Coordination Chemistry of Higher Oxidation States. Part 15*. Cobalt(III) Complexes of Bi- and Multi-dentate Phenylphosphines

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Abstract

Six-coordinate cobalt(III) complexes *trans*-$[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2X_2]ClO_4$, *fac*-$[Co\{PhP(CH_2CH_2PPh_2)_2\}X_3]$, *cis*-$[Co\{P(CH_2CH_2PPh_2)_3\}X_2]ClO_4$ and *cis*-β-$[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2X_2]PF_6$ (X = Cl, Br) have been prepared by halogen oxidation of the Co(II) analogues, and characterised by IR, electronic and ^{31}P NMR spectroscopy. The failure to obtain complexes with X = I, and with some related ligands is discussed, and the rather low stability of the above complexes is rationalised in terms of steric crowding at the metal centre.

Introduction

Cobalt(III) complexes of bi- or poly-dentate alkyl substituted phosphines or arsines, are readily prepared by air-oxidation of alcoholic solutions of the ligands and cobalt(II) halides. Typical examples include those with $o\text{-}C_6H_4(AsMe_2)_2$ [2], $MeAs(o\text{-}C_6H_4AsMe_2)_2$ [3], $As(CH_2CH_2CH_2AsMe_2)_3$ [4], $[Me_2As(CH_2)_3As(Ph)CH_2\text{-}]_2$ [5] and $o\text{-}C_6H_4(PMe_2)_2$ [6]. In contrast aryl phosphine complexes of cobalt(II) do not air-oxidise, and halogen oxidation has been reported only for *cis*-$Ph_2PCH{=}CHPPh_2$ [7] and (briefly) $P(o\text{-}C_6H_4PPh_2)_3$ [8] complexes. We have recently examined the halogen oxidation of polydentate phosphine and arsine complexes of nickel(II) [9], palladium(II) [10] and platinum(II) [11] and the present study was undertaken for purposes of comparison.

Results

Data on the new cobalt(II) complexes used in the present study, and upon several known complexes for which it was unavailable, are given in Table I. Based upon this we assign monomeric five coordinate structures, probably square pyramids [15] to $[Co\{PhP(CH_2CH_2PPh_2)_2\}X_2]$ and $[Co\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}X_2]$ (X = Cl, Br, I). In contrast the IR and electronic spectra of the 1:1 complexes of the triarsine $MeC(CH_2AsMe_2)_3$, contain the characteristic [16] absorptions of CoX_4^{2-} ions, and are formulated $[Co\{MeC(CH_2AsMe_2)_3\}_2][CoX_4]$. The data does not allow us to distinguish between 5 and 6-coordinate geometries for the cations, although the paucity of low-spin octahedral Co(II) complexes [17], favours the former.

Cobalt(III)

Halogen (Cl_2 or Br_2) oxidation of $[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2X]ClO_4$ (X = Cl, Br) gave the diamagnetic $[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2X_2]ClO_4$ (Table II) which are identified as the *trans* isomers on the basis of (a) single ^{31}P NMR resonances (Table III), (b) one IR active ν(CoX) vibration at relatively high frequency [18]—402 cm^{-1} (Cl), 346 cm^{-1} (Br), and (c) the low energy of the first d–d transition [5, 7]. Attempts to prepare *cis*-$[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2Cl_2]ClO_4$ by sequential treatment [19] of the *trans* isomer with silver acetate and Cl^-, resulted only in recovery of the *trans* isomer. Although steric crowding may destabilise the *cis* isomer, the easy reduction of these complexes would lead to facile *cis* → *trans* conversion by a Co(II) catalysed route [19]. The $[Co\{Ph_2PCH_2PPh_2\}_2X]ClO_4$ [20] decompose immediately on treatment with halogens, and as reported by Miskowski *et al.* [7], we find that $[Co(Ph_2PCH_2CH_2PPh_2)_2X_2]^+$ appear to form in solution but decompose during attempts at isolation.

Cautious halogen oxidation of the corresponding cobalt(II) complexes in dry CH_2Cl_2/CCl_4, produced deep purple $[Co\{PhP(CH_2CH_2PPh_2)_2\}X_3]$ (X = Cl, Br), but reaction of $[Co\{PhP(CH_2CH_2PPh_2)_2\}I_2]$ and I_2 in CH_2Cl_2, or of $[Co\{PhP(CH_2CH_2PPh_2)_2\}Cl_3]$ and KI in ethanol–CH_2Cl_2 gave only a greenish-yellow cobalt(II) phosphine oxide complex. The $[Co\{PhP(CH_2CH_2PPh_2)_2\}X_3]$ are fairly stable solids, but decompose slowly in solution, evident both in their high conductances (for non-electrolytes) which rise with time, and by the presence of some phosphine oxide (^{31}P NMR evidence). The ^{31}P NMR spectra (Table III) suggest only one isomer is present but do not distinguish between *mer* and *fac*. The far IR spectra show two ν(Co–X) vibrations, as

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*Part 14, ref. [1].

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TABLE I. Cobalt(II) Complexes Analytical and Physical Data.

Complex	Colour	C%^{a}	H%	Λ_M^{b}	E_{max} 10^3 cm^{-1} (ϵ_{mol} dm^3 cm^{-1} mol^{-1})^{c}	IR ν(CoX) cm^{-1} ^{d}
$[Co\{PhP(CH_2CH_2PPh_2)_2\}Cl_2]^{e}$	orange	61.2(61.4)	5.1(5.0)	55	14.45(16),21.93(2056),24.27sh	318(s),334(sh)
$[Co\{PhP(CH_2CH_2PPh_2)_2\}Br_2]$	pink–brown	55.0(54.1)	4.5(4.4)	120	13.66(64),18.25sh,21.93(2100)	292(m)
$[Co\{PhP(CH_2CH_2PPh_2)_2\}I_2]$	brown	47.9(48.1)	4.0(3.9)	77	12.88(94),17.36(475),21.83(2030),24.63sh	
$[Co\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Cl_2]$	green	24.9(25.7)	5.5(5.3)	insol	(dr)15.24,16.55,22.52	364(m),312(s)
$[Co\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_2]$	red–orange	22.0(21.9)	4.5(4.5)	decomp	(dr)13.90,18.40,19.6,23.3	274(m)
$[Co\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}I_2]$	brown	18.9(18.9)	3.9(3.9)	insol	(dr)13.70,14.95,17.00,21.00	
$[Co\{P(CH_2CH_2PPh_2)_3\}Cl]ClO_4^{f}$	brown	58.6(58.3)	4.8(4.9)	100^{h}	12.50(117),16.45(560),21.19(2490),27.78(4956)	
$[Co\{P(CH_2CH_2PPh_2)_3\}Br]ClO_4^{g}$	brown	55.3(55.8)	4.6(4.6)	111^{h}	12.31(107),16.34(477),20.83(2260)	
$[Co\{MeC(CH_2AsMe_2)_3\}_2]CoCl_4$	dull green	26.5(25.7)	5.3(5.2)	insol	(dr)14.49,15.06,15.82,16.39,22.22(sh),24.27	286(br)
$[Co\{MeC(CH_2AsMe_2)_3\}_2]CoBr_4$	green–brown	22.0(21.9)	4.6(4.5)	insol	(dr)13.85,14.29,14.97,15.63,21.28,22.83	226(br)

[a] Calculated values in parenthesis. [b] 10^{-3} Molar solutions in MeCN 1:1 electrolytes have Λ_M *ca.* 120–160 ohm^{-1} cm^2 mol^{-1}. [c] CH_2Cl_2 solution, except dr = diffuse reflectance. [d] Tentative assignments. Identification of ν(CoX) is made difficult by strong ligand absorptions in the same region. [e] Ref. 12. [f] Ref. 13. [g] Ref. 14 (isolated as PF_6^- salt). [h] 10^{-3} Molar in CH_3NO_2 1:1 electrolytes have Λ_M = 70–110 ohm^{-1} cm^2 mol^{-1}.

TABLE II. Cobalt(III) Complexes.

Complex	Colour	C%^{a}	H%	Λ_M^{b} ohm^{-1} cm^2 mol^{-1}	E_{max} 10^3 cm^{-1} (ϵ_{mol} dm^3 cm^{-1} mol^{-1})^{c}	ν(CoX) cm^{-1} ^{d}
trans-$[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2Cl_2]ClO_4$	yellow–green	64.4(64.2)	4.1(4.3)		16.0(155),25.3(34000),31.75(11500)	402
trans-$[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2Br_2]ClO_4$	orange	59.2(59.5)	4.0(4.0)		14.95(135),23.8(sh),25.3(19000),27.75(18600)	346
fac-$[Co\{PhP(CH_2CH_2PPh_2)_2\}Cl_3]$	purple	58.1(58.3)	4.6(4.7)	*ca.* 40	15.3(sh),19.1(1425),22.5(sh)	306(br)
fac-$[Co\{PhP(CH_2CH_2PPh_2)_2\}Br_3]$	purple-brown	49.2(49.0)	4.0(4.0)	*ca.* 60	14.45(sh),18.05(1670),24.5(sh)	272(sh),260(br)
cis-$[Co\{P(CH_2CH_2PPh_2)_3\}Cl_2]ClO_4$	red	55.7(56.0)	4.8(4.7)	115	19.46(2025)	
cis-$[Co\{P(CH_2CH_2PPh_2)_3\}Br_2]ClO_4$	red	50.8(51.0)	4.1(4.2)	98	18.8(1650)	
$[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2Cl_2]PF_6$	orange-brown	53.4(53.3)	4.5(4.4)	99	16.56(sh),19.08(sh),26.31(4580)	
$[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2Br_2]PF_6$	red-brown	48.6(48.7)	4.1(4.1)	94	18.52(1090),25.38(4750)	

[a] Calculated values in parenthesis. [b] $MeNO_2$ 10^{-3} mol dm^{-3} 1:1 electrolytes have Λ_M 70–110 ohm^{-1} cm^2 mol^{-1}. [c] CH_2Cl_2 solution. [d] Also *trans* $[Co\{Ph_2PCHCHPPh_2\}_2Cl_2]ClO_4$ 402 cm^{-1}; $[Co\{Ph_2PCHCHPPh_2\}_2Br_2]ClO_4$ 330 cm^{-1}.

TABLE III. ^{31}P NMR Data[a].

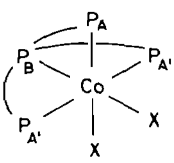
Complex	δ(P) free ligand	δ(P) complex	Δ (δP$_{complex}$ − δP$_{ligand}$)
trans-$[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2Cl_2]ClO_4$	−2.1	47.35	49.45
trans-$[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2Br_2]ClO_4$		42.2	44.3
fac-$[Co\{PhP(CH_2CH_2PPh_2)_2\}Cl_3]$	Ph_2P– −12.1, PhP $<$ −15.8	Ph_2P– 44.0, PhP $<$ 89.2	56.1, 105.0
fac-$[Co\{PhP(CH_2CH_2PPh_2)_2\}Br_3]$		Ph_2P– 54.2, PhP $<$ 100.0	66.3, 115.8
cis-$[Co\{P(CH_2CH_2PPh_2)_3\}Cl_2]ClO_4$	Ph_2P– −12.1, P $<$ −16.6	Ph_2P– 49.0[b], 46.6[c], P $<$ 116.3	61.1, 58.7, 132.9
cis-$[Co\{P(CH_2CH_2PPh_2)_3\}Br_2]ClO_4$		Ph_2P– 56.0[b], 50.2[c], P $<$ 127.3	68.1, 62.3, 143.9
cis-β-$[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2Cl_2]PF_6$	Ph_2P– −12.1, PhP $<$ −16.0	Ph_2P– 38.7, 36.7[d] PhP $<$ 102.9, 104.7[d]	50.8, 48.8, 118.9, 120.7
cis-β-$[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2Br_2]PF_6$		Ph_2P 40.2, 38.4[d], PhP $<$ 107.0, 108.8[d]	52.3, 50.5, 123.0, 124.8

[a] Freshly prepared $CDCl_3$ solutions δ relative H_3PO_4, +δ values to high frequency. [b] P_A. [c] $P_{A'}$ of Fig. 1. [d] See text.

expected (a_1 + e) for *fac* isomers, and lack the higher frequency vibration (b_1) expected for the *trans* CoX_2 unit of a *mer* isomer. The electronic spectra are also similar to those of $[Co\{MeAs(o\text{-}C_6H_4AsMe_2)_2\}X_3]$ believed [3, 21] to be *fac* isomers, although the triphosphine has been found to give *mer* isomers with Cr(III) [22], Pt(IV) [11] and probably Ni(III) [9]. Other workers [23] have noted that donor groups with high *trans* influence (like $\text{-}PR_2$) tend to occupy *cis* positions on Co(III) which would favour the *fac* isomer.

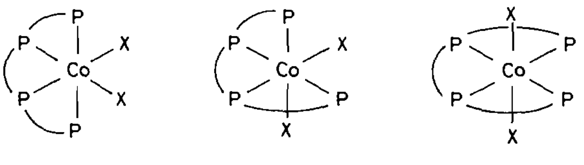
Chlorination of the brown halide-bridged dimer $[MeC(CH_2PPh_2)_3CoCl_2Co(Ph_2PCH_2)_3CMe](PF_6)_2$ [24] produced a bright green solid, but this could not be obtained with a reproducible composition. Unexpectedly the Co(II) triarsine ($MeAs(CH_2CH_2CH_2AsMe_2)_2$, $MeC(CH_2AsMe_2)_3$) complexes were recovered unchanged, after treatment with X_2/CCl_4, and after stirring for 2 days in EtOH/HX with free access of air. This contrasts with the ready oxidation of complexes of $MeAs(o\text{-}C_6H_4AsMe_2)_2$ [3] and $As(CH_2CH_2CH_2AsMe_2)_3$ [4].

Dark red $[Co\{P(CH_2CH_2PPh_2)_3\}Cl_2]ClO_4$ was produced by treatment of the Co(II) analogue with Cl_2 or NOCl, and the bromide was obtained using Br_2.† These complexes are 1:1 electrolytes, and the ^{31}P NMR spectra confirm structure (I). A similar structure has been established [25] by an X-ray of $[Co\{N(CH_2CH_2PPh_2)_3\}Cl_2]BF_4$. Attempts to prepare the iodo analogue by metathesis with KI/EtOH caused reduction to Co(II).



(I)

The tripod arsine $As(CH_2CH_2CH_2AsMe_2)_3$ has been shown by Meek *at al.* [4] to give $[Co(As_4)X_2]ClO_4$ (Cl, Br *and* I) which have analogous structures to (I), in this case readily assigned from the ^1H NMR spectra (Table IV). Although tripodal ligands if bound as tetradentates can only coordinate as in (I), open chain analogues have a wider range of possibilities available (II) [5].



cis α (a) cis β (b) trans (c)

(II)

For complexes of $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$, the central phosphorus atoms are asymmetric centres and hence *meso* and *racemic* diastereoisomers are expected. However the commercial ligand contains‡ only one diastereoisomer and X-ray studies [27] of two iron complexes reveal this is the *meso* form. The orange-brown $[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2X_2]PF_6$ (Table II) are 1:1 electrolytes in freshly prepared nitromethane solutions, but the solutions decompose on standing. The far IR spectra are dominated by absorptions of the phosphine ligand, and the ν(CoX) have not been identified. However the electronic spectra are clearly

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†Reaction of $[Co\{P(CH_2CH_2PPh_2)_3\}Br]ClO_4$ with NOBr gave a red solid with IR. Absorptions at *ca.* 1535, 1570 cm^{-1}, indicating a nitrosyl (NO^-) species.

‡Our sample had Mp 162–166 °C compared to 168–171 °C and 99–101 °C for the two isomers [26].

TABLE IV. ^{1}H NMR Spectral Data[a].

	Me_2As (*trans* X)	Me_2As (*trans* As)
$[Co\{As(CH_2CH_2CH_2AsMe_2)_3\}Cl_2]ClO_4$	1.55	1.67, 1.70
$[Co\{As(CH_2CH_2CH_2AsMe_2)_3\}Br_2]ClO_4$	1.60	1.69, 1.72
$[Co\{As(CH_2CH_2CH_2AsMe_2)_3\}I_2]ClO_4$	1.85	1.75, 1.78

[a] δ Scale relative to TMS in $CDCl_3$. Free ligand $-AsMe_2$ = 0.90.

different from those of *trans* $[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2X_2]^+$ and the *trans* isomers of linear tetraarsines [5, 28], ruling out the presence of significant amounts of the *trans* isomer **IIc**. Distinction of *cis* α and *cis* β isomers on the basis of electronic spectroscopy is less clear, although those in Table II are more reminiscent of *cis* β-$[Co(\text{tetraarsine})Cl_2]^+$ [5, 28]. Furthermore if, as outlined above, the tetraphosphine is the *meso* diastereoisomer, the *cis* α complex is not expected since the chelate terminal arms are constrained to move towards *the same* apical position. The ^{31}P NMR spectra of these two complexes reveal considerable decomposition occurs in solution on standing, and resonances characteristic of oxidised/halogenated phosphines are present especially in the bromide spectra. The spectra of the Co(III) complexes (Table III) shows four inequivalent phosphorus atoms (intensity 1:1:1:1) consistent only with this *cis*-β geometry proposed. We do not know for certain within each pair (*i.e.* PhP < and Ph_2P-) which resonance is *trans* P and which *trans* X, although comparison with the complexes of $P(CH_2CH_2PPh_2)_3$, would suggest the higher frequency signal of each pair is due to P *trans* X. In view of the decomposition observed in solution, the ^{31}P spectra do not allow us to rule out the presence of small amounts of a second isomer, although the identification of the major species as the *cis*-β isomer is unequivocal.

All of the ^{31}P NMR spectra (Table III) have broad resonances (linewidth *ca.* 50 Hz) which is probably due to scalar broadening by the quadrupolar cobalt (I = 7/2, ^{59}Co), [29] and P–P couplings were not resolved.

Discussion

This study has shown that cobalt(III) complexes can be isolated with certain phenylphosphines ($o\text{-}C_6H_4(PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, $PhP(CH_2CH_2PPh_2)_2$, $[\text{-}CH_2P(Ph)CH_2CH_2PPh_2]_2$), but not with others ($Ph_2P(CH_2)_nPPh_2$ (n = 1, 2), $MeC(CH_2PPh_2)_3$), whilst qualitatively $CoP_4X_2^+$ units appear more stable than $CoP_3X_3^0$. Similar trends are evident with $As(CH_2CH_2CH_2AsMe_2)_3$ and $MeAs(CH_2CH_2CH_2AsMe_2)_2$, which respectively do and do not form Co(III) compounds. The ready formation of $[Co\{MeAs(o\text{-}C_6H_4AsMe_2)_2\}X_3]$ [3] whilst $MeAs(CH_2CH_2CH_2AsMe_2)_2$ and $MeC(CH_2AsMe_2)_3$ fail to give similar complexes may be due to the more favourable ring size (5) in the former, and to the '*o*-phenylene backbone effect' observed in other systems [6, 9] (essentially resistance to dissociation due to its rigidity). Studies of other high valent metal complexes (Pd(IV), Ni(III), *etc.*) with multidentate phosphines [9–11] have revealed that usually the metal binds sufficient halide ions to neutralise the formal charge, and then fills the remaining coordination sites with neutral donors. The observed stability $CoP_4X_2^+ > CoP_3X_3^0$ conflicts with this trend, and possibly reflects the low ligand field effect of halide ions on 3d metals, since for t_{2g}^6Co(III), there will be significant gains in LFSE, from replacement of X^- by the strong field P(As) donors. Detailed analysis of the electronic spectra of the complexes in Table II, is not possible due to the low symmetry, and the limited number of d–d transitions observed[§], but approximations [30] suggest that for the phenylphosphine complexes Dq is *ca.* 1900–2200 cm^{-1}, and B *ca.* 450–550 cm^{-1} rather similar Dq values and smaller B's than found in cobalt(III) amines.

The ^{31}P NMR coordination shifts in Table 3 are generally similar to those found in other complexes of these and similar ligands [31, 32], the large high frequency shifts of the phosphorus atoms in five membered rings being explained in terms of Δ_R, the ring contribution [32]. The complexes of $P(CH_2CH_2PPh_2)_3$ reveal that δP shifts to high frequency with *trans* ligand P < Cl < Br, but the absolute differences $\delta P_{trans\ P}$ and $\delta P_{trans\ X}$ are small (*ca.* ≤ 5 ppm), so that distinction of *mer* or *fac* CoP_3X_3 geometry for example, is uncertain from δP data.

It is apparent that although we have obtained Co(III) complexes of various phenylphosphines, these are much less robust than the corresponding amines and alkyl-phosphine or -arsine compounds. Although electronic factors will not be of negligible importance, the major features in the phenylphosphine complexes are probably steric.

[§] We believe that bands with $\epsilon_{max} \leq$ *ca.* 25000 cm^{-1} are essientially d–d in character, *cf.* [5, 8, 23, 28], although some workers [7] suggest that charge transfer bands lie as low as *ca.* 20000 cm^{-1}.

X-ray structural data on polyphosphine complexes of other 3d metal ions, *e.g.* Cr(III), Fe(II), Co(II) [22, 27, 33, 34], reveal that there is considerable crowding about the metal centre, and destabilising steric interactions will become increasingly important as the metal covalent radii decrease, on moving along the 3d period. Certainly the instability of $[Co(Ph_2PCH_2CH_2PPh_2)_2X_2]^+$ is predictable from the crowded nature of $[Co(Ph_2PCH_2CH_2PPh_2)_2X]^+$ [34], where the sixth coordination site is effectively 'filled' by the ligands *o*-phenyl-H's. The inability to obtain cobalt(III) iodocomplexes with phenylphosphines (whereas examples with alkyl phosphine or arsine multidentates readily form) is in keeping with the large size of I^- which would exacerbate the steric problems, although this effect is no doubt reinforced by the weakly oxidising nature of I_2.

Experimental

Physical measurements were made as described elsewhere [9–11]. ^{31}P NMR spectra were obtained for freshly prepared $CDCl_3$ solutions on a Bruker AM360, referenced to 85% H_3PO_4 (+ve δ values to high frequency).

The following cobalt complexes were made by literature methods: (X = Cl, Br or I) $[Co(Ph_2PCH_2PPh_2)_2X]ClO_4$ [20], $[Co(Ph_2PCH_2CH_2PPh_2)_2X]ClO_4$ [35] $[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2X]ClO_4$ [36], $[Co\{PhP(CH_2CH_2PPh_2)_2\}X_2]$ [12]. $[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2X]PF_6$ and $[Co_2\{MeC(CH_2PPh_2)_3\}_2X_2](PF_6)_2$ were made as described in Refs. [13, 24] using $NaPF_6$ instead of $NaBPh_4$. Attempts to obtain these as ClO_4^- salts, lead to mixtures containing CoX_4^{2-} and ClO_4^- as anions. $[Co\{P(CH_2CH_2PPh_2)_3\}X]ClO_4$ were made by refluxing together $Co(H_2O)_6X_2$, the ligand and $LiClO_4$ in a 1:1:4 mol ratio in ethanol. When chlorinated solvents were used (X = Br) some chloride was incorporated in the product.

$[Co\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}X_2]$ (X = Cl, Br, I)

The ligand (0.19 g, 0.5 mmol) was added under nitrogen to an ethanol solution (10 cm^3) of the appropriate $Co(H_2O)_6X_2$ (0.5 mmol). After stirring for 2 hours, the precipitated solids were filtered off, rinsed with ethanol and vacuum dried. $[Co\{MeC(CH_2AsMe_2)_3\}_2][CoX_4]$ were made similarly. $[Co\{As(CH_2CH_2CH_2AsMe_2)_3\}X_2]ClO_4$ [4] and $[Co(Ph_2PCHCHPPh_2)_2X_2]ClO_4$ [7] were made as described.

$[Co\{PhP(CH_2CH_2PPh_2)_2\}X_3]$

To a suspension of the cobalt(II) complex (1 mmol) in dry CCl_4 (10 cm^3) was added a slight excess of the appropriate halogen in CCl_4, and the mixture stirred for 1/2 hour. The solids produced were isolated by filtration, and dissolved in the minimum amount of dry CH_2Cl_2 containing a little free X_2. After filtration, the solutions were concentrated under reduced pressure, and the products dried *in vacuo* (*ca.* 80%).

$[Co\{P(CH_2CH_2PPh_2)_3\}Cl_2]ClO_4$

Nitrosyl chloride made as described elsewhere [9] was distilled on a frozen solution of $[Co\{P(CH_2CH_2PPh_2)_3\}Cl]ClO_4$ (1 mmol) in CH_2Cl_2. The mixture was allowed to warm up to room temperature, and then the solvent and excess NOCl removed *in vacuo*. Yield *ca.* quantitative.

$[Co\{P(CH_2CH_2PPh_2)_3\}X_2]ClO_4$, $[Co\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2X_2]PF_6$, $[Co\{o\text{-}C_6H_4(PPh_2)_2\}_2X_2]ClO_4$

A concentrated solution of the appropriate cobalt(II) complex (1 mmol) in CH_2Cl_2–CCl_4 (1:1 v/v 20 cm^3) was treated with excess of the halogen (*ca.* 1.2 mmol), and the mixture stirred at room temperature for 30 minutes. The solutions were filtered and concentrated under reduced pressure, to yield the solid complexes, which were isolated by filtration and dried *in vacuo* 50–70%.

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References

1 Part 14. S. K. Harbron and W. Levason, *J. Chem. Soc., Dalton Trans.*, in press.
2 R. S. Nyholm, *J. Chem. Soc.*, 2071 (1950).
3 R. G. Cunninghame, R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 5800 (1964).
4 G. Kordosky, G. S. Benner and D. W. Meek, *Inorg. Chim. Acta, 7*, 605 (1973).
5 B. Bosnich, W. G. Jackson and S. B. Wild, *J. Am. Chem. Soc., 95*, 8269 (1973); *ibid., Inorg. Chem., 13*, 1121 (1974).
6 L. F. Warren and M. A. Bennett, *Inorg. Chem., 15*, 3126 (1976).
7 V. M. Miskovski, J. L. Robbins, G. S. Hammond and H. B. Gray, *J. Am. Chem. Soc., 98*, 2477 (1976).
8 J. G. Hartley, D. G. E. Kerfoot and L. M. Venanzi, *Inorg. Chim. Acta, 1*, 145 (1967).
9 L. R. Gray, S. J. Higgins, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, 459 (1984).
10 L. R. Gray, D. J. Gulliver, W. Levason and M. Webster, *J. Chem. Soc., Dalton Trans.*, 133 (1983).
11 D. J. Gulliver, K. G. Smith and W. Levason, *J. Chem. Soc., Dalton Trans.*, 2153 (1982).
12 R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem., 10*, 1841 (1971).
13 R. B. King, R. N. Kapoor, M. S. Saran and P. N. Kapoor, *Inorg. Chem., 10*, 1851 (1971).
14 M. DiVaira, *J. Chem. Soc., Dalton Trans.*, 2360 (1975).

15 T. E. Nappier and D. W. Meek, *Inorg. Chim. Acta, 7*, 235 (1973).

16 F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc., 83*, 4690 (1961); A. Sabatini and L. Sacconi, *J. Am. Chem. Soc., 86*, 17 (1964).

17 J. R. Hartman, E. J. Hintsa and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 386 (1984).

18 J. Lewis, R. S. Nyholm and G. A. Rodley, *J. Chem. Soc.*, 1483 (1965).

19 B. K. W. Baylis and J. C. Bailar, *Inorg. Chem., 9*, 641 (1970); B. Bosnich, W. G. Jackson and J. W. Mclaren, *Inorg. Chem., 13*, 1133 (1974).

20 K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta, 14*, 121 (1975).

21 R. G. Cunninghame, R. S. Nyholm and M. L. Tobe, *J. Chem. Soc. A*, 227 (1971).

22 L. R. Gray, A. L. Hale, W. Levason, F. P. McCullough and M. Webster, *J. Chem. Soc., Dalton Trans.*, 47 (1984), and refs. therein.

23 I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto and S. Ooi, *Bull. Chem. Soc. Jpn., 54*, 2663 (1981).

24 C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chem., 14*, 2513 (1975).

25 M. DiVaira, A. Meli and L. Sacconi, *Cryst. Struct. Commun., 6*, 727 (1977).

26 R. B. King, P. R. Heckley and J. C. Cloyd Jr., *Z. Naturforsch. Teil B, 29*, 574 (1974).

27 M. Bacci and C. A. Ghilardi, *Inorg. Chem., 13*, 2398 (1974); C. A. Ghilardi, S. Midollini, L. Sacconi and P. Stoppioni, *J. Organomet. Chem., 205*, 193 (1981).

28 B. Bosnich, S. T. D. Lo and E. A. Sullivan, *Inorg. Chem., 14*, 2305 (1975).

29 M. Bressan, R. Ettorre and P. Rigo, *J. Organomet. Chem., 144*, 215 (1978).

30 A. L. Hale, Ph.D. Thesis, Southampton (1983).

31 R. B. King and J. C. Cloyd Jr., *Inorg. Chem., 14*, 1550 (1975).

32 P. E. Garrou, *Chem. Rev., 81*, 229 (1981).

33 F. Cecconi, M. DiVaira, S. Midollini, A. Orlandini and L. Sacconi, *Inorg. Chem., 20*, 3423 (1981).

34 J. K. Stalick, P. W. R. Corfield and D. W. Meek, *Inorg. Chem., 12*, 1668 (1973).

35 A. Sacco and A. Gorieri, *Gazz. Chim. Ital., 93*, 687 (1963).

36 W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta, 14*, 127 (1975).