_3PN). IR (cm^{-1}): 1263 w, 1044 vs, 985 m, 775 m, 739 mw, 481 s, 153 m. MS (*m/z*): 1486 (M^+), 1457 ($M^+ - Et$), 1359, 988, 619, 373, 246, 134, 132, 105, 104, 76. Crystals of **7**·CH_3CN were obtained by subsequent recrystallization of **3** from dichloromethane and acetonitrile. We assume that **7** was formed in trace amounts by the adventious reaction of **3** with grease (Bayer silicone, used to seal glass joints).

[CdI(NPMe₃)]₄ (4). A mixture of 4.00 g of CdI_2 (10.92 mmol), 2.16 g of NaF (51.4 mmol), and 35.0 mL of $Me_3SiNPMe_3$ (203.1 mmol) was thermolyzed at 200 °C for 18 h. After the evolution of gaseous Me_3SiF had ceased, excess $Me_3SiNPMe_3$ was removed *in vacuo*. After extraction with a total volume of 80 mL of CH_2Cl_2, filtration and evaporation of solvent, the slightly yellowish material was recrystallized from a mixture of 10 mL of toluene, 3 mL of acetonitrile, and 0.5 mL of dichloromethane. Yield: 0.76 g (0.6 mmol, 21%). Anal. Calcd for $C_{12}H_{36}N_4P_4I_4Cd_4$ (1317.58 g/mol): C, 10.94; H, 2.75; N, 4.25. Found: C, 11.33; H, 2.88: N, 4.34. ^1H NMR (C_7D_8): δ 1.15 (d, $J = 12.5$ Hz, (($C\underline{H}_3)_3P$). ^{13}C NMR (CD_2Cl_2): δ 21.47 (d, $^1J_{P-C} = 63.3$ Hz, ($\underline{C}H_3)_3P$). ^{31}P NMR (C_7D_8): δ 28.0 (Me_3PN). IR (cm^{-1}): 1303 s, 1292 s, 1060 vs, 935 vs, 858 s, 738 s, 468 vs, 161 m. MS (*m/z*): 1318 (M^+), 1228, 1191, 861, 771, 535, 408, 331, 204, 91, 76.

[CdMe(NPEt₃)]₄ (5). Compound **5** has been obtained *via* a different route described earlier.[10] To a suspension of 4.03 g (3.1 mmol) of **2** in 100 mL of *n*-hexane was added at room temperature 8.1 mL of MeLi (1.6 mol/L in diethyl ether). The mixture was refluxed for 2.5 h, after which ca. 10 mL of solvent was removed under reduced pressure, and then the mixture was filtered while still warm. After removal of solvents *in vacuo*, 8 mL of *n*-hexane was added and the suspension was subsequently treated in an ultrasonic bath. Filtration and drying in high vacuum gave 3.00 g of **5** (2.9 mmol, 93%). Anal. Calcd for $C_{28}H_{72}N_4P_4Cd_4$ (1038.44 g/mol): C, 32.39; H, 6.99; N, 5.40. Found: C, 32.17; H, 7.28; N, 5.38. ^1H NMR (CD_2Cl_2): δ −0.29 (s, 3H, $C\underline{H}_3Cd$), 0.97 (dt, $J = 7.6$, 15.3 Hz, 9H, ($C\underline{H}_3CH_2)_3P$), 1.45 (dq, $J = 7.6$, 11.6 Hz, 6H, ($CH_3C\underline{H}_2)_3P$). ^{13}C NMR (C_6D_6): δ −8.62 (s, $\underline{C}H_3Cd$), 7.11 (s, ($\underline{C}H_3CH_2)_3P$), 23.44 (d, $^1J_{P-C} = 59.5$ Hz, ($CH_3\underline{C}H_2)_3P$). ^{31}P NMR (n-C_6H_{14}): δ 29.4 (Et_3PN). IR (cm^{-1}): 1263 m, 1081 vs, 981 m, 769 s, 756 s, 737 m, 627 m, 474 s, 445 s. MS (*m/z*): 1023 ($M^+ - Me$), 881, 624, 507, 492, 134, 133, 132, 129, 105, 104, 76.

[Cd(C₂SiMe₃)(NPEt₃)]₄ (6). A solution of 10.3 mmol of LiC_2SiMe_3 in 46.8 mL of THF/Et_2O {prepared by dropwise addition of 6.8 mL of MeLi (1.6 mol/L, in diethyl ether; 10.88 mmol) to a solution of 2.32 mL (10.3 mmol) of $Me_3SiC_2SiMe_3$ in 40 mL of THF and subsequent refluxing for ca. 30 min} was added, at 35 °C, to a suspension of 3.27 g (2.52 mmol) of **2** in 45 mL of *n*-hexane, resulting in a clear solution. After an additional 5 min of stirring, solvents were removed *in vacuo*. Extraction twice with 30 mL portions of *n*-hexane gave **6** as thick, colorless needles upon cooling to 4 °C. Evaporation of solvent and

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subsequent washing with less than 5 mL of *n*-hexane, followed by filtration and drying in high vacuum afforded spectroscopically pure **6** in almost quantitative yield: 3.24 g (2.37 mmol, 94%). **6** is moderately soluble in *n*-hexane and has excellent solubility in benzene and toluene. Anal. Calcd for $C_{44}H_{96}N_4P_4Si_4Cd_4$ (1367.15 g/mol): C, 38.66; H, 7.08; N, 4.10. Found: C, 38.90; H, 7.25: N, 4.03. ^{1}H NMR (C_6D_6): δ 0.17 (s, 9H, $C\underline{H}_3Si$), 1.00 (dt, $J = 7.8$, 14.5 Hz, 9H, $(C\underline{H}_3CH_2)_3P$), 1.62 (dq, $J = 7.8$, 16.2 Hz, 6H, $(CH_3C\underline{H}_2)_3P$). ^{13}C NMR ($C_6D_6$): δ 1.19 (s, $\underline{C}H_3Si$), 7.22 (s, $(\underline{C}H_3CH_2)_3P$), 22.76 (d, $^1J_{P-C} = 59.1$ Hz, $(CH_3\underline{C}H_2)_3P$), 55.71 (s, $Cd\underline{C}CSi(CH_3)_3$), 115.11 (s, $CdC\underline{C}Si(CH_3)_3$). ^{31}P NMR ($C_6D_6$): δ 37.6 (Et_3PN). ^{29}Si NMR (C_6D_6): δ −25.0 (Me_3Si). IR (cm^{-1}): 2044 s, 1260 sh, 1245 vs, 1060 vs, 985 m, 855 vs, 837 vs, 773 vs, 759 vs, 717 st, 690 vs, 602 w, 480 vs. MS (*m*/*z*): 1367 (M^+), 1337, 1322, 1270, 1235, 1138, 1026, 995, 928, 684, 587, 552, 475, 378, 343, 246, 134, 132, 105, 104, 98, 76, 73.

Results and Discussion

Syntheses. Refluxing a mixture of anhydrous cadmium dihalide and a manifold excess of $Me_3SiNPEt_3$ in the presence of NaF for several hours leads to the formation of gaseous Me_3SiF, eq 1 {X = Cl (**1**), Br (**2**), I (**3**)}.

$$CdX_2 + Me_3SiNPEt_3 + NaF \rightarrow \tfrac{1}{4}\,[CdX(NPEt_3)]_4 + NaX + Me_3SiF\uparrow \quad (1)$$

Halogeno cubanes $[CdX(NPEt_3)]_4$ **1**−**3** can be extracted from the mixtures, in which one halogen function per cadmium remains. Yields are best in the case of iodine.[16] Even after prolonged reaction times, no homoleptic $[Cd(NPEt_3)_2]_n$ species can be isolated. No phosphoraniminato complexes are formed when $CdCl_2$ or $CdBr_2$ are treated with P-methyl derivative $Me_3SiNPMe_3$ under the same conditions as above. However, when CdI_2 is used, formation of $[CdI(NPMe_3)]_4$ **4** is observed, albeit in low yield.[16] In order to test the factors responsible for tetramer formation, P-phenyl derivative $Me_3SiNPPh_3$ was employed, but none of the cadmium dihalides showed any substantial reaction. Similar findings in the case of the lighter congener zinc suggest that low reactivity of bulky silylated phosphoranimines can be attributed to steric hindrance rather than electronic effects.[2g]

Suspensions of the bromo derivative **2** in *n*-hexane react with organolithium compounds LiR′ (Et_2O/THF solutions) to give organocadmium complexes $[CdR'(NPEt_3)]_4$ {R′ = Me (**5**), C_2SiMe_3 (**6**)}, eq 2. According to ^{31}P-NMR spectra of the reaction mixtures, these transmetalation reactions proceed quantitatively.

$$[CdBr(NPEt_3)]_4 + 4LiR' \rightarrow [CdR'(NPEt_3)]_4 + 4LiBr \quad (2)$$

Spectroscopic Studies. Table 1 summarizes the principal infrared vibrational frequencies of P-ethyl-substituted phosphoraniminato heterocubanes **1**−**3**, **5**, and **6**, as well as comparative NMR data. The conspicuous feature of all infrared spectra is that only one ν(CdN) and one ν(CdX) {X = Cl (**1**), Br (**2**), I (**3**), C (**5**, **6**)} of the $[(Cd{-}X/R')_4N_4]$ framework as well as only one ν(NP) of the ligand is observed. This is due to the high symmetry (T_d) of the complexes, which, according to selection rules, allows for F_2 vibrations only, which are triply degenerate.[17] IR data are therefore in agreement with cubane-type molecular structures as determined by single X-ray crystallography, see below. Figure 1 shows the IR and FIR spectra of the bromo derivative $[CdBr(NPEt_3)]_4$, **2**, as a representative example. The most characteristic absorptions are ν(NP) at 1047 cm^{-1} and ν(CdN) at 483 cm^{-1}. As can be seen in Table 1, absorptions arising from the N−P moiety are unaffected by the nature of the exocyclic function in heterocubane halides **1**−**3**. The substitution of a methyl function for halide at cadmium in compound **5**, however, leads to an increase of the absorption energy of the N−P fundamental (1081 cm^{-1}). Replacement of the halide at cadmium by an ethinyl function in complex **6** is also accompanied by an increase of the N−P absorption energy (1060 cm^{-1}). Since the absorption energy can be used as a probe for the strength of the N−P bond of the phosphoraniminato ligand, these observations suggests that organometallic substitution leads to a strengthening of the N−P bonds. In addition, carbon substitution for the halide at the cadmium atoms shifts the ^{31}P NMR resonances to higher field (Table 1) indicating that P atoms in organometallic derivatives **5** and **6** bear less positive charge.[18] In contrast, IR absorptions of the Cd−N framework lie at essentially the same energy, irrespective of the exocyclic function at cadmium.

Table 1. Spectroscopic Data of Triethylphosphoraniminato Complexes **1**−**6**

δ/ν	(X = Cl) **1**	(X = Br) **2**	(X = I) **3**	(X = CH_3) **5**	(X = C_2TMS) **6**
δ ^{31}P (ppm)	44.4	44.4	44.3	29.4	37.6
solvent	CD_2Cl_2	CD_2Cl_2	CD_2Cl_2	*n*-C_6H_{14}	C_6D_6
νCd−N (cm^{-1})	483	483	481	474	480
νCd−X (cm^{-1})	289	206	153	445	480[a]
νN−P (cm^{-1})	1048	1047	1044	1081	1060

[a] Tentative assigment.

Tetrameric molecular ions are found in the mass spectra of **3**, **4**, and **6**, under electron impact conditions: $[Cd_4I_4(NPEt_3)_4]^+$ (*m*/*z* 1486 au), $[Cd_4I_4(NPMe_3)_4]^+$ (*m*/*z* 1318 au) and $[Cd_4(C_2SiMe_3)_4(NPEt_3)_4]^+$ (*m*/*z* 1367 au). In the mass spectra of **1**, **2**, and **5**, however, peaks are recorded which are due to the loss of only one ethyl or methyl group, arising from the species $[Cd_4Cl_4(NPEt_3)_3(NPEt_2)]^+$ (*m*/*z* 1091 au), $[Cd_4Br_4(NPEt_3)_3(NPEt_2)]^+$ (*m*/*z* 1269 au), and $[Cd_4Me_3(NPEt_3)_4]^+$ (*m*/*z* 1023 au). The presence of peaks with high intensities corresponding to tetrameric units in the mass spectra suggest that the $[Cd_4N_4]$ frameworks are stabilized by strong Cd−N bonds, consistent with good thermal stabilities of compounds **1**−**4**. In addition, trimeric, dimeric, and monomeric species as well as fragments of the (NPR_3^-) ligand are detected in high relative intensities in most spectra.

Single Crystal X-ray Structures

Crystal Structures of Symmetrical Cubanes. We have been able to carry out single crystal X-ray structure determinations of compounds **1**, **2**, **3**, and **6**. Crystal, data collection, and refinement parameters are given in Table 2. Table 3 contains relevant average bond lengths and angles. Figure 2 shows the molecular structure of $[CdCl(NPEt_3)]_4$, **1** as a representative example of halogeno derivatives **1**, **2**, and **3**. The molecular structure of organocadmium compound **6** with exocyclic (trimethylsilyl)ethinyl ligands is shown in Figure 3.

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(16) We regard these observations as reflections of Cd−X bond enthalpies. The Cd−I bond is most easily cleaved (free enthalpies of formation: CdI_2, −201.4 kJ/mol; $CdBr_2$, −296.3 kJ/mol; $CdCl_2$, −343.9 kJ/mol; Lide, D. R., Ed.; *Handbook of Chemistry and Physics*, 74th ed.; CRC Press Inc.: Boca Raton, FL, 1993). Since the boiling point of $Me_3SiNPMe_3$ is lower than that of $Me_3SiNPEt_3$, only the iodine derivative is formed.

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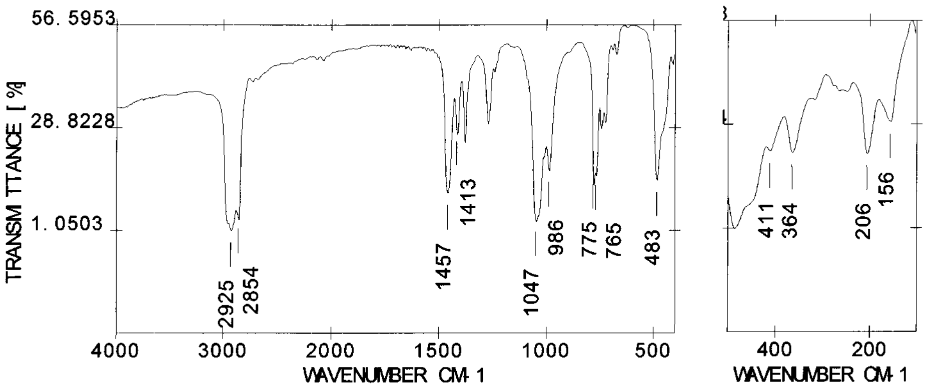

Figure 1. IR and FIR spectra of [CdBr(NPEt$_3$)]$_4$ (**2**).

Table 2. Crystallographic Data for Complexes **1**, **2**, **3**, **6**, and **7**

	1·CH$_2$Cl$_2$	**2**·2C$_7$H$_8$	**3**·3C$_7$H$_8$	**6**	**7**·CH$_3$CN
chemical formula	$C_{25}H_{62}N_4P_4Cl_6Cd_4$	$C_{38}H_{76}N_4P_4Br_4Cd_4$	$C_{45}H_{84}N_4P_4I_4Cd_4$	$C_{44}H_{96}N_4P_4Si_4Cd_4$	$C_{23}H_{57}N_4P_4I_4OSiCd_4$
fw (g/mol)	1204.97	1482.15	1762.24	1367.09	1483.93
space group	P2$_1$ (No. 4)	P2$_{1/n}$ (No. 14)	R3m (No. 160)	I2/a (No. 15)	P2$_{1/c}$ (No. 14)
a (Å)	1100.7(3)	2160.1(3)	1784.2(2)	1979.4(1)	2011.1(9)
b (Å)	1098.8(3)	1184.2(2)	1784.2(2)	1060.0(2)	1199.13(8)
c (Å)	1852.8(2)	2355.0(3)	1729.0(3)	3209.4(2)	2065.5(10)
α (deg)	90	90	90	90	90
β (deg)	90.57(2)	116.65(1)	90	107.512(7)	111.44(2)
γ (deg)	90	90	120	90	90
V (Å^3)	2240.8(9)	5429.4(14)	4766.6(11)	6421.5(11)	4638(3)
Z	2	4	3	4	4
T (K)	223(2)	213(2)	223(2)	190(2)	203(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
D_{calc} (g/cm^3)	1.786	1.813	1.842	1.414	2.125
μ(Mo Kα) (cm^{-1})	239.5	463.6	339.4	151.0	462.1
R[a]	0.058	0.065	0.040	0.036	0.039
R_w[b]	0.143	0.114	0.097	0.086	0.081

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

Table 3. Average Bond Lengths and Bond Angles in Complexes **1**, **2**, **3**, and **6**[a]

d (pm)/ ∠ (deg)	(X = Cl) **1**	(X = Br) **2**	(X = I) **3**	(X = C$_2$SiMe$_3$) **6**
Cd−N	227.9(13)	225.9(12)	227.0(8)	229.4(4)
Cd−X	239.5(5)	249.9(2)	267.7(2)	213.4(5)
N−P	158.5(13)	159.1(12)	160.0(14)	158.1(4)
N−Cd−N	89.4(5)	89.2(4)	88.8(4)	88.14(13)
Cd−N−Cd	90.5(5)	90.9(4)	90.7(4)	91.83(13)
N−P−C	113.1(10)	113.1(9)	113.0(6)	113.8(7)
N−Cd−X	125.0(4)	125.9(3)	126.1(3)	126.05(19)
Cd−N−P	124.8(7)	124.7(7)	124.8(7)	123.86(19)

[a] Esd's (in parentheses) correspond to the largest standard deviation observed.

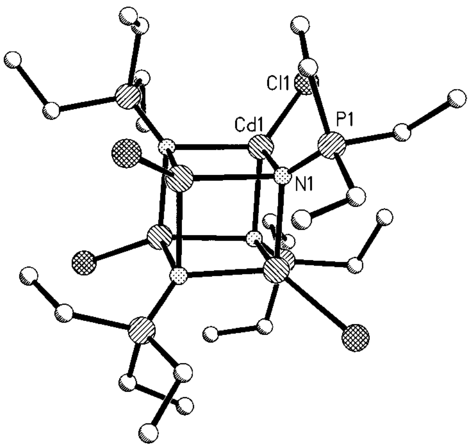

Figure 2. Molecular structure of [CdCl(NPEt$_3$)]$_4$ (**1**). H atoms have been omitted for clarity. Compounds [CdBr(NPEt$_3$)]$_4$ (**2**) and [CdI(NPEt$_3$)$_4$] (**3**) possess the same molecular structure.

All complexes possess heterocubane structures, in which four cadmium atoms and four *μ*$_3$-nitrogen atoms of the phosphoraniminato ligands are placed at the vertices of almost undistorted cubic frameworks. Cubic bond angles Cd−N−Cd differ by less than 1.8°, and N−Cd−N by less than −1.9° from the ideal cubic geometry (Table 3). Cubanes **1** and **2** show no crystallographic symmetry, whereas complexes **3** and **6** possess an axis of higher symmetry (*C*$_3$ and *C*$_2$, respectively).

All distances between N and P atoms in the phosphoraniminato ligands lie in the range of N═P double bonds, for which 155−164 pm is accepted in the literature.[19] As mentioned above, absorption frequencies of N−P fundamentals suggest a strengthening of the N−P bond upon exchanging the halide function with carbon, which is in accordance with an increased electron density around the phosphorus nuclei as determined by ^{31}P NMR. However, these arguments cannot be supported by X-ray crystallographic data, with the average N−P distance in the acetylene derivative [Cd(C$_2$SiMe$_3$)(NPEt$_3$)]$_4$, **6** (158.1(4) pm), being as short as those in halogeno derivatives [CdCl(NPEt$_3$)]$_4$, **1** (158.5(13) pm), [CdBr(NPEt$_3$)]$_4$, **2** (159.1(12) pm), and [CdI(NPEt$_3$)]$_4$, **3** (160.0(14) pm). The measured Cd−N bond lengths (227.9(13) pm in **1**, 225.9(12) pm in **2**, 227.0(8) pm in **3**, and 229.4(4) pm in **6**) are also essentially uneffected

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(19) (a) Hoard, L. G.; Jacobsen, R. A. *J. Chem. Soc. A* **1966**, 1203. (b) Cameron, A. F.; Hair, N. J.; Morris, D. G. *Acta Crystallogr.* **1974**, *30B*, 221. (c) Adamson, G. W.; Bart, J. C. *J. Chem. Soc. A* **1970**, 1452.

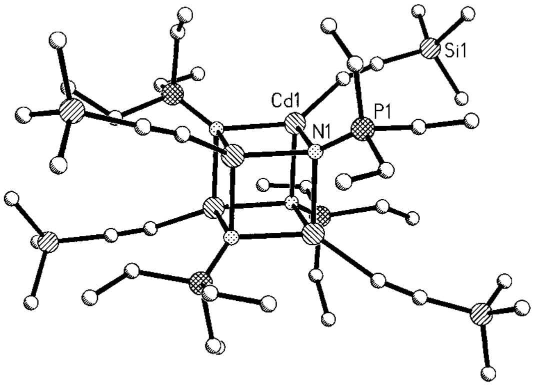

Figure 3. Molecular structure of [Cd(C$_2$SiMe$_3$)(NPEt$_3$)]$_4$ (**6**). H atoms have been omitted for clarity.

by the nature of the exocyclic function at cadmium. The Cd−N bond lengths in cadmium phosphoraniminato heterocubanes lie in the same range as those found in tris(pyrazolyl)borato complexes of cadmium (222−226 pm), in which Cd is also ligated by a (*N*,*N*,*N*)-donor set.[20,21] Only in (hydrogentris(3-*tert*-butyl-5-methylpyrazolyl)borato-*N*,*N*′,*N*″)methylcadmium has a longer Cd−N distance been reported (231.1(7) pm), probably due to steric hindrance of the 3-*tert*-butyl-5-methylpyrazolyl moiety.[20] Consequently, Cd−C distances are especially short in the latter compound (207.4(19) pm), notwithstanding that the carbon ligand is CH_3 with sp^3-hybridized carbon. Therefore, the measured Cd−C distances in [Cd(C$_2$SiMe$_3$)(NPEt$_3$)]$_4$ (**6**) with sp-hybridized carbon ligands seem very long (mean value 213.4(5) pm), but they are in good agreement with those found in bis(phenylethinyl)cadmium−TMEDA complex (214.2(9) pm).[22] Exocyclic Cd−Cl bonds in chloro compound **1** are 4 pm longer than the distance observed in (hydrogentris(3-*tert*-butylpyrazolyl)borato-*N*,*N*′,*N*″)chlorocadmium (235.5(2) pm).[21]

In summary, short N−P bond lengths are found in cadmium phosphoraniminato heterocubanes. Since second-row element nitrogen cannot have a valence greater than 4, short N−P bonds can only be rationalized by an electrostatic σ-bond strengthening contribution. In comparison with the corresponding [Zn$_4$N$_4$] heterocubanes, the lengths of [Cd$_4$N$_4$] cube edges are enlarged by *circa* 20 pm which corresponds to the difference in covalent radii of the two metals.[23]

Crystal Structure of [Cd$_4$I$_4$(OSiMe$_3$)(NPEt$_3$)$_3$]·CH$_3$CN (7·CH$_3$CN). Crystal, data collection, and refinement parameters are given in Table 2. Table 4 contains relevant average bond lengths and angles. As can be seen in Figure 4, one of the phosphoraniminato ligands has been replaced by a silyloxy group in **7** (Figure 4).[24] In the crystal structure **7** has no symmetry, yet the molecule is best described as having local C_{3v} symmetry, with the C_3 axis going through the Si−O and the Cd2−I2 bonds. As to exocyclic bonds, all four Cd−I bond lengths are essentially the same (266.9(1) pm), as are N−P bond distances (mean value 159.3(5)). Again, the latter are well in the range of N=P double bonds.[19] On the other hand, according to local C_{3v} symmetry, the cubic system is distorted in that three different cube edges occur. Cd−N bond lengths including Cd2 (located opposite of the silyloxy function) are significantly longer (228.4(5) pm) than those Cd−N bond lengths including cadmium atoms bound to O (224.6(5) pm). The longest edges are the three Cd−O distances which are 231.5(4) pm in average. Naturally, the cube angles vary substantially in **7**. Angles at nonmetal atoms are larger than 90°, and angles at Cd vary from 87.2(2)° (N−Cd1/3/4−O) to 90.2(2)° (N−Cd1/3/4−N). In conclusion, this “three-quarter-heterocubane” is distorted in that the cube is compressed at the Cd2 vertex and pulled out at the O vertex.

Table 4. Average Bond Lengths and Bond Angles in **7**[a]

d (pm) /∠ (deg)	**7**	∠ (deg)	**7**
Cd2−N	228.4(5)	N−Cd1/3/4−O	87.2(2)
Cd1/3/4−N	224.6(5)	Cd−O−Cd	91.0(2)
Cd1/3/4−O	231.5(4)	Cd2−N−Cd1/3/4	90.6(2)
N−P	159.3(5)	Cd1/3/4−N−Cd1/3/4	94.4(2)
Cd2−I2	266.9(1)	N−P−C	112.9(6)
Cd1/3/4−I1/3/4	266.9(1)	N−Cd−I	127.8(1)
		Cd−N−P	123.8(3)
N−Cd2−N	88.3(2)	Cd−O−Si	124.5(2)
N−Cd1/3/4−N	90.2(2)	O1−Si−C	110.1(4)

[a] Esd’s (in parentheses) correspond to the largest standard deviation observed.

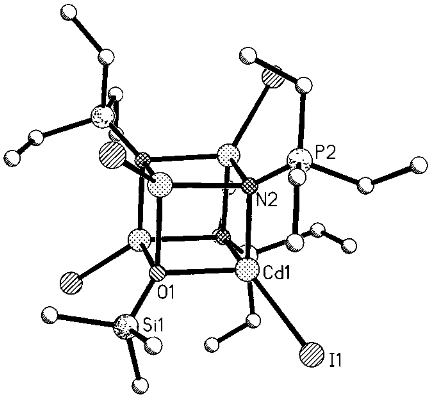

Figure 4. Molecular structure of [Cd$_4$I$_4$(OSiMe$_3$)(NPEt$_3$)$_3$] (**7**). H atoms have been omitted for clarity.

Concluding Remarks. Halogenocadmium cluster compounds with a [Cd$_4$N$_4$] cubane core can be prepared by simple thermolysis procedures. Crystal structures of these thermally stable phosphoraniminato complexes of cadmium are reported for the first time. With one remaining halogen function still intact, organometallic derivatization has been achieved by transmetalation from organolithiums. We expect organocadmium phosphoraniminato complexes to be capable of transferring organic substituents R′ onto electrophiles, with the (NPR$_3^-$) ligand not being transferred, thereby acting as a “dummy ligand”.[25] The high covalent character of the Cd−C bond promises high functional group compatibility in organic synthesis.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged. We thank Prof. Dr. Dr. h. c. K. Dehnicke for encouragement and helpful discussions throughout this work. M.K. thanks the Fonds

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(24) We have recently described an organozinc complex in which one (NPR$_3$) moiety is replaced by an iodine atom, [Zn$_4$(n-Bu)$_4$I(NPMe$_3$)$_3$]; see ref 2f. Exchange of the metal moiety has also been accomplished in an organozinc complex, in which the (RZn) vertex is replaced by a LiBr molecule. We will report on this shortly: Krieger, M.; Gould, R. O.; Dehnicke, K. Unpublished results.

(25) For recent examples of RR′M transferring only one group in organozinc chemistry, see: Berger, S.; Langer, F.; Lutz, C.; Knochel, P.; Mobley, T. A.; Reddy, C. K. *Angew. Chem.* **1997**, *109*, 1603 and references cited therein.

der Chemischen Industrie as well as the Graduiertenkolleg “Metallorganische Chemie” for doctoral fellowships.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of {[CdCl(NPEt$_3$)]$_4$] (**1**), [CdBr(NPEt$_3$)]$_4$ (**2**), [CdI(NPEt$_3$)]$_4$] (**3**), [Cd(C$_2$SiMe$_3$)(NPEt$_3$)]$_4$ (**6**), and [Cd$_4$I$_4$(OSiMe$_3$)(NPEt$_3$)$_3$] (**7**)} are available on the Internet only. Access information is given on any current masthead page.

IC9710364