Co-ordination Chemistry of Higher Oxidation States. Part 33.[1] Five-co-ordinate Diphosphine Complexes of Cobalt(III), $[Co\{Ph_2P(CH_2)_nPPh_2\}X_3]$ (n = 4 or 5, X = Cl or Br)†

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Oxidation of $[Co\{Ph_2P(CH_2)_nPPh_2\}X_2]$ (n = 4 or 5, X = Cl or Br) with NOX in CH_2Cl_2 produces intensely coloured $[Co\{Ph_2P(CH_2)_nPPh_2\}X_3]$, which are rare examples of five-co-ordinate cobalt(III) complexes. The complexes have been characterised by analysis, magnetic measurements ($\mu_{eff.}$ = *ca.* 3), i.r. and u.v.–visible spectroscopies. First co-ordination sphere bond lengths for the complexes with n = 4 have been obtained from cobalt *K*-edge extended *X*-ray absorption fine structure data. The properties of these complexes are compared with those of the monodentate phosphine analogues $[Co(PR_3)_2X_3]$. Attempts to obtain similar complexes with shorter backbone diphosphines have been unsuccessful.

Five-co-ordinate trigonal-bipyramidal phosphine complexes of cobalt(III) and nickel(III) $[M(PR_3)_2X_3]$ (M = Co or Ni, X = Cl or Br) can be prepared by nitrosyl halide oxidation of the corresponding $[M(PR_3)_2X_2]$.[2–4] For nickel(III), diphosphine complexes $[Ni(L–L)X_3]$ [L–L = $Ph_2PCH_2CH_2PPh_2$, *o*-$C_6H_4(PPh_2)_2$, $Me_2PCH_2CH_2PMe_2$, *etc.*] are also readily prepared and have distorted square-pyramidal geometries.[5] The close similarity between the complexes of the two metals with monodentate phosphines suggests that similar complexes of cobalt(III) with diphosphines should also exist, although none has been reported, indeed five-co-ordination is generally rare for Co^{III}. In contrast six-co-ordinate cobalt(III) diphosphines $[Co(L–L)_3]^{3+}$ and *cis*- and *trans*-$[Co(L–L)_2X_2]^+$ are well known.[6–8]

Results and Discussion

The synthetic route to $[Ni(L–L)X_3]$ is halogen oxidation of solutions of the corresponding $[Ni(L–L)X_2]$,[5] and hence the obvious route to cobalt(III) complexes is similar oxidation of $[Co(L–L)X_2]$. This proves to be a major problem in that few genuinely monomeric $[Co(L–L)X_2]$ are known. Usually reaction of a diphosphine with cobalt(II) halides yields materials which are mainly $[Co(L–L)_2X]X$ or $[Co(L–L)_2X]_2[CoX_4]$.[9] Even when materials with a 1:1 stoicheiometry are obtained, *e.g.* with *o*-$C_6H_4(PPh_2)_2$, $Ph_2PCH_2CH_2PPh_2$, or *cis*-$Me_2AsCH{=}CHAsMe_2$,[10–12] the spectroscopic data mostly suggest a $[Co(L–L)_2][CoX_4]$ formulation. This formation of [cation][anion] species rather than $[Co(L–L)X_2]$ seems to be the norm for two-carbon backboned diphosphines. All our attempts to prepare the reported $[Co(Ph_2PCH_2CH_2PPh_2)X_2]$[13] (X = Cl or Br) have been unsuccessful; in every case the corresponding diphosphine dioxide complexes were obtained, a result recently established by others for X = Cl *via* an *X*-ray study.[14] Genuine monomeric 1:1 complexes appear to be limited to ligands with longer backbones $[Ph_2P(CH_2)_nPPh_2$, n = 3—5] or with bulky terminal groups $[(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$, n = 3—5].[15,16,‡] Hence the attempts to prepare the $[Co(L–L)X_3]$ complexes are considerably restricted by the available starting materials. Unlike nickel, where some $[Ni(L–L)_2X_2]$ are halogen oxidised to $[Ni(L–L)X_3]$ with cleavage of one bidentate ligand, similar reactions with $[Co(L–L)_2X_2]$ generally proceed only as far as $[Co(L–L)_2X_2]^+$.[8,18]

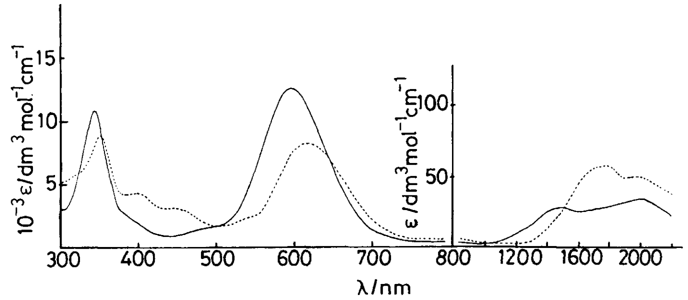

Figure 1. U.v.–visible spectra of $[Co\{Ph_2P(CH_2)_5PPh_2\}X_3]$ in CH_2Cl_2 solution. Solid line X = Cl, broken line X = Br

Oxidation of $[Co\{Ph_2P(CH_2)_nPPh_2\}X_2]$ (n = 4 or 5, X = Cl or Br) with NOX in CH_2Cl_2 at low temperature gave intense blue-black (X = Cl) or green-black (X = Br) solutions, from which $[Co\{Ph_2P(CH_2)_nPPh_2\}X_3]$ materials were obtained upon removal of the solvent. The complexes are reasonably soluble in chlorocarbon solvents, much more so than the cobalt(II) starting materials, although the solutions are completely decomposed in a few days. In the solid state the complexes have somewhat longer shelf-lives than the monodentate analogues.[4] Selected physical data are given in the Table. Similar treatment of $[Co\{Ph_2P(CH_2)_3PPh_2\}Br_2]$ gave a dark brown material which was too unstable to characterise, whilst the corresponding chloride decomposed to $[CoCl_4]^{2-}$ and diphosphine dioxide. The treatment of $[Co\{(C_6H_{11})_2P(CH_2)_4P(C_6H_{11})_2\}X_2]$ with NOX did not produce any reaction, the colour of the solutions remaining unchanged. For the four isolated cobalt(III) complexes (Table) the i.r. spectra showed no evidence of phosphine oxide or nitrosyl groups, whilst in the far-i.r. region two or three halogen-sensitive bands were observed for each, consistent with a low-symmetry cobalt environment. The magnetic moments correspond to two unpaired electrons, and the u.v.–visible spectra (Figure 1 shows typical examples) are very similar to those of D_{3h} $[Co(PR_3)_2X_3]$,[4] which strongly supports a five-co-ordinate

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† *Non-S.I. unit employed:* eV $\simeq$ 1.60 × 10^{-19} J.

‡ After completion of this work $[Co(Pr^i_2PCH_2CH_2PPr^i_2)Cl_2]$ was reported.[17]

Table. Physical, spectroscopic, and structural data for $[Co\{Ph_2P(CH_2)_nPPh_2\}X_3]$ (n = 4 or 5; X = Cl or Br)

Complex	Colour	$\mu_{eff.}$[a]	Infrared/cm^{-1} ν(Co–X)[b]
$[Co\{Ph_2P(CH_2)_4PPh_2\}Cl_3]$	Deep blue	3.00	355, 340, 300
$[Co\{Ph_2P(CH_2)_5PPh_2\}Cl_3]$	Blue-black	2.98	358, 338, 302
$[Co\{Ph_2P(CH_2)_4PPh_2\}Br_3]$	Dark green	3.04	—[c]
$[Co\{Ph_2P(CH_2)_5PPh_2\}Br_3]$	Green-black	3.06	290, 279, —[c]

	Electronic spectra/10^3 cm^{-1} (ε/dm^3 cm^{-1} mol^{-1})[d]							
$[Co\{Ph_2P(CH_2)_4PPh_2\}Cl_3]$	4.93 (45),	6.76 (39),	16.8 (10 790),	20.1 (1 600),	—	25.6 (1 580),	29.0 (9 190)	
$[Co\{Ph_2P(CH_2)_5PPh_2\}Cl_3]$	4.98 (26),	6.71 (26),	16.8 (13 100),	20.2 (1 640),	—	25.4 (2 460),	29.1 (11 290)	
$[Co\{Ph_2P(CH_2)_4PPh_2\}Br_3]$	—	—	16.2 (7 350),	19.5 (1 850),	21.9 (2 950),	24.9 (3 770),	28.4 (7 240)	
$[Co\{Ph_2P(CH_2)_5PPh_2\}Br_3]$	5.00 (62),	5.62 (66),	16.2 (7 210),	19.3 (1 050),	22.2 (2 770),	25.1 (3 600),	28.5 (7 580),	30.7 (4 070)

	Refined EXAFS parameters						
	d(Co–X)/Å	d(Co–P)/Å	$2\sigma^2$/Å^2	E_o/eV	VPI	f.i.[e]	R[f]/%
$[Co\{Ph_2P(CH_2)_4PPh_2\}Cl_3]$	2.18(2)	2.30(2)	0.012, 0.010	21.4	−4.55	0.50	11.6
$[Co\{Ph_2P(CH_2)_4PPh_2\}Br_3]$	2.38(2)	2.34(2)	0.011, 0.011	13.9	−5.50	0.64	11.8

[a] Measured in $CHCl_3$ solution by the Evans n.m.r. method (D. F. Evans, *J. Chem. Soc.*, 1959, 2003). [b] Nujol Mull, plastic plates. [c] Obscured by other bands. [d] Measured as *ca.* 10^{-4} mol dm^{-3} solutions in CH_2Cl_2. [e] Fit index defined as $\sum_i [(\chi_i^T - \chi_i^E)k_i^3]^2$. [f] $R = (\int|\chi^T - \chi^E|k^3dk/\int|\chi^E|k^3dk) \times 100\%$.

geometry. The steric constraints of the chelating diphosphines preclude a regular D_{3h} geometry (as do the inequivalent halides deduced from the i.r. spectra). Repeated attempts to produce crystals for an *X*-ray crystallographic study have been frustrated by the poor solution stability, and thus the detailed molecular geometry cannot be established. It seems highly likely that an 'intermediate' geometry of C_s symmetry, which is established for a variety of complexes of five-co-ordinate Co^{II} and Ni^{II} with chelating ligands,[19,20] is present in these materials. The close resemblance between the u.v.–visible spectra of these four materials and those of the corresponding $[Co(PR_3)_2X_3]$[4] leads to a tentative assignment of the strong bands at *ca.* 16 500 cm^{-1} as P $\sigma \longrightarrow$ Co charge transfer,* the features at *ca.* 22 000 cm^{-1} for the bromides as Br $\pi \longrightarrow$ Co charge transfer, whilst the bands at *ca.* 29 000 cm^{-1} are P $\sigma \longrightarrow$ Co (in the case of the chlorides the Cl $\pi \longrightarrow$ Co transition may be coincident[4]). This leaves the weaker features at *ca.* 5 000—7 000, 20 000, and 25 000 cm^{-1}, as *d–d* transitions.

Although attempts to obtain single crystals have failed, first co-ordination sphere bond-length data have been obtained *via* Co *K*-edge extended *X*-ray absorption fine structure (EXAFS), a similar approach having been successful for $[Co(PR_3)_2X_3]$.[4] This technique does not normally afford angular information, but provides internuclear distances about the primary absorber, and information about the number and nature of the atoms surrounding the primary absorber (in this case the cobalt centre).[21]

Cobalt *K*-edge EXAFS data were recorded at room temperature in transmission mode on solid samples dispersed in boron nitride. The pre-edge background was removed by subtracting a third-order polynomial fitted to the pre-edge region from the whole spectrum, whilst the atomic component of the oscillatory part of the spectrum was approximated using spline functions. Curve fitting was performed on k^3-weighted Fourier-filtered (0—5 Å) data using the curved wave theory implemented in EXCURVE[22] and *ab initio* phase shifts calculated in the usual manner[22] were used without modification. Data on suitable model compounds are presented in ref. 4. The calculated spectra obtained are shown in Figure 2 plotted against un-Fourier filtered EXAFS together with the respective Fourier transforms. The refined bond distances and the other EXAFS parameters are shown in the Table. The bond distances obtained for $[Co\{Ph_2P(CH_2)_4PPh_2\}X_3]$, d(Co–P) = 2.30(2) and 2.34(2) Å respectively for the chloride and bromide, and d(Co–Cl) = 2.18(2) and d(Co–Br) = 2.38(2) Å, compare well with those recently obtained for the monodentate complexes $[Co(PR_3)_2X_3]$.[4] There are a number of potential dangers in fitting two scattering shells at similar distances especially if as in the case of $[Co\{Ph_2P(CH_2)_4PPh_2\}Cl_3]$ the back-scatterers are of similar mass. Care must therefore be taken to demonstrate the validity of the fits in such systems. In the present complexes all attempts to fit the data to single-shell models resulted in markedly poorer fits [fit index (f.i.) > 1.5, R > 20%; *cf.* two-shell model, f.i. = 0.5, 0.64 and R = 11.6, 11.8 for X = Cl and Br respectively] and in uncharacteristic Debye–Waller factors. The effect of varying the co-ordination numbers (*e.g.* two X groups instead of three) also led to poorer fits (f.i. > 0.9, R > 15%). Examination of the statistics showed that some correlation between the parameters was present, but that in all cases these correlations fell within acceptable limits [the largest between the d(Co–P) and the Debye–Waller factor of Co–Br in the bromide complex is 0.68: correlations less than 0.8 are normally judged acceptable], and therefore the fitting of two shells can be regarded with some confidence.

Experimental

Near-i.r. spectra were recorded on a Varian Cary 2300 spectrometer and other physical measurements were made as described in previous parts of this series. The cobalt(II) diphosphine complexes $[Co\{Ph_2P(CH_2)_nPPh_2\}X_2]$ were made by literature methods.[15]

Cobalt(III) *Complexes: General Method.*—The complex $[Co\{Ph_2P(CH_2)_4PPh_2\}Cl_2]$ (0.04 mmol) was suspended in dry dinitrogen-purged CH_2Cl_2 and cooled to −80 °C (acetone slush). Pure NOCl was distilled into the reaction vessel under static vacuum, and the solution stirred for 15 min. Most of the solid dissolved forming a very dark purple solution. This was filtered to remove unreacted starting material, and taken to dryness *in vacuo*, leaving a deep blue-black solid. The bromides were prepared similarly, except that a solution of NOBr in CH_2Cl_2 was added *via* a syringe (Found: C, 57.6; H, 5.1. Calc.

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* In view of the uncertainty over the geometry, it does not seem reasonable to assign symmetry labels to the cobalt *d* orbitals involved in the transition.

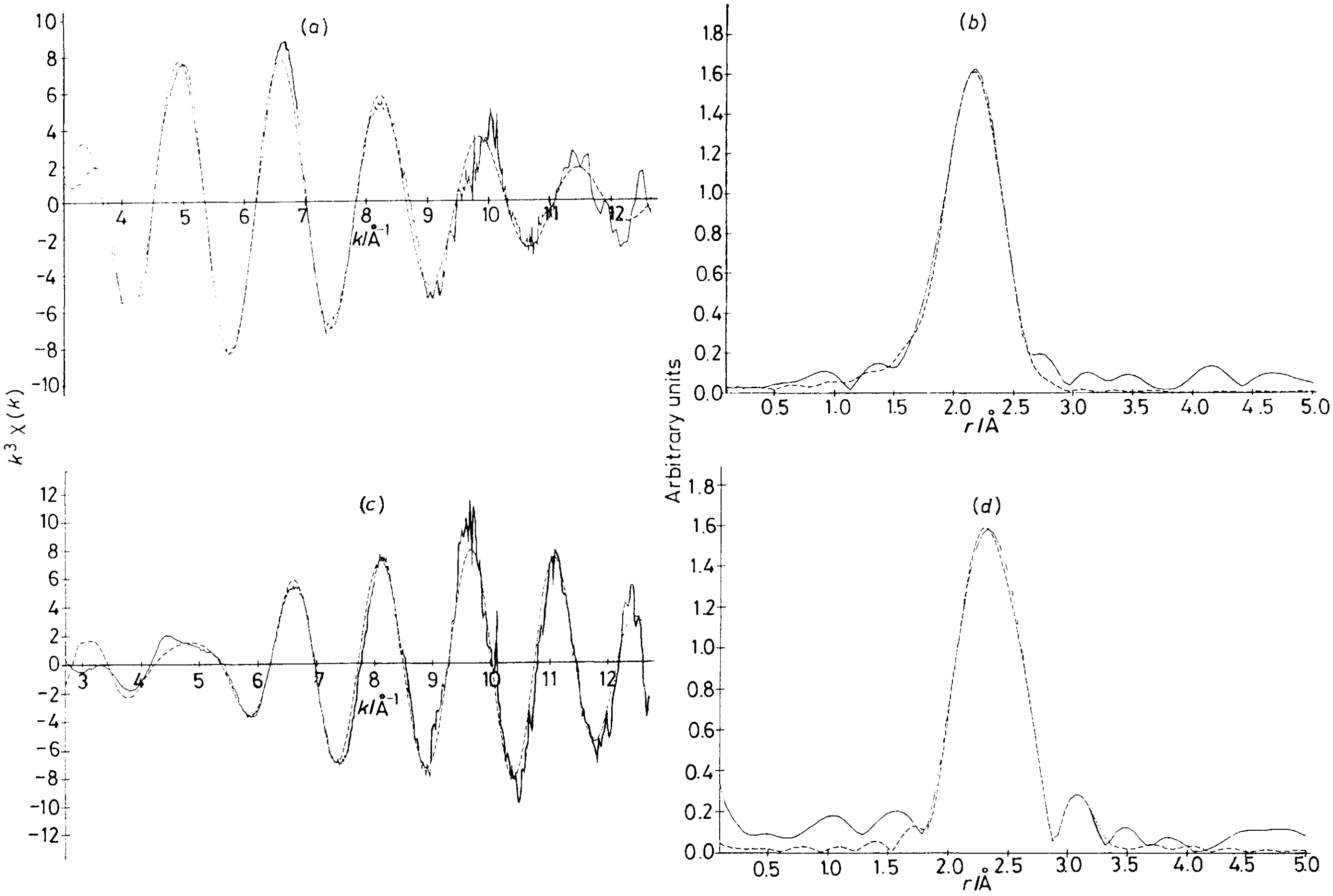

Figure 2. Background-subtracted raw EXAFS of $[Co\{Ph_2P(CH_2)_4PPh_2\}X_3]$ and their Fourier transforms: (*a*), (*b*) X = Cl; (*c*), (*d*) X = Br. Full line, experimental data; broken line, calculated data

for $[Co\{Ph_2P(CH_2)_4PPh_2\}Cl_3]$: C, 56.8; H, 4.8. Found: C, 47.0; H, 4.0. Calc. for $[Co\{Ph_2P(CH_2)_4PPh_2\}Br_3]$: C, 46.4; H, 3.9. Found: C, 56.9; H, 5.3. Calc. for $[Co\{Ph_2P(CH_2)_5PPh_2\}Cl_3]$: C, 57.5; H, 5.0. Found: C, 46.6; H, 4.2. Calc. for $[Co\{Ph_2P(CH_2)_5PPh_2\}Br_3]$: C, 47.1; H, 4.1%).

EXAFS.—The Co *K*-edge data were recorded at the Synchrotron Radiation Source, Daresbury, on station 8.1 using a double-crystal silicon(111) monochromator. The operating energy was 2 GeV at an average current of 150 mA. Measurements were made in transmission mode on freshly prepared solid samples diluted with BN (*ca.* 10% Co by mass) and held between Sellotape strips in aluminium spacers (path length ≈ 1 mm). No hydrolysis or decomposition of the samples was evident either by visual inspection or by extraction from the BN with CH_2Cl_2 and subsequent spectroscopic study. The programs PAXAS[23] and EXCURVE[22] were used in the data analysis.

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