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Structural and spectroscopic studies of cobalt(II) complexes incorporating the bidentate phosphine ligand $Ph_2PCH_2Si(CH_3)_2CH_2PPh_2$

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Abstract—A series of cobalt(II) complexes of general formula $[CoX_2L^2]$ (X = Cl, Br, I, NO_3, ClO_4, NCS; $L^2 = Ph_2PCH_2Si(CH_3)_2CH_2PPh_2$) have been synthesised and characterised by electronic and infrared spectroscopy and by magnetic moment studies. The bidentate phosphine ligand is an analogue of 1,3-bis(diphenylphosphino)propane (dppp). X-ray analysis of the $[CoBr_2L^2]$ complex proves tetrahedral geometry at the metal centre with the bidentate phosphine exhibiting a bite angle of 101.54(6)°. A range of evidence supports the existence of tetrahedral geometry about the metal in all the complexes in both the solid state and solution. Electronic spectroscopy is diagnostic for the tetrahedral d^7 metal ion in each case, with the ν_2 and ν_3 transitions clearly visible. Calculations of D_q and B', the RACAH parameter, have been performed for each complex; the relative magnitudes of B' indicate that the metal-phosphorus bonds are of increased covalency in comparison with Co(dppp) analogues. Magnetic moment studies show values of μ_B in the range 4.4–4.9 B.M., as expected for tetrahedral cobalt(II). IR studies show that the nitrate and perchlorate ions in the respective complexes are bound in monodentate fashion, while the $[Co(NCS)_2(L^2)]$ complex exhibits N-bonded thiocyanate groups. © 1997 Elsevier Science Ltd

Keywords: cobalt II; bidentate phosphine; X-ray structure; spectroscopic studies.

Tertiary phosphine ligands form an extensive part of the known co-ordination chemistry of the transition metals [1]. Bidentate phosphine ligands comprise an integral part of this chemistry, with the ligand 1,2-bis(diphenylphosphino)ethane (dppe) perhaps the most widely studied. The bidentates offer greater stability than their monodentate equivalents, and influence control over the stereochemistry, co-ordination number and stoichiometry of their complexes [2]. There is interest [3] in observing the effects that varying the length of the backbone in $R_2P(CH_2)_nPR_2$ ligands has upon the stereochemistry of metal complexes. Transition metal complexes of the tertiary phosphines are also of interest as homogeneous catalysts; the nature of the complex can influence selectivity, reactivity and stability [4].

The incorporation of silicon into the backbone of phosphine ligands was first carried out in 1962 [5]. Alyea and co-workers [6] subsequently reported the preparation of the novel ligand 2,2-dimethyl-2-sila-1,3-bis(diphenylphosphino)propane, $Ph_2PCH_2Si(CH_3)_2CH_2PPh_2$, subsequently denoted L^2. This ligand is a cousin of the more renowned 1,3-bis(diphenylphosphino)propane (dppp), but the presence of the dimethylsilyl backbone confers several advantages over the dppp analogue: L^2 is highly soluble in organic solvents, and the dimethylsilyl group provides a sensitive NMR probe. The crystal structure of $[Ni(NO_3)_2L^2]$ was reported in 1987 [7]. The complex provided a rare example of *allogons*, where both square planar and tetrahedral forms occur for the same complex; the square planar form was structurally characterised.

Cobalt(II) combines with diphosphines in 1 : 1, 1 : 2 and, rarely, 1 : 1.5 stoichiometry [1]. Studies again revolve around dppe-type ligands, with pseudo-tetrahedral geometries reported for $[Co(dppm)X_2]$ [8] and $[Co(dppe)X_2]$ [9] (X = Cl, Br, I). Complexes with dppp, the analogue of L^2, are also known; the pseudo-

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tetrahedral [Co(dppp)(SPh)$_2$] [10] is a rare example of a crystallographically characterised four co-ordinate cobalt(II)-dppp complex. Complexes of general formula [Co(dppp)$_{1.5}$X$_2$] (X = CN, NCS) have also been reported [11]. These latter compounds were thought to exhibit a dimeric structure in which one of the dppp groups acted as a bidentate bridging ligand between the two cobalt centres.

The scope of the research reported here was to synthesise a range of complexes of general formula [CoX$_2$L^2] and investigate their co-ordination properties by structural, magnetic and spectroscopic (electronic, infrared) studies. Characterisation of these species would afford a direct comparison between L^2 and dppp complexes of cobalt(II) and also provide some insight into the different bonding properties of the two ligands. A further objective was to use spectroscopic techniques to determine the mode of co-ordination of the nitrate, perchlorate and thiocyanate ligands in the respective complexes.

EXPERIMENTAL

General comments

Ligand L^2 was prepared according to the literature method [6]. All complexes were prepared and handled under a nitrogen atmosphere using standard Schlenk techniques. The solvents used were reagent grade and were dried and distilled immediately prior to use. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Az. UV–vis spectra were recorded on CsI plates as Nujol mulls on a Cary-14 UV-visible spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer 180 double beam spectrometer. Magnetic moment measurements were performed by the Evans method[12] on a Varian EM 360 NMR spectrometer.

X-ray crystallography

Diffraction-quality crystals of (1) were obtained by slow evaporation of a dichloromethane solution of the complex. The crystallographic data are summarised in Table 1. X-ray measurements were made on an Enraf–Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-K_α radiation. Data were collected in the range $4 \leqslant 2\theta \leqslant 55°$ and corrected for Lorentz, polarisation and absorption effects. The structure was solved using the heavy-atom method and the NRCVAX [13] program system. Final refinement was performed with SHELXL-93 [14] using all F^2 data, with all non-H atoms allowed anisotropic motion and hydrogen atoms allowed for as riding atoms.

Table 1. Crystallographic data for [CoBr$_2$L^2] (**1**)

formula	$C_{28}H_{30}Br_2CoP_2Si$
fw	675.30
colour	green
space group	$P2_1/n$
a (Å)	9.4893(8)
b (Å)	18.457(2)
c (Å)	16.632(2)
β (deg)	90.122(8)
V (Å^3)	2912.9(5)
Z	4
T (°C)	20
λ (Mo-K_α Å)	0.70930
ρ_{calcd} (g cm^{-3})	1.540
μ (mm^{-1})	3.499
R^a	0.0531
R_w^a	0.0758

[a] Residuals calculated for reflections with $I > 2\sigma(I)$; $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[CoX$_2$(Ph$_2$PCH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)] (X = Cl, Br, NO$_3$, ClO$_4$)

Addition of the ligand dissolved in dichloromethane to stirred solutions of the cobalt(II) salts in ethanol (60 cm^3) and dimethoxypropane (2 cm^3) in a 1 : 1 molar ratio produced the immediate deposition of blue to green coloured precipitates. After stirring for 4 h at room temperature the precipitates were filtered, washed with ethanol and dry ether and pumped dry overnight. Yields 60–75%. Anal.Calcd for $C_{28}H_{30}CoCl_2P_2Si$: 57.35; H, 5.16. Found: C, 57.43; H, 5.38. Anal. Calcd for $C_{28}H_{30}CoBr_2P_2Si$: C, 49.80; H, 4.48. Found: C, 49.96; H, 4.46. Anal. Calcd for $C_{28}H_{30}CoN_2O_6P_2Si$: C, 52.59; H, 4.73; N, 4.38. Found: C, 52.59; H, 5.08; N, 4.34. Anal. Calcd for $C_{28}H_{30}CoCl_2O_8P_2Si$: C, 47.07; H, 4.23. Found: C, 47.11; H, 4.39.

CAUTION! Perchlorate salts of metal complexes containing organic ligands are potentially explosive. Only small amounts of such complexes should be made, and should be handled with great care [15].

[CoI$_2$(Ph$_2$PCH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)]

To a solution of [CoCl$_2$(Ph$_2$PCH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)] (0.3 g, 0.5 mmol) in dichloromethane (120 cm^3), a solution of potassium iodide (0.35 g, 2.1 mmol) in hot ethanol (40 cm^3) was added. The solution turned purple immediately. After 3 h the green precipitate that appeared was filtered, washed with ethanol and pumped dry overnight. Yield 65%. Anal. Calcd for $C_{28}H_{30}CoI_2P_2Si$: C, 43.71; H, 3.93. Found: C, 43.78; H, 3.98.

[Co(NCS)$_2$(Ph$_2$PCH$_2$Si(CH$_3$)$_2$CH$_2$PPh$_2$)]

Equimolar amounts of an ethanolic solution of Co(NCS)$_2$ and a dichloromethane solution of the

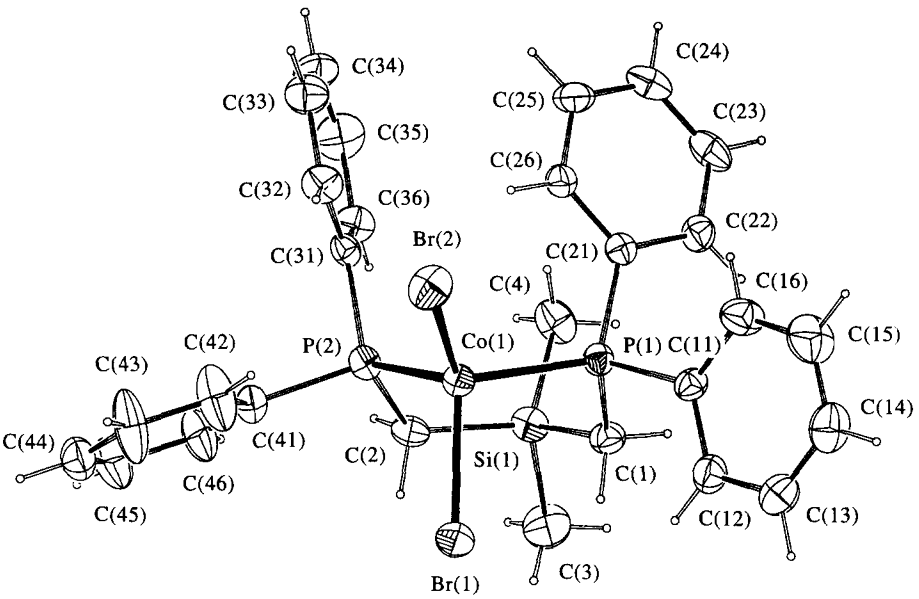


Fig. 1. ORTEP view of **1**. Thermal ellipsoids are drawn at the 30% probability level.

ligand were added together and stirred for 1 h. The resultant green precipitate was filtered, washed with ethanol and dry ether and dried *in vacuo* overnight. Yield 62%. Anal. Calcd for $C_{30}H_{30}CoN_2P_2S_2Si$: C, 57.05; H, 4.79; N, 4.43. Found: C, 57.21; H, 4.93; N, 4.50.

RESULTS AND DISCUSSION

Crystal structure of $[CoBr_2(Ph_2PCH_2Si(CH_3)_2CH_2PPh_2)]$ (**1**)

An ORTEP [16] view of the molecule appears in Fig. 1, and selected bond lengths and angles are given in Table 2. The metal centre is tetrahedral, bound to two bromine atoms [Co(1)—Br(1) 2.360(1), Co—Br(2) 2.347(1) Å] and the two phosphorus donor sites on the bidentate ligand. The Co—P distances [Co(1)—P(1) 2.344(2), Co(1)—P(2) 2.364(2) Å] compare closely with values noted in the two structurally characterised four co-ordinate Co-dppp complexes ($[CpCo(dppp)(SPh)]PF_6$ [17] Co—P 2.225, $[Co(dppp)(SPh)_2]$ [10] Co—P 2.346 Å). Angles around the metal centre range from 101.54(6) [P(1)—Co(1)—P(2)] to 117.54(4)° [Br(1)—Co(1)—B(2)]. The six membered chelate ring comprising Co(1), P(1), C(1), Si(1), C(2), P(2) adopts a chair conformation; it is noteworthy that the equivalent chelate ring in $[Ni(NO_3)_2L^2]$ [7] adopts a boat conformation. This difference is presumably due to the square planar metal centre in the nickel analogue. The chelate bite angle in (**1**) is 101.54(6)° [P(1)—Co(1)—P(2)]; this compares to much lower values observed in the dppp complexes, the enhanced value reflecting the incorporation of the larger silicon

Table 2. Selected bond distances (Å) and angles (°) for the crystal structure of $[CoBr_2L^2]$ (**1**)

Co(1)—Br(1)	2.360(1)	P(1)—C(11)	1.804(6)
Co(1)—Br(2)	2.347(1)	P(1)—C(21)	1.816(6)
Co(1)—P(1)	2.344(2)	P(2)—C(2)	1.821(5)
Co(1)—P(2)	2.364(2)	P(2)—C(31)	1.812(6)
P(1)—C(1)	1.823(5)	P(2)—C(41)	1.823(6)
Br(1)—Co(1)—Br(2)	117.54(4)	C(1)—Si(1)—C(3)	106.3(3)
Br(1)—Co(1)—P(1)	102.31(5)	C(1)—Si(1)—C(4)	111.3(3)
Br(1)—Co(1)—P(2)	101.93(5)	C(2)—Si(1)—C(3)	105.1(3)
Br(2)—Co(1)—P(1)	113.86(5)	C(2)—Si(1)—C(4)	114.0(3)
Br(2)—Co(1)—P(2)	117.30(5)	Co(1)—P(1)—C(11)	115.0(2)
P(1)—Co(1)—P(2)	101.54(6)	Co(1)—P(1)—C(21)	116.8(2)
Co(1)—P(1)—C(1)	107.1(2)	Co(1)—P(2)—C(31)	117.9(2)
Co(1)—P(2)—C(2)	107.9(2)	Co(1)—P(2)—C(41)	113.3(2)
C(1)—Si(1)—C(2)	111.0(3)		

atom into the ligand backbone. The C—Si—C angles in complex (**1**) range from 105.1(3) [C(2)—Si(1)—C(3)] to 114.0(3)° (C(2)—Si(1)—C(4)), with the C(1)—Si(1)—C(2) backbone at 111.0(3)°.

Electronic spectra

The electronic spectra of tetrahedral complexes of cobalt(II) show three electronic transitions from the $^4A_2$ ground state. ν_1 ($^4A_2 \rightarrow {}^4T_2$) occurs in the range 3000–5000 cm^{-1} and is rarely observed. ν_2 [$^4A_2 \rightarrow {}^4T_1(F)$] is usually a broad band which appears in the near IR region, while ν_3 [$^4A_2 \rightarrow {}^4T_1$(P)] is broad and intense, with noticeable fine structure. Unfortunately the broadness of these latter two bands renders their assignment somewhat arbitrary. However, electronic spectroscopy can be used to ascertain metal geometry: the structures of [CoX$_2$(L)] (X = Cl, Br and L = dppe, dppp) and [Co(dppe)$_2$I]I were identified as tetrahedral and pentaco-ordinate, respectively, on the basis of their electronic spectra [18a].

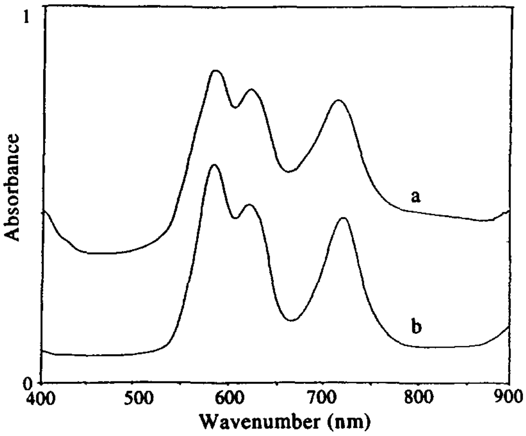


Fig. 2. UV–vis spectra of [CoCl$_2$L^2]: (a) solid state, (b) dichloromethane solution. The absorbance (y-axis) scale has arbitrary units.

The electronic spectroscopic data for the cobalt(II) complexes are presented in Table 3. The solid state and solution UV–vis spectra are very similar: the spectra in the visible range for CoCl$_2$L^2 appear in Fig. 2. Bands corresponding to the ν_2 transition appear in the near-IR region; they are typically broad, with a degree of splitting observed. Dynamic Jahn–Teller effects in the excited states are almost certainly responsible for the energy spread. The bands arising from ν_3 appear in the range 13,000–20,000 cm^{-1}. The assignment of ν_2 and ν_3 allows calculation of ligand field strength Dq and the RACAH parameter B; for example, the chloride complex has average values of $\nu_2 = 7775$ cm^{-1} and $\nu_3 = 16{,}310$ cm^{-1}. These values are calculated using the method reported by Drago [18b]. B is a measure of electron–electron repulsion and has a lower value in complexes as compared with the free ion: it is hence denoted B′. Values for Dq and B′ also appear in Table 3.

On the basis of the Dq values calculated for the cobalt(II) complexes here, it is possible to assign the spectrochemical series as $I^- < Br^- < Cl^- \leqslant ClO_4^- < NO_3^- \leqslant NCS^-$. This is consistent with previously reported complexes [19,20]. Calculation of Dq for [CoX$_2$(dppp)] (X = Cl, Br, I) using data given in Ref. [18a] resulted in slightly lower values than in the analogous L^2 systems here. Thus L^2 shows a slightly greater ligand field strength and a different bonding ability than dppp. It is also possible to determine that the thiocyanate ligands in [Co(NCS)$_2$L^2] are N-bonded to the metal centre; if the ligand was S-bonded it would appear between Br$^-$ and Cl$^-$ in the spectrochemical series. B′ values for all the complexes are 60–73% of the free ion values, reflecting an appreciable orbital overlap. The intensities of the bands in the

Table 3. UV–vis data[a] for [CoX$_2$L^2] complexes

X	UV–vis λ_{max}, nm (ε^b, M^{-1} cm^{-1})	D_q (cm^{-1})	B′[c] (cm^{-1})
Cl	598 (1160), 629 (960), 725 (850), 847 sh., 1205 (160), 1449 (200)	454	697[d]
Br	624 (1180), 666 (1130), 741 (970), 877 sh., 1266 (160), 1471 (170)	438	657
I	675 (1150), 714 (980), 763 (880), 847 sh., 1299 (150), 1493 (120)	432	586[d]
NO$_3$	598 (770), 629 (800), 730 (530), 862 sh., 1190 (150), 1408 (180)	464	680
ClO$_4$	600 (940), 629 (800), 730 (740), 1205 (170), 1449 (200)	455	695
NCS	575 (640), 625 (800), 1163 (220), 1449 (120)	466	713

[a] in CH$_2$Cl$_2$.
[b] extinction coefficient.
[c] RACAH parameter for Co^{2+} = 971 cm^{-1}.
[d] values of B′ for [CoX$_2$(dppp)] 705 (Cl), 678 (I) cm^{-1} (calculated from data in Ref. [18]).

electronic spectra are due in large part to molecular orbital mixing i.e. covalency [9]. The extinction coefficients of the L^2 complexes are higher than those of analogous dppp systems, again reflecting increased covalency. Lower values of the RACAH parameter B′ for $[CoCl_2L^2]$ and $[CoI_2L^2]$ compared to their dppp analogues also suggests increased covalency in the Co—P bonds in the L^2 complexes.

Magnetic moment studies

Magnetic moments for the complexes were measured by the Evans method [12] and were corrected for ligand diamagnetism and temperature-independent paramagnetism (T.I.P.). The values, which appear in Table 4, fall in the range 4.4–4.9 μ_B and are similar to those for other pseudotetrahedral cobalt(II)–phosphine complexes [21]. The values are slightly higher for complexes of L^2 than the dppp analogues ($\mu_B = 4.43$ (Cl), 4.47 (Br), 4.56 (I) B.M.], indicative of more regular tetrahedral geometry around the metal; this is a reflection of the larger chelate ring available in L^2. The data are also consistent with the $S = 3/2$ ground state with a significant orbital contribution to the magnetic moment ($\mu_{eff} = 3.87$ B.M. (spin only)]. The magnetic moment order ($I^- > Br^- > Cl^- \geqslant NO_3^- > ClO_4^- > NCS^-$) is concurrent with the order established by Cotton [19] and Nicolini [22] for tetrahedral $[CoX_2(L)_2]$ (L = amine) complexes.

Infrared spectra

All the complexes display characteristic ligand bands [23]. The halide complexes each show characteristic Co–X stretching frequencies, with ν(Co—Cl) 320, ν(Co—Br) 270, ν(Co—I) 224 cm^{-1}. The presence of these bands is indicative of terminal Co-halide bonds [24]. Co—P stretches are assigned in the region 210–250 cm^{-1} and, although weak, their appearance is consistent with tetrahedral geometry. For the complex $[Co(NCS)_2L^2]$ the infrared spectrum confirms the presence of N-bonded thiocyanate; Bailey *et al.* [25] established IR patterns in M–NCS, M–SCN and M–NCS–M′ systems and concluded that for S-bonded thiocyanate, the characteristic IR stretch appeared at 2130–2160 cm^{-1}. The band at 2050 cm^{-1} in the complex here is concurrent with the N-bonded form. Signals at 790 [ν(CS)] and 485 [δ(NCS)] cm^{-1} provide additional confirmation.

Table 4. Magnetic data[a] for $[CoX_2L^2]$ complexes

X	$\chi_g{}^b \times 10^{-6}$ c.g.s.	$\chi_m{}^b \times 10^{-6}$ c.g.s.	$\mu_{eff}{}^d$ (B.M.)
Cl	13.43	8693.3	4.6
Br	12.72	9430.7	4.8
I	11.43	9664.5	4.9
NO_3	12.04	8510.3	4.6
ClO_4	10.29	8189.2	4.5
NCS	10.99	7766.2	4.4

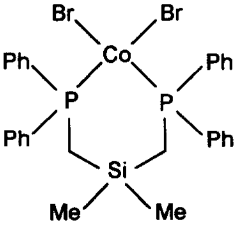
[a] in CH_2Cl_2 at 303 K.
[b] gram susceptibility.
[c] molar susceptibility, corrected for T.I.P. (500×10^{-6} c.g.s. units) and diamagnetism (L^2 correction = 262.1×10^{-6} c.g.s. units)
[d] $\mu \pm 0.1$ B.M.

Electronic spectroscopy and magnetic moment studies point to a tetrahedral geometry for $[Co(NO_3)_2L^2]$, with each nitrate ligand bound in monodentate fashion. The extent of splitting of the ν_3 band is often used to determine mono- or bidentate coordination of nitrate ions, with a separation of > 150 cm^{-1} implying a bidentate mode, and a corresponding value < 150 cm^{-1} pointing towards monodenticity. In this case bands at 1380 and 1280 cm^{-1} (ν_3) have a separation of 100 cm^{-1}: other bands at 1005 (ν_1), 830 (ν_2) and 750, 720 (ν_4) are consistent with monodentate NO_3^- groups. The previously-reported [7] $Ni(NO_3)_2$ complex of L^2 also shows monodentate nitrate, with a ν_3 splitting of 85 cm^{-1}.

The perchlorate complex $[Co(ClO_4)_2L^2]$ shows a split in the fundamental ν_3 (1100, 1030) and ν_4 (640, 605 cm^{-1}) modes, suggesting monodentate ClO_4^- of C_{3v} symmetry. Observation of bands for ν_2 (920) and ν_6 (440 cm^{-1}) verifies the monodentate nature of the perchlorate [26]. Tetrahedral perchlorate usually has four modes of vibration with only ν_3 and ν_4 IR active. However, monodentate co-ordination lowers the symmetry to C_{3v} and the extra modes thus appear.

CONCLUSIONS

The novel ditertiary phosphine ligand L^2, an analogue of dppp, readily forms 1 : 1 complexes with cobalt(II) salts (anions = Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, NCS^-). The electronic and infrared spectroscopic and magnetic moment data indicate that Co^{II} has tetrahedral geometry in both the solid state and solution. The IR evidence shows that the nitrate and perchlorate anions are monodentate and that the thiocyanate group is N-bonded. The electronic spectral and magnetic data suggest that the Co—P bonds in



(1)

Scheme 1.

the L^2 complexes are of increased covalent character than those in corresponding dppp analogues, and that the L^2 ligand chelates better to the tetrahedral sites. Verification of the metal geometry and these deductions was obtained by the X-ray structural determination of the $[CoBr_2L^2]$ complex, in which the bidentate L^2 phosphine ligand exhibits a bite of 101.54(6)°.

Supplementary data—Tables of X-ray experimental details and crystallographic data, all atomic coordinates, anisotropic displacement parameters and bond distances and angles for the crystal structure of (**1**) (15 pages). Ordering information is given on any current masthead page.

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