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Spectroscopic and crystallographic characterisation of cadmium complexes incorporating a bidentate phosphine ligand

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The 1 : 1 stoichiometric addition of the bidentate phosphine ligand 2,2-dimethyl-2-sila-1,3-bis(diphenylphosphino)propane (L^2) to a range of cadmium(II) salts produced a series of moisture-sensitive complexes of general formula [$CdX_2(L^2)$] (X = Cl **1**, Br, I, SCN or NO_3). These complexes have been investigated by vibrational and multinuclear (^{31}P and ^{113}Cd) NMR spectroscopy and by X-ray crystallography. Complex **1** crystallises in the orthorhombic space group $P2_12_12_1$, with $a = 9.2862(10)$, $b = 15.386(2)$, $c = 20.724(3)$ Å, $U = 2960.9(6)$ Å^3 and $Z = 4$. The metal centre exhibits four-co-ordinate, tetrahedral geometry, with the ligand bound in a bidentate manner. Both the solution- and solid-state cross-polarisation magic angle spinning ^{31}P NMR spectra of the complexes show clearly resolved $^{113}Cd-^{31}P$ and $^{111}Cd-^{31}P$ one bond couplings in a $^{113}Cd : ^{111}Cd$ ratio of 1.044 : 1.046 as expected. Vibrational spectroscopy indicates that each complex is mononuclear, with no evidence for bridging species; [$Cd(NO_3)_2(L^2)$] features monodentate nitrate groups. The addition of 2 equivalents of the ligand to cadmium perchlorate yields a complex which has been established as [$Cd(L^2)_2$][ClO_4]$_2$ by spectroscopic and conductance studies.

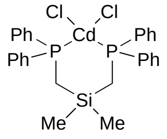
The complex [Cd(dmpe){TeSi(SiMe$_3$)$_3$}$_2$][1] [dmpe = 1,2-bis(dimethylphosphino)ethane] is the only structurally characterised cadmium species incorporating a bidentate ditertiary phosphine ligand reported to date. Wymore and Bailar[2] reported the preparation of [$CdBr_2$(depe)] [depe = 1,2-bis(diethylphosphino)ethane] *via* the addition of water to a dimethylformamide (dmf) solution of [($CdBr_2$)$_3$(depe)$_2$]; addition of $CdBr_2$ regenerated the starting material. Cadmium halide complexes with dppe [1,2-bis(diphenylphosphino)ethane] and dppb [1,4-bis(diphenylphosphino)butane] were shown[3] to be four-co-ordinate, monomeric moieties, characterised by vibrational spectroscopy.[4]

The general insolubility of metal complexes of ditertiary phosphine ligands has commonly precluded their study by multinuclear NMR spectroscopy; in order to overcome this problem we have synthesised[5] the ligand 2,2-dimethyl-2-sila-1,3-bis(diphenylphosphino)propane (L^2). The incorporation of a dimethyl silicon component in the ligand backbone not only increases complex solubility but also provides an excellent NMR spectroscopic handle.

We have recently reported the complexation of a range of cobalt(II)[6] and mercury(II)[7] salts with L^2, to form four-co-ordinate, tetrahedral species of general formula [$MX_2(L^2)$] (X = Cl, Br, I, NO_3 or SCN). Cadmium is extremely amenable to NMR spectroscopic study, as it has two isotopes of non-zero spin, ^{113}Cd ($I = \frac{1}{2}$) and ^{111}Cd ($I = \frac{1}{2}$). Colton and Dakternieks[8] studied monodentate phosphine complexes of cadmium *via* low-temperature Fourier-transform NMR spectroscopic techniques. The generation of analogous cadmium(II) salts should thus allow characterisation by multinuclear (^{113}Cd and ^{31}P) NMR and vibrational spectroscopy and engender crystal formation for an X-ray study.

Results and Discussion

The 1 : 1 stoichiometric addition of a dichloromethane solution of L^2 to a series of cadmium(II) salts produced a range of moisture-sensitive complexes denoted as [$CdX_2(L^2)$] (X = Cl **1**, Br, I, NO_3 or SCN). Reaction between cadmium perchlorate and 2 equivalents of the phosphine ligand yielded [$Cd(L^2)_2$][ClO_4]$_2$.



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Multinuclear (^1H, ^{31}P and ^{113}Cd) NMR spectroscopic studies were performed on these six cadmium complexes. The ^1H NMR spectra of the 1 : 1 species show apparent triplets for the P–CH_2 backbone protons. The splitting is due to two bond and four bond virtual coupling to the two phosphorus atoms; the appearance of a triplet is due to $^4J(^{31}P-^1H)$ being much smaller than $^2J(^{31}P-^1H)$ and hence having a minor contribution to the total coupling constant ($^2J + {^4J} = 5.4$–6.2 Hz). Three bond couplings to the cadmium centres are also clearly visible, with ^3J(Cd–H) 26.1–29.4 Hz. The coupling constants for the two NMR-active cadmium nuclei are not clearly resolved and hence the J(Cd–H) values quoted are approximate average values of the two. The chemical shifts for the P–CH_2 protons appear downfield from the free ligand value (complexes δ 1.84–2.08, free ligand 1.50), reflecting the expected increase in deshielding upon complexation to the metal centres. The dimethylsilyl protons appear as a singlet in each case (δ −0.29 to −0.33), indicating the equivalence of the two methyl groups. The NMR spectrum of the 2 : 1 perchlorate complex is complicated and not clearly resolved, and coupling constants are hence not observed.

Solution-state ^{31}P NMR spectroscopic studies reveal the chemical environments of the phosphorus atoms; data are presented in Table 1. Chemical shift and coupling constant values for cadmium(II) complexes are dependent on temperature, concentration, magnetic field and solvent,[8] while previous studies[9] have shown that for complexes of monodenate phosphines, anion and phosphine exchange are rapid on the NMR timescale. The room-temperature ^{31}P NMR spectra of the cadmium halide and nitrate species here each show a sharp central resonance for the phosphorus atoms, with clearly resolved satellites arising from $^1J(^{113}Cd-^{31}P)$ and $^1J(^{111}Cd-^{31}P)$ couplings. The ^{31}P NMR spectrum of [$Cd(NO_3)_2(L^2)$] appears in Fig. 1. The thiocyanate complex, however, gives a broad spectrum, with cadmium–phosphorus coupling not readily apparent; thus it is

Table 1 Multinuclear (^{31}P and ^{113}Cd) NMR spectroscopic data[a] for the cadmium complexes

Complex	$\delta^{31}P^{b}$ (ppm)	$\delta^{113}Cd^{c}$ (ppm)	$^1J(^{113}Cd{-}^{31}P)^{d}$/Hz	$^1J(^{111}Cd{-}^{31}P)^{d}$/Hz
1	−15.5	415 (t)	1248.5	1195.8
2	−18.3	389 (t)	1154.6	1106.3
3	−25.0	317 (t)	974.8	933.8
4	−8.6	92 (t)	1756.4	1679.4
5	−10.7		Broad, no coupling	Broad, no coupling
6	−5.4		1111.7	1064.3
Free L^2	−21.0			

[a] Complexes in CH_2Cl_2. [b] At 298 K, relative to external 85% H_3PO_4. [c] At 183 K, referenced to 4 M $Cd(NO_3)_2$, t = triplet. [d] At 298 K.

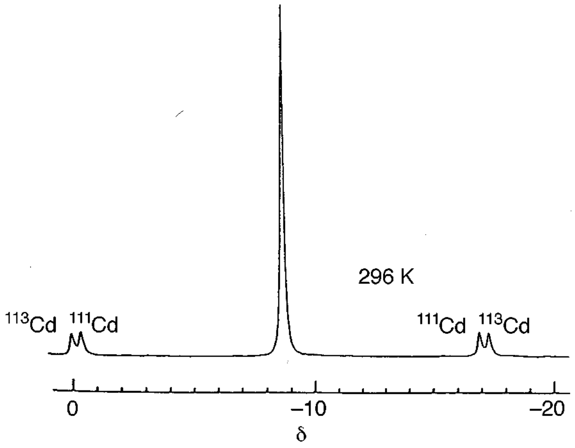

Fig. 1 The ^{31}P NMR spectrum of $[Cd(NO_3)_2(L^2)]$ at 298 K

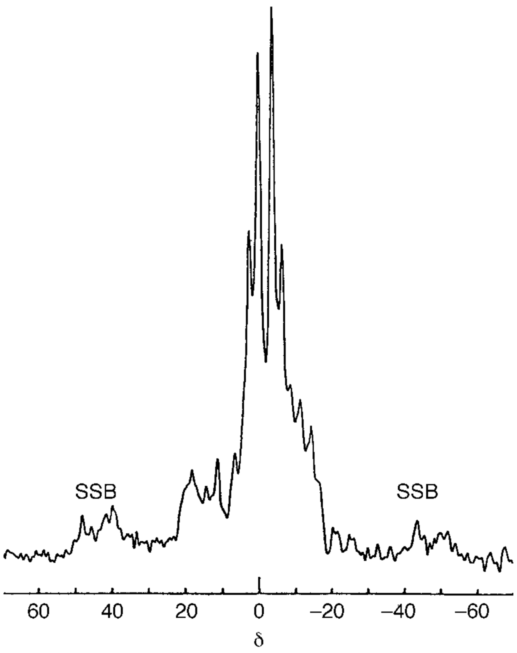

Fig. 2 The CP-MAS solid-state ^{31}P NMR spectrum of $[Cd(NO_3)_2(L^2)]$ (SSB = spinning side band)

clear that thiocyanate exchange occurs at room temperature: upon cooling to 243 K, coupling to the cadmium centre becomes visible [$^1J(^{113}Cd{-}^{31}P)$ 1435.5 and $^1J(^{111}Cd{-}^{31}P)$ 1384.3 Hz], while at lower temperatures the insolubility of the thiocyanate complex precludes NMR spectroscopic study.

Both $^1J(^{113}Cd{-}^{31}P)$ and $^1J(^{111}Cd{-}^{31}P)$ couplings in the halide and nitrate complexes are clearly resolved, with a $^{113}Cd:^{111}Cd$ ratio of 1.044:1.046. This is in accordance with the gyromagnetic ratio calculated for the two nuclei, and remains constant at variable temperature. The values of the Cd−P coupling constants are comparable to those observed in related monodentate phosphine complexes[10] and are much smaller than those values noted in analogous Hg–L^2 complexes[7] {*e.g.* $^1J(M{-}P)$ = 3684 $[HgCl_2(L^2)]$, 1248 and 1196 Hz $[CdCl_2(L^2)]$}. The magnitudes of the chemical shifts and coupling constants in the L^2 complexes here and in the monodenate phosphine analogues vary in the order NO_3 > SCN > Cl > Br > I and increase as the temperature is decreased: this trend is readily explained by the strengthening of the M−P bonds as phosphine exchange slows upon cooling. For metals such as cadmium and mercury, in which d orbital participation is not important, the magnitude of the M−P coupling in their complexes is purely a reflection of σ bond effects.

Although the ring contribution, Δ_R, to δ_P cannot be accurately calculated as there are no chemical shift data available for 1:2 cadmium complexes with the monodentate analogue PPh_2Pr, data for PPh_2Et have been recorded.[11] The co-ordination chemical shift for $[CdI_2(PPh_2Et)]$ was estimated as δ −2.5 from the spectrum at 183 K, while the value of δ −2.8 was noted in the L^2 complex. Thus Δ_R can be calculated to be −0.3 ppm, a very small upfield shift owing to the chelate ring. The Cd−P coupling constants for $[CdI_2(PPh_2Et)]$ were measured as 1143.3 (^{111}Cd) and 1195.7 Hz (^{113}Cd) at 183 K, and are hence larger than the values observed for L^2. Thus the decrease in M−P coupling constants in the chelate complex is attributable to a decrease in the valence s electron density at the metal nucleus compared with the monodenate species. This suggests that L^2 does not span the tetrahedral angle and interact as strongly with the cadmium centre as do two monodenate phosphine ligands: this is borne out by the crystal structure of **1**, as discussed later.

The cross-polarisation magic angle spinning (CP-MAS) solid-state ^{31}P NMR spectrum of $[Cd(NO_3)_2(L^2)]$ is shown in Fig. 2. An AB pattern can be clearly observed for the two inequivalent phosphorus atoms. The non-equivalence of the two phosphorus atoms can be explained by the distorted tetrahedral geometry and by crystal packing effects, as subsequently discussed in the structural analysis. The cadmium satellites are not fully resolved, hence the M−P coupling constants were estimated by using the value of 78 Hz that is observed for the difference between $^1J(^{111}Cd{-}^{31}P)$ and $^1J(^{113}Cd{-}^{31}P)$ in the solution-state ^{31}P NMR spectrum. The observed average coupling constant is thus calculated to be 1784 Hz, with derived individual values of $^1J(^{111}Cd{-}^{31}P) = (1784 - 39) = 1745$ and $^1J(^{113}Cd{-}^{31}P) = (1784 + 39) = 1823$ Hz. This gives an expected ratio of 1.045:1 for $^{113}Cd:^{111}Cd$. It should be noted that the value of 78 Hz from the solution spectrum may differ slightly from that which would be observed in the solid state, and hence the *J* values are not precise; a clear conclusion, however, is that the larger *J* values observed in the solid state reflect stronger M−P bonds than are present in solution. The two bond $^{31}P{-}^{31}P$ coupling through the cadmium centre can be calculated as 211 Hz. The CP-MAS spectrum of $[Cd(L^2)_2][ClO_4]_2$ shows a single broad resonance at δ −4.11, similar to the value observed in solution. The Cd−P satellites are not observed.

The ^{113}Cd NMR spectroscopic studies were performed on the halide and nitrate complexes and the results are shown in Table 1. The spectra each showed triplets with a 1:2:1 intensity,

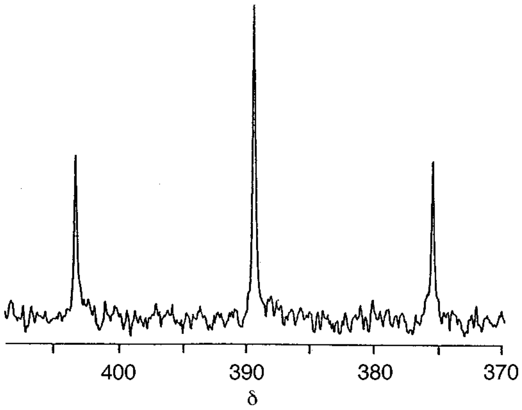

Fig. 3 The ^{113}Cd NMR spectrum of $[CdBr_2(L^2)]$ at 183 K

revealing metal co-ordination to two phosphorus atoms; the spectrum of the bromide complex is shown in Fig. 3. The $^{1}J(^{113}Cd-^{31}P)$ coupling constants were calculated and correlate with those noted from the ^{31}P NMR spectra. The thiocyanate and 1:2 perchlorate complexes were of insufficient solubility to allow ^{113}Cd NMR spectroscopy. The linear correlation between δ_{Cd} and the electronegativity of the attached halide, and that between the chemical shift and coupling constant, imply that the latter values are largely determined by σ bond effects, as previously suggested; similar trends were noted[8,10] for cadmium(II) complexes of monodentate phosphines.

Vibrational spectroscopic studies performed on the complexes confirmed the presence of four-co-ordinate mononuclear species. Assignments of ν(M–X) and ν(M–P) were made on the basis of similar observations reported for monodentate phosphine complexes.[4] The halide and thiocyanate complexes each show characteristic terminal Cd–X stretches in the IR and Raman spectra, with no evidence for bridging X groups. The thiocyanate shows clear signals assigned to ν(CN) 2080, ν(CS) 830, 790 and δ(SCN) 460 cm^{-1}, and indicate co-ordination through the S atom.

In general it is difficult to distinguish between mono- and bidentate co-ordination in nitrate groups.[12] However, Alyea and co-workers[13] showed that the extent of separation of the ν_3 band may give some indication; values greater than 150 cm^{-1} often point towards bidentate co-ordination, while values less than 150 cm^{-1} may infer monodenticity. In this case, ν_3 appears at 1440 and 1290 cm^{-1} and hence the separation is exactly 150 cm^{-1}. However, the trend for formation of four-co-ordinate $[MX_2(L^2)]$ complexes[6,7] implies that the two nitrate groups are almost certainly bound in a monodentate fashion.

Molar conductance measurements performed on freshly prepared nitromethane solutions (10^{-3} M) revealed that the 1:1 complexes were all non-electrolytes. However, the perchlorate complex showed a value of 161.1 Ω^{-1} cm^{2} mol^{-1}; this value is in the range for a 1:2 electrolyte[14] and thus confirms the assignment of the complex as $[Cd(L^2)_2][ClO_4]_2$. Clearly this also rules out the possibility of the formation of $[Cd(L^2)_2][CdX_4]$ or $[CdX(L^2)_2]X$ species.

Recrystallisation from dichloromethane afforded colourless needle crystals of complex **1**. A view of the complex is in Fig. 4, and selected bond lengths and angles are given in Table 2. Complex **1** contains a four-co-ordinate distorted tetrahedral metal centre, with the ligand L^2 bound in a bidentate fashion, Cd–P(1) 2.580(2), Cd–P(2) 2.553(2) Å and P(1)–Cd–P(2) 97.94(6)°. The Cd–P bond lengths, which are significantly different from each other, are also considerably shorter than those noted in $[Cd(dmpe)\{TeSi(SiMe_3)_3\}_2]$ [Cd–P mean 2.701(5) Å], although this may well be a reflection of the bulky silyl groups on the latter compound. The Cd–Cl bond lengths differ slightly at Cd–Cl(1) 2.403(2), Cd–Cl(2) 2.440(2) Å, but fall within the expected range. The metal geometry is significantly distorted from tetrahedral with angles ranging from 97.94(6) [P(1)–Cd–P(2)] to 120.68(7)° [Cl(1)–Cd–Cl(2)]. This can be attributed in part to the high steric crowding about the cadmium due to the phenyl groups. There is also evidence for an intermolecular C(43)–H(43)···Cl(2) interaction [H(43)···Cl(2*) 2.74, C(43)···Cl(2*) 3.616(11) Å, C(43)–H(43)···Cl(2*) 158°; Cl(2*) at $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. The combination of the steric effects and the crystal packing thus explains the distortion from idealised tetrahedral geometry and the non-equivalence of the phosphorus atoms in the solid state.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Cd–Cl(1)	2.403(2)	P(1)–C(1)	1.815(6)
Cd–Cl(2)	2.440(2)	P(1)–C(21)	1.810(6)
Cd–P(1)	2.580(2)	P(2)–C(2)	1.826(6)
Cd–P(2)	2.553(2)	P(2)–C(31)	1.806(7)
P(1)–C(1)	1.811(7)	P(2)–C(41)	1.806(5)
Cl(1)–Cd–Cl(2)	120.68(7)	Cd–P(2)–C(2)	104.4(2)
Cl(1)–Cd–P(1)	113.05(6)	Cd–P(2)–C(31)	118.0(2)
Cl(1)–Cd–P(2)	120.12(6)	Cd–P(2)–C(41)	114.2(2)
Cl(2)–Cd–P(1)	102.44(7)	C(1)–Si–C(2)	113.5(3)
Cl(2)–Cd–P(2)	98.89(6)	C(1)–Si–C(3)	105.3(3)
P(1)–Cd–P(2)	97.94(6)	C(1)–Si–C(4)	113.2(3)
Cd–P(1)–C(1)	110.1(2)	C(2)–Si–C(3)	104.4(3)
Cd–P(1)–C(11)	113.6(2)	C(2)–Si–C(4)	110.8(3)
Cd–P(1)–C(21)	113.1(2)	C(3)–Si–C(4)	109.1(4)

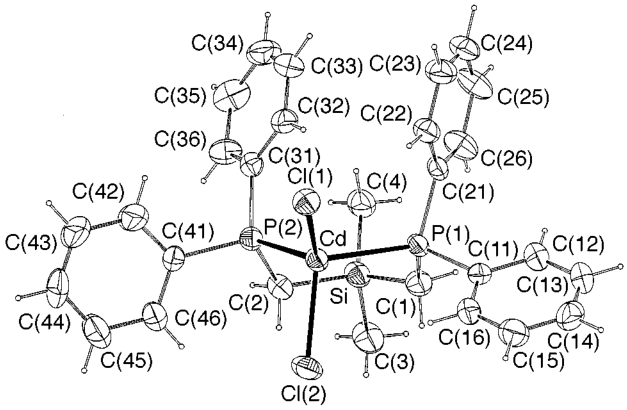

Fig. 4 A view of the crystal structure of complex **1**, with thermal ellipsoids at the 30% probability level

The ligand chelate bite angle is considerably smaller than the values of 101.54(6) and 105.28(6)° in the analogous $[CoBr_2(L^2)]$[6] and $[HgI_2(L^2)]$[7] complexes, respectively. The six-membered chelate ring defined by Cd, P(1), P(2), C(1), C(2) and Si adopts a chair conformation, with torsion angles ranging from −45.6(2) [P(2)–Cd–P(1)–C(1)] to −66.2(4)° [Cd–P(2)–C(2)–Si].

In summary, the addition of 1 equivalent of L^2 to cadmium(II) salts produces mononuclear four-co-ordinate tetrahedral metal species, which are of sufficient solubility to engender multinuclear NMR spectroscopic studies.

Experimental

The cadmium salts were purchased from Aldrich Chemical Co. and used as supplied. All solvents used were reagent grade and were distilled immediately prior to use. A stock solution of L^2 in dichloromethane (1 g, 10 cm^{3}) was prepared. The NMR spectra were recorded on a Bruker WH-400 FT-NMR spectrometer at 400.1 (^{1}H, ref. SiMe$_4$), 162.0 (^{31}P) and 88.7 MHz (^{113}Cd). Solid-state ^{31}P NMR spectra were recorded on a Bruker CXP-200 using the CP-MAS technique. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 180 double-beam spectrometer. Elemental analyses were performed by M. H. W. Laboratories, Phoenix, AZ.

Preparation of [CdCl$_2$(L^2)] 1

To a stirred solution of cadmium chloride (0.80 g, 4.40 mmol) in ethanol (50 cm^3), a dichloromethane solution of L^2 (2.00 g, 4.38 mmol) was added dropwise. The white precipitate that formed immediately was stirred for 20 min, filtered, washed with ethanol and dry diethyl ether and dried *in vacuo* overnight. Yield 2.10 g (72%), m.p. 235 °C (Found: C, 52.42; H, 4.70. $C_{28}H_{30}CdCl_2P_2Si$ requires C, 52.56; H, 4.72%). ν_{max}/cm^{-1} (Nujol) 280vs, 255vs (Cd–Cl), 148w and 134w (Cd–P). δ_H(CDCl$_3$) 7.78–7.31 (20 H, m, 4 C$_6$H$_5$P), 1.84 [4 H, t, *J*(P–H) 5.4, *J*(Cd–H) 28.6 Hz, 2 CH$_2$] and −0.29 (6 H, s, SiMe$_2$).

Preparation of [CdBr$_2$(L^2)] 2

To a stirred solution of cadmium bromide (1.10 g, 4.04 mmol) in ethanol (50 cm^3), L^2 (1.85 g, 4.05 mmol) in dichloromethane was added dropwise, yielding the immediate deposition of a white precipitate. The reaction mixture was stirred for 30 min, and the precipitate was filtered, washed with ethanol and dry diethyl ether and dried *in vacuo* overnight. Yield 2.03 g (68%), m.p. 245 °C (Found: C, 46.36; H, 4.35. $C_{28}H_{30}Br_2CdP_2Si$ requires C, 46.15; H, 4.15%). ν_{max}/cm^{-1} (Nujol) 202vs, 178vs (Cd–Br) and 136w (Cd–P). δ_H(CDCl$_3$) 7.72–7.36 (20 H, m, 4 C$_6$H$_5$P), 1.87 [4 H, t, *J*(P–H) 5.7, *J*(Cd–H) 26.8 Hz, 2 CH$_2$] and −0.29 (6 H, s, SiMe$_2$).

Preparation of [CdI$_2$(L^2)] 3

A dichloromethane solution of L^2 (2.00 g, 4.38 mmol) was added dropwise with stirring to a solution of cadmium iodide (1.50 g, 4.10 mmol) in ethanol (50 cm^3). A white precipitate formed immediately. After stirring for 20 min the precipitate was filtered, washed with ethanol and dry diethyl ether and dried *in vacuo* overnight. Yield 2.65 g (80%), m.p. 215 °C (Found: C, 41.00; H, 3.85. $C_{28}H_{30}CdI_2P_2Si$ requires C, 40.87; H, 3.67%). ν_{max}/cm^{-1} (Nujol) 172s, 158s (Cd–I) and 134w (Cd–P). δ_H(CDCl$_3$) 7.79–7.27 (20 H, m, 4 C$_6$H$_5$P), 1.90 [4 H, t, *J*(P–H) 5.6, *J*(Cd–H) 26.1 Hz, 2 CH$_2$] and −0.31 (6 H, s, SiMe$_2$).

Preparation of [Cd(NO$_3$)$_2$(L^2)] 4

A stirred solution of cadmium nitrate (1.20 g, 5.08 mmol) in ethanol (50 cm^3) was treated with a dichloromethane solution of L^2 (2.00 g, 4.38 mmol) and the reaction mixture was stirred for 4 h. The resultant white precipitate was filtered, washed with ethanol and dry diethyl ether and dried *in vacuo* overnight. Yield 2.27 g (65%), m.p. 232 °C (Found: C, 48.33; H, 4.37; N, 4.05. $C_{28}H_{30}CdN_2O_6P_2Si$ requires C, 48.53; H, 4.36; N, 4.04%). ν_{max}/cm^{-1} (Nujol) 1440s, 1290vs, 1015s, 840s, 745m, 720s (NO$_3$) and 140w (Cd–P). δ_H(CDCl$_3$) 7.62–7.36 (20 H, m, 4 C$_6$H$_5$P), 1.96 [4 H, t, *J*(P–H) 6.2, *J*(Cd–H) 29.0 Hz, 2 CH$_2$] and −0.33 (6 H, s, SiMe$_2$).

Preparation of [Cd(SCN)$_2$(L^2)] 5

To a stirred solution of cadmium thiocyanate (1.00 g, 4.38 mmol) in hot ethanol (50 cm^3), a solution of L^2 (2.00 g, 4.38 mmol) in dichloromethane was added and the reaction mixture was stirred for 4 h. A white precipitate resulted; this was filtered, washed with ethanol and dry diethyl ether and dried *in vacuo* overnight. Yield 2.05 g (73%), m.p. 154 °C (Found: C, 52.49; H, 4.38; N, 4.41. $C_{30}H_{30}CdN_2P_2S_2Si$ requires C, 52.59; H, 4.41; N, 4.09%). ν_{max}/cm^{-1} (Nujol) 2080vs (CN), 830vs, 790s (CS), 460m (NCS), 260s (Cd–SCN) and 190vs (Cd–P). δ_H(CDCl$_3$) 7.66–7.48 (20 H, m, 4 C$_6$H$_5$P), 2.08 [4 H, t, *J*(P–H) 6.0, *J*(Cd–H) 29.4 Hz, 2 CH$_2$] and −0.32 (6 H, s, SiMe$_2$).

Preparation of [Cd(L^2)$_2$][ClO$_4$]$_2$ 6

Cadmium perchlorate (0.80 g, 2.57 mmol) dissolved in ethanol (50 cm^3) and a dichloromethane solution of L^2 (2.35 g, 5.15 mmol) were mixed in a 1 : 2 molar ratio and stirred for 2 h at 50 °C. The white precipitate that formed immediately was filtered, washed with ethanol and dry diethyl ether and dried *in vacuo* overnight. Yield 2.20 g (70%), m.p. 190 °C (Found: C, 54.33; H, 5.36. $C_{56}H_{60}CdCl_2O_8P_2Si$ requires C, 54.93; H, 4.94%). ν_{max}/cm^{-1} (Nujol) 1090vs (br) and 620s (ClO$_4$). δ_H(CDCl$_3$) 7.91–7.23 (20 H, m, 4 C$_6$H$_5$P), 1.70–1.61 (4 H, d, 2 CH$_2$) and −0.01 (6 H, s, SiMe$_2$).

Table 3 Summary of crystal data, data collection, structure solution and refinement details for complex **1**

Crystal data	
Empirical formula	$C_{28}H_{30}CdCl_2P_2Si$
M	639.85
Colour, habit	Colourless, needle
Crystal size/mm	0.42 × 0.18 × 0.17
Crystal system	Orthorhombic
a/Å	9.2862(10)
b/Å	15.386(2)
c/Å	20.724(3)
U/Å^3	2960.9(6)
Space group	$P2_12_12_1$
Z	4
F(000)	1296
D_{calc}/g cm^{-3}	1.435
μ/mm^{-1}	1.082
Data acquisition[a]	
T/K	294(1)
θ Range/°	9.8–15.0
Max. θ (°) for reflections	24.91
hkl Range of reflections[a]	−11 to 11; −18 to 18; −24 to 24
Variation in 2 standard reflections	1.8%
Reflections measured	5913
Unique reflections	5172
With $I > 2\sigma(I)$	3151
Absorption correction type	ψ Scans
Minimum, maximum absorption correction	0.8038, 0.9980
Structure solution and refinement[b]	
Refinement	On F^2
Solution method	Direct methods
Hydrogen atom treatment	Riding
No. variables in least squares	301
Weights: *k* in $w = 1/(\sigma^2 F_o^2 + k)$ $[P = (F_o^2 + 2F_c^2)/3]$	$(0.0362P)^2$
R, *R′*, *S*	0.043, 0.088, 0.94
Density range in final Δ-map/e Å^{-3}	−0.298, 0.501
Final shift/error ratio	0.001
Flack parameter	−0.08(4)

[a] Data collection on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatised Mo-Kα radiation (λ 0.71067 Å). Two octants of data were collected, one with $+h, +k, +l$, the other with $-h, -k, -l$ indices. [b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs[15] for refinement with observed data on *F*, or with SHELXL 93[16] for refinement with all data on F^2.

Crystal structure of complex 1

The slow evaporation of solvent from a dichloromethane solution of the complex yielded colourless, needle crystals of **1**. A summary of the crystal data, solution and refinement parameters appears in Table 3. X-Ray measurements were made on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. Data were collected in the range $4 \leqslant 2\theta \leqslant 55°$ and corrected for Lorentz, polarisation and absorption effects. Molecule **1** as synthesised is achiral, but it crystallises in the chiral space group $P2_12_12_1$. The analysis establishes the absolute structure of the crystal studied. All non-H atoms were allowed anisotropic motion and hydrogen atoms allowed for as riding atoms. An absorption correction was applied, based on ψ scan data.[17]

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References

1 P. J. Bonasia and J. Arnold, *Inorg. Chem.*, 1992, **31**, 2508.
2 C. E. Wymore and J. C. Bailar jun., *J. Inorg. Nucl. Chem.*, 1960, **14**, 42.
3 S. S. Sandhu, R. Dass and M. Gupta, *J. Indian Chem. Soc.*, 1970, **47**, 1137.
4 G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.
5 E. C. Alyea, K. J. Fisher, R. P. Shakya and A. E. Vougioukas, *Synth. React. Inorg. Met.-Org. Chem.*, 1988, **18**, 163.
6 P. R. Meehan, E. C. Alyea, R. P. Shakya and G. Ferguson, *Polyhedron*, 1997, accepted for publication.
7 E. C. Alyea, P. R. Meehan, R. P. Shakya and G. Ferguson, *Inorg. Chem.*, 1997, accepted for publication.
8 R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1980, **33**, 1677.
9 R. Colton and D. Dakternieks, *Aust. J. Chem.*, 1981, **34**, 323.
10 R. G. Goel, W. P. Henry and N. K. Jha, *Inorg. Chem.*, 1982, **21**, 2551.
11 B. E. Mann, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 595.
12 C. C. Addison, N. Logand, S. C. Wallwork and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.
13 P. H. Merrell, E. C. Alyea and L. Ecott, *Inorg. Chim. Acta*, 1982, **59**, 25.
14 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
15 E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.
16 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
17 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

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