Inorganic Grignard Analogues. Reaction of Cobalt Powder with Triorganodiiodophosphorus Compounds to form [PR_3I][$Co(PR_3)I_3$]. Crystal Structure of [PPh_3I][$Co(PPh_3)I_3$], and Isolation of the Novel Complexes [PPh_3I][$Co(PPh_3)IBr_2$] and [$SbPh_3I$][$Co(SbPh_3)I_3$]†

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The reactions of a large number of triorganodiiododophosphorus compounds, R_3PI_2 [R_3 = Et_3, $Pr^n{}_3$, $Bu^n{}_3$, $PhMe_2$, Ph_2Me, Ph_2Pr^n, Ph_3 (*o*-, *m*- or *p*-MeC_6H_4)Ph_2, or (*m*-MeC_6H_4)$_3$], with unactivated cobalt metal in dry diethyl ether have been studied. All reactions produce the novel ionic complexes [PR_3I][$Co(PR_3)I_3$] in quantitative yield, illustrated crystallographically for [PPh_3I][$Co(PPh_3)I_3$]. However, where R_3 = $PhMe_2$ both the ionic complex and the cobalt(III) complex [$Co(PPhMe_2)_2I_3$] are produced from the same reaction. The previously reported isolation of the 'frozen transition-state complex' [$Co(PBu^n{}_3)_3I_8$] from the reaction of $Bu^n{}_3PI_2$ with cobalt powder has been reinvestigated; when allowed to proceed to completion, the reaction produces the ionic complex described above. The compound Ph_3PIBr reacts with cobalt powder to produce the mixed-halide ionic complex [PR_3I][$Co(PR_3)IBr_2$]. All the complexes [PR_3I][$Co(PR_3)I_3$] have been studied using Raman and visible spectroscopy, the latter confirming the tetrahedral geometry of the cobalt anion. Very little reaction is observed with the corresponding dibromophosphorus compounds, R_3PBr_2, but in some cases visible spectroscopic studies on the trace of complex formed suggest a tetrahedral cobalt(II) species, perhaps similar to the iodo-complexes described above. Additionally, Ph_3SbI_2 reacts with cobalt metal in an analogous way to Ph_3PI_2 to produce the novel complex [$SbPh_3I$][$Co(SbPh_3)I_3$].

The chemistry of transition-metal complexes of tertiary phosphines is, perhaps, the widest and most actively studied area of inorganic chemistry. The usual method of synthesis is the reaction of a metal salt, *i.e.* an oxidised metal, with phosphine ligands.[1] Recently, our group has developed a novel synthetic route to existing and unusual phosphine complexes.[2-5] Rather than an oxidised metal, this approach starts with an oxidised ligand, *e.g.* a dihalogenotriorganophosphorus compound, R_3PX_2 (X = Br[6] or I[7,8]), although other oxidised Group 15 ligands, R_3AsX_2 and R_3SbX_2, can also be used, and crude metal powders [equation (1)]. This type of reaction may be seen to produce an inorganic Grignard complex [equations (2) and (3)]. Although reaction (2) frequently needs an additional reagent, *e.g.* MeI or I_2, to activate the magnesium, our method needs no such additional reagents. This is highly unusual and quite unexpected. The use of metallic reagents is rare, but not unknown, in inorganic chemistry, but all other workers have previously employed 'activated' metals. Thus, Timms[9] and Green[10] and their co-workers have produced metal complexes by employing metal vapours, whilst Hudnall and Rieke[11] used finely dispersed metals. Tuck and co-workers[12] have developed the electrolytic reaction of anodic or cathodic metals to produce Schiff-base and other complexes.

$$M + R_3PX_2 \longrightarrow M(PR_3)_yX_n + \text{, in some instances, other products} \quad (1)$$

$$\text{Grignard complex: } C\text{–}X + Mg \longrightarrow C\text{–}Mg\text{–}X \quad (2)$$

$$\text{Our complexes: } P\text{–}X + M \longrightarrow P\text{–}M\text{–}X \quad (3)$$

However, these latter techniques all involve experimental difficulties or limitations. High temperatures are necessary for vapour-phase reactions in order to render the reactants volatile, and subsequent co-condensation of the vapours requires very low temperatures. Moreover, whilst involatile ligands can be treated with dispersed metals in solution, the formation of these solutions can be laborious. Electrolytic syntheses are quite straightforward, but the range of applicable ligands is restricted.

Cobalt(II) phosphine complexes have been extensively studied, and their nature is well understood. By far the most familiar are the monomeric tetrahedral [$Co(PR_3)_2X_2$] species, readily synthesised by reaction of CoX_2 with 2 mol equivalents of PR_3 in a suitable solvent.[13] Recently, a more unusual 1:1 complex, $Co(PPh_3)I_2$, has been prepared using an excess of CoI_2 and shown to be a halide-bridged dimer by X-ray crystallographic methods.[14] In addition to the extensive carbonyl chemistry associated with cobalt complexes,[15] some cobalt(I) phosphine complexes have been reported, *e.g.* [$Co(PMe_3)_3Br$].

Cobalt(II) halides typically form 1:2 complexes with tertiary phosphines; however with PMe_3 the situation is more interesting and [$Co(PMe_3)_2X_2$], [$Co(PMe_3)_3X_2$] and [$Co(PMe_3)_4X$]$^+$ can be isolated, depending on reaction conditions.[16,17] The reaction of CoX_2 with PMe_3 under oxidising conditions never resulted in the formation of any cobalt(III)/phosphine complex.

In addition to the species mentioned above, tetrahedral cobalt(II) complexes containing the [$Co(PPh_3)X_3$]$^-$ (X = Br or I) anion have been isolated by Cotton and co-workers.[13] Although no X-ray crystallographic studies have been performed on complex cobalt(II) anions of this kind, they have been assigned tetrahedral geometry based on magnetic susceptibility,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and spectroscopic data for the complexes $[PR_3I][Co(PR_3)I_3]$

Compound	Colour	Analysis (%) C	H	I	ν(P–I)/cm⁻¹
$[P(C_6H_4Me\text{-}m)_3I][Co\{P(C_6H_4Me\text{-}m)_3\}I_3]$	Lime green	43.2 (42.9)	3.8 (3.6)	42.9 (43.2)	149
$[P(C_6H_4Me\text{-}p)Ph_2I][Co\{P(C_6H_4Me\text{-}p)Ph_2\}I_3]$	Green	39.6 (40.7)	3.3 (3.0)	46.2 (45.4)	169
$[P(C_6H_4Me\text{-}m)Ph_2I][Co\{P(C_6H_4Me\text{-}m)Ph_2\}I_3]$	Green	39.7 (40.7)	2.7 (3.0)	45.3 (45.4)	164
$[P(C_6H_4Me\text{-}o)Ph_2I][Co\{P(C_6H_4Me\text{-}o)Ph_2\}I_3]$	Green	42.2 (40.7)	2.8 (3.0)	45.4 (45.4)	172
$[PPh_3I][Co(PPh_3)I_3]$	Lime green	39.2 (39.6)	2.7 (2.7)	45.6 (46.5)	160
$[PPh_2Pr^nI][Co(PPh_2Pr^n)I_3]$	Mint green	35.4 (35.2)	3.2 (3.3)	49.4 (49.6)	182
$[PPh_2MeI][Co(PPh_2Me)I_3]$	Pale green	32.6 (32.3)	2.5 (2.7)	52.3 (52.5)	186
$[PPhMe_2I][Co(PPhMe_2)I_3]$	Pale green	22.9 (22.8)	2.9 (2.6)	60.5 (60.3)	208
$[PBu^n{}_3I][Co(PBu^n{}_3)I_3]$	Green	28.7 (29.7)	5.2 (5.6)	52.1 (52.3)	206
$[P(CH_2CH_2Ph)_3I][Co\{P(CH_2CH_2Ph)_3\}I_3]$	Blue-green	45.9 (46.9)	4.6 (4.4)	39.7 (41.4)	163
$[PPh_3I][Co(PPh_3)IBr_2]$	Green	43.6 (43.3)	2.9 (3.0)	26.0 (25.5)*	159
$[PPr^n{}_3I][Co(PPr^n{}_3)I_3]$	Green	24.2 (24.4)	4.6 (4.7)	56.8 (57.3)	209
$[PEt_3I][Co(PEt_3)I_3]$	Green	17.9 (18.0)	3.7 (3.8)	63.5 (63.3)	235

* Br 15.8 (16.0%).

Table 2 Electronic band positions for the complexes $[PR_3I][Co(PR_3)I_3]$ in diethyl ether

Complex	λ*/nm Band 1	Band 2	Band 3
$[P(C_6H_4Me\text{-}m)_3I][Co\{P(C_6H_4Me\text{-}m)_3\}I_3]$	724 (600)	690 (649)	647 (463)
$[P(C_6H_4Me\text{-}p)Ph_2I][Co\{P(C_6H_4Me\text{-}p)Ph_2\}I_3]$	712 (522)	669 (565)	640 (465)
$[P(C_6H_4Me\text{-}m)Ph_2I][Co\{P(C_6H_4Me\text{-}m)Ph_2\}I_3]$	717 (480)	678 (585)	640 (483)
$[P(C_6H_4Me\text{-}o)Ph_2I][Co\{P(C_6H_4Me\text{-}o)Ph_2\}I_3]$	715 (406)	671 (527)	640 (552)
$[PPh_3I][Co(PPh_3)I_3]$	718 (562)	696 (580)	620 (380)
$[PPh_2Pr^nI][Co(PPh_2Pr^n)I_3]$	720 (sh) (547)	699 (620)	645 (493)
$[PPh_2MeI][Co(PPh_2Me)I_3]$		698 (622)	644 (481)
$[PPhMe_2I][Co(PPhMe_2)I_3]$	716 (493)	668 (565)	617 (466)
$[P(CH_2CH_2Ph)_3I][Co\{P(CH_2CH_2Ph)_3\}I_3]$	715 (536)	673 (581)	620 (sh) (370)
$[PBu^n{}_3I][Co(PBu^n{}_3)I_3]$	718 (620)	676 (638)	640 (566)
$[PPr^n{}_3I][Co(PPr^n{}_3)I_3]$	718 (618)	666 (699)	639 (551)
$[PEt_3I][Co(PEt_3)I_3]$	716 (628)	667 (692)	618 (472)
$[PPh_3I][Co_2(PPh_3)IBr_2]$	713 (559)	679 (572)	620 (sh) (401)

* Absorption coefficients are shown in parentheses in dm³ mol⁻¹ cm⁻¹.

electronic spectroscopic and conductivity measurements.[13] Tetraalkylammonium species, $[NR_4]^+$, form the cations in these complexes and LaMar and co-workers[18] have studied ion–ion interactions therein.

Cobalt(III) complexes containing monodentate phosphine ligands are rare, and only one halide complex has been the subject of a crystallographic study.[19] A low-precision X-ray study of $[Co(PEt_3)_2Cl_3]$ by Beurskens and co-workers[19] showed it to be a molecular trigonal-bipyramidal complex with axial phosphine ligands. A detailed spectroscopic study of $[Co(PR_3)_2X_3]$ (R_3 = Me_3, Et_3, $PhMe_2$, $PhEt_2$ or Ph_2Et; X = Cl or Br) has been reported by Levason *et al.*[20] These complexes were synthesised by the oxidation of the respective cobalt(II) species with NOX. It is notable that these workers report that it was not possible to oxidise the cobalt(II) complex by the addition of an excess of dihalogen.

As stated above, we are currently engaged in a detailed study of the reaction of dihalogenotriorganophosphorus compounds, R_3PX_2 (X = Br or I), with unactivated coarse-grain transition-metal[2–5] and main-group[21] metal powders to produce metal phosphine complexes. Our results so far have shown that, as well as established complexes, novel isomers of known complexes[2] and complexes containing the metal atom in an unusually high oxidation state[2,4] are all available from this new synthetic route.

Recently we reported[4] the reaction of 2 mol equivalents of Me_3PI_2 and $Bu^n{}_3PI_2$ with cobalt metal powder to produce $[Co(PMe_3)_2I_3]$ and $[Co(PBu^n{}_3)_3I_8]$, respectively. The latter was isolated prior to reaction completion and may be considered as a 'frozen transition state' or 'snapshot' of the mechanism. The former complex, $[Co(PMe_3)_2I_3]$, was isolated quantitatively from the reaction of $2Me_3PI_2$ with cobalt powder, the other product diiodine being detected spectrophotometrically; this cobalt(III) complex was synthesised directly, without the use of any subsequent oxidising agent.

In view of these results we have extended our studies to include a wide range of diiodo- and dibromo-triorganophosphorus compounds and their reaction with cobalt metal powder. In particular, the reaction of 2 mol equivalents of $Bu^n{}_3PI_2$ with cobalt powder has been reinvestigated, and allowed to proceed to completion. We also report the reaction of the mixed-halogen compound Ph_3PIBr and the stibine Ph_3SbI_2 with cobalt powder.

Results and Discussion

Reaction [equation (4)] of coarse-grain unactivated reagent-grade cobalt metal powder with 2 mol equivalents of the R_3PI_2 compounds [R_3 = $(m\text{-}MeC_6H_4)_3$, (o-, m- or p-$MeC_6H_4)Ph_2$, Ph_3, $(PhCH_2CH_2)_3$, Ph_2Pr^n, $PhMe_2$, Ph_2Me, $Bu^n{}_3$, $Pr^n{}_3$ or Et_3] in diethyl ether yielded the complexes $[PR_3I][Co(PR_3)I_3]$ (Table 1). Reactions times vary, but were typically 15 d at room temperature (r.t.) or 5 d at 60 °C in sealed tubes, see Experimental section. Yields are quantitative; characterisation data are contained in Tables 1 and 2.

$$2R_3PI_2 + Co \xrightarrow[15\ \mathrm{d,\ r.t.;\ or\ 5\ d,\ 60\ ^\circ C}]{Et_2O} [PR_3I][Co(PR_3)I_3] \quad (4)$$

Single crystals of $[PPh_3I][Co(PPh_3)I_3]\cdot OEt_2$ suitable for X-ray work were grown from diethyl ether. The structure is shown in Fig. 1. This ionic material contains a tetrahedral cobalt(II) anion, the charge being balanced by the iodophosphonium cation, $[PPh_3I]^+$. Bond lengths and angles are in Table 3, fractional atomic coordinates for the non-hydrogen atoms in Table 4. No complex of this structure has previously been crystallographically characterised; indeed no complexes containing the $[Co(PPh_3)I_3]^-$ anion have been crystallographically characterised, despite the fact that its existence has been postulated for more than 30 years.[13] However, tetrahedral anions of $[CoLCl_3]^-$ (L = PPh_3, pyridine) have been crystallographically identified.[22,23]

The electronic transitions in the visible region of the $[PR_3I][Co(PR_3)I_3]$ complexes are listed in Table 2; all complexes display electronic spectra typical of cobalt(II) in a tetrahedral environment.[24] In each spectrum three close bands are observed, and the energy of these, together with their moderate absorption coefficients, are typical of d–d transitions in tetrahedral cobalt(II) complexes.[24] The present complexes are all subtly different shades of green; this is not to be unexpected, since variation of R in the $[Co(PR_3)I_3]^-$ moiety will have only a marginal effect on the overall ligand field at the cobalt(II) centre.

The low-frequency Raman spectra of the $[PR_3I][Co(PR_3)I_3]$ complexes, Table 1, all exhibit a dominant ν(P–I) band. We have previously reported[8] the ν(P–I) Raman bands for all the R_3PI_2 compounds employed in the present study, and therefore assignments for the $[PR_3I][Co(PR_3)I_3]$ complexes can be made with confidence. In fact, little or no shift in ν(P–I) is observed from R_3PI_2 to $[PR_3I][Co(PR_3)I_3]$.

Table 3 Selected bond lengths (Å) and angles (°) in $[PPh_3I][Co(PPh_3)I_3]\cdot OEt_2$

I(1)–Co	2.572(7)	P(1)–C(1)	1.77(3)
I(2)–Co	2.565(9)	I(4)–P(2)	2.38(1)
I(3)–Co	2.567(7)	P(2)–C(19)	1.83(4)
Co–P(1)	2.37(1)		
I(1)–Co–I(2)	106.5(2)	I(3)–Co–P(1)	113(1)
I(1)–Co–I(3)	114.3(3)	I(4)–P(2)–C(25)	109(1)
I(1)–Co–P(1)	109.5(3)	I(4)–P(2)–C(19)	107(1)
I(2)–Co–I(3)	113.9(3)	I(4)–P(2)–C(31)	111(1)
I(2)–Co–P(1)	107.7(4)		

Reaction of $PhMe_2PI_2$.—The reaction of 2 mol equivalents of $PhMe_2PI_2$ with cobalt metal powder has proven to be a special case. After 5 d at 60 °C a pale green solid and a black solution resulted. Isolation of the green solid by standard Schlenk techniques revealed it to be the familiar $[PPhMe_2I][Co(PPhMe_2)I_3]$, Table 1. The low-frequency Raman spectrum exhibited a ν(P–I) band at 208 cm^{-1}, very close to that of $PhMe_2PI_2$ at 204 cm^{-1}. Dissolution of this solid in diethyl ether subsequently yielded a visible spectrum much like those of the other $[PR_3I][Co(PR_3)I_3]$ complexes, Table 2.

Careful concentration of the black filtrate from this reaction under an inert atmosphere yielded black crystals of $[Co(PPhMe_2)_2I_3]$ [Found (Calc.): C, 26.7 (26.8); H, 3.2 (3.1); I, 52.9 (53.2%)]. We have previously reported[4] the reaction (5).

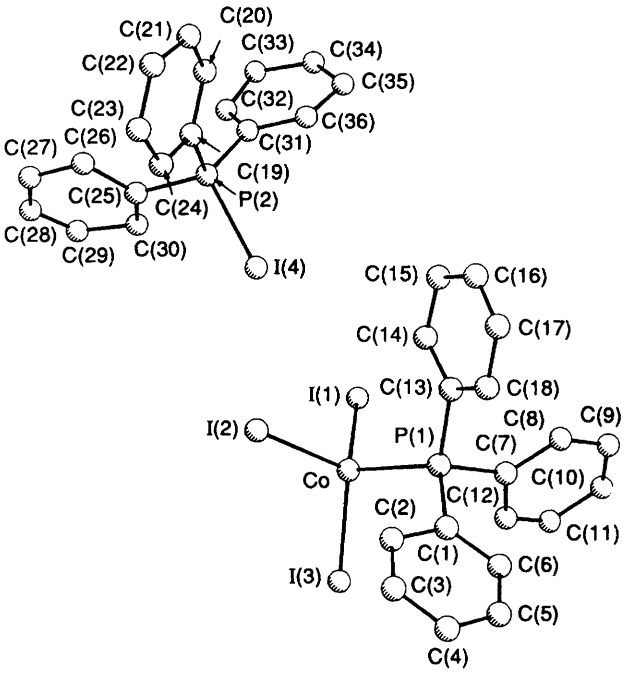

Fig. 1 The crystal structure of $[PPh_3I][Co(PPh_3)I_3]\cdot OEt_2$. Hydrogen atoms and diethyl ether of crystallisation are omitted for clarity

Table 4 Fractional atomic coordinates for the non-hydrogen atoms in $[PPh_3I][Co(PPh_3)I_3]\cdot OEt_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I(1)	0.3438(3)	0.3631(2)	0.4210(3)	P(2)	0.805(1)	0.4259(6)	0.147(1)
I(2)	0.6306(3)	0.2617(2)	0.5487(3)	C(19)	0.902(4)	0.367(2)	0.081(4)
I(3)	0.3307(3)	0.2720(2)	0.7717(3)	C(20)	0.915(4)	0.363(2)	−0.051(4)
Co	0.3956(6)	0.2654(3)	0.5428(5)	C(21)	0.996(5)	0.320(3)	−0.101(4)
P(1)	0.282(1)	0.1610(5)	0.418(1)	C(22)	1.071(5)	0.285(2)	−0.018(5)
C(1)	0.288(3)	0.092(2)	0.505(3)	C(23)	1.055(4)	0.288(2)	0.111(4)
C(2)	0.409(4)	0.084(2)	0.570(3)	C(24)	0.968(5)	0.325(3)	0.160(5)
C(3)	0.423(4)	0.027(2)	0.635(4)	C(25)	0.909(4)	0.491(2)	0.266(4)
C(4)	0.328(5)	−0.021(2)	0.643(4)	C(26)	1.041(5)	0.495(2)	0.261(4)
C(5)	0.213(4)	−0.007(2)	0.582(4)	C(27)	1.116(4)	0.552(2)	0.349(4)
C(6)	0.191(4)	0.045(2)	0.515(4)	C(28)	1.070(5)	0.601(2)	0.425(4)
C(7)	0.119(4)	0.163(2)	0.370(3)	C(29)	0.956(5)	0.599(2)	0.424(4)
C(8)	0.044(5)	0.135(2)	0.247(4)	C(30)	0.860(4)	0.544(3)	0.340(4)
C(9)	−0.087(5)	0.143(2)	0.213(5)	C(31)	0.720(4)	0.460(2)	0.020(4)
C(10)	−0.136(4)	0.171(2)	0.305(5)	C(32)	0.741(4)	0.526(2)	0.004(4)
C(11)	−0.064(5)	0.201(2)	0.431(4)	C(33)	0.682(5)	0.551(3)	−0.103(5)
C(12)	0.052(4)	0.195(2)	0.466(4)	C(34)	0.587(5)	0.501(3)	−0.198(4)
C(13)	0.334(4)	0.132(2)	0.256(3)	C(35)	0.555(5)	0.437(3)	−0.182(5)
C(14)	0.383(4)	0.182(2)	0.196(4)	C(36)	0.625(4)	0.415(2)	−0.073(4)
C(15)	0.415(4)	0.160(2)	0.070(4)	O	0.878(4)	0.121(2)	0.862(4)
C(16)	0.399(4)	0.089(3)	0.024(4)	C(37)	0.779(6)	0.146(3)	0.795(5)
C(17)	0.359(5)	0.044(3)	0.087(5)	C(38)	0.695(5)	0.167(3)	0.889(6)
C(18)	0.319(4)	0.065(3)	0.208(4)	C(39)	0.978(8)	0.100(4)	0.793(6)
I(4)	0.6664(3)	0.3687(2)	0.2656(3)	C(40)	1.079(7)	0.072(4)	0.863(8)

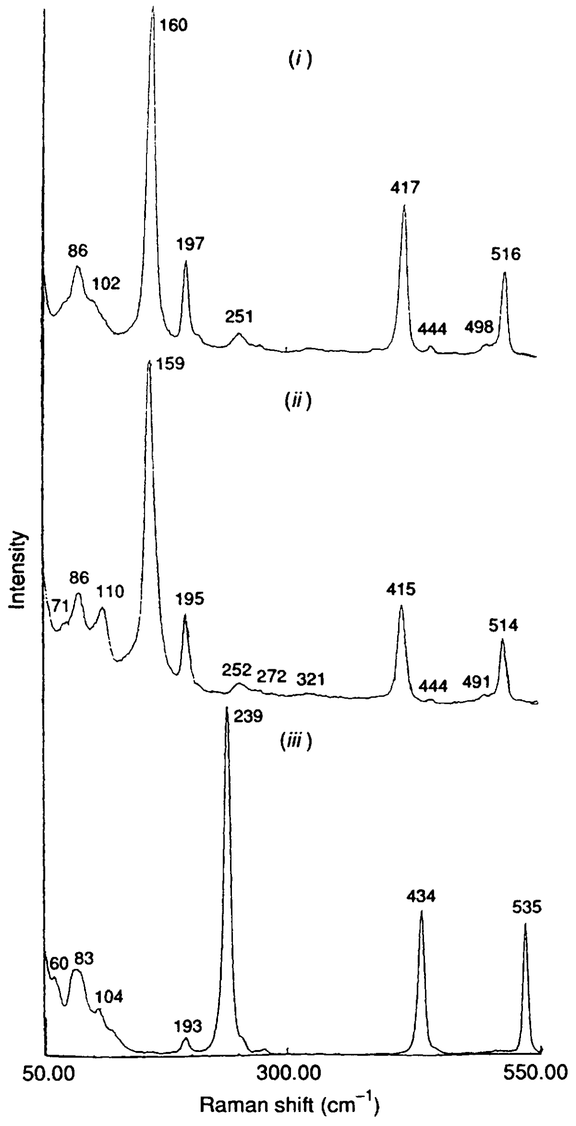

Fig. 2 Comparison of the low-frequency Raman spectra of (*i*) Ph_3PI_2, (*ii*) $[PPh_3I][Co(PPh_3)I_3]$ and (*iii*) Ph_3PBr_2

$$2Me_3PI_2 + Co \xrightarrow[Et_2O]{60\,°C,\ 4\ d} [Co(PMe_3)_2I_3] + \tfrac{1}{2}I_2 \qquad (5)$$

However, in that reaction the cobalt(III) species is produced quantitatively, and no evidence for the ionic cobalt(II) species was observed. In the reaction of the diiodophosphoranes with cobalt metal described here the ionic $[PR_3I][Co(PR_3)I_3]$ is quantitatively produced in every case except where $R_3 = PhMe_2$. It therefore appears that in this case an equilibrium exists, from which both the cobalt(III) complex, $[Co(PPhMe_2)_2I_3]$, and the cobalt(II) species, $[PPhMe_2I][Co(PPhMe_2)I_3]$, may be isolated. We can, therefore, postulate an overall reaction (6). Like equation (5), this reaction scheme necessitates the

$$4PhMe_2PI_2 + 2Co \longrightarrow [PPhMe_2I][Co(PPhMe_2)I_3] + [Co(PPhMe_2)_2I_3] + \tfrac{1}{2}I_2 \qquad (6)$$

production of 0.5 mol equivalent of molecular iodine; this, however, was not quantitatively detected. The intensely black solution produced by dissolution of the black crystals of $[Co(PPhMe_2)_2I_3]$ in diethyl ether was not stable and quantitative estimation of I_2 by measurement of the absorption coefficient of the diiodine band at *ca.* 466 nm was not possible. Nonetheless, bands due to $[Co(PPhMe_2)_2I_3]$ were observed at 350, 472 and 613 nm, quite similar to those observed for the cobalt(III) complex $[Co(PMe_3)_2I_3]$.[4] We have previously reported the crystal structure of $[Co(PMe_3)_2I_3]$[4] and since the electronic spectrum of this complex is so similar to that of $[Co(PPhMe_2)_2I_3]$ we can assign a *trans*-trigonal-bipyramidal configuration to the latter.

We have also investigated the reaction of 2 equivalents of the mixed-halogen compound Ph_3PIBr with cobalt powder; after 5 d at 60 °C a pale green solid is produced of empirical formula $Co(PPh_3)_2I_2Br_2$, **1**. The low-frequency Raman spectrum displays an intense band at 159 cm^{-1} which, by comparison with the spectra of Ph_3PI_2 and $[PPh_3I][Co(PPh_3)I_3]$, can be confidently assigned to ν(P–I), and no evidence for a band at 239 cm^{-1}, the ν(P–Br) of Ph_3PBr_2,[25] was observed. The low-frequency Raman spectra of **1**, Ph_3PI_2 and Ph_3PBr_2 are illustrated in Fig. 2, from which it can be seen that the cationic fragment of **1** must be the iodophosphonium ion, PPh_3I^+. Further, we can deduce that the anion is $[Co(PPh_3)IBr_2]^-$, a rare example of a tetrahedral mixed-halide cobaltate(II) ion; the visible spectrum of this $[PPh_3I][Co(PPh_3)IBr_2]$ complex exhibits bands at 620 (sh), 679 (ε_{max} = 572 dm^3 mol^{-1} cm^{-1}) and 713 nm, similar to those of the complexes described earlier, Table 2.*

Reaction of Diiodotriphenylantimony.—Reaction of 2 mol equivalents of pale yellow Ph_3SbI_2 with cobalt powder in diethyl ether at 60 °C for 5 d yielded a green complex **2**, in quantitative yield, the empirical formula of which corresponds to $Co(SbPh_3)_2I_4$ [Found (Calc.): C, 33.9 (34.2); H, 2.4 (2.7); Co, 4.6 (4.9); I, 39.9 (40.4); Sb, 19.2 (18.6%)]. The X-ray powder diffraction patterns of **2** and Ph_3SbI_2 were distinctly different, thus ruling out the possibility that **2** is merely a statistical mixture of Ph_3SbI_2 and cobalt metal. Moreover, when the low-frequency Raman spectra are compared, Fig. 3, the shoulder at 118 cm^{-1} for **2** can be assigned to ν(Sb–I), and the further shoulder at 164 cm^{-1}, by comparison with the phosphorus-containing compounds, is assigned to ν(Co–I).

The peak at 221 cm^{-1}, absent in the spectrum of Ph_3SbI_2, is tentatively assigned to ν(Co–Sb). Clearly, **2** is a stibine analogue to the majority of the phosphine complexes reported here, *i.e.* $[SbPh_3I][Co(SbPh_3)I_3]$, and, since the donor power of Ph_3Sb towards cobalt(II) must be normally seen as almost negligible, represents yet another example of unusual compounds to be synthesised by our new strategy. A final piece of evidence that **2** may be formulated as above comes from its electronic spectrum which exhibits a broad absorption at 674 nm (ε_{max} = 391 dm^3 mol^{-1} cm^{-1}), which is quite similar to those recorded for the analogous phosphine complexes, Table 2.

Dibromotriorganophosphorus Compounds.—In vivid contrast to the reaction of Ph_3PI_2, Ph_3PIBr and Ph_3SbI_2 with cobalt metal powder, the reaction of Ph_3PBr_2 is not straightforward and does not proceed to completion. After *ca.* 3 months of refluxing 2 mol equivalents of Ph_3PBr_2 with cobalt powder in diethyl ether a very pale blue colour had developed in the solvent. A white solid and unreacted cobalt metal were also present in the reaction vessel. The white solid was subsequently shown to be

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* A referee queried the stability of $[Co(PPh_3)IBr_2]^-$ towards dissociation in diethyl ether solution. If it disproportionated in solution the products would be $[Co(PPh_3)I_3]^-$ and $[Co(PPh_3)Br_3]^-$, *viz.* $3[Co(PPh_3)IBr_2]^- \longrightarrow [Co(PPh_3)I_3]^- + 2[Co(PPh_3)Br_3]^-$. This would lead to the presence of a more complicated visible spectrum with bands due to $[Co(PPh_3)I_3]^-$ and $[Co(PPh_3)Br_3]^-$ in a 1:2 ratio. However, the spectrum of $[Co(PPh_3)IBr_2]^-$ is much the same as those of the other $[Co(PR_3)I_3]^-$ complexes, *i.e.* indicative of a single cobalt-containing moiety, but is sufficiently different from that recorded for $[Co(PPh_3)I_3]^-$, Table 2. The spectra of $[Co(PPh_3)IBr_2]^-$ and $[Co(PPh_3)I_3]^-$ are similar, however, as expected.

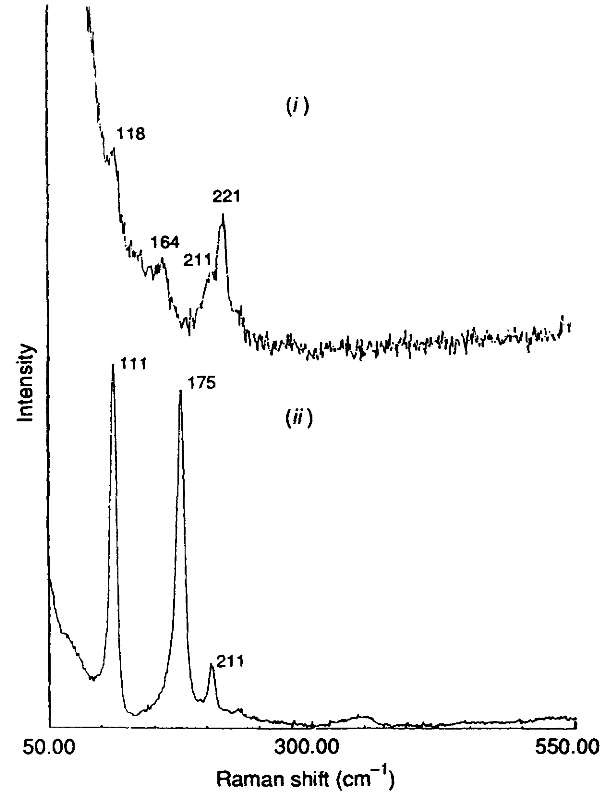

Fig. 3 Comparison of the low-frequency Raman spectra of (*i*) $[SbPh_3I][Co(SbPh_3)I_3]$ and (*ii*) Ph_3SbI_2

Ph_3PBr_2 by elemental analyses and Raman spectroscopy. The blue filtrate exhibited visible spectral bands at 644, 672 and 704 nm, suggesting the formation of a tetrahedral cobalt(II) species, but we nonetheless must conclude that Ph_3PBr_2 gives only a very slight reaction with cobalt powder under these conditions.

We must draw attention to this failure of reaction of cobalt with these dibromo-derivatives, and contrast it with the ready reaction of a range of such species, R_3PBr_2 (R_3 = Ph_3, $PhMe_2$, $Bu^n{}_3$ or $Pr^n{}_3$), with manganese powder to form $[Mn(PR_3)X_2]$,[5] and with nickel powder.[25] With the latter a spectrum of reactivity has been observed, *e.g.* Ph_3PBr_2 and $Ph_2Pr^nPBr_2$ form $[PR_3Br][Ni(PR_3)Br_3]$, and $PhMe_2PBr_2$ gives a mixture of $[PPhMe_2Br][Ni(PPhMe_2)Br_3]$ and planar $[Ni(PPhMe_2)_2Br_2]$.[25] On the other hand, nickel powder shows no reaction with Me_3PBr_2, Et_3PBr_2 and $Pr^n{}_3PBr_2$. This wide range of reactivity further illustrates the subtlety of this novel synthetic method, as was seen earlier.[2–5]

Oxidation Products.—In order to investigate the air oxidation of the complexes $[PR_3I][Co(PR_3)I_3]$, samples of $[PR_3I][Co(PR_3)I_3]$ (R = Et or *m*-MeC_6H_4) were dissolved in diethyl ether and exposed to the atmosphere. After *ca.* 4 d blue crystals appeared in the flasks. Samples of these were isolated and in both cases the crystals exhibited a strong infrared ν(P=O) at *ca.* 1130 and 1155 cm^{-1}, respectively. Elemental analysis of the blue crystals identified them as $[Co(OPEt_3)_2I_2]$ and $[Co\{OP(C_6H_4Me\text{-}m)_3\}_2I_2]$ respectively [Found (Calc.): C, 24.9 (24.8); H, 5.1 (5.2); I, 43.9 (43.7); C, 52.7 (52.9); H, 4.1 (4.4); I, 26.4 (26.7%)].

Conclusion

Synthesis of the previously unknown ionic cobalt(II) complexes $[PR_3I][Co(PR_3)I_3]$ from the direct reaction of 2 equivalents of R_3PI_2 with unactivated cobalt metal powder has been established, and the yields are quantitative. No reaction scheme for the synthesis of these complexes from CoI_2 and tertiary phosphine has been reported and their synthesis from conventional methods may well be difficult.

The reaction of 2 equivalents of $PhMe_2PI_2$ with cobalt metal produces both the ionic complex $[PPhMe_2I][Co(PPhMe_2)I_3]$ and the cobalt(III) complex $[Co(PPhMe_2)_2I_3]$. We have previously reported the reaction of Me_3PI_2 with cobalt powder to produce only $[Co(PMe_3)_2I_3]$ and, therefore, where R_3 = $PhMe_2$ an equilibrium is set up and both the cobalt-(II) and -(III) complexes may be isolated from the same reaction mixture.

The reaction of the analogous R_3PBr_2 with cobalt metal powder either does not proceed at all or results in the detection of a trace quantity of a cobalt(II) complex, possibly analogous to the corresponding iodo-complexes described earlier. The failure of this reaction is noteworthy since dibromophosphoranes react readily with other metals (*e.g.*. iron, manganese and nickel) to produce a metal complex in quantitative yield.

The reaction of 2 equivalents of Ph_3SbI_2 with cobalt powder produces the complex $[SbPh_3I][Co(SbPh_3)I_3]$. No complex of this type has been reported before and this result suggests that, as well as the now established reaction of dihalogenotriorganophosphorus compounds with metal powders, Group 15 analogues of stoichiometry R_3EI_2 (E = As, Sb or Bi) may also react with metal powder to produce novel metal complexes.

The mixed-halogeno ligand Ph_3PIBr reacts with cobalt powder to form $[PPh_3I][Co(PPh_3)IBr_2]$.

Finally it is interesting that, despite the ubiquity of the cobalt(II) phosphine complexes $[Co(PR_3)_2X_2]$ in the literature and their ready formation from the reaction of CoX_2 and tertiary phosphine, no evidence for their formation from the reaction of R_3PI_2 with cobalt powder was noted in this study. This suggests that the latter reaction proceeds in a different way compared to the reaction of metal salts with tertiary phosphines and is further evidence that the reaction of metal powders with R_3PX_2 represents a completely new synthetic route to both familiar and novel metal tertiary phosphine complexes.

Experimental

All the cobalt complexes described are moisture sensitive therefore strictly anaerobic and anhydrous conditions were adhered to during their synthesis. The synthesis of the phosphoranes R_3PI_2 has been described elsewhere[8] and the bromophosphoranes, R_3PBr_2, are prepared in an analogous manner.[26] Diethyl ether was obtained from BDH, dried over sodium wire for *ca.* 1 d and then distilled over CaH_2 in an inert atmosphere prior to use; it was distilled directly into the reaction vessel and degassed with nitrogen sparge. Standard reagent-grade coarse-grain cobalt metal powder obtained from Aldrich was used as received. After isolation, any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box.

The same reaction technique was employed in the synthesis of all the complexes described in order to establish a reactivity pattern. The synthesis of $[PPh_3I][Co(PPh_3)I_3]$ is typical. Diiodotriphenylphosphorane (1.611 g, 3.12 mmol) was dissolved in diethyl ether (*ca.* 100 cm^3) and subsequently cobalt powder (0.092 g, 1.56 mmol) was added. After *ca.* 5 d the resultant bright green solid formed was isolated by standard Schlenk techniques and dried *in vacuo*. It was then transferred to pre-dried argon-filled ampoules which were subsequently flame sealed.

Elemental analyses (Table 1) were performed by the analytical laboratory of this department. Electronic spectra were recorded on a Varian Cary 610, Cecil 6000 or Shimadzu UV-2101PC spectrophotometer. Raman spectra were recorded by the University of Manchester Raman service using a Coherent Innova 90 5W argon-ion laser and a SPEX 1403 double monochromator (focal length 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research Inc. TE 177

Table 5 Crystal data and details of refinement for $[PPh_3I][Co(PPh_3)I_3]\cdot OEt_2$

M	1165.25
Crystal system	Triclinic
Space group	$P1$ (no. 2)
a/Å	10.908(7)
b/Å	20.186(10)
c/Å	10.340(6)
α/°	98.63(3)
β/°	99.15(3)
γ/°	97.78(3)
U/Å^3	2192
Z	2
D_c/g cm^{-3}	1.765
$F(000)$	1114
μ/cm^{-1}	32.77
Total data measured	6614
Maximum 2θ/°	50
No. of unique reflections	6147
No. of observed reflections $[I_o > 3\sigma(I_o)]$	1708
No. of parameters	254
ρ_{min}, ρ_{max}/e Å^{-3}	−0.81, 2.01
Maximum least-squares shift-to-error ratio	0.04
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.03
Final R	0.079
Final R'	0.086

RF-005 cooler housing. The data were processed on a SPEX DM1B data station.

X-Ray Crystallography Study.—A triangular crystal (0.35 × 0.35 × 0.15 mm) was mounted in a Lindeman tube under dry-box conditions (argon). All measurements were performed on a Rigaku AFC6S diffractometer using graphite-monochromated Mo-Kα radiation. Crystal data and refinement details are presented in Table 5.

Lorentz, polarisation, decomposition (55%), and absorption (azimuthal scans; minimum, maximum transmission 0.50, 1.35) corrections were applied.

The structure was solved by direct methods.[27] Iodine, cobalt and phosphorus atoms and the diethyl ether solvent molecule were refined anisotropically and the remaining non-hydrogen atoms isotropically. Hydrogen atoms were constrained to chemically reasonable positions. The presence of diethyl ether solvate led to substantial decomposition and consequently a reduced number of structure factors and slightly elevated R factors. Neutral atom scattering factors were taken from ref. 28(*a*). Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were taken from ref. 28(*b*). All calculations were performed using the TEXSAN crystallographic software package.[29]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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