

Syntheses of Pentamethylcyclopentadienylcobalt(III) Compounds and Reactions of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{solvent})_3]\text{X}_2$ (solvent = acetonitrile or acetone, $\text{X} = \text{BF}_4$ or PF_6)

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The complexes $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\text{L}]$ [$\text{L} = \text{PMe}_2\text{Ph}$, $\text{P}(\text{OPh})_3$, or CNBu^t] and $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\text{I}]$ ($\text{L} = \text{CNBu}^t$) are prepared by reaction of $[\{\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\}_n]$ with the appropriate Lewis base, L. The preparation and properties of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{solvent})_n]\text{X}_2$ [solvent = NCMe , $n = 3$, $\text{X} = \text{PF}_6$ (6); solvent = OCMe_3 , n believed to be 3, $\text{X} = \text{PF}_6$ (8a) or BF_4 (8b)] are described including the rapid solvolysis of the hexafluorophosphate anion of (8a). Reaction of the complexes (6) or (8) with the appropriate small ligand L yields $[\text{Co}(\text{C}_5\text{Me}_5)\text{L}_3]^{2+}$ [$\text{L} = \text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$, pyridine, or CNBu^t] whereas larger ligands with (6) give $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_2\text{L}]^{2+}$ [$\text{L} = \text{PMe}_2\text{Ph}$, $\text{P}(\text{OPh})_3$, or PPh_3]. One equivalent of 1,10-phenanthroline (phen) and MeCN react with (6) to give $[\text{Co}(\text{C}_5\text{Me}_5)(\text{phen})(\text{NCMe})]^{2+}$ whereas excess of phen gives $[\text{Co}(\text{phen})_3]^{2+}$; a similar displacement of the C_5Me_5 ligand occurs when $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ reacts with $\text{Ag}[\text{PF}_6]$ in dimethyl sulphoxide to give $[\text{Co}(\text{OSMe}_2)_n][\text{PF}_6]_2$. These reactions have been contrasted with those of the analogous complexes $[\text{M}(\text{C}_5\text{Me}_5)(\text{solvent})_n][\text{PF}_6]_2$ ($\text{M} = \text{Rh}$ or Ir).

COMPLEXES of the type $[\text{M}(\eta\text{-C}_5\text{Me}_5)(\text{solvent})_3][\text{PF}_6]_2$ ($\text{M} = \text{Rh}$ or Ir ; solvent = acetonitrile, dimethyl sulphoxide, or pyridine) are readily prepared by the reaction of $[\{\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2\}_2]$ with $\text{Ag}[\text{PF}_6]$ in the appropriate solvent.^{1,2} Although similar complexes with weakly co-ordinating solvents (*e.g.* acetone, dichloromethane, or methanol) can not be isolated in the solid state they are readily generated in solution and have proved to be valuable intermediates for synthesis since these solvent molecules are readily displaced by arenes,² phosphorus-donor ligands,³ phenol,⁴ and mono-, di-, and tri-olefins.⁵

In view of the ability of these rhodium and iridium tris(solvent) complexes to react with such a wide range of molecules we decided to prepare and investigate the reactivity of the analogous cobalt cations, $[\text{Co}(\text{C}_5\text{Me}_5)(\text{solvent})_3]^{2+}$ generated from $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (1) or $[\{\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\}_n]$ (2). Little is known of the reactivity of pentamethylcyclopentadienylcobalt(III) halides in contrast to the detailed chemistry of $[\{\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2\}_2]$ ⁶ and therefore we also briefly examined the reactions of Lewis bases with complexes (1) and (2). The reactions studied are summarised in the Scheme.

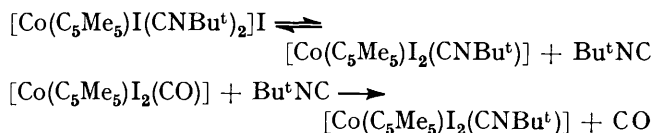
RESULTS AND DISCUSSION

The complexes $[\{\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\}_n]$ ⁷ and $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ ⁸ are readily prepared from $[\text{Co}_2(\text{CO})_8]$ and acetylpentamethylcyclopenta-1,3-diene *via* the dicarbonyl complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{CO})_2]$. However, the synthesis of acetylpentamethylcyclopenta-1,3-diene is not a trivial problem. Treatment of hexamethylbicyclo[2.2.0]hexadiene (hexamethyl-Dewar benzene) with 3-chloroperbenzoic acid has been reported to yield acetylpentamethylcyclopenta-1,3-diene in up to 40% yield⁹ although we found that this method gave very variable results. An alternative procedure (see Experimental section) which is convenient, cheaper, and consistently gives higher yields (*ca.* 40–50%) is based on the reported oxidation of hexamethyl-Dewar benzene by mercury(II) acetate.^{10,11} Recently, an improved route to pentamethylcyclopentadiene which does not involve hexamethyl-Dewar benzene has also been described.¹²

Contrary to a previous report,⁸ it was found that triphenylphosphine does not displace the carbonyl group from the complex $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (1) at 25 °C even after 6 d, whilst in refluxing tetrahydrofuran both PPh_3 and trimethyl phosphite gave a mixture of products which were difficult to separate. By comparison, $[\{\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\}_n]$ reacted readily at room temperature with phosphorus-donor ligands to give the monomeric complexes $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{L})]$ [$\text{L} = \text{PPh}_3$,⁸ PMe_2Ph (3a), or $\text{P}(\text{OPh})_3$ (3b)]. Both complexes (1) and (2) reacted rapidly with *t*-butyl isocyanide at 25 °C to give initially $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CNBu}^t)]$ (4) and then, with an excess of free ligand, the ionic complex $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}(\text{CNBu}^t)_2\text{I}]$ (5). Powell and Mays¹³ have reported similar reactions of $[\text{Co}(\text{C}_5\text{H}_5)\text{I}_2(\text{CO})]$ and they also suggested that the following equilibrium exists in solution:



When L is a weakly co-ordinating ligand (*e.g.* acetonitrile) the equilibrium was reported to lie to the right whereas for strongly co-ordinating ligands (*e.g.* isocyanides) the equilibrium lies to the left. In order to detect the presence of such an equilibrium in a dichloromethane solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}(\text{CNBu}^t)_2\text{I}]$, 1 mol equivalent of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ was added. It was reasoned that if any dissociation of co-ordinated Bu^tNC took place the following reactions should occur:

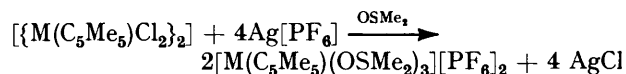


The i.r. spectrum of the mixture did not change over a period of a week and thus there is no evidence that dissociation of Bu^tNC occurs when (5) is dissolved in dichloromethane. In keeping with this proposal that the *t*-butyl isocyanide ligands are strongly bonded in the pentamethylcyclopentadienylcobalt complexes, $[\text{Co}(\text{C}_5\text{R}_5)\text{I}_2(\text{CNBu}^t)]$ ($\text{R} = \text{Me}$) exhibits $\nu(\text{CN})$ at 2 181 cm^{-1} , significantly lower than that of the unsubstituted complex ($\text{R} = \text{H}$), $\nu(\text{CN})$ at 2 205 cm^{-1} .¹⁴

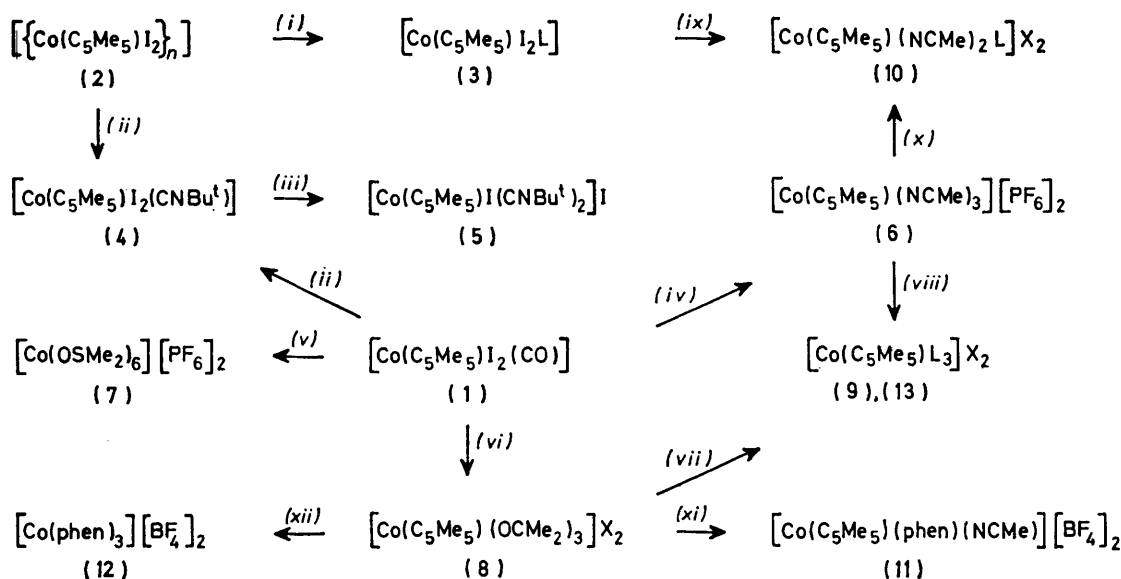
Preparation and Properties of Pentamethylcyclopentadienylcobalt Solvent Complexes.—(a) *Acetonitrile.* Treatment of an acetonitrile solution of either $[\text{Co}(\text{C}_5\text{Me}_5)_2(\text{CO})]$ or $[\{\text{Co}(\text{C}_5\text{Me}_5)_2\}_n]$ with 2 mol equivalents of silver(I) hexafluorophosphate gave the tris(acetonitrile) complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ (6). The complex is stable in air and was recovered unchanged after heating to 220 °C in air. It is soluble in acetonitrile and trifluoroacetic acid but it was found to be either insoluble or to undergo decomposition in other solvents. For example, the ^1H n.m.r. spectrum of an $[\text{D}_6\text{H}_6]$ acetone solution showed a broad resonance due to co-ordinated acetonitrile (δ 2.68–2.75) and two singlets in the C_5Me_5 region (δ 1.47 and 1.57). Addition of acetonitrile to this

placement of co-ordinated acetonitrile by acetone occurs.²

(b) *Dimethyl sulphoxide.* The complexes $[\text{M}(\text{C}_5\text{Me}_5)(\text{OSMe}_2)_3][\text{PF}_6]_2$ ($\text{M} = \text{Rh}$ or Ir) have been prepared by the reaction:²



It was anticipated that the analogous reaction of $[\text{Co}(\text{C}_5\text{Me}_5)_2(\text{CO})]$ with $\text{Ag}[\text{PF}_6]$ in dimethyl sulphoxide would give the complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{SMe}_2\text{O})_3][\text{PF}_6]_2$. Although we believe this to be an intermediate, cleavage of the $\text{Co}-\text{C}_5\text{Me}_5$ bond occurred with concomitant reduction of the metal and the paramagnetic complex



SCHEME (i) $\text{L} = \text{PMe}_2\text{Ph}$ (3a) or $\text{P}(\text{OPh})_3$ (3b); (ii) 1 equivalent Bu^tNC ; (iii) excess of Bu^tNC ; (iv) 2 equivalents $\text{Ag}[\text{PF}_6]$ in MeCN ; (v) 2 equivalents $\text{Ag}[\text{PF}_6]$ in SMe_2O ; (vi) 2 equivalents $\text{Ag}[\text{PF}_6]$ ($\text{X} = \text{PF}_6$) or $\text{Ag}[\text{BF}_4]$ ($\text{X} = \text{BF}_4$) in acetone; (vii) $\text{X} = \text{BF}_4$, $\text{L} = \text{P}(\text{OMe})_3$ (9a), $\text{P}(\text{OEt})_3$ (9b), or pyridine; $\text{X} = \text{PF}_6$, $\text{L} = \text{Bu}^t\text{NC}$ (13); (viii) $\text{L} = \text{Bu}^t\text{NC}$, $\text{X} = \text{PF}_6$ (13); (ix) 2 equivalents $\text{Ag}[\text{BF}_4]$ in MeCN [$\text{L} = \text{PMe}_2\text{Ph}$, $\text{X} = \text{BF}_4$ (10a)]; (x) $\text{X} = \text{PF}_6$, $\text{L} = \text{P}(\text{OPh})_3$ (10b) or PPh_3 (10c); (xi) 1 equivalent phen + MeCN ; (xii) excess of phen

solution caused the resonance at δ 1.47 to disappear leaving the singlet at δ 1.57 as the only C_5Me_5 signal. These observations indicate that the following exchange process occurs in acetone:



The exchange process is slow on the n.m.r. time scale. {In the above spectrum the signal due to free acetonitrile (δ 2.05) was obscured by the $[\text{D}_6\text{H}_6]$ acetone multiplet.} The ^1H n.m.r. spectrum of (6) in $[\text{D}_6\text{H}_6]$ acetonitrile showed, in addition to the signal of the C_5Me_5 ligand (δ 1.40), resonances due to both co-ordinated and free acetonitrile (δ 2.48 and 2.01 respectively), again indicating that exchange between co-ordinated and non-co-ordinated solvent molecules is slow.

It is of interest to note that whilst the complexes $[\text{M}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ ($\text{M} = \text{Rh}$ or Ir) undergo similar slow exchange processes in acetonitrile no dis-

$[\text{Co}(\text{OSMe}_2)_6][\text{PF}_6]_2$ (7) was isolated. The i.r. spectrum of the product [$\nu(\text{SO})$ at 950 cm^{-1}] indicated that the SMe_2O ligands were co-ordinated through the oxygen atoms and the spectrum closely resembled that reported for the related oxygen-bonded complex $[\text{Co}(\text{OSMe}_2)_6][\text{CoCl}_4]^{15}$

The ring-cleavage reaction suggests that the $\text{Co}^{\text{III}}-\text{C}_5\text{Me}_5$ bond is significantly weaker than the $\text{M}^{\text{III}}-\text{C}_5\text{Me}_5$ bonds ($\text{M} = \text{Rh}$ or Ir).

(c) *Acetone.* When an acetone solution of $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ is allowed to stand for 18 h at 54 °C a solvolysis reaction occurs to give the difluorophosphate complex $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\text{PF}_2\text{O}_2)_3][\text{PF}_6]$ which has been characterised by X-ray crystallography;¹ the corresponding iridium complex $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ undergoes a similar solvolysis followed by further reactions resulting after 72 h at 50 °C in the formation of the hydroxypentadienyl complex ion, $[\text{Ir}(\text{C}_5\text{Me}_5)\{\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{OH})\text{CH}_2\}]^+$.^{16a} In view of these re-

markable reactions it was of particular interest to examine the behaviour of the complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ (8a).

On treatment with $\text{Ag}[\text{PF}_6]$, acetone solutions of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ or $[\{\text{Co}(\text{C}_5\text{Me}_5)\text{I}\}_n]$ gave a deep blue solution and a precipitate of silver(I) iodide, which was filtered off. The blue solution quickly darkened and within 2 h a small amount of insoluble black material was deposited; after 24 h, etching of the glass container was observed. The nature of the species present in solution was investigated by ^1H and ^{31}P n.m.r. spectroscopy using solutions prepared in $[\text{C}_6\text{H}_6]$ acetone. Initially the ^1H n.m.r. spectrum showed only a singlet (δ 1.30) which we assign to the C_5Me_5 ligand of $[\text{Co}(\text{C}_5\text{Me}_5)\{\text{OC}(\text{CD}_3)_2\}_3][\text{PF}_6]_2$ but within 1 h this signal was replaced by another singlet (δ 0.99) which in turn broadened slowly and disappeared (*ca.* 6 h) leaving a number of weak broad signals. The ^{31}P n.m.r. spectrum of the solution recorded within 5 min of its preparation already showed a triplet [δ -3.1; $J(\text{PF}) = 947$ Hz] in addition to the septet of the PF_6 anion [δ -143.8; $J(\text{PF}) = 707$ Hz]. This spectrum closely resembles that of $[\text{Rh}_2(\text{C}_5\text{Me}_5)_2(\text{PF}_2\text{O}_2)_3][\text{PF}_6]$ [δ -11.1 (t), $J(\text{PF}) = 952$ Hz; δ -143.9 (septet), $J(\text{PF}) = 708$ Hz]. In contrast to the rhodium difluorophosphate complex the product formed initially from $[\text{Co}(\text{C}_5\text{Me}_5)\{\text{OC}(\text{CD}_3)_2\}_3][\text{PF}_6]_2$ underwent further reaction and within 30 min the ^{31}P n.m.r. spectrum contained an additional triplet [δ -2.5, $J(\text{PF}) = 940$ Hz] along with other minor peaks. All these signals broadened and decayed within 4 h at room temperature leaving only the PF_6 septet.

Several attempts were made to isolate the species present by addition of excess of diethyl ether to acetone solutions of (8a) which had been allowed to stand for short periods (10–30 min). The blue solids obtained by this procedure could be recrystallised from chloroform and ether mixtures and appeared quite stable in air but decomposed slowly in chloroform solution and more rapidly in acetone. Although the analytical data of the blue solids were variable the spectroscopic properties were consistent and closely resembled those of $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\text{PF}_2\text{O}_2)_3][\text{PF}_6]$ [^1H n.m.r., $[\text{C}_6\text{H}_6]$ chloroform, δ 0.87(s); ^{31}P n.m.r., $[\text{C}_6\text{H}_6]$ chloroform, δ -3.2 (t), $J(\text{PF}) = 948$ Hz; δ -145.1 (septet), $J(\text{PF}) = 707$ Hz]. In particular the i.r. spectra (Nujol) contained bands at 1 148 and 1 310 cm^{-1} and at 854 and 870 cm^{-1} , assigned to $\nu(\text{PO})$ and $\nu(\text{PF})$ respectively of a PF_2O_2 ligand.¹⁶ A band at 835 cm^{-1} characteristic of the PF_6 anion was also present.

Summarising, the complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ appears to undergo a very rapid solvolysis reaction of the PF_6 anions to give a difluorophosphate complex which is unstable in solution and decomposes to give several unidentified products. The initial solvolysis reaction is complete within minutes at ambient temperature whereas the analogous reactions of the complexes $[\text{M}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ required 18 h at 54 °C for $\text{M} = \text{Rh}$ and *ca.* 12 d at 35 °C for $\text{M} = \text{Ir}$.¹⁷ Although the mechanism

of the solvolysis of the PF_6 anions in these complexes is unknown the metal clearly plays an important role in the reaction.

When $\text{Ag}[\text{BF}_4]$ rather than $\text{Ag}[\text{PF}_6]$ is allowed to react with an acetone solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ the complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ (8b) is believed to be formed. This complex is considerably more stable than the PF_6 analogue; the ^1H n.m.r. spectrum in $[\text{C}_6\text{H}_6]$ -acetone initially contained one singlet in the C_5Me_5 region (δ 1.29) which decayed over 72 h at 35 °C to give a complex spectrum.

Reactions of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{solvent})_3]^{2+}$ (6: solvent = NCMe; 8: solvent = OCMe_2).—(a) *With phosphorus-donor ligands.* Addition of trimethyl phosphite or triethyl phosphite to acetone solutions of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ gave the tris(phosphite) complexes $[\text{Co}(\text{C}_5\text{Me}_5)\{\text{P}(\text{OR})_3\}_3][\text{BF}_4]_2$ [$\text{R} = \text{Me}$ (9a) or Et (9b)]. The presence of three phosphite ligands in both complexes is clearly indicated by the ^1H n.m.r. spectra which show the C_5Me_5 resonances as quartets [$J(\text{PH}) = 3$ Hz]. The complex $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ undergoes analogous reactions with $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OEt})_3$ whereas the iridium tris(acetone) complex reacts with $\text{P}(\text{OMe})_3$ to give $[\text{Ir}(\text{C}_5\text{Me}_5)\text{H}\{\text{P}(\text{OMe})_3\}_2][\text{PF}_6]_3$.

Trimethyl phosphite and triethyl phosphite are relatively small ligands (cone angle $\theta = 107$ and 109° respectively);¹⁸ with bulkier ligands no pentamethylcyclopentadienylcobalt tris(ligand) complexes were formed. For example, neither $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ nor $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ gave stable complexes when treated with excess of PMe_2Ph ($\theta = 122^\circ$); ^1H n.m.r. studies of the latter reaction clearly showed that co-ordination of only two phosphine ligands occurred in solution since the C_5Me_5 resonance appeared as a triplet (δ 1.30, $J = 2$ Hz). The monophosphine adduct $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_2(\text{PMe}_2\text{Ph})][\text{BF}_4]_2$ (10a) was isolated in 78% yield from the reaction of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{PMe}_2\text{Ph})]$ with two equivalents of $\text{Ag}[\text{BF}_4]$ in acetonitrile. It is interesting to note that although $[\text{Co}(\text{C}_5\text{Me}_5)(\text{PMe}_2\text{Ph})_3][\text{PF}_6]_2$ could not be prepared, the corresponding rhodium compound is stable.³

Treatment of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ with excess of triphenyl phosphite ($\theta = 128^\circ$) or triphenylphosphine ($\theta = 145^\circ$) gave only the monosubstituted products $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_2\text{L}][\text{PF}_6]_2$ [$\text{L} = \text{P}(\text{OPh})_3$ (10b) or PPh_3 (10c)]. The tris(acetone) complex (8b) appeared to react similarly although the bis(acetone) adducts $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_2\text{L}][\text{BF}_4]_2$ proved too unstable to isolate in the solid state. The ^1H n.m.r. spectrum of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_2(\text{PPh}_3)][\text{PF}_6]_2$ and a large excess of triphenylphosphine showed no indication of the formation of a bis(phosphine) adduct; in contrast, although no bis(phosphine) adduct could be isolated from the reaction of $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{NCMe})_2(\text{PPh}_3)][\text{PF}_6]$ and triphenylphosphine, such a species clearly exists in solution since the ^1H n.m.r. spectrum of the reaction mixture contained a triplet in the C_5Me_5 region [δ 1.37, $J(\text{PH}) = 3$ Hz] in addition to a signal due to free acetonitrile.³

Again in contrast to the cobalt analogue, the compounds $[\text{M}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ ($\text{M} = \text{Rh}$ or Ir) react with excess of triphenyl phosphite to give the *ortho*-metallated compounds $[\text{M}(\text{C}_5\text{Me}_5)\{\text{C}_6\text{H}_4\text{OP}(\text{OPh})_2\}\{\text{P}(\text{OPh})_3\}][\text{PF}_6]$ rather than the simple monosubstituted products $[\text{M}(\text{C}_5\text{Me}_5)(\text{NCMe})_2\{\text{P}(\text{OPh})_3\}][\text{PF}_6]_2$.³

These observations indicate that co-ordination of donor ligands to cobalt bearing a pentamethylcyclopentadienyl ligand depends markedly upon the steric properties of the donor ligands.

(b) *With nitrogen-donor ligands.* The complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ reacted with 1 mol equivalent of 1,10-phenanthroline (phen) to give a dark red complex of composition $[\text{Co}(\text{C}_5\text{Me}_5)(\text{phen})][\text{BF}_4]_2 \cdot n \text{H}_2\text{O}$ (n varied between 0.4 and 1.5). The i.r. spectrum of the product confirmed that it contained water [$\nu(\text{OH})$ at 3 300–3 400 cm^{-1}] and not acetone; exhaustive pumping under vacuum at 82 °C failed to remove water which was probably co-ordinated to the cobalt. Recrystallisation of the red solid from acetonitrile and diethyl ether, however, did give the well defined complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{phen})(\text{NCMe})][\text{BF}_4]_2$ (11) which was characterised by elemental analysis and ^1H n.m.r. and i.r. spectroscopy.

Addition of more than 1 mol equivalent of 1,10-phenanthroline to an acetone solution of (8b) led to the formation of $[\text{Co}(\text{phen})_3][\text{BF}_4]_2$ (12) which was the sole product when 3 mol equivalents were added. In contrast, $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ reacts with excess of 1,10-phenanthroline to give the complex $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{phen})_2][\text{PF}_6]_2$.¹⁷ The displacement of the C_5Me_5 ligand from cobalt by 1,10-phenanthroline is analogous to the reaction with dimethyl sulphoxide and again illustrates the relative weakness of the $\text{Co}-\text{C}_5\text{Me}_5$ bond in contrast to the exceedingly stable rhodium- and iridium-pentamethylcyclopentadienyl bonds.

Reaction of excess of pyridine with $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ gave a purple oil which was formulated as $[\text{Co}(\text{C}_5\text{Me}_5)(\text{py})_3][\text{BF}_4]_2$ on the basis of ^1H n.m.r. spectroscopy $\{^2\text{H}_2\}$ dichloromethane: δ 1.01(s), 15 H; 7.36–7.96 (m, br), 9 H; 8.86 (d, $J = 5$ Hz), 6 H}. The pyridine ligands proved to be very labile and all attempts to recrystallise the product led to decomposition. For example, in solution acetone displaced the pyridine ligands; similar displacement of acetonitrile was observed when $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ was dissolved in acetone.

(c) *Reactions with Bu^tNC , dienes, and arenes.* Treatment of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{solvent})_3][\text{PF}_6]_2$ (solvent = NCMe or OCMe_2) with excess of *t*-butyl isocyanide gave the tris(isocyanide) complex $[\text{Co}(\text{C}_5\text{Me}_5)(\text{CNBu}^t)_3][\text{PF}_6]_2$ (13). Comparison of the i.r. spectra of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CNBu}^t)]$ (4), $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}(\text{CNBu}^t)_2]\text{I}$ (5), and $[\text{Co}(\text{C}_5\text{Me}_5)(\text{CNBu}^t)_3][\text{PF}_6]_2$ (Table) shows that $\nu(\text{CN})$ increases with increasing positive charge on the complex. Co-ordinated isocyanide ligands have been shown to be susceptible to nucleophilic attack to give carbene complexes¹⁹ but reaction of the complexes (4), (5), and (13) with sodium

methoxide or trimethylamine did not give any characterisable products; Powell and Mays¹³ reported similar negative results for the reactions of $[\text{Co}(\text{C}_5\text{H}_5)\text{I}(\text{CNC}_6\text{H}_4\text{-OMe-}p)_2]^+$ with these reagents.

Cyclopentadiene reacts with $[\text{M}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ within minutes to give a quantitative yield of the corresponding cyclopentadienyl complex $[\text{M}(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_5)][\text{PF}_6]$ ($\text{M} = \text{Rh}$ or Ir).⁵ In contrast, the cobalt acetone complex (8b) reacted slowly (16 h) with cyclopentadiene in acetone to give a mixture of products. Removal of the solvent *in vacuo* and recrystallisation of the residue from dichloromethane and diethyl ether yielded a small amount of yellow solid which was formulated as $[\text{Co}(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_5)][\text{BF}_4]$ on the basis of ^1H n.m.r. spectroscopy $\{^2\text{H}_6\}$ acetone: δ 2.17(s), 15 H; 5.50(s), 5 H}. Cyclo-octa-1,5-diene and butadiene did not react with $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$.

The reactions of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3]\text{X}_2$ ($\text{X} = \text{BF}_4$ or PF_6) with arenes are discussed fully in the following paper²⁰ but it is appropriate to point out that, whereas the corresponding rhodium and iridium complexes react with a wide range of arenes to give complexes of the type $[\text{M}(\text{C}_5\text{Me}_5)(\text{arene})][\text{PF}_6]_2$ ($\text{M} = \text{Rh}$ or Ir),² only the cobalt indole complex $[\text{Co}(\text{C}_5\text{Me}_5)(\eta^6\text{-C}_8\text{H}_7\text{N})][\text{PF}_6]_2$ was successfully prepared by this procedure.

The tris(acetonitrile) complex (6) did not react with indole or cyclopentadiene.

Conclusions.—Dicationic pentamethylcyclopentadienylcobalt solvent complexes are useful for preparing ionic complexes of the type $[\text{Co}(\text{C}_5\text{Me}_5)\text{L}^1_2\text{L}^2]\text{X}_2$ [$\text{X} = \text{BF}_4$ or PF_6 ; $\text{L}^1 = \text{NCMe}$, $\text{L}^2 = \text{PPh}_3$, $\text{P}(\text{OPh})_3$, or PMe_2Ph ; $\text{L}^1_2 = \text{phen}$, $\text{L}^2 = \text{NCMe}$; $\text{L}^1 = \text{L}^2 = \text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$, py , or CNBu^t] which are unknown for the unsubstituted $\text{Co}(\eta\text{-C}_5\text{H}_5)$ system. It is clear from this study, however, that whereas the corresponding rhodium and iridium complexes are extremely valuable intermediates in synthesis there are several factors which severely limit the use of complexes of the type $[\text{Co}(\text{C}_5\text{Me}_5)(\text{solvent})_3]\text{X}_2$ (solvent = OCMe_2 or NCMe ; $\text{X} = \text{BF}_4$ or PF_6). The first is the relative instability of these solvent complexes as illustrated by the rapid decomposition of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ (8a) or the displacement of co-ordinated acetonitrile from $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ (6) in acetone solution. The ready cleavage of the metal-pentamethylcyclopentadienyl bond by dimethyl sulphoxide and 1,10-phenanthroline also highlights a limitation of the pentamethylcyclopentadienylcobalt system, whilst the reactions of the complexes (6) and (8b) with phosphorus-donor ligands demonstrate that the steric bulk of the pentamethylcyclopentadienyl ligand causes severe constraint on the number and size of the other ligands on cobalt. Finally, although the rhodium and iridium analogues react readily with dienes and arenes, the cation $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3]^{2+}$ showed little tendency to react with such π -acids illustrating that despite the considerable electron-donating ability of the pentamethylcyclopentadienyl ligand the cobalt atom is a typical 'hard' centre.

Complex	Analytical and spectroscopic data ^a				I.r. (Nujol) (cm ⁻¹)	¹ H n.m.r. (δ)		
	Analysis (%)					C ₅ Me ₅	Other methyls	Other
	C	H	N	I				
(3a) [Co(C ₅ Me ₅)I ₂ (PMe ₂ Ph)]	37.1 (36.9)	4.6 (4.5)		43.1 (43.3)		1.68 [d, J(PH) = 1] ^b	2.06 [d, J(PH) = 10]	Ph, 7.3—7.6 (m, 3 H); 7.9—8.3 (m, 2 H)
(3b) [Co(C ₅ Me ₅)I ₂ {P(OPh) ₃ }]	44.6 (44.3)	4.0 (4.0)		33.2 (33.5)		2.08 [d, J(PH) = 3.5] ^b		Ph, 7.02m
(4) [Co(C ₅ Me ₅)I ₂ (CNBu ^t)]	34.2 (33.9)	4.8 (4.6)	2.7 (3.0)	47.8 (47.8)	ν(CN) 2 181s	2.06s ^b	1.54s	
(5) [Co(C ₅ Me ₅)I(CNBu ^t) ₂]I	39.0 (39.1)	5.5 (5.4)	4.4 (4.6)	41.7 (41.3)	ν(CN) 2 196s, 2 228s	2.03s ^b	1.58s	
(6) [Co(C ₅ Me ₅)(NCMe) ₃][PF ₆] ₂ ^c	31.6 (31.6)	4.2 (4.0)	6.9 (6.9)		ν(NC) 2 302w, 2 327w	1.37s ^d	2.30s	
(7) [Co(OSMe ₂) ₆][PF ₆] ₂	17.8 (17.6)	4.4 (4.4)			ν(SO) 950s			
(9a) [Co(C ₅ Me ₅){P(OMe) ₃ }] ₃ [BF ₄] ₂ ^e	30.8 (30.8)	5.7 (5.7)			ν(PO) 1 178m	1.82 [q, J(PH) = 3]	4.26m	
(9b) [Co(C ₅ Me ₅){P(OEt) ₃ }] ₃ [BF ₄] ₂	38.8 (38.8)	7.0 (6.8)			ν(PO) 1 158m	1.85 [q, J(PH) = 3]	1.49 [t, J(Me- CH ₂) = 7.5]	CH ₂ , 4.28—4.75m
(10a) [Co(C ₅ Me ₅)(NCMe) ₂ (PMe ₂ Ph)]- [BF ₄] ₂	44.3 (44.9)	5.6 (5.5)	4.7 (4.8)			1.45 [d, J(PH) = 2]	1.45 [d, J(PH) = 1] PMe ₂ Ph, 2.01 [d, J(PH) = 11.5]	Ph, 7.61—8.17m
(10b) [Co(C ₅ Me ₅)(NCMe) ₂ {P(OPh) ₃ }] [PF ₆] ₂	44.2 (44.1)	3.9 (4.1)	3.3 (3.2)		ν(NC) 2 308m, 2 330m	1.72 [d, J(PH) = 4.5]	2.26 [d, J(PH) = 2]	Ph, 7.25—7.60m
(10c) [Co(C ₅ Me ₅)(NCMe) ₂ (PPh ₃)] ₂ [PF ₆] ₂	46.9 (46.6)	4.3 (4.4)	3.2 (3.4)		ν(NC) 2 300m, 2 328m	1.33 [d, J(PH) = 2]	2.51 [d, J(PH) = 1.5]	Ph, 7.20—7.48 (m, 3 H), 7.65—7.75 (m, 2 H)
(11) [Co(C ₅ Me ₅)(phen)(NCMe)] ₂ [BF ₄] ₂	49.0 (48.9)	4.5 (4.5)	7.3 (7.1)		ν(NC) 2 312w, 2 330 (sh)	1.47s	2.26s	phen, H ^{3,8} 8.37, H ^{5,6} 8.82, H ^{2,7} 9.2; J(H ² H ³) = 5.5, J(H ² H ⁴) = 8; J(H ² H ⁴) = 1.5
(12) [Co(phen) ₃][BF ₄] ₂	55.9 (55.9)	3.1 (3.1)	10.5 (10.8)					
(13) [Co(C ₅ Me ₅)(CNBu ^t) ₃][PF ₆] ₂ ^f	41.0 (40.9)	5.8 (5.8)	6.0 (5.7)		ν(CN) 2 229s, 2 240s	1.37s	2.30s	

^a Calculated analysis figures are given in parentheses; unless stated otherwise, n.m.r. spectra were recorded in [²H₆]acetone using SiMe₄ as internal standard (*J* values in Hz). ^b Recorded in [²H₁]chloroform. ^c ¹³C-¹H n.m.r. recorded in CF₃CO₂H containing ca. 10% [²H₁]chloroform: 4.2 (MeCN), 10.6 (C₅Me₅), 102.7 (C₅Me₅), 133.4 (MeCN). ^d Recorded in CF₃CO₂H. ^e ¹³C-¹H n.m.r. data: 10.6 (C₅Me₅), 58.1 (OMe), 108.6 (C₅Me₅). ^f ¹³C-¹H n.m.r. data: 10.2 (C₅Me₅), 29.8 (CNCMe₃), 62.6 (CNCMe₃), 109.4 (C₅Me₅), 129.7 (CNCMe₃).

EXPERIMENTAL

All reactions were carried out under dinitrogen. Acetone and dichloromethane were dried over anhydrous CaCl₂ and CaH₂ respectively and distilled before use; other solvents were of reagent grade and were dried by standing over molecular sieves. The complexes [Co(C₅Me₅)I₂(CO)]⁸ and [Co(C₅Me₅)I₂]_n⁷ were prepared as described previously. Elemental analyses were carried out by the microanalytical department of this university. Hydrogen-1 n.m.r. spectra were recorded on Varian Associates HA 100 or Perkin-Elmer R34 220 MHz spectrometers, ¹³C and ³¹P n.m.r. spectra on a JEOL PFT 100 spectrometer; ³¹P spectra were calibrated using 85% H₃PO₄ as an external reference. Infrared spectra were recorded using a Perkin-Elmer 157 G grating spectrometer; all hexafluorophosphate salts showed a strong band at ca. 840 cm⁻¹ and all tetrafluoroborate salts a very broad, strong band at ca. 1 000—1 100 cm⁻¹.

5-Acetylpentamethylcyclopenta-1,3-diene.—A slurry of hexamethylbicyclo[2.2.0]hexa-2,5-diene (11.2 g, 70 mmol) and Hg[O₂CMe]₂ (22.6 g, 70 mmol) in 50% aqueous tetrahydrofuran (thf) (300 cm³) was stirred for 24 h. Acetic

acid (10 cm³) was added and the mixture boiled gently for 1 h in order to complete the reaction. The cooled solution was decanted from the metallic mercury residue and the product was extracted into diethyl ether (3 × 100 cm³). After drying over anhydrous sodium carbonate for 3 h, the ether extracts were filtered and reduced to a yellow oil *in vacuo*. The product was extracted into pentane and on cooling (−40 °C) gave 5-acetylpentamethylcyclopenta-1,3-diene as a white crystalline solid (6.26 g, 52%). The ¹H n.m.r. spectrum of the product was identical to that reported by King and Efraty.⁹

(Dimethylphenylphosphine)di-iodo(η-pentamethylcyclopentadienyl)cobalt(III), (3a).—The complex [(Co(C₅Me₅)I₂]₂ (200 mg, 0.22 mmol) and dimethylphenylphosphine (65 mg, 0.47 mmol) were stirred in dichloromethane (5 cm³) for 10 min. After removal of the solvent *in vacuo*, the residual dark green oil was dissolved in chloroform (10 cm³) and filtered through a short alumina column (0.5 × 2 cm). Concentration of the chloroform solution and addition of pentane yielded black crystals of [Co(C₅Me₅)I₂(PMe₂Ph)] (180 mg, 76%).

Di-iodo(η-pentamethylcyclopentadienyl)(triphenyl phosphite)cobalt(III), (3b).—The complex $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\{\text{P}(\text{OPh})_3\}]$ (275 mg, 81%) was obtained as black needle-shaped crystals from $[\{\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2\}]_2$ (200 mg, 0.22 mmol) and triphenyl phosphite (150 mg, 0.45 mmol) by the method described above for $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{PMe}_2\text{Ph})]$.

Di-iodo(η-pentamethylcyclopentadienyl)(t-butyl isocyanide)cobalt(III), (4).—*t*-Butyl isocyanide (35 mg, 0.42 mmol) in dichloromethane (5 cm³) was added slowly to a stirred solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (200 mg, 0.42 mmol) in dichloromethane (10 cm³). The solution was reduced to a brown solid *in vacuo* and this solid was extracted into diethyl ether until the washings were colourless. The ether solution was filtered, reduced to a brown solid *in vacuo*, and recrystallised from dichloromethane and pentane to give $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CNBu}^t)]$ (200 mg, 90%).

Iodo(η-pentamethylcyclopentadienyl)bis(t-butyl isocyanide)cobalt(III) Iodide, (5).—*t*-Butyl isocyanide (500 mg, 6.0 mmol) was added to a stirred solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (200 mg, 0.42 mmol) in dichloromethane (10 cm³). The solution was reduced *in vacuo* to a green solid, which was recrystallised from acetone and diethyl ether to give dark green crystals of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}(\text{CNBu}^t)_2\text{I}]$ (240 mg, 93%).

Tris(acetonitrile)(η-pentamethylcyclopentadienyl)cobalt(III) Hexafluorophosphate, (6).—Silver(I) hexafluorophosphate (430 mg, 1.7 mmol) was added to a stirred solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (400 mg, 0.85 mmol) in acetonitrile (30 cm³) and after 5 min the precipitate of AgI was removed by filtration through a cellulose column (1 × 3 cm). Addition of diethyl ether to the filtrate precipitated a red solid which was recrystallised from acetonitrile and ether to give dark red crystals of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ (475 mg, 92%).

Hexakis(dimethyl sulphoxide)cobalt(II) Hexafluorophosphate, (7).—The salt $\text{Ag}[\text{PF}_6]$ (210 mg, 0.85 mmol) was added to a solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (200 mg, 0.42 mmol) in dmsO (20 cm³). After stirring for 10 min the precipitate was removed by filtration through a small cellulose column (1 × 3 cm) and addition of dichloromethane and diethyl ether precipitated $[\text{Co}(\text{OSMe}_2)_6][\text{PF}_6]_2$ (320 mg, 93%) as a pink solid.

Reaction of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ with $\text{Ag}[\text{PF}_6]$ in Acetone.—The salt $\text{Ag}[\text{PF}_6]$ (315 mg, 1.27 mmol) was added to a stirred solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (300 mg, 0.63 mmol) in acetone (15 cm³). After 5 min the mixture was filtered through a cellulose column (1 × 3 cm) to remove the fine precipitate of AgI. The residue and column were washed with acetone (15 cm³) and the combined filtrate and washings were concentrated to ca. 10 cm³. The resulting blue solution, believed to contain $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$, darkened rapidly and decomposed completely within 70 min. Consequently, reactions involving acetone solutions of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ were always carried out using freshly prepared solutions.

Reaction of $\text{Ag}[\text{BF}_4]$ with $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ in Acetone.—An acetone solution of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ was prepared from $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ and $\text{Ag}[\text{BF}_4]$ using the procedure described above for $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$.

(η-Pentamethylcyclopentadienyl)tris(trimethyl phosphite)cobalt(III) Tetrafluoroborate, (9a).—A brown solution was formed upon addition of $\text{P}(\text{OMe})_3$ (0.5 g, 4.1 mmol) to an acetone solution of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$, prepared from $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (200 mg, 0.42 mmol) and $\text{Ag}[\text{BF}_4]$ (165 mg, 0.84 mmol) as described above. After stirring for 20 min, the solution was filtered, concentrated, and sub-

sequent addition of diethyl ether precipitated a yellow solid which was recrystallised from acetone and ether to give pale yellow crystals of $[\text{Co}(\text{C}_5\text{Me}_5)\{\text{P}(\text{OMe})_3\}_3][\text{BF}_4]_2$ (275 mg, 89%).

(η-Pentamethylcyclopentadienyl)tris(triethyl phosphite)cobalt(III) Tetrafluoroborate, (9b).—The complex $[\text{Co}(\text{C}_5\text{Me}_5)\{\text{P}(\text{OEt})_3\}_3][\text{BF}_4]_2$, a pale yellow crystalline solid, was prepared from $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ and $\text{P}(\text{OEt})_3$ in 85% yield in the same manner as its trimethyl phosphite analogue.

Bis(acetonitrile)(dimethylphenylphosphine)(η-pentamethylcyclopentadienyl)cobalt(III) Tetrafluoroborate, (10a).—The salt $\text{Ag}[\text{BF}_4]$ (60 mg, 0.31 mmol) was added to a solution of $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{PMe}_2\text{Ph})]$ (90 mg, 0.15 mmol) in acetonitrile (10 cm³) and the mixture stirred for 30 min before being filtered through a cellulose column (1 × 3 cm). Addition of diethyl ether yielded an orange oil. This was recrystallised from acetonitrile and ether at -25 °C to give orange crystals of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_2(\text{PMe}_2\text{Ph})][\text{BF}_4]_2$ (70 mg, 78%).

Bis(acetonitrile)(η-pentamethylcyclopentadienyl)(triphenylphosphine)cobalt(III) Hexafluorophosphate, (10c).—Triphenylphosphine (800 mg, 3.1 mmol) was added to a suspension of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ (200 mg, 0.33 mmol) in dichloromethane (15 cm³) and the mixture stirred for 20 h. After filtration, the resulting orange solution was concentrated to ca. 5 cm³. Addition of diethyl ether gave orange crystals of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_2(\text{PPh}_3)][\text{PF}_6]_2$ which were recrystallised from dichloromethane and ether (225 mg, 82%).

Bis(acetonitrile)(η-pentamethylcyclopentadienyl)(triphenyl phosphite)cobalt(III) Hexafluorophosphate, (10b).—Red crystals of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_2\{\text{P}(\text{OPh})_3\}][\text{PF}_6]_2$ were obtained in 81% yield from $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})_3][\text{PF}_6]_2$ and $\text{P}(\text{OPh})_3$ using the procedure described above for compound (10c).

Acetonitrile(η-pentamethylcyclopentadienyl)(1,10-phenanthroline)cobalt(III) Tetrafluoroborate, (11).—A solution of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{BF}_4]_2$ in acetone (10 cm³) was prepared from $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (200 mg, 0.42 mmol) and $\text{Ag}[\text{BF}_4]$ (165 mg, 0.84 mmol) as previously described. 1,10-Phenanthroline (76 mg, 0.42 mmol) in acetone (10 cm³) was added to the stirred solution over a period of 5 min. The mixture was then concentrated to ca. 5 cm³ and a small amount of yellow solid was filtered off. This was identified as $[\text{Co}(\text{phen})_3][\text{BF}_4]_2$ by elemental analysis and its characteristic ¹H n.m.r. spectrum.²¹ Addition of diethyl ether to the filtrate gave a purple solid, believed to be $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OH})_2(\text{phen})][\text{BF}_4]_2$ which was recrystallised from acetonitrile and ether to give dark red crystals of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{NCMe})(\text{phen})][\text{BF}_4]_2$ (210 mg, 85%).

(η-Pentamethylcyclopentadienyl)tris(t-butyl isocyanide)cobalt(III) Hexafluorophosphate, (13).—An acetone solution of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)_3][\text{PF}_6]_2$ was prepared from $[\text{Co}(\text{C}_5\text{Me}_5)\text{I}_2(\text{CO})]$ (300 mg, 0.63 mmol) and $\text{Ag}[\text{PF}_6]$ (320 mg, 1.26 mmol) as previously described. Addition of Bu^tNC (2 g, 24 mmol), followed by concentration and addition of diethyl ether, precipitated an orange solid. Recrystallisation from acetone and ether yielded pale yellow crystals of $[\text{Co}(\text{C}_5\text{Me}_5)(\text{CNBu}^t)_3][\text{PF}_6]_2$ (415 mg, 90%).

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