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Coordination Chemistry of Higher Oxidation States. 30.[1] Five-Coordinate Cobalt(III) Phosphine Complexes. Spectroscopic and Cobalt K-Edge EXAFS Studies

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The complexes $[Co(PR_3)_2X_3]$ (X = Cl, Br; PR_3 = PMe_3, PEt_3, PMe_2Ph, PEt_2Ph, $PEtPh_2$; X = Br, PR_3 = PPh_3) have been prepared by oxidation of the corresponding $[Co(PR_3)_2X_2]$ in dichloromethane with NOX at low temperatures. The intensely colored, paramagnetic (μ = 2.9–3.3 μ_B) Co(III) complexes are formulated as five-coordinate trigonal-bipyramidal species on the basis of vibrational and UV-visible spectroscopic studies and FAB mass spectra. Detailed assignments for the d-d and charge-transfer transitions in the UV-visible spectra are proposed. First-coordination-sphere bond lengths for the complexes $[Co(PEt_3)_2X_3]$ and $[Co(PEt_2Ph)_2X_3]$ were obtained by cobalt and bromine K-edge EXAFS spectroscopy (extended X-ray absorption fine structure), along with similar data for the model compounds $[Co(PPh_3)_2X_2]$. For the cobalt(III) complexes average bond lengths are Co–P = 2.30 Å, Co–Cl = 2.20 Å, and Co–Br = 2.36 Å.

Introduction

Diamagnetic six-coordinate cobalt(III) complexes of amine ligands are very familiar and played a central role in the development of coordination chemistry. Analogues with other group 15 and 16 ligands are less numerous but are readily obtained, e.g. $[Co(H_2O)_6]^{3+}$,[2a] $[Co(S_2CNR_2)_3]$,[2b] $[Co(Se_2CNR_2)_3]$,[2c] $[Co(L\text{-}L)_3]^{3+}$ (L-L = bidentate, P, As, or Sb donor ligand),[2d] and $[Co(L\text{-}L)_2X_2]^+$ (X = Cl, Br).[2e-g] Four-coordination is rare, but planar complexes of 1,2-dithiolato, biuretato, and Schiff base ligands[3] have been characterized.

A small number of five-coordinate square-pyramidal materials are known, including [Co(Schiff base)R][4a,b] (R = alkyl), [Co(Schiff base)X],[4c-e] and $[Co(corrole)PPh_3]$.[4f,g] Monodentate phosphine complexes $[Co(PR_3)_2X_3]$ were prepared by Jensen,[5,6] but only the PEt_3 complexes were obtained in pure form, and apart from a relatively low-precision X-ray study of the chloride complex,[7] which confirmed a trigonal-bipyramidal geometry, they have not been further studied. Here we report a systematic investigation of a series of such complexes.

Results and Discussion

Jensen et al.[5] prepared $[Co(PEt_3)_2Cl_3]$ from $[Co(PEt_3)_2Cl_2]$ and neat nitrosyl chloride, NOCl, and the corresponding bromide from $[Co(PEt_3)_2Br_2]$ and NOBr in benzene. After surveying a number of solvent systems and reaction conditions, we found that the best route to $[Co(PR_3)_2X_3]$ (R_3 = Me_3, Et_3, Et_2Ph, $EtPh_2$, Me_2Ph; X = Cl, Br; R_3 = Ph_3, X = Br) was oxidation of $[Co(PR_3)_2X_2]$ with NOX in dichloromethane at -80 °C followed by rapid removal of the solvent in vacuo at low temperatures. Since the products are unstable in solution and extraordinarily soluble in most organic media, attempted purification by recrystallization is ineffective (indeed it often *decreases* purity). Samples with acceptable analytical and spectroscopic purity (i.e. absence of phosphine oxide or nitrosyl vibrations in the IR spectra and of Co(II) features in the visible spectra) are best obtained by using pure starting materials and rigorously dry solvents and by careful control of the reaction conditions. Attempts to halogen oxidize these cobalt(II) tertiary phosphine complexes result in oxidation of the phosphine, not the metal center. The $[Co(PCy_3)_2X_2]$ complexes (Cy = cyclohexyl) are not oxidized with NOX, and while $[Co(PPh_3)_2Cl_2]$ in CH_2Cl_2 darkens on treatment with NOCl at -80 °C, the color fades upon slight warming. The very unstable $[Co(AsEt_3)_2X_2]$[8] complexes decompose on reaction with NOX. Nitrosyl iodide is unknown at room temperature,[9] and diiodine does not oxidize $[Co(PEt_3)_2I_2]$.[10]

The cobalt(III) chloro complexes are dichroic, intensely blue-purple solids and the bromides very dark green, with the exception of the PMe_3 and PMe_2Ph complexes, which are very dark red. They are all very soluble in halocarbons, alcohols, ethers, arenes, and pentane, less soluble in hexane, and effectively insoluble in water. As pure dry solids $[Co(PR_3)_2X_3]$ can be kept at -20 °C for some months, but impure samples are less stable, and all decompose rapidly at room temperature in the air (between $^1/_2$ and 48 h depending upon the phosphine present) to blue oils containing Co(II) and phosphine oxide. Qualitatively the bromides are more stable than the corresponding chlorides, reflecting better binding of the phosphine to the softer bromocobalt center, and with PR_3 the stability varies in the order $PPh_3 < PPh_2Et < PEt_2Ph < PMe_3 \approx PMe_2Ph < PEt_3$. In solution, when UV-visible spectroscopy was used for monitoring, the $[Co(PEt_3)_2Br_3]$ in dichloromethane showed no decomposition in 3 h, while at the other extreme the triphenylphosphine complex was completely decomposed in ca. 10 min.

The mononuclear nature of $[Co(PEt_3)_2X_3]$ was confirmed by FAB mass spectrometry, and the X-ray study[7] of the chloride showed the geometry to be trigonal bipyramidal with axial phosphines. Comparison of the far-IR spectra of corresponding chloro and bromo complexes revealed a single medium-intensity

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(1) Part 29: Jenkinson, J. J.; Levason, W.; Perry, R. J.; Spicer, M. D. *J. Chem. Soc., Dalton Trans.* **1989**, 453.

(2) Representative references: (a) Johnson, D. A.; Sharpe, A. G. *J. Chem. Soc. A* **1966**, 798. (b) Bond, A. M.; Hendrickson, A. R.; Martin, R. L.; Moir, J. E.; Page, D. R. *Inorg. Chem.* **1983**, *22*, 3440. (c) Bond, A. M.; Colton, R.; Mann, D. R.; Moir, J. E. *Aust. J. Chem.* **1986**, *39*, 1385. (d) Jewiss, H. C.; Levason, W.; Webster, M. *Inorg. Chem.* **1986**, *25*, 1997. (e) Cloyd, J. C.; Meek, D. W. *Inorg. Chim. Acta* **1972**, *6*, 480. (f) Bosnich, B.; Jackson, W. G.; McClaren, J. W. *Inorg. Chem.* **1974**, *13*, 1133. (g) Jewiss, H. C.; Levason, W.; Spicer, M. D.; Webster, M. *Inorg. Chem.* **1987**, *26*, 2102.

(3) (a) Eisenberg, R.; Dori, Z.; Gray, H. B.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 741. (b) Baker-Hawkes, M. J.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 4870. (c) Rao, C. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428. (d) Fikar, R.; Koch, S. A.; Millar, M. M. *Inorg. Chem.* **1985**, *24*, 3311. (e) Birker, P. J. M. W. L.; Bour, J. J.; Steggerda, J. J. *Inorg. Chem.* **1973**, *12*, 1254. (f) Birker, P. J. M. W. L.; Beurskens, P. T. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 218. (g) Brewer, J. C.; Collins, T. J.; Smith, M. R.; Sanstasiero, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 423.

(4) (a) Costa, G.; Mestroni, G.; Stefani, L. *J. Organomet. Chem.* **1966**, *6*, 181; **1967**, *7*, 493. (b) Bruckner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1969**, *3*, 308. (c) Higson, B. M.; McKenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1972**, 269. (d) McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1976**, *16*, 9. (e) Bailey, N. A.; McKenzie, E. D.; Worthington, J. M. *J. Chem. Soc., Dalton Trans.* **1977**, 763. (f) Coulon, M.; Johnson, A. W.; Overend, W. R.; Rajapaska, D.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2281. (g) Hitchcock, P. B.; McLaughlin, G. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1927.

(5) Jensen, K. A.; Nygaard, B.; Pedersen, C. T. *Acta Chem. Scand.* **1963**, *17*, 1126.

(6) Jensen, K. A.; Jørgensen, C. K. *Acta Chem. Scand.* **1965**, *19*, 451.

(7) Van Enckevort, W. J. P.; Hendriks, H. M.; Beurskens, P. T. *Cryst. Struct. Commun.* **1977**, *6*, 531.

(8) Hatfield, W. E.; Yoke, J. T. *Inorg. Chem.* **1962**, *1*, 475.

(9) It may exist in low-temperature matrices. See: Feuerhahn, M.; Hilbig, W.; Minkwitz, R.; Engelhardt, U. *Spectrochim. Acta* **1978**, *34A*, 1065.

(10) $[Ni(PMe_3)_2I_3]$ has been made serendipitously from $[\{Ni(\mu\text{-}{}^tBu_2As)(PMe_3)_2\}_2]$ and diiodine (Chandler, D.; Jones, R. A.; Whittlesey, B. R. *J. Coord. Chem.* **1987**, *16*, 19), and it is possible that the Co(III) analogues may be capable of existence.

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Table I. Selected Physical Data

complex	color	μ_{eff}, μ_B[a]	e′(Co–X), cm^{-1} [b]	anal., %[c] C	H
$[Co(PMe_3)_2Cl_3]$	red–black	3.20	345	22.6 (22.7)	6.0 (5.7)
$[Co(PEt_3)_2Cl_3]$	mauve–black	3.25	349	36.2 (35.9)	7.3 (7.5)
$[Co(PEt_2Ph)_2Cl_3]$	mauve–black	3.24	362	48.6 (48.3)	6.3 (6.1)
$[Co(PEtPh_2)_2Cl_3]$	dark blue	3.28	356	57.3 (56.6)	5.3 (5.1)
$[Co(PMe_2Ph)_2Cl_3]$	mauve–black	3.16		43.9 (43.5)	5.2 (5.0)
$[Co(PMe_3)_2Br_3]$	red–black	3.09	244	15.8 (16.0)	4.0 (4.3)
$[Co(PEt_3)_2Br_3]$	green–black	2.93	245	27.3 (26.9)	5.8 (5.7)
$[Co(PEt_2Ph)_2Br_3]$	green–black	3.00	247	37.7 (38.1)	4.9 (4.8)
$[Co(PEtPh_2)_2Br_3]$	green–black	3.04	263	47.0 (46.5)	4.3 (4.2)
$[Co(PMe_2Ph)_2Br_3]$	mauve–black	3.21		33.3 (33.4)	3.9 (3.9)
$[Co(PPh_3)_2Br_3]$	green–black	3.17	230	52.8 (52.5)	3.9 (3.7)

[a] Evans NMR method in $CHCl_3$ (±0.1 μ_B). [b] IR spectra, Nujol mulls. [c] Calculated values in parentheses.

Table II. UV–Visible Spectral Data[a]

complex	$e'' \to e'$	$P(\sigma) \to e'$	$e' \to a_1'$	$Br(\pi) \to e'$	$e'' \to a_1'$	$P(\sigma) \to a_1'$[b]	$Br(\pi) \to a_1'$
$[Co(PMe_3)_2Cl_3]$	5.31 (20), 6.90 (21)	19.6 (2440)	22.9 (430)		27.0 (sh)	32.4 (1730)	
$[Co(PEt_3)_2Cl_3]$	4.95 (49), 6.53 (35)	17.8 (4300)	21.9 (600)		27.6 (750)	30.7 (2500)	
$[Co(PEt_2Ph)_2Cl_3]$	5.26 (44), 6.50 (42)	17.3 (6100)	21.5 (600)		26.7 (950)	29.7 (5400)	
$[Co(PEtPh_2)_2Cl_3]$	*c*	16.8 (1200)	21.1 (180)		26.3 (230)	29.0 (900)	
$[Co(PMe_2Ph)_2Cl_3]$	*c*	18.2 (2100)	21.8 (800)		27.3 (1600)	30.6 (3100)	
$[Co(PMe_3)_2Br_3]$	5.49 (22), 6.69 (32)	19.0 (2095)		23.3 (1220)	27.0 (640)	32.0 (2090)	
$[Co(PEt_3)_2Br_3]$	6.02 (25), 6.90 (sh)	17.1 (6700)	20.6 (sh)	23.2 (3800)	27.8 (sh)	30.3 (5700)	34.5 (9800)
$[Co(PEt_2Ph)_2Br_3]$	5.38 (sh), 6.54 (60)	16.7 (5900)	19.7 (sh)	22.9 (2200)	26.0 (2680)	29.1 (6900)	33.1 (4100)
$[Co(PEtPh_2)_2Br_3]$	6.45 (50)	16.3 (6800)	19.2 (sh)	22.3 (2900)	25.3 (3400)	28.5 (7000)	33.1 (3700)
$[Co(PMe_2Ph)_2Br_3]$	*c*	17.8 (3000)	20.0 (sh)	23.0 (1500)	27.2 (1400)	29.9 (3500)	33.3 (2100)
$[Co(PPh_3)_2Br_3]$	*c*	15.7 (3950)	18.9 (sh)	21.6 (1540)	24.2 (2020)	28.0 (3400)	32.5 (2800)

[a] E_{max}, 10^3 cm^{-1} (ϵmol, dm^3 mol^{-1} cm^{-1}) for solutions ca 10^{-4} mol dm^{-3} in CH_2Cl_2. [b] For the chlorides $Cl(\pi) \to e'$ and $P(\sigma) \to a_1'$ are coincident (see text). [c] Not measured.

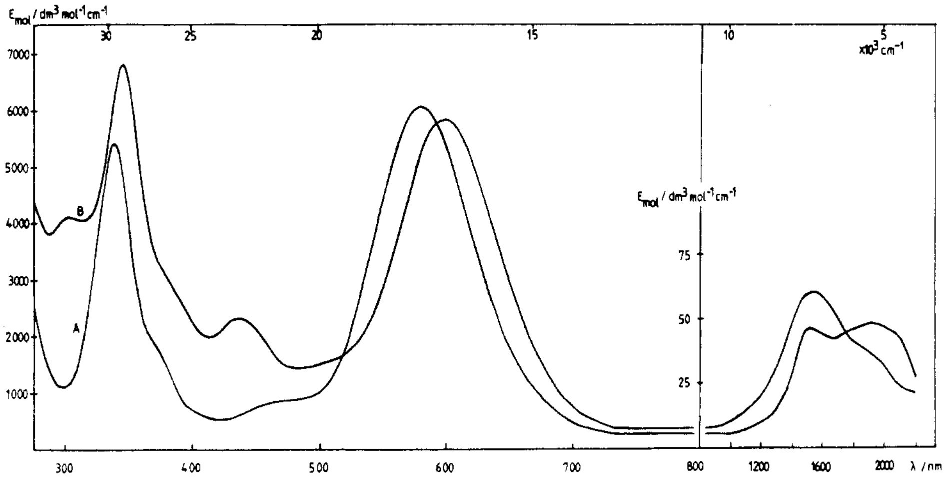

Figure 1. UV–visible spectra of $[Co(PEt_2Ph)_2X_3]$: (A) X = Cl; (B) X = Br.

band in each assignable as e′(Co–X) in D_{3h} symmetry (Table I). From this and the general similarity of the UV-visible spectra (Table II), a D_{3h} structure is proposed for all the complexes. In D_{3h} symmetry the d-orbital ordering is expected to be d_{xz}, d_{yz} (e″) < d_{xy}, $d_{x^2-y^2}$ (e′) < d_{z^2} (a_1'), leading in a d^6 low-spin configuration to a ground state of $(e'')^4(e')^2(a_1')^0$ and an expected spin-only magnetic moment of 2.83 μ_B. The experimental magnetic moments (Table I) are in the range 2.9–3.3 μ_B.

The most striking property of these complexes is the very intense color. An early study by Jensen and Jørgensen[6] of $[Co(PEt_3)_2Cl_3]$ found bands in the electronic spectrum at 18 000 and 27 000 cm^{-1} with $\epsilon_{mol} \geq 2000$ dm^3 mol^{-1} cm^{-1} but concluded that, despite the high extinction coefficients, the data did not allow a definite assignment, arguments in favor of both d–d and charge-transfer transitions being possible. The larger number of examples in the present study, particularly by extension of the measurements into the near-IR region, has allowed a definite assignment (Table II). Typical spectra are shown in Figure 1. The assignment of the d–d bands is based upon the ligand field treatment of Norgett et al.[11] previously applied to tripodal tetraphosphine complexes of Fe(II) with C_{3v} symmetry. The model is directly transferable to the isoelectronic $[Co(PR_3)_2X_3]$ in D_{3h} symmetry. The two weak overlapping bands in the 5000–7000-cm^{-1} region are assigned as e″ → e′ (there are two transitions associated with this one-electron process[11]). A weak band at ca. 21 000–23 000 cm^{-1} in the chlorides and the corresponding shoulder at 19 000–21 000 cm^{-1} in the bromides is assigned as $e' \to a_1'$, and the third expected transition $e'' \to a_1'$ is the medium-intensity band or shoulder in the ca. 27 000-cm^{-1} region. This leaves the intense absorptions at 16 000–18 000 and 28 000–32 000 cm^{-1} as charge-transfer (ligand to metal) transitions. The charge-transfer transitions have been assigned by using Jørgensen's optical electronegativity concept,[12] which assumes that the transition energies may be related to the electronegativity differences between the donor (χ_{opt}(ligand)) and acceptor (χ_{opt}(metal)) orbitals. If χ_{opt}(Co(III)) is taken as 2.3,

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(11) Norgett, M. J.; Thornley, J. H. M.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 540.

(12) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

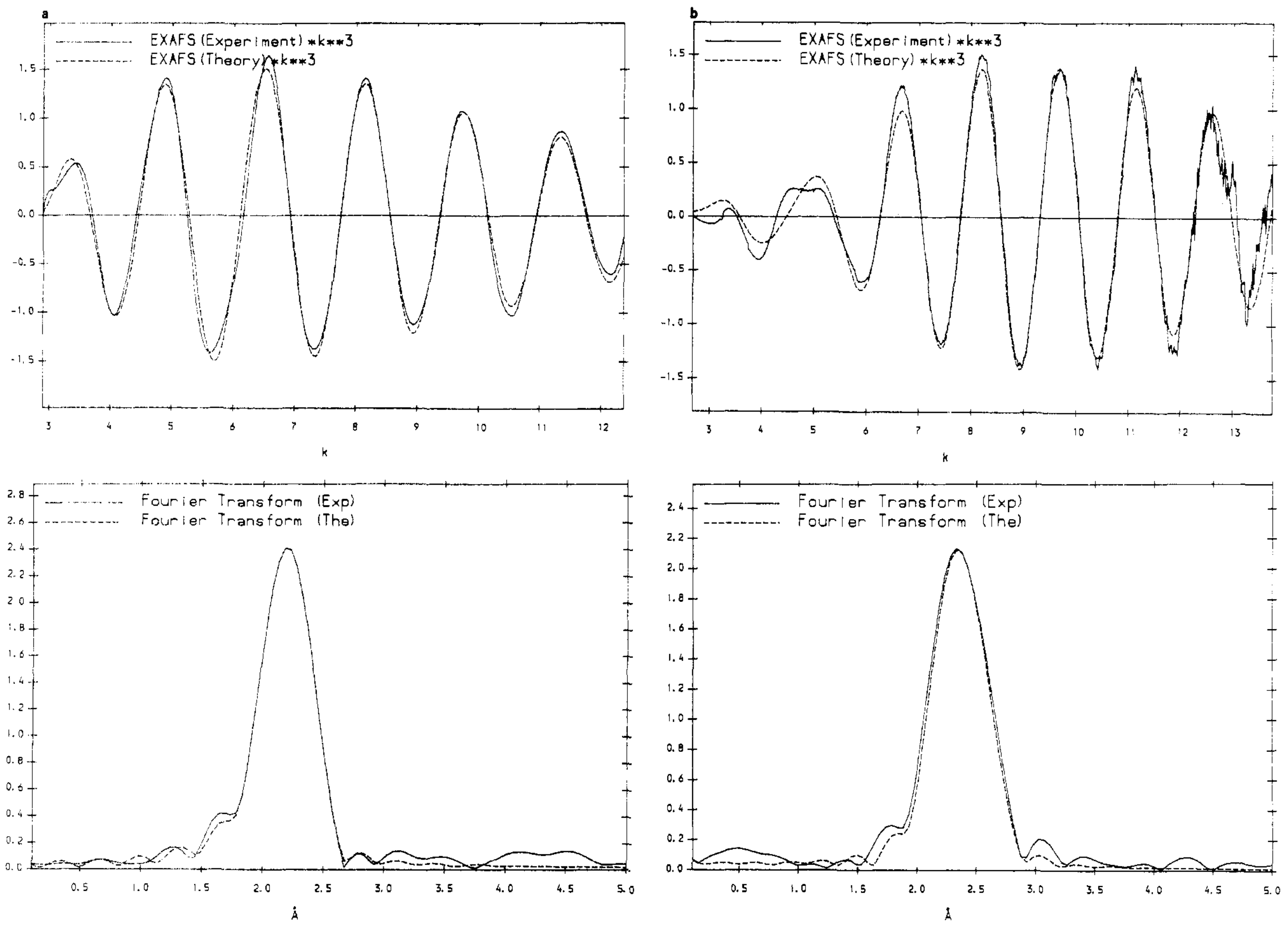

Figure 2. Background-subtracted EXAFS spectra and the Fourier transforms for $[Co(PEt_3)_2X_3]$: (a) X = Cl; (b) X = Br (—, experimental data; - - -, calculated data).

$\chi_{opt}(P)$ as 2.6, $\chi_{opt}(Cl)$ as 3.0, and $\chi_{opt}(Br)$ as 2.8,[12] E_{obs}, the energy of the lower charge-transfer transition $P(\sigma) \rightarrow Co^{III}(e')$, is

$$E_{obs} = 30000[\chi_{opt}(P) - \chi_{opt}(Co(III))] + E(e'\text{-}e'') + SPE$$

where $E(e'\text{-}e'')$ is the energy separation between the e′ and e″ orbitals and SPE is the correction for spin pairing, $D = \sim 3000$ cm^{-1}.[12] Putting $E(e'\text{-}e'')$ as ca. 6000 cm^{-1} from the d–d transition energy above gives $E_{obs} = \sim 18000$ cm^{-1}, in excellent agreement with experiment. The second $P(\sigma) \rightarrow Co^{III}$ charge-transfer band is to the a_1' level, for which the predicted energy is

$$E_{obs} = 30000[\chi_{opt}(P) - \chi_{opt}(Co(III))] + E(a_1'\text{-}e'') + SPE$$

Using the a_1'–e″ separation as ca. 27 000 cm^{-1} and an SPE in this case involving a change in spin state from $S = 1$ to $S = {}^3/_2$ corresponding to $-2D$ (ca. −6000 cm^{-1}),[12] leads to E_{obs} = ca. 30 000 cm^{-1}. Similar calculations predict $Cl(\pi) \rightarrow Co^{III}(e')$ as ca. 31 000 cm^{-1}, $Br(\pi) \rightarrow Co^{III}(e')$ as ca. 24 000 cm^{-1}, and $Br(\pi) \rightarrow Co^{III}(a_1')$ as ca. 36 000 cm^{-1}. These predicted charge-transfer transitions correlate well with the observed spectra (Table II), and one should note that $Cl(\pi) \rightarrow Co^{III}(e')$ and $P(\sigma) \rightarrow Co^{III}(a_1')$ are approximately coincident. Within the limitations of these calculations the agreement with experiment is excellent.

Co K-Edge EXAFS Data. In view of the solution instability of these complexes, which prevented the production of good-quality single crystals for an X-ray study, we used Co K-edge EXAFS data, supplemented by Br K-edge data, to obtain structural information. We have shown previously that a combination of spectroscopic data to define the ligand field and metal EXAFS data to provide first-coordination-sphere bond lengths can result in an essentially complete description of unstable metal coordination complexes such as nickel(IV) or iron(IV) diphosphines.[13,14]

Cobalt and bromine K-edge spectra were recorded in the transmission mode on room-temperature samples diluted with BN. The pre-edge background was removed by fitting the pre-edge region to a cubic polynomial and subtracting this from the whole spectrum. The post-edge background was obtained by using inverse polynomials of order 6 and subtracting these from the post-edge region. The k^3-weighted EXAFS spectrum thus obtained was used for curve fitting without Fourier filtering. The fitting employed single-scattering, curved-wave theory contained within the SEXCURVE program with ab initio phase shifts and backscattering factors calculated in the usual manner.[15] Figure 2 shows typical examples of the background-subtracted EXAFS data and their Fourier transforms. The model compounds $[Co(PPh_3)_2X_2]$ and $[Co(PEt_3)_2Cl_3]$, which have known first-coordination-sphere bond lengths, were used to assess the transferability of phase-shift parameters, and the calculated phase shifts were found to be satisfactory in each case. The results are shown in Table III. Comparison of the first-coordination-sphere bond lengths in the model compounds $[Co(PPh_3)_2X_2]$ as determined by these EXAFS measurements with the X-ray-determined bond lengths shows satisfactory agreement and indicates that the results from the Co(III) compounds may be viewed with some confidence.

In the treatment of the EXAFS data two potential problems were considered. For the bromide complexes it was thought possible that the bromines might dominate the backscattering, but attempts to fit the data without the inclusion of the phosphorus or to fit a single-shell model led to markedly poorer fits and higher R factors (see the supplementary material). For the chlorides the very similar backscattering powers of chlorine and phosphorus and the relatively similar bond lengths expected raised the question

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(13) Higgins, S. J.; Levason, W.; Feiters, M. C.; Steel, A. T. *J. Chem. Soc., Dalton Trans.* **1986**, 317.

(14) Harbron, S. K.; Higgins, S. J.; Levason, W.; Feiters, M. C.; Steel, A. T. *Inorg. Chem.* **1987**, *25*, 1789.

(15) Gurman, S. J.; Binsted, N.; Ross, I. *J. Phys. C* **1984**, *17*, 143; **1986**, *19*, 1845.

Table III. Structural Data

complex	technique	*d*(Co–P), Å	*d*(Co–X), Å	$2\sigma^2$, Å^2	E_0	FI[a]	*R*,[b] %	ref
$[Co(PPh_3)_2Cl_2]$	EXAFS	2.36	2.20	0.010, 0.010	17.4	0.17	7.74	this work
	X-ray	2.384 (1)	2.212 (1)					*c*
$[Co(PEt_3)_2Cl_3]$	EXAFS	2.30	2.18	0.009, 0.006	13.7	0.44	7.53	this work
	X-ray	2.280 (3)	2.196 (2)					7
$[Co(PEt_2Ph_2)Cl_3]$	EXAFS	2.29	2.21	0.010, 0.006	18.8	0.46	7.54	this work
$[Co(PPh_3)_2Br_2]$	EXAFS	2.37	2.33	0.009, 0.005	19.7	1.18	14.35	this work
	X-ray	2.385 (2)	2.349 (2)					*c*
$[Co(PEt_3)_2Br_3]$	EXAFS	2.32	2.37	0.014, 0.009	13.2	0.92	13.58	this work
$[Co(PEt_2Ph)_2Br_3]$	EXAFS	2.29	2.35	0.012, 0.010	18.5	1.47	13.72	this work
$[Co(PEt_2Ph)_2Br_3]$	EXAFS[d]		2.37	0.010	14.1	0.07	10.58	this work

[a] Fit index defined as $\sum_i(\chi_i^T - \chi_i^E)(Ki)^3$. [b] *R* factors defined as $\int|\chi^T - \chi^E|\kappa^3\,d\kappa/\int|\chi^E|\,d\kappa \times 100\%$. [c] Carlin, R. L.; Chirico, R. D.; Sinn, E.; Mennenga, G.; de Jongh, L. J. *Inorg. Chem.* **1982**, *21*, 2218. [d] Bromine K-edge.

of whether a two-shell fit was justified or whether a single shell was more appropriate. The fit for the two-shell model gave slightly lower *R* factors, and examination of the statistics showed that although there was some correlation between the two shells, they were not so highly correlated as to make separate fitting unreasonable. Thus, on the basis of the data treatment we believe that the bond lengths quoted in Table III are reliable to within the currently accepted precision (±0.02 Å).

X-ray data on other cobalt(III) phosphines is limited to the six-coordinate species $[Co(PMe_3)_3(NCS)_3]$[16] ($Co{-}P_{trans\,P}$ = 2.294 (3) Å (av)), *trans*-$[Co\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^+$ [17] ($Co{-}P_{trans\,P}$ = 2.241 Å (av)), and $[Co(dmgH)_2(PPh_3)X]$ ($dmgH_2$ = dimethylglyoxime: X = Cl, Co–P = 2.327 (4) Å;[18] X = Br, Co–P = 2.331 (4) Å[19]) and to the square-pyramidal $[Co(corrole)PPh_3]$[4g] (Co–P = 2.210 (5) Å). Cobalt(III)–halogen bond lengths for comparison purposes are Co–Cl = 2.251 (1) Å in *trans*-$[Co(dmgH)_2(PPh_3)Cl]$[18] and 2.253 Å (av) in $[Co\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^+$,[17] while corresponding Co(III)–Br distances are 2.445 (2) Å in *trans*-$[Co(dmgH)_2Br(PPh_3)]$[19] and 2.38 (1) Å (av) in $[Co(dmgH)_2Br_2]^-$.[20] The Co–P and Co–X bond lengths for the present five-coordinate phosphine complexes are thus very similar to those in six-coordinate Co(III) species.

Experimental Section

Near-IR spectra were measured on a Varian Cary 2300 instrument. Other physical measurements were made as described in previous parts of this series.

Co(II) Compounds. The $[Co(PR_3)_2X_2]$ (R_3 = Et_3, Et_2Ph, $EtPh_2$, Ph_3; X = Cl, Br) were prepared by literature methods.[21,22] Complexes of PMe_2Ph and PMe_3 were prepared as described below.

$[Co(PMe_2Ph)_2X_2]$. Anhydrous cobalt(II) halide (0.5 mmol) was suspended in dry dichloromethane (20 cm^3) purged with dinitrogen and the ligand (0.95 mmol) added dropwise. The mixture was stirred for 2 h, during which time a dark blue solution was formed. Unreacted CoX_2 was filtered off and the solution reduced to half-volume. As the complexes were not readily isolated in crystalline form (usually oily materials were produced), the solutions were used for in situ oxidations.

$[Co(PMe_3)_2X_2]$. Anhydrous CoX_2 (0.8 mmol) and $[\{Ag(PMe_3)I\}_4]$ (0.4 mmol) were suspended in dry, rigorously oxygen-free dichloromethane and stirred for 2 h. The resulting dark blue solution was filtered to remove AgI and unreacted CoX_2 and taken to dryness in vacuo. The slightly sticky solid produced was used directly for the oxidations.

Co(III) Complexes. General Method. $[Co(PR_3)_2X_2]$ (0.5 mmol) was dissolved in the minimum quantity of dry, dinitrogen-purged dichloromethane and the solution cooled to −80 °C (acetone slush). Pure NOCl was distilled into the solution under static vacuum, whereupon a rapid color change from deep blue to deep blue–purple was observed. The solvent was removed as rapidly as possible in vacuo to leave a dark blue–purple solid. The bromides were prepared in a similar manner, except that NOBr was added as a dichloromethane solution via a syringe.

FAB Mass Spectra. FAB mass spectra were obtained with 3-nitrobenzyl alcohol as matrix liquid. The parent peaks (*m*/*e*) are as follows. $[Co(PEt_3)_2Br_2]$: 457, 455, 453 (M^+). $[Co(PEt_3)_2Cl_3]$: 406, 404, 402, 400 (M^+). $[Co(PEt_3)_2Br_3]$: 540, 538, 536, 534 (M^+).

EXAFS. The Co K-edge EXAFS measurements were recorded at the Daresbury Synchrotron Radiation Source (operating at 2 GeV and an average current of 150 mA) on Station 8.1 using a double-crystal silicon 111 monochromator and the bromine K-edge measurements similarly on Station 9.2 using a silicon 220 monochromator. Measurements were made at the cobalt and bromine K-edges in transmission mode on freshly prepared solid samples (<48 h old) diluted with BN (10–20% Co complex), held between "Sellotape" strips in aluminum holders (~1-mm thickness). No hydrolysis or decomposition of the samples was evident during these measurements, as judged by visual inspection and in some cases by extraction from the BN with dichloromethane and subsequent spectroscopic studies. The programs used in the data treatment were PAXAS[23] and SEXCURVE.[15]

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Registry No. $[Co(PMe_3)_2Cl_3]$, 92766-32-0; $[Co(PEt_3)_2Cl_3]$, 64520-43-0; $[Co(PEt_2Ph)_2Cl_3]$, 120311-63-9; $[Co(PEtPh_2)Cl_3]$, 120311-64-0; $[Co(PMe_2Ph)Cl_3]$, 120311-65-1; $[Co(PMe_3)_2Br_3]$, 92766-17-1; $[Co(PEt_3)_2Br_3]$, 120311-66-2; $[Co(PEt_2Ph)_2Br_3]$, 120311-67-3; $[Co(PEtPh_2)_2Br_3]$, 120311-68-4; $[Co(PMe_2Ph)_2Br_3]$, 120311-69-5; $[Co(PPh_3)_2Br_3]$, 120311-70-8; $[Co(PPh_3)_2Cl_2]$, 14126-40-0; $[Co(PPh_3)_2Br_2]$, 14126-32-0; $[Co(PEt_3)_2Cl_2]$, 14784-62-7; $[Co(PEt_3)_2Br_2]$, 14784-57-7; $[Co(PEt_2Ph)_2Cl_2]$, 14916-43-9; $[Co(PEt_2Ph)_2Br_2]$, 14916-42-8; $[Co(PEtPh)_2Cl_2]$, 14916-45-1; $[Co(PEtPh)_2Br_2]$, 14916-44-0; $[Co(PMe_2Ph)_2Cl_2]$, 52133-21-8; $[Co(PMe_3)_2Cl_2]$, 53432-22-7; $[Co(PMe_3)_2Br_2]$, 53432-23-8; $[\{Ag(PMe_3)I\}_4]$, 12389-34-3; NOCl, 2696-92-6; NOBr, 13444-87-6; $[Co(PMe_2Ph)_2Cl_2]$, 52487-04-4.

Supplementary Material Available: A table giving single-shell fits of the EXAFS data and correlation tables for $Co(PEt_3)_2Cl_3$ and $Co(PEt_3)_2Br_3$ (1 page). Ordering information is given on any current masthead page.

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(16) Alnaji, O.; Peres, Y.; Dahan, F.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chem.* **1986**, *25*, 1385.

(17) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126.

(18) Bruckner, S.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1974**, 1017.

(19) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *Gazz. Chim. Ital.* **1981**, *111*, 147.

(20) Leban, I. *Vestn. Slov. Kem. Drus.* **1975**, *22*, 27; *Chem. Abstr.* **1977**, *86*, 64008s.

(21) Cotton, F. A.; Faust, O. D.; Goodgame, D. M. L.; Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 1780.

(22) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1961**, 285.

(23) Binsted, N. "PAXAS: Microcomputer program for pre- and post-edge background subtraction"; University of Southampton, 1988.