Invited Review

Organometallic Complexes Containing Bonds Between Transition Metals and Group IIIB Metals

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Contents

Abbreviations

M	metal	THF	tetrahydrofuran
L	ligand	DMF	dimethylform-amide
X	halogen	py	pyridine
Q	organometallic group	bipy	2,2'-bipyridyl
R	organic group	phen	1,10-phenanthroline
Me	methyl	5,6-Me$_2$-phen	5,6-dimethyl-1,10-phenanthroline
Et	ethyl	acac⁻	2,4-pentandionate
Pr	propyl	oxine⁻	anion of 8-hydroxyquinoline
Bu	butyl	diglyme	diethylene glycol dimethyl ether
Ph	phenyl	siphos	tris(trimethylsilyl-methyl)phosphine
OAc	acetate	dmgH$_2$	dimethylglyoxime

1. Introduction

During the past decade or two, there has been considerable interest in metal–metal bonded organometallic complexes. Among those containing bonds between transition metals and metals of Group IIB–IVB, complexes involving metals of Group IIIB have received the least attention in contrast to the ubiquity of those with metals of Group IIB[1,2] or IVB.[3–8]

This review is concerned with the recent advances in the study of transition metal–Group IIIB metal bonded complexes and the literature is covered up to June 1974. A general survey reveals that in these complexes, particularly those of the lighter elements, the interplay between the Lewis acidity of the Group IIIB metals and the nucleophilicity of the transition metal carbonyl anions is much manifested and is deemed to be more important an influencing factor for complexes containing Group IIIB metals than for those of Group IIB or IVB. Despite this incongruity, an attempt has been made to draw meaningful comparisons whenever possible. There is ample evidence that isoelectronic pairs of Group IIB and IIIB, or Group IIIB and IVB complexes of the similar kind bear significant resemblance in properties and are probably isostructural.
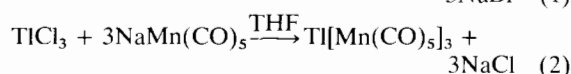
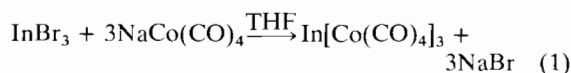Transition metal–boron complexes are not included in this review for the fact that boron is generally regarded as a non-metal or a metalloid rather than a metal and most of its compounds display somewhat different chemical properties from those of its heavier congeners, *e.g.* catenation in boron compounds, and that species containing transition metal–boron bonds have been adequately treated in a recent review.[9]

2. General Synthetic Methods

Several well established methods have been employed in the preparation of complexes containing transition metals bonded to Group IIIB metals. Important syntheses of new complexes by chemical transformation of compounds with incipient transition metal-Group IIIB metal bonds are also included in this section.
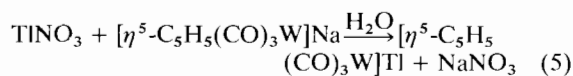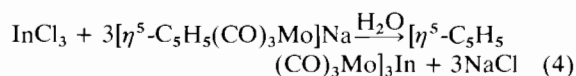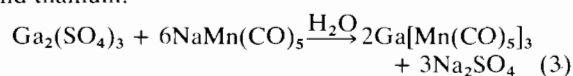
A. Metathetical Reactions

Most of the complexes described herein have been made by treating the corresponding metal halides or other salts with transition metal carbonyl anions as typified by the following reactions:[10, 11]

$$InBr_3 + 3NaCo(CO)_4 \xrightarrow{THF} In[Co(CO)_4]_3 + 3NaBr \quad (1)$$

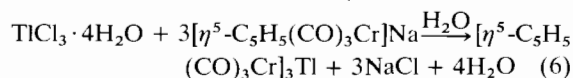$$TlCl_3 + 3NaMn(CO)_5 \xrightarrow{THF} Tl[Mn(CO)_5]_3 + 3NaCl \quad (2)$$

These reactions are usually carried out in ethereal solvents especially tetrahydrofuran, but the yield of the product very often depends upon the ease and effectiveness in separating the complex from the alkali metal halide. It is therefore essential to remove the last traces of the ethereal solvent prior to extraction with another solvent.

An alternative to this procedure is to perform the reaction in aqueous solution provided that neither the reactants nor the products are decomposed by water. Since the only other product (the inorganic salt) is retained in solution, the ready isolation of a relatively pure product accrues to the advantage of this method, which has been successfully utilized in the preparation of some transition metal complexes of gallium, indium and thallium:[12–15]

$$Ga_2(SO_4)_3 + 6NaMn(CO)_5 \xrightarrow{H_2O} 2Ga[Mn(CO)_5]_3 + 3Na_2SO_4 \quad (3)$$

$$InCl_3 + 3[\eta^5\text{-}C_5H_5(CO)_3Mo]Na \xrightarrow{H_2O} [\eta^5\text{-}C_5H_5(CO)_3Mo]_3In + 3NaCl \quad (4)$$

$$TlNO_3 + [\eta^5\text{-}C_5H_5(CO)_3W]Na \xrightarrow{H_2O} [\eta^5\text{-}C_5H_5(CO)_3W]Tl + NaNO_3 \quad (5)$$
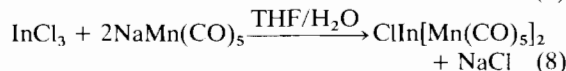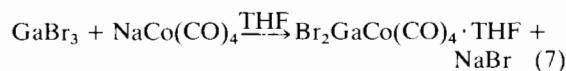
If the Group IIIB metal halide or other salt used is only slightly or slowly hydrolysed in aqueous solution, the metathetical reaction can still be carried out in water by adding an aqueous solution of the metal carbonyl anion to the solid metal salt. For example,[14]

$$TlCl_3 \cdot 4H_2O + 3[\eta^5\text{-}C_5H_5(CO)_3Cr]Na \xrightarrow{H_2O} [\eta^5\text{-}C_5H_5(CO)_3Cr]_3Tl + 3NaCl + 4H_2O \quad (6)$$

However, this procedure could not be applied to transition metal–aluminium complexes which are rapidly decomposed by water affording the corresponding transition metal hydrides in high yields.[16]

Complexes containing one or two transition metal–Group IIIB metal bonds may be obtained by reacting in appropriate molar ratios:[10, 17]
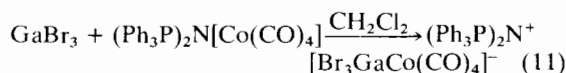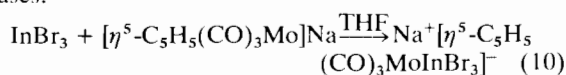
$$GaBr_3 + NaCo(CO)_4 \xrightarrow{THF} Br_2GaCo(CO)_4 \cdot THF + NaBr \quad (7)$$

$$InCl_3 + 2NaMn(CO)_5 \xrightarrow{THF/H_2O} ClIn[Mn(CO)_5]_2 + NaCl \quad (8)$$

With the notable exception of $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2$ TlCl,[18, 19] this procedure appears to find little application in the synthesis of unsymmetrically substituted thallium(III) complexes since equilibria such as

$$3Q_2TlX \rightleftharpoons 2Q_3Tl + TlX_3 \quad (9)$$
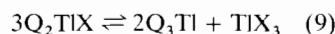
where Q is a transition metal group, lie far to the right for most systems. It is remarkable that the reactions of Ph$_2$TlCl and PhTlCl$_2$ with NaMn(CO)$_5$ *(vide infra)* have been reported to yield, *inter alia*, some unsymmetrically substituted complexes which are stable under the reaction conditions.[20]

Inasmuch as Group IIIB metal halides are potential Lewis acids, a fairly strong interaction is expected to occur between the metal halide and the metal carbonyl anion. Indeed, stable adducts can be isolated in some cases:[13, 21]

$$InBr_3 + [\eta^5\text{-}C_5H_5(CO)_3Mo]Na \xrightarrow{THF} Na^+[\eta^5\text{-}C_5H_5(CO)_3MoInBr_3]^- \quad (10)$$

$$GaBr_3 + (Ph_3P)_2N[Co(CO)_4] \xrightarrow{CH_2Cl_2} (Ph_3P)_2N^+[Br_3GaCo(CO)_4]^- \quad (11)$$

It is now apparent that the type of products obtainable from such reactions may be anticipated from a consideration of the nucleophilicity of the attacking as well as the leaving group(s) on the one hand, and the Lewis acidity of the Group IIIB metal in question on the other hand. Consistent with this contention is the non-isolation of Ga[Co(CO)$_4$]$_3$ from the reaction of gallium(III) bromide with an excess of [Co(CO)$_4$]$^-$ ion which is a weak nucleophile; the only isolable product is the disubstituted complex BrGa[Co(CO)$_4$]$_2 \cdot$ THF.[10]

B. Insertion Reactions

The insertion of halides of low-valent gallium and indium into the metal–metal or metal–halogen bonds of transition metal organometallic complexes provides a useful synthetic route to complexes containing one or two transition metal–Group IIIB metal bonds.[22–24] These reactions occur under a variety of conditions depending on the nature of the transition metal substrate. Thus gallium(I) tetrabromogallate(III) readily reacts with Co$_2$(CO)$_8$ in tetrahydrofuran at room temperature to give Br$_2$GaCo(CO)$_4 \cdot$ THF,[10] while with Mn$_2$(CO)$_{10}$, heating is required to effect the insertion to produce

$Br_2GaMn(CO)_5$.[23] The nature of the solvent in these insertion reactions could be a critical factor as in the reaction of indium(I) bromide with $Co_2(CO)_8$ giving $BrIn[Co(CO)_4]_2$ in tetrahydrofuran and $Br_3In_3Co_4(CO)_{15}$ in benzene.[10,24–26]

By contrast, the insertion of indium(I) halides into the metal–halogen bonds of inorganic or organometallic complexes takes place more readily under rather mild conditions to afford transition metal–indium bonded complexes such as *trans*-$Rh(InCl_2)CO(PPh_3)_2$ and η^5-$C_5H_5(CO)_3MoInCl_2$.[13,22]

The reaction of a transition metal derivative of thallium(I) with an appropriate dimeric transition metal carbonyl complex is essentially analogous, thus providing a convenient if not the only route to mixed thallium (III) complexes:[14]

$$[\eta^5\text{-}C_5H_5(CO)_3W]Tl + Co_2(CO)_8 \xrightarrow{THF} [\eta^5\text{-}C_5H_5 \atop (CO)_3W]Tl[Co(CO)_4]_2 \quad (12)$$
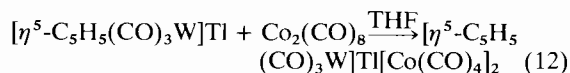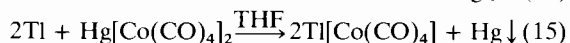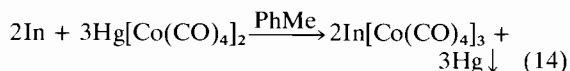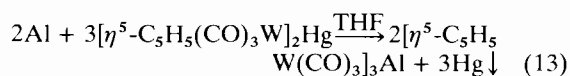
C. Exchange Reactions

Two types of exchange reactions involving metal–metal bonded species can be recognized.

(i) Metal exchange (or transmetallation) reactions

The metal exchange reactions constitute the basis of one of the most facile syntheses of transition metal–Group IIIB metal bonded complexes. The majority of such reactions involves the interaction of a Group IIIB metal with transition metal derivatives of a Group IIB metal:[14,16,27]
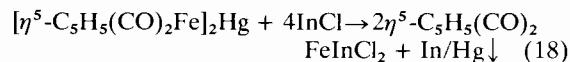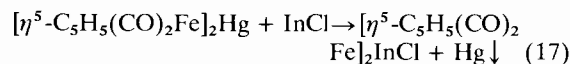
$$2Al + 3[\eta^5\text{-}C_5H_5(CO)_3W]_2Hg \xrightarrow{THF} 2[\eta^5\text{-}C_5H_5 \atop W(CO)_3]_3Al + 3Hg\downarrow \quad (13)$$

$$2In + 3Hg[Co(CO)_4]_2 \xrightarrow{PhMe} 2In[Co(CO)_4]_3 + 3Hg\downarrow \quad (14)$$

$$2Tl + Hg[Co(CO)_4]_2 \xrightarrow{THF} 2Tl[Co(CO)_4] + Hg\downarrow \quad (15)$$

or with transition metal complexes of another Group IIIB metal:[11]

$$In + Tl[Mn(CO)_5]_3 \xrightarrow{THF} In[Mn(CO)_5]_3 + Tl\downarrow \quad (16)$$
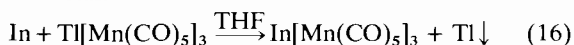
The course of such reactions which usually proceed to completion, can be readily monitored by infrared spectroscopy. However, there is evidence that some of these reactions may be reversed and the position of the equilibrium largely depends upon the nature of the solvent used. Thus, treatment of $Tl[Co(CO)_4]$ with an excess of metallic mercury in toluene [the reverse of equation (15)] gives an equilibrium mixture containing $Hg[Co(CO)_4]_2$ and some unreacted $Tl[Co(CO)_4]$.[14]

Indium(I) halides react with transition metal derivatives of Group IIB metals to afford complexes of the type Q_2InX and $QInX_2$ (Q = transition metal group; X = halogen) depending on the stoichiometry of the reactants and the reaction conditions. In general, the

formation of the disubstituted complexes Q_2InX is favoured by higher reaction temperature and by a deficiency of the low-valent metal halide.[13,22]

$$[\eta^5\text{-}C_5H_5(CO)_2Fe]_2Hg + InCl \rightarrow [\eta^5\text{-}C_5H_5(CO)_2 \atop Fe]_2InCl + Hg\downarrow \quad (17)$$

$$[\eta^5\text{-}C_5H_5(CO)_2Fe]_2Hg + 4InCl \rightarrow 2\eta^5\text{-}C_5H_5(CO)_2 \atop FeInCl_2 + In/Hg\downarrow \quad (18)$$

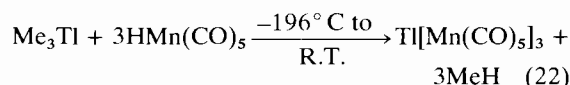### (ii) Group exchange (or redistribution) reactions
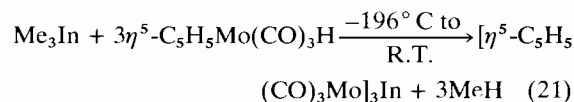
Group IIIB metal complexes containing one or two transition metal groups, Q, may be obtained by the following redistribution reactions:
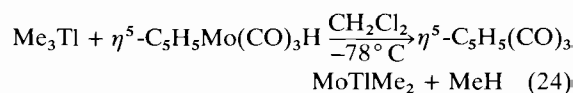
$$2Q_3M + MX_3 \rightleftharpoons 3Q_2MX \quad (19)$$

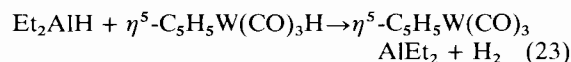$$Q_3M + 2MX_3 \rightleftharpoons 3QMX_2 \quad (20)$$
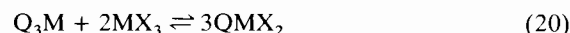
whilst a 1:1 reaction often yields a mixture consisting of an essentially equivalent amount of Q_2MX and QMX_2. Although synthetic uses of these reactions have not been fully investigated, existing evidence seems to suggest that the equilibria lie far to the right for the lighter Group IIIB metals. Thus, whereas the indium complexes $XIn[Mn(CO)_5]_2$ and $X_2InMn(CO)_5$ (X = Cl and Br) have been prepared by these reactions,[17] the corresponding thallium(III) complexes could not be isolated under similar conditions.[11]

D. Reactions of Metal Alkyls with Metal Carbonyl Hydrides

Most monomeric metal carbonyl hydrides are sufficiently acidic to react with main-group alkyls or hydrides to furnish metal–metal bonded complexes. Several transition metal derivatives of Group IIIB metals have been synthesized by this method:[13,28]

$$Me_3In + 3\eta^5\text{-}C_5H_5Mo(CO)_3H \xrightarrow[R.T.]{-196°\,C\ to} [\eta^5\text{-}C_5H_5 \atop (CO)_3Mo]_3In + 3MeH \quad (21)$$

$$Me_3Tl + 3HMn(CO)_5 \xrightarrow[R.T.]{-196°\,C\ to} Tl[Mn(CO)_5]_3 + 3MeH \quad (22)$$

Although in these reactions the mono- or di-alkyl derivatives could not be isolated even with a deficiency of the metal carbonyl hydrides,[13,28] the O-bonded aluminium complexes η^5-$C_5H_5ML(CO)_2AlR_2$ (M = Mo or W; R = Me or Et; L = CO or phosphines)[29–31] and the unique Mo–Tl bonded complex η^5-$C_5H_5(CO)_3$ $MoTlMe_2$[32] have been obtained from analogous reactions, *e.g.*

$$Et_2AlH + \eta^5\text{-}C_5H_5W(CO)_3H \rightarrow \eta^5\text{-}C_5H_5W(CO)_3 \atop AlEt_2 + H_2 \quad (23)$$

$$Me_3Tl + \eta^5\text{-}C_5H_5Mo(CO)_3H \xrightarrow[-78°\,C]{CH_2Cl_2} \eta^5\text{-}C_5H_5(CO)_3 \atop MoTlMe_2 + MeH \quad (24)$$

The failure to isolate complexes of the types Q_2MR and QMR_2 (Q = transition metal group; R = alkyl) in other systems may well be attributed[33] to either that the remaining metal–carbon bonds are too reactive toward further cleavage or that these complexes are too unstable to permit isolation and promptly disproportionate according to the reverse of equations (19) and (20) or simply decompose. The credibility of this statement must await further synthetic studies in this area, especially in view of the well-known stability of Group IIIB organometallic halides of the types RMX_2 and R_2MX and the ubiquity of Group IVB organometallic complexes with transition metals,[2–8] and in the light of the recent findings that complexes such as Ph_2 $TlMn(CO)_5$[20] and η^5-$C_5H_5(CO)_3MoTlMe_2$[32] are reasonably stable once they have been isolated.
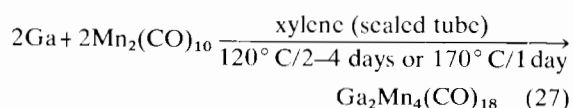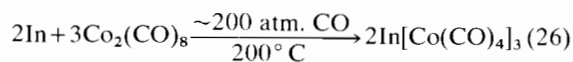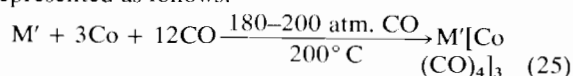
E. Miscellaneous Specific Reactions

Reactions which lack general applications but may be used in the synthesis of a restricted class or type of complexes are discussed in this section.

(i) Adduct formation reactions

Lewis acid–base interaction between a transition metal carbonyl group and a tervalent Group IIIB metal compound leads to the formation of a fairly wide range of adducts most of which are bonded through the carbonyl oxygen atom(s). If the coordination directly involves the transition metal, dative metal–metal bonds similar to those in coordination compounds would result. Such metal–metal bonds are thought to occur in the following complexes: $[\eta^5$-$C_5H_5(CO)_3WInPh_3]^-$,[34] $[Br_3InM(CO)_5]^{2-}$ (M = Cr or W),[35] $(\eta^5$-$Ph_3PC_5H_4)$ $(CO)_3MM'Br_3$ (M = Mo or W; M' = Ga or In),[36] $[Br_3M'$ $Fe(CO)_4]^{2-}$ and $[Br_3M'Co(CO)_4]^-$ (M' = Ga or In).[21]

(ii) High temperature and pressure syntheses

A number of cobalt and manganese carbonyl derivatives including the first transition metal–Group IIIB metal bonded complexes, $M'[Co(CO)_4]_3$ (M' = In or Tl) and $TlCo(CO)_4$,[37] have been prepared by a high temperature and pressure reaction in an autoclave or a sealed Carius tube. Typical examples[37–39,72] are represented as follows:

$$M' + 3Co + 12CO \xrightarrow[200°C]{180–200 \text{ atm. CO}} M'[Co(CO)_4]_3 \quad (25)$$

$$2In + 3Co_2(CO)_8 \xrightarrow[200°C]{\sim 200 \text{ atm. CO}} 2In[Co(CO)_4]_3 \quad (26)$$

$$2Ga + 2Mn_2(CO)_{10} \xrightarrow[120°C/2–4 \text{ days or } 170°C/1 \text{ day}]{\text{xylene (sealed tube)}} Ga_2Mn_4(CO)_{18} \quad (27)$$

(iii) Oxidative elimination reactions

The thermal reaction between C_5H_5Tl and $L_3Mo(CO)_3$ (L = CO[40] or PPh_3[41]) in tetrahydrofuran gives, *inter*

alia, the thallium(III) complexes $[\eta^5$-$C_5H_5(CO)_2LMo]_3$ Tl. The difficulty in isolating the pure product from the reaction mixture has rendered this reaction of little synthetic value.

(iv) Disproportionation of unstable low-valent species

A rather unusual synthesis for the transition metal complexes of thallium(III) as typified by the reaction:[42–44]

$$3TlNO_3 + 3NaMn(CO)_5 \xrightarrow{H_2O \text{ or}}_{THF} 3Tl[Mn(CO)_5]$$
$$\rightarrow Tl[Mn(CO)_5]_3 + 2Tl \quad (28)$$
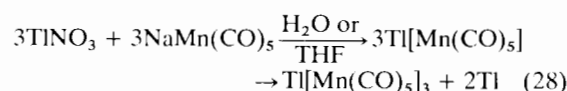
involves an unstable thallium(I) species. This reaction which is reminiscent of the disproportionation of the transient organothallium(I) compounds according to the equation:[45]

$$3Tl + 3RLi \rightarrow 3'TlR' \rightarrow TlR_3 + 2Tl \quad (29)$$

largely reflects the relative stability (under anaerobic conditions) of the thallium(I) and the thallium(III) derivatives. These reactions are further discussed in Section 6.

3. Transition Metal–Aluminium Complexes

Aluminium(III), being the strongest Lewis acid among the tervalent Group IIIB metals, shows a marked tendency to interact with electron-rich centres, thus posing an intriguing problem regarding the actual site of coordination. In the case of transition metal carbonyls, the relatively electron-rich oxygen atom of the carbonyl group provides a favourable site for attachment. Coordination of this kind, (I), is almost invariably accom-

$$M–C{\equiv}O \rightarrow AlR_3 \quad \text{(I)}$$

panied by a shift to lower wavenumbers for at least one of the carbonyl stretching absorptions.[46] Oxygen-bonded adducts with trialkylaluminium or aluminium(III) halides have been reported for a fairly wide range of metal carbonyl complexes including $(\eta^5$-$Ph_3PC_5H_4)$ $Mo(CO)_3$,[47] $Mo(CO)_2L_2L'_2$ (L_2 = phen or 5,6-Me_2 phen; L' = PPh_3 or L'_2 = phen),[48] $[\eta^5$-C_5H_5Mo $(CO)_3]_2$,[49] *trans*-$[ReCl(CO)(PMePh_2)_4]$,[50] $Fe_2(CO)_9$,[51] $[\eta^5$-$C_5H_5M(CO)_2]_2$ (M = $Fe^{49,52,53}$ or $Ru^{49,53}$), $[\eta^5$-$C_5H_5Fe(CO)]_4$,[49,52,53] $M_3(CO)_{12}$ (M = Fe or Ru),[51] Co_2 $(CO)_8$,[51,53,55] $[\eta^5$-$C_5H_5Ni(CO)_2]_2$ and $(\eta^5$-$C_5H_5)_3Ni_3$ $(CO)_2$.[49,51] On the other hand with metal carbonyl halides, the interaction of aluminium(III) halides may well occur through the transition metal-bound halogen atom, (II), as in the adducts X_3Al–$XMn(CO)_5$ and

$$M–X \cdots AlX_3 \quad \text{(II)}$$

η^5-$C_5H_5Fe(CO)_2X$–AlX_3 (X = Cl, Br or I).[56]

TABLE I. Transition Metal–Aluminium Complexes.

Complex	Colour	Method of Preparation[a]	Physical Data[b]
$[(\eta^5\text{-}C_5H_5)(C_5H_4)TiHAlEt_2]_2$	red	c	IR, NMR,[57] X-ray[60]
$[(\eta^5\text{-}C_5H_5)(C_5H_4)NbHAlEt_3]_2$[d]		E(i)[61]	
$(\eta^5\text{-}C_5H_5)_2(CO)NbHAlEt_3$[d]		E(i)[61]	
$(\eta^5\text{-}C_5H_5)_2(C_2H_4)NbHAlEt_3$[d]		E(i)[61]	
$(\eta^5\text{-}C_5H_5)_2(Me_3P)NbHAlEt_3$[d]		E(i)[61]	
$(\eta^5\text{-}C_5H_5)_2NbH_2AlEt_2$[d]		D[61]	
$(\eta^5\text{-}C_5H_5)_2H_2MoAlMe_3$	yellow	E(i)[61]	IR, NMR
$(\eta^5\text{-}C_5H_5)_2H_2MoAlEt_3$	yellow	E(i)[61]	IR, NMR
$(\eta^5\text{-}C_5H_5)_2H_2MoAlPh_3$	yellow	E(i)[61]	IR, NMR
$\eta^5\text{-}C_5H_5Mo(CO)_3AlMe_2$[e,f]	yellow	D[29]	
$\eta^5\text{-}C_5H_5Mo(CO)_3AlEt_2$[e,f]	yellow	D[29]	
$\eta^5\text{-}C_5H_5Mo(CO)_3AlBu^i_2$[e,f]	yellow	D[29]	
$\eta^5\text{-}C_5H_5(Ph_2MeP)Mo(CO)_2AlMe_2$[f]	yellow	D[29]	IR, NMR
$\eta^5\text{-}C_5H_5(Ph_3P)Mo(CO)_2AlMe_2$[f]	yellow	D[29]	
$(\eta^5\text{-}C_5H_5)_2H_2WAlMe_3$	yellow	E(i)[62, 63]	IR, NMR
$(\eta^5\text{-}C_5H_5)_2H_2WAlMe_2H$	yellow	E(i)[62]	IR, NMR
$(\eta^5\text{-}C_5H_5)_2H_2WAlEt_3$	yellow	E(i)[62]	IR, NMR
$(\eta^5\text{-}C_5H_5)_2H_2WAlPh_3$	yellow	E(i)[62]	IR, NMR
$\eta^5\text{-}C_5H_5W(CO)_3AlMe_2$[f]	D[30]	X-ray[31]	
$\eta^5\text{-}C_5H_5W(CO)_3AlEt_2$[f]		D[30]	
$[Bu^n_4N][\eta^5\text{-}C_5H_5W(CO)_3AlPh_3]$[f]	bright yellow	E(i)34	IR
$[\eta^5\text{-}C_5H_5W(CO)_3]_3Al\cdot3THF$[f]	light yellow	C(i)[16]	IR, X-ray
$(\eta^5\text{-}C_5H_5)_2HReAlMe_3$	yellow	E(i)[63]	
$[Me_2NAlFe(CO)_3Br_2]_2$		g	IR, MS[64]
$Me_2NAlFe(CO)_3Br_2\cdot THF$	red brown	g	MS, NMR[64]
$(\mu\text{–}Me_2N)(\mu\text{–}Me_2NCO_2)[AlFe(CO)_3Br_2]_2$	brown	g	IR[64]
$[Me_2NC(O)AlFe(CO)_2(PBu^n_3)Br_2]_2$	red brown	g	IR[64]
$AlCo_3(CO)_9$	deep red	A[65]	IR, MS
$Al[Co(CO)_4]_3$		D[66]	
$(Ph_3P)_2Pt(AlMe_3)_2$	orange red	E(iii)[67]	IR, ESR

[a]The lettering of the preparative methods follows that in Section 2. [b]Unless otherwise stated, the references to the physical data correspond to those for the preparations: IR = infrared, FIR = far-infrared, R = Raman, NMR = nuclear magnetic resonance, ESR = electron spin resonance, MS = mass spectrometry. [c]See text and ref. 57 and 59. [d]Formulated as hydride bridged. [e]Not isolated. [f]Oxygen bonded. [g]See text and ref. 64.

Nevertheless, metal–metal interaction in these complexes seems to be the least likely. Reported complexes (Table I) at one time or another thought to contain a transition metal–aluminium bond are discussed below.

A. Complexes of Group IVA and VA Metals

The reaction of $(Et_3Al)_2$ with $(\eta^5\text{-}C_5H_5)_2TiPh_2$, $(\eta^5\text{-}C_5H_5)_2TiCl_2$, or $(\eta^5\text{-}C_5H_5)_2TiCl$ affords a Ti–Al complex which has been formulated[57] as $[(C_5H_5)(C_5H_4)Ti HAlEt_2]_2$ (Figure 1) on the basis of spectroscopic evidence, consideration of its molecular dimensions from models, and by analogy with the well known structure of the so-called "niobocene," $[(C_5H_5)(C_5H_4) NbH]_2$.[58] The complex has been shown to be identical with that previously isolated by Natta and co-workers.[59] Its structure has been subsequently determined by X-ray
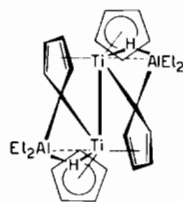
Figure 1. Suggested structure for $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$.[57]

crystallography as containing a Ti–Al bond of length 279.2 ± 1.1 pm. However, no attempt has been made to locate the hydrogen atoms.

The related cyclopentadienyl complexes, $[(\eta^5\text{-}C_5H_5)(C_5H_4)NbH]_2$, $(\eta^5\text{-}C_5H_5)_2NbLH$ (L = CO, C_2H_4 or

PMe$_3$), and (η^5-C$_5$H$_5$)$_2$TaH$_3$, react with (Et$_3$Al)$_2$ to afford hydrogen-bridged complexes of the types, [(η^5-C$_5$H$_5$)(C$_5$H$_4$)Nb–H–AlEt$_3$]$_2$, (η^5-C$_5$H$_5$)$_2$LNb–H–AlEt$_3$, and (η^5-C$_5$H$_5$)$_2$H$_2$Ta–H–AlEt$_3$, while (η^5-C$_5$H$_5$)$_2$NbH$_3$ eliminates a mole of ethane to yield (η^5-C$_5$H$_5$)$_2$NbH$_2$ AlEt$_2$.[61] The presence of transition metal–aluminium bonds in these complexes must await confirmation from structural studies.

B. Complexes of Group VIA and VIIA Metals

The hydrides, (η^5-C$_5$H$_5$)$_2$MH$_2$ (M = Mo[62] or W[62, 63]) and (η^5-C$_5$H$_5$)$_2$ReH,[63] form yellow crystalline 1:1 adducts with (R$_3$Al)$_2$ (R = Me, Et, or Ph) and (Me$_2$ AlH)$_3$. The infrared spectra of these adducts both in the solid state and in solution are virtually the superposition of those of the two compounds[62, 63] with a slight shift in the ν(M–H) absorption observable only in that of the complex (η^5-C$_5$H$_5$)$_2$WH$_2$·AlMe$_3$.[63] Low temperature (–50° C) NMR studies have found no evidence for the non-equivalence in the hydride or the methyl groups thus eliminating all possible electron-deficient (bridging) structures such as (III). These observations
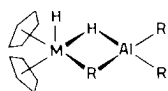
(III)

strongly suggest that these complexes are metal–metal bonded.[62, 63] Although most of the complexes slowly decompose on standing at room temperature,[62] NMR studies have demonstrated that the adduct (η^5-C$_5$H$_5$)$_2$ WH$_2$·AlMe$_3$ undergoes rapid exchange with either of its components and that these exchanges cease at about –50°C.[63] Attempts to isolate the adduct (η^5-C$_5$H$_5$)$_2$ WH$_2$·AlH$_3$ have been unsuccessful.[62]

The air- and moisture-sensitive complexes [η^5-C$_5$H$_5$ (L)M(CO)$_2$AlR$_2$]$_n$ (M = Mo,[29] L = CO, PMePh$_2$, or PPh$_3$; R = Me, Et, or Bu^i; M = W,[30] L = CO, R = Me or Et; n = 1 or 2) have been prepared by protolysis of aluminium alkyls or hydrides with the corresponding cyclopentadienylmetal carbonyl hydride. The lack of metal–metal bonds in these complexes has been unequivocally established by an X-ray structural analysis on [η^5-C$_5$H$_5$(CO)W(CO)$_2$AlMe$_2$]$_2$, (IV), which con-
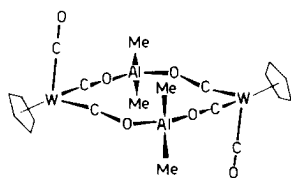
(IV)

tains a twelve-membered ring with O,O'-bonded dimethylaluminium groups.[31]

The complex, [η^5-C$_5$H$_5$W(CO)$_3$]$_3$Al·3THF, has been obtained by a metal exchange reaction [equation

(13)]. Determination of its crystal structure has revealed an O-bonded structure, (V), with the three tetrahy-
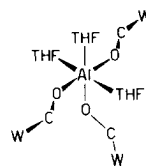

(V)

drofuran molecules occupying the *meridianal* positions of an octahedrally coordinated aluminium atom; the other three coordination sites are being taken up by the carbonyl oxygen atoms from the three η^5-C$_5$H$_5$W (CO)$_3$ groups. This extremely air-sensitive complex is rapidly hydrolysed by moisture to give the hydride, η^5-C$_5$H$_5$W(CO)$_3$H, forms the trifluoroacetyl derivative η^5-C$_5$H$_5$(CO)$_3$WCOCF$_3$ on addition of trifluoroacetic anhydride, and generates the salt Et$_4$N[η^5-C$_5$H$_5$W (CO)$_3$] when treated with Et$_4$NBr.[16]

Unlike Ph$_3$In *(vide infra)*, (Ph$_3$Al)$_2$ forms an O-bonded adduct with [η^5-C$_5$H$_5$W(CO)$_3$]$^-$.[34]

C. Complexes of Group VIII Metals

The reaction of Fe$_3$(CO)$_{12}$ with (Me$_2$NAlBr$_2$)$_2$ in refluxing benzene furnishes the dimeric complex, (VI) which readily undergoes a bridge-splitting reaction with tetrahydrofuran to yield the monomeric (VII), carbon dioxide insertion to form the N,N-dimethylcarbamate (VIII), and with tri-n-butylphosphine, carbonyl substitution at iron with concomitant carbonyl insertion at the Al–N bond to afford (IX).[64] It is noteworthy that
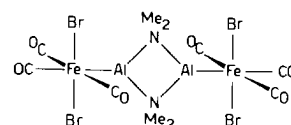
(VI)
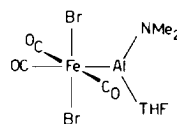
(VII)
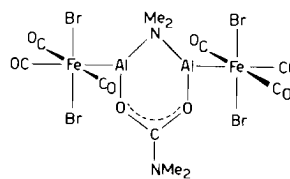
(VIII)
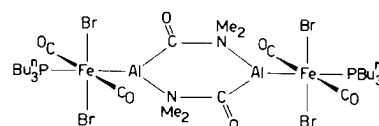
(IX)

the formulation of these interesting complexes as aluminium(I) derivatives in order to be consistent with the existing physical data and chemical evidence is singularly unnecessary.

The cluster complex $AlCo_3(CO)_9$ was inadvertently obtained from the metathesis between $NaCo(CO)_4$ and Al_2Cl_6 in benzene. The presence of bridging carbonyl groups in this complex clearly suggests a structure closely resembling that of $Co_4(CO)_{12}$.[65] Protolysis of $(Et_3Al)_2$ with $HCo(CO)_4$ has been reported in a patent as to generate the complex $Al[Co(CO)_4]_3$, which has been used as a catalyst in the polymerization of, for example, ethylene in the presence of carbon dioxide to $HO(C_2H_4)_nCOOH$.[66]

An orange–red 1:2 adduct of formula $(Ph_3P)_2Pt$ $(AlMe_3)_2$ has been obtained from the reaction of $(Me_3Al)_2$ with $(Ph_3P)_3Pt$ or $(Ph_3P)_2PtSiF_4$ and has been characterized by elemental analysis and ESR spectroscopy.[67]

4. Transition Metal–Gallium Complexes

Only several complexes containing transition metal–gallium bonds have been described (Table II).

A. Complexes of Group VIA Metals

There is NMR evidence for the partial complexation between $(\eta^5\text{-}C_5H_5)_2WH_2$ and Me_3Ga which is accompanied by a distinct colour change. However, no stable adduct could be isolated and the Me_3Ga can be removed on evacuation.[63] Attempts to isolate the gallane adduct $(\eta^5\text{-}C_5H_5)_2WH_2GaH_3$ have also been unsuccessful.[62]

The adduct $(\eta^5\text{-}Ph_3PC_5H_4)(CO)_3MoGaBr_3$ has been made from its components and formulated as metal–metal bonded on the basis of its infrared spectrum which shows a shift to higher wave numbers in the $\nu(CO)$ modes. This follows from the fact that the Lewis acid group $GaBr_3$ drains some electron density away from the metal[36] and not from the carbonyl oxygen atom as in the case of the corresponding trimethylaluminium adduct which is O-bonded.[47]

B. Complexes of Group VIIA Metals

The partial complexation of $(\eta^5\text{-}C_5H_5)_2ReH$ with Me_3Ga which is analogous to that of $(\eta^5\text{-}C_5H_5)_2WH_2$ has been briefly mentioned.[63]

The stoichiometry of the complex, $Br_2GaMn(CO)_5$, which is the product of the sealed tube reaction:[23]

$$Ga[GaBr_4] + Mn_2(CO)_{10} \xrightarrow[19hr]{190°\,C} 2Br_2GaMn(CO)_5 \quad (30)$$
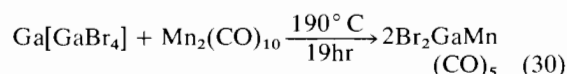
has been established from mass spectral studies. The corresponding chloro-complex has been isolated as the tetrahydrofuran adduct from the metathesis between $GaCl_3$ and $NaMn(CO)_5$ in equimolar quantities; the presence of a Mn–Ga bond in this complex has been substantiated by the intense $\nu(Mn–Ga)$ mode at 149 cm^{-1} in its far-infrared spectrum.[68]

Heating a xylene solution of $Mn_2(CO)_{10}$ with metallic gallium in an autoclave at 120° C for 2–4 days or at 170° C for a day [equation (27)] affords the unusual cluster complex, $Ga_2Mn_4(CO)_{18}$, the formulation of which is based on its vibrational spectra which exhibit strong absorptions attributable to the $\nu(Ga–Ga)$

TABLE II. Transition Metal–Gallium Complexes.

Complex	Colour	Method of Preparation[a]	Physical Data[a]
$(\eta^5\text{–}Ph_3PC_5H_4)(CO)_3MoGaBr_3$	white	E(i)[36]	IR
$(\eta^5\text{-}C_5H_5)_2H_2WGaMe_3$[b]	golden yellow	E(i)[63]	NMR
$Cl_2GaMn(CO)_5 \cdot THF$	yellow	A[68]	IR, FIR
$Br_2GaMn(CO)_5$	yellow	B[23]	IR, MS
$Ga_2Mn_4(CO)_{18}$	red	E(ii)[39,72]	IR, FIR, R, MS
$Ga[Mn(CO)_5]_3$	yellow	A[12]	IR, MS
$(\eta^5\text{-}C_5H_5)_2HReGaMe_3$		E(i)[63]	
$[(Ph_3P)_2N]_2[Br_3GaFe(CO)_4]$		E(i)[21]	IR
$Cl_2GaCo(CO)_4 \cdot THF$	white	A, B[10]	IR
$Br_2GaCo(CO)_4 \cdot THF$	pale yellow	A, B[10]	IR
$I_2GaCo(CO)_4 \cdot THF$[c]		B[10]	
$Br(acac)GaCo(CO)_4$	pale yellow	d	IR[10]
$[(Ph_3P)_2N][Br_3GaCo(CO)_4]$		E(i)[21]	IR
$ClGa[Co(CO)_4]_2 \cdot THF$	lemon yellow	A[10]	IR
$BrGa[Co(CO)_4]_2 \cdot THF$	lemon yellow	A[10]	IR
$(acac)Ga[Co(CO)_4]_2$	yellow	d	IR[10]

[a]See footnotes in Table I. [b]Dissociates on evacuation. [c]Not isolated pure. [d]From the reaction with an equimolar amount of Tl(acac).[10]

and $\nu(Mn-Ga)$ vibrations and its mass spectrum. The complex $Ga[Mn(CO)_5]_3$ has also been prepared according to equation (3).[12]

C. Complexes of Group VIII Metals

Among the Group VIII transition metals, only complexes with Co–Ga bonds have been studied in detail. Treatment of gallium(III) halides with $NaCo(CO)_4$ in tetrahydrofuran in appropriate molar ratios yields the complexes, $XGa[Co(CO)_4]_2 \cdot THF$ (X = Cl or Br) and $X_2GaCo(CO)_4 \cdot THF$ (X = Cl, Br or I).[10] The dihalo-complexes are also obtained from the reaction of $Ga[GaX_4]$ with $Co_2(CO)_8$ in tetrahydrofuran at room temperature. These complexes are converted to the four-coordinate acetylacetonato derivatives, $(acac)Ga[Co(CO)_4]_2$ and $Br(acac)GaCo(CO)_4$, using $Tl(acac)$. The non-isolation of the complex $Ga[Co(CO)_4]_3$ from the reaction of $GaBr_3$ with an excess of $NaCo(CO)_4$ in tetrahydrofuran[10] has been discussed in Section 2.A.

The interaction of $GaBr_3$ with $(Ph_3P)_2N[Co(CO)_4]$ and with $(Ph_3P)_2N[HFe(CO)_4]$ in dichloromethane or tetrahydrofuran leads to the formation of the adducts $[(Ph_3P)_2N[]Br_3GaCo(CO)_4]$ and $[(Ph_3P)_2N]_2[Br_3GaFe(CO)_4]$ respectively.[21] The isolation of these adducts as opposed to the probable metathetical reaction reflects the important role played by the cation concerned in reactions of this kind.

5. Transition Metal–Indium Complexes

The general availability of the indium starting materials, the greater stability of most of its complexes to moisture and aerial oxidation, and the much diminished Lewis acidity of indium(III), which is often favourably compared with that of cadmium(II) or tin(IV), are the major factors that have been grossly exploited during the more recent extensive investigation of transition metal–indium complexes (Table III).

TABLE III. Transition Metall–Indium Complexes.

Complex	Colour	Method of Preparation[a]	Physical Data[a]
$[(Ph_3P)_2N]_2[Br_3InCr(CO)_5]$		b	IR^{69}
$(\eta^5-Ph_3PC_5H_4)(CO)_3MoInBr_3$	white	E(i)[36]	IR
$\eta^5-C_5H_5(CO)_3MoInCl_2$	light yellow	A. B[13, 32]	IR,[13, 70]NMR, MS[70]
$[Et_4N][\eta^5-C_5H_5(CO)_3MoInBr_3]$	pale yellow	E(i)[13, 70]	IR
$[\eta^5-C_5H_5(CO)_3Mo]_2InCl$	yellow	A. B,[c]C(i)[13, 22]	IR,[13, 70]NMR, MS[70]
$[\eta^5-C_5H_5(CO)_3Mo]_2InBr$	yellow	A. B, C(i)[13, 22]	IR,[13, 70]NMR, MS[70]
$[\eta^5-C_5H_5(CO)_3Mo]_3In$	bright yellow	A. C(i), D[13]	IR,[13, 70]NMR, MS[70]
$[(Ph_3P)_2N]_2[Br_3InW(CO)_5]$		b	IR^{69}
$(\eta^5-Ph_3PC_5H_4)(CO)_3WInBr_3$	white	E(i)[36]	IR
$[Bu^t N][\eta^5-C_5H_5(CO)_3WInPh_3]$	pale yellow	E(i)[34]	IR
$[\eta^5-C_5H_5(CO)_3W]_2InCl$	yellow	A. B, C(i)[13, 22]	IR,[13, 70]NMR, MS[70]
$[\eta^5-C_5H_5(CO)_3W]_3In$	bright yellow	A. C(i), D[13]	IR,[13, 70]NMR, MS[70]
$Cl_2InMn(CO)_5$	light yellow	A,[17]B[22]	IR, MS[17]
$Br_2InMn(CO)_5$	lemon yellow	A,[17]B[22]	IR. MS[17]
$[Me_4N][Cl_3InMn(CO)_5]$	pale yellow	E(i)[17]	IR
$[Et_4N][Br_3InMn(CO)_5]$	pale yellow	E(i)[17]	IR
$ClIn[Mn(CO)_5]_2$	yellow	A,[17] B[22]	IR, MS[17]
$BrIn[Mn(CO)_5]_2$	yellow	A,[17] B[22, 23]	IR[17]
$\{(MeCN)_2In[Mn(CO)_5]_2\}[ClO_4]$	colourless	d	IR[17]
$\{py_2In[Mn(CO)_5]_2\}[ClO_4]$	colourless	d	IR[17]
$\{phen_2In[Mn(CO)_5]_2\}[ClO_4]$	colourless	d	IR[17]
$[Me_4N]\{Cl_2In[Mn(CO)_5]_2\}$	yellow	E(i)[17]	IR
$[Et_4N]\{Br_2In[Mn(CO)_5]_2\}$	lemon yellow	E(i)[17]	IR
$[Et_4N]_2\{Br_3In[Mn(CO)_5]_2\}$	yellow	E(i)[17]	IR
$(acac)In[Mn(CO)_5]_2$	yellow	e	IR[17, 23]
$(oxine)In[Mn(CO)_5]_2$	bright yellow	d	IR[17]
$In[Mn(CO)_5]_3$	orange yellow	A,[17] C(i),[11] E(ii)[39]	IR, MS[17] FIR[39]
$Ph_3POIn[Mn(CO)_5]_3$		E(i)[f, 78]	IR
$[Me_4N]\{ClIn[Mn(CO)_5]_3\}$	bright yellow	E(i)[17]	IR
$[Et_4N]\{BrIn[Mn(CO)_5]_3\}$	orange	E(i)[17]	IR
$[Ph_4As]\{In[Mn(CO)_5]_4\}$		E(i)[78]	
$In_2Mn_4(CO)_{18}$	ruby red	g	
$Cl_2InRe(CO)_5$	pale yellow	A, B[13]	IR, MS[13, 70]
$ClIn[Re(CO)_5]_2$	yellow	A, B[c, 13]	IR, MS[13, 70]
$In[Re(CO)_5]_3$	intense yellow	A, C(i), D[13]	IR, MS[13, 70]

TABLE III. (Cont.)

Complex	Colour	Method of Preparation[a]	Physical Data[a]
$[(Ph_3P)_2N]_2[Br_3InFe(CO)_4]$		E(i)[21]	IR
$[(Ph_3P)_2N][Br_2InFe(CO)_4]$		<u>h</u>	IR[21]
$[(Ph_3P)_2N][pyBr_2InFe(CO)_4]$		<u>h</u>	IR[21]
$[(Ph_3P)_2N][(Et_3N)Br_2InFe(CO)_4]$		<u>h</u>	IR[21]
$\eta^5\text{-}C_5H_5(CO)_2FeInCl_2$	yellow	A, B[13,22]	IR,[13,70]NMR, MS[70]
$\eta^5\text{-}C_5H_5(CO)_2FeInBr_2$	yellow	A, B[13,22]	IR,[13,70]
$\eta^5\text{-}C_5H_5(CO)_2FeInBr_2\cdot THF$	yellow	A, B[13]	IR,[13,70]
$[\eta^5\text{-}C_5H_5(CO)_2Fe]_2InCl$	yellow-brown	A, B, C(i)[13,22]	IR,[13,70]NMR, MS[70]
$[(Ph_3P)_2N][Br_3InCo(CO)_4]$		E(i)[21]	IR
$ClIn[Co(CO)_4]_2\cdot THF$	yellow	A, B, C(i)[13,22]	IR,[13] MS[70]
$BrIn[Co(CO)_4]_2\cdot THF$	bright yellow	A,[10] B[10,24]	IR
$ClIn[Co(CO)_4]_2$	yellow	A, B, C(i)[13,22]	IR,[13] MS[70]
$BrIn[Co(CO)_4]_2$	orange	A,[10] B[10,24]	IR
$(acac)In[Co(CO)_4]_2$	bright yellow	<u>i</u>	IR[10]
$[Et_4N]\{Br_2In[Co(CO)_4]_2\}$	yellow	E(i)[15]	X-ray[85]
$In[Co(CO)_4]_3$	red	A,[10] C(i),[27] E(ii)[37,38]	IR[10]
$In[Co(CO)_3PPh_3]_3$		<u>j</u>	IR[79]
$Ph_3POIn[Co(CO)_4]_3$		E(i)[79,83]	
$Ph_3POIn[Co(CO)_3PPh_3]_3$		E(i)[79]	
$[Ph_4As][Cl\{In[Co(CO)_4]_3\}_2]$		E(i)[79,83]	
$[Ph_4As]\{In[Co(CO)_4]_4\}$	red	E(i)[79,83]	
$[Ph_4As]\{In[Co(CO)_3PPh_3]_4\}$		E(i)[79]	
$Br_3In_3Co_4(CO)_{15}$	orange	B[10,24]	IR,[10] X-ray[25,26]
$trans\text{-}[Rh(InCl_2)(CO)(PPh_3)_2]$	orange	B[22]	IR[70]
$(Et_3P)_2Pt(InCl_2)_2$	orange	B[22]	
$trans\text{-}[Pt(InCl_2)(SiPh_3)(PMe_2Ph)_2]$	orange	B[86]	FIR
$[(Et_3P)_2(p\text{-}MeOC_6H_4NC)PtInCl_2][ClO_4]$	orange	B[22]	IR[70]
$Ph_3PAuInCl_2$	orange	B[22]	IR, FIR[70]

[a]See footnotes of Table I. [b]See text an ref. 69. [c]Reaction incomplete. [d]See text and ref. 17. [e]See text and ref. 17 and 23. [f]Not isolated. [g]See text and ref. 72. [h]See text and ref. 21. [i]See text and ref. 10. [j]See text and ref. 79.

It is evident from the results of these studies that the chemical behaviour of transition metal–indium complexes which constitute the largest group among the Group IIIB metal derivatives, is, as expected, intermediate between those containing transition metal–gallium and –thallium bonds. Of particular significance is the tendency of indium to form stable mixed complexes of the types QMX_2 and Q_2MX (Q = transition metal group; X = halogen) although no analogous organoindium derivatives have yet been isolated. The following discussion attempts to delineate the similarities (or differences) between isoelectronic pairs of transition metal–cadmium and –indium complexes or of transition metal–indium and –tin complexes.

No complexes of Group IVA or VA have been described.

A. Complexes of Group VIA Metals

On the basis of infrared evidence, the 1:1 adducts between the ylide complexes $(\eta^5\text{-}Ph_3PC_5H_4)M(CO)_3$ (M = Mo or W) and $InBr_3$ (*cf.* the $GaBr_3$ adduct) have been formulated as metal–metal bonded.[36] Similar dative metal–metal bonding has been surmised for the adduct, $[Bu^t_4N][\eta^5\text{-}C_5H_5(CO)_3WInPh_3]$, which shows $\nu(CO)$ vibrations in its infrared spectrum rather different from that of the aluminium analogue.[34]

Interaction of InBr with $[M_2(CO)_{10}]^{2-}$ (M = Cr or W) in a tetrahydrofuran–dichloromethane mixture affords the complexes $[Br_3InM(CO)_5]^{2-}$ along with a deposition of metallic indium. In marked contrast to this reaction:

$$[(Ph_3P)_2N]_2[M_2(CO)_{10}] + 6InBr \xrightarrow{THF/CH_2Cl_2} 2[(Ph_3P)_2N]_2[Br_3InM(CO)_5] + 4In \quad (31)$$
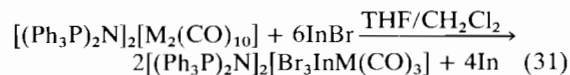
are those of GeI_2 and SnI_2 which gives the "insertion" products $\{I_2M'[M(CO)_5]_2\}^{2-}$ (M' = Ge or Sn).[69]

The series of complexes, $[\eta^5\text{-}C_5H_5(CO)_3M]_nInX_{3-n}$ (M = Mo or W; X = Cl or Br; n = 1, 2, or 3), have been synthesized by a number of methods (see Table III) including the metathetical reaction,[13] the insertion reaction, and the exchange reaction.[13,22] The trisubstituted complexes (n = 3) have also been obtained in high yield from the reaction of the corresponding hydride

η^5-C$_5$H$_5$M(CO)$_3$H and Me$_3$In. In the latter reaction the intermediate complexes, [η^5-C$_5$H$_5$(CO)$_3$M]$_n$InMe$_{3-n}$ (n = 1 or 2), could not be isolated even when a deficiency of the carbonyl hydride is used.[13] The structures of these complexes have been established by infrared,[13,70] mass and NMR spectroscopy.[70] The complex [η^5-C$_5$H$_5$(CO)$_3$W]$_3$In and its isoelectronic cadmium analogue {[η^5-C$_5$H$_5$(CO)$_3$W]$_3$Cd}$^{-71}$ may well have the same structure with planar M′W$_3$ (M′ = Cd or In) moiety. Attempts to prepare η^5-C$_5$H$_5$(CO)$_3$MoInBr$_2$ have been unsuccessful; the isolable product from the reaction mixture has been identified as the adduct [η^5-C$_5$H$_5$(CO)$_3$MoInBr$_3$]$^{-}$.[13,70] The reason for this unusual behaviour has been discussed in Section 2.A.

B. Complexes of Group VIIA Metals

Metathetical reactions between NaMn(CO)$_5$ and InX$_3$ (X = Cl or Br) in appropriate molar ratios have been employed in the synthesis of the complexes X$_{3-n}$In[Mn(CO)$_5$]$_n$ (n = 1, 2, or 3).[17] In addition, the tri-substituted complex, In[Mn(CO)$_5$]$_3$, has been obtained from a high-yield metal exchange reaction [equation (16)][11] and as a by-product in the direct reaction between metallic indium and Mn$_2$(CO)$_{10}$ in an autoclave at 140° C for 14 days.[39] The latter reaction also generates the ruby red complex, In$_2$[Mn(CO)$_5$]$_4$, of unknown structure.[72]

The mixed complexes X$_{3-n}$In[Mn(CO)$_5$]$_n$ (n = 1 or 2) have been shown to be dimeric in the vapour phase and presumably so in the solid state, (X) and (XI), but monomeric in polar solvents probably due to the

(X)

(XI)
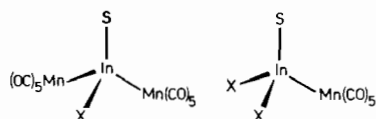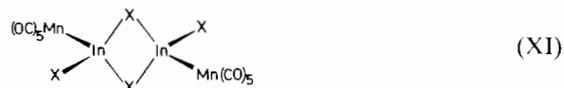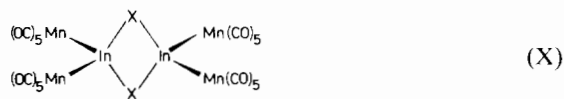
(XII)   (XIII)

formation of weak adducts with the solvent molecule, S, as in (XII) and (XIII). The presence of metal–metal bonds in In[Mn(CO)$_5$]$_3$ has been substantiated by far-infrared[39] and mass spectral studies.[17,70]

Redistribution reactions between InX$_3$ (X = Cl or Br) and the complexes X$_{3-n}$In[Mn(CO)$_5$]$_n$ (n = 1, 2, or 3) have been studied and in solution, the position of the following equilibria:
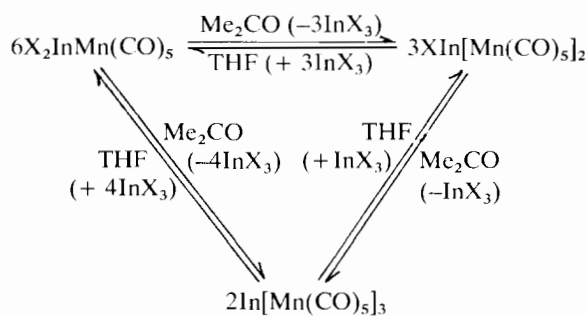
largely depends upon the nature of the solvent used as well as the stoichiometry of the reaction mixture.[70]

The complexes X$_{3-n}$In[Mn(CO)$_5$]$_n$ (n = 1, 2, or 3) undergo extensive ionization in dimethylformamide solution yielding the [Mn(CO)$_5$]$^{-}$ anion. However, in acetonitrile, all these complexes show similar and within experimental error, superimposable terminal carbonyl stretching absorptions which are not due to the [Mn(CO)$_5$]$^{-}$ anion. In the case of In[Mn(CO)$_5$]$_3$, two additional peaks are observed in the lower frequency region which may be ascribed to this anion. Partial ionization of the metal–metal bonds according to the equations:

$$\text{In[Mn(CO)}_5\text{]}_3 \rightleftharpoons \text{In[Mn(CO)}_5\text{]}_2{}^+ + \text{Mn(CO)}_5{}^- \quad (32)$$

$$\text{XIn[Mn(CO)}_5\text{]}_2 \rightleftharpoons \text{In[Mn(CO)}_5\text{]}_2{}^+ + \text{X}^- \quad (33)$$

$$2\text{X}_2\text{InMn(CO)}_5 \rightleftharpoons \text{In[Mn(CO)}_5\text{]}_2{}^+ + \text{InX}_4{}^- \quad (34)$$
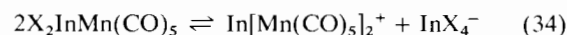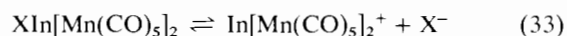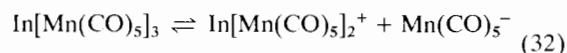
has been invoked to explain this anomalous behaviour. In accordance with these, the cation In[Mn(CO)$_5$]$_2{}^+$ has been isolated as the acetonitrile adduct {(MeCN)$_2$In[Mn(CO)$_5$]$_2$}$^+$ by treating the complexes XIn[Mn(CO)$_5$]$_2$ (X = Cl or Br) with silver perchlorate in acetonitrile and from the metathesis:

$$2\text{X}_2\text{InMn(CO)}_5 + \text{Me}_4\text{N}^+\text{ClO}_4{}^- \xrightarrow{\text{MeCN}}$$
$$\{(\text{MeCN})_2\text{In[Mn(CO)}_5\text{]}_2\}^+[\text{ClO}_4]^-$$
$$+ \text{Me}_4\text{N}^+\text{InX}_4{}^- \quad (35)$$
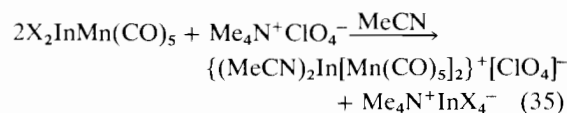
Attempts to isolate the cation by protonation of In[Mn(CO)$_5$]$_3$ with HClO$_4$ or HPF$_6$ in water have been unsuccessful.[17,73] The similarity between the infrared spectrum of the cation and those of the complexes L$_2$Cd[M(CO)$_5$]$_2$ (M = Mn[74] or Re[75]; L = amines) indicates that it probably possesses an analogous C$_{2v}$ structure. Addition of pyridine or 1,10-phenanthroline to {(MeCN)$_2$In[Mn(CO)$_5$]$_2$}$^+$[ClO$_4$]$^-$ yields the corresponding adduct {L$_2$In[Mn(CO)$_5$]$_2$}[ClO$_4$] (L = py or phen).[17,73] The pyridine complex is isoelectronic and probably isostructural with the cadmium complex py$_2$Cd[Mn(CO)$_5$]$_2$,[74] while the 1,10-phenanthroline complex may well contain a six-coordinate indium atom.[17]

Halogens and hydrogen halides cleave one, two, or all three of the Mn–In bonds of In[Mn(CO)$_5$]$_3$, the

volatile by-products being $XMn(CO)_5$ (X = Cl or Br) or $HMn(CO)_5$.[17] These reactions differ considerably from those of the thallium analogue, $Tl[Mn(CO)_5]_3$ (*vide infra*). With halide ions, however, the complexes $X_{3-n}In[Mn(CO)_5]_n$ (X = Cl or Br; n = 1, 2, or 3) afford 1:1 adducts of the general formula $\{X_{4-n}In[Mn(CO)_5]_2\}^-$ (n = 1, 2, or 3)[17] which are isoelectronic and probably isosteric with the tetrahedral Mn–Sn bonded complexes, $X_{4-n}Sn[Mn(CO)_5]_n$, which have C_{3v} (N = 1 or 3) or C_{2v} (n = 2) structures.[3,6,76–78] The 1:2 adduct $[Et_4N]_2\{Br_3In[Mn(CO)_5]_2\}$ has also been isolated.[17] The complex $In[Mn(CO)_5]_3$ also forms 1:1 adducts with Ph_3PO and the $[Mn(CO)_5]^-$ anion.[79] The isolation of the anionic complex $\{In[Mn(CO)_5]_4\}^-$ bears the significant implication that the hitherto unknown isoelectronic tin complex, $Sn[Mn(CO)_5]_4$, should be capable of existence unless the fourth $Mn(CO)_5$ group in the former complex is not bonded through a Mn–In bond. It is noteworthy that a previous attempt to synthesize $Sn[Mn(CO)_5]_4$ by treating $SnCl_4$ with more than four molar equivalents of $NaMn(CO)_5$ in tetrahydrofuran was unsuccessful and the failure has been attributed to steric effects.[80a]

Treatment of the complexes, $XIn[Mn(CO)_5]_2$ (X = Cl or Br), with Na(acac),[17] Tl(acac) or acetylacetone in the presence of a base,[23] and with 8-hydroxyquinoline gives respectively the chelate complexes, $(acac)In[Mn(CO)_5]_2$ and $(oxine)In[Mn(CO)_5]_2$.

The rhenium complexes, $Cl_{3-n}In[Re(CO)_5]_n$ (n = 1, 2, or 3) have been similarly prepared by the metathetical reaction, insertion reaction and from the reaction of $HRe(CO)_5$ with Me_3In, and characterized by their infrared and mass spectra.[13,70]

C. Complexes of Group VIII and IB Metals

(i) The iron subgroup

The reaction of $InBr_3$ with the anion $[Fe(CO)_4]^{2-}$ in tetrahydrofuran or $[HFe(CO)_4]^-$ in dichloromethane furnishes the 1:1 adduct $[Br_3InFe(CO)_4]^{2-}$, along with a varying amount of the complex $[Br_2InFe(CO)_4]^-$ which readily adds on an amine to yield the complexes $[LBr_2InFe(CO)_4]^-$ (L = py or Et_3N). The following reversible equilibrium in dichloromethane has been established:

$$[Br_3InFe(CO)_4]^{2-} \rightleftharpoons [Br_2InFe(CO)_4]^- + Br^- \quad (36)$$
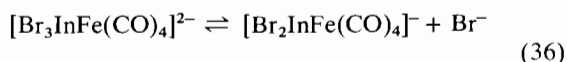
and found to be largely dependent upon the concentration of the added bromide ion.[21]

The complexes $[\eta^5\text{-}C_5H_5(CO)_2Fe]_nInX_{3-n}$ (X = Cl, n = 1 or 2; X = Br, n = 1) have been prepared by the insertion of InX into the Fe–Fe and Fe–Cl bonds of the complexes $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and $\eta^5\text{-}C_5H_5Fe(CO)_2Cl$ respectively, from the interaction of InX with the mercurial, $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2Hg$, according to equations (17) and (18),[13,22] and from the metathetical reactions between InX_3 and $[\eta^5\text{-}C_5H_5(CO)_2$

Fe]Na in 1:1 and 1:2 molar ratios.[13] These complexes which resemble $[\eta^5\text{-}C_5H_5(CO)_3Mo]_nInX_{3-n}$ in physical properties and chemical reactivity, have been characterized by infrared[13] and NMR spectroscopy, and the fragmentation pathways in their mass spectra[70] are similar to those of the mercury complexes, $\eta^5\text{-}C_5H_5(CO)_2FeHgX$ (X = Cl or Br).[80b] Conspicuous by its absence from Table III is the trisubstituted complex, $[\eta^5\text{-}C_5H_5(CO)_2Fe]_3In$, which could not be isolated pure.[13]

(ii) The cobalt subgroup

The reaction of $[(Ph_3P)_2N][Co(CO)_4]$ with $InBr_3$ is entirely analogous to the gallium derivative yielding the 1:1 adduct $[(Ph_3P)_2N][Br_3InCo(CO)_4]$.[21]

The complex, $In[Co(CO)_4]_3$, which has been more extensively investigated, can be synthesized by several methods including the metathetical reaction [equation (1)],[10] the metal exchange reaction [equation (14)],[27] and the high temperature and pressure syntheses [equations (25) and (26)].[37,38] The complex has also been obtained from a reaction involving the use of the more exotic reagent $Tl[Co(CO)_4]$:[81]

$$InCl_3 + 3Tl[Co(CO)_4] \xrightarrow{\text{THF}} In[Co(CO)_4]_3 + 3TlCl \quad (37)$$

The presence of Co–In bonds in its approximately C_{3h} structure has been unequivocally established by an X-ray structural analysis, the average Co–In bond distance being 259.4 ± 0.3 pm.[27] This complex has been employed as a catalyst, either by itself[38] or in the presence of $Et_2O \cdot BF_3$,[82] in the stereospecific dimerization of bicyclo[2,2,1]hepta-2,5-diene.

Both $In[Co(CO)_4]_3$ and its triphenylphosphine derivative, $In[Co(CO)_3PPh_3]_3$, form 1:1 adducts with $Co(CO)_3L^-$ (L = CO or PPh_3) and with Ph_3PO.[79,83] The far-infrared spectrum of the red crystalline anionic complex $[Ph_4As]\{In[Co(CO)_4]_4\}$ exhibits a strong absorption at 128 cm^{-1} assignable to the $\nu(Co–In)$ mode.[83] Like its isoelectronic tin analogue, $Sn[Co(CO)_4]_4$,[84] this anionic complex is eminently probable to possess a tetrahedrally coordinated indium atom. Addition of $Ph_4As^+Cl^-$ to $In[Co(CO)_4]_3$ leads to the formation of the novel chlorine bridged adduct, $[Ph_4As][Cl\{In[Co(CO)_4]_3\}_2]$,[79,83] although attempts to isolate the simple 1:1 adduct, $\{ClIn[Co(CO)_4]_3\}^-$, have been unsuccessful generating only the chlorine bridged complex.[79]

Metathesis between InX_3 and $NaCo(CO)_4$ in 1:2 molar ratio or insertion of InX into the Co–Co bond of $Co_2(CO)_8$ in tetrahydrofuran affords the complexes $XIn[Co(CO)_4]_2 \cdot THF$ (X = Cl[13,22] or Br[10,24]) in high yield. The chloro-complex has also been prepared from the interaction of InCl with $Hg[Co(CO)_4]_2$ in the same solvent.[13,22] These four-coordinate complexes readily lose the coordinated solvent molecule

to furnish the complexes $XIn[Co(CO)_4]_2$ which are dimeric with halogen bridges.[10,70] The bromo-complex reacts with Tl(acac) to form the yellow chelate complex, $(acac)Tl[Co(CO)_4]_2$,[10] and with bromide ion, the anionic adduct $\{Br_2In[Co(CO)_4]_2\}^-$ is produced.[15] X-ray structural studies on the complex $[Et_4N]\{Br_2In[Co(CO)_4]_2\}$ have shown that its C_{2v} structure contains a tetrahedrally coordinated indium atom with an average Co–In bond distance of 265.2 ± 1.3 pm[85] and is presumably isostructural with the isoelectronic tin complex, $Cl_2Sn[Co(CO)_4]_2$.[84]

When the reaction between InBr and $Co_2(CO)_8$ is performed in benzene, an orange crystalline complex is obtained. The identity of this product, which was first formulated as $Br_3In_3Co_4(CO)_{16}$ on the basis of a complete elemental analysis and its infrared spectrum,[10,24] has now been established by X-ray crystallography as having the composition $Br_3In_3Co_4(CO)_{15}$ and the structure as depicted in Figure 2.[25,26]
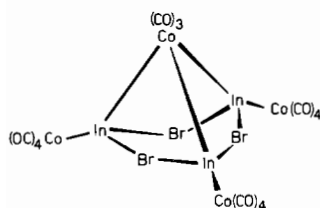

Figure 2. Structure for $Br_3In_3Co_4(CO)_{15}$.[25,26]

The insertion of InCl into the Rh–Cl bond of *trans*-$RhCl(CO)(PPh_3)_2$ is accomplished at room temperature yielding the orange complex, *trans*-$Rh(InCl_2)(CO)(PPh_3)_2$.[22]

(iii) The nickel subgroup and group IB metals

Metal complexes of these groups have not been investigated in any detail and only a few organometallic or inorganic complexes have been described, namely, $(Et_3P)_2Pt(InCl_2)_2$,[22] *trans*-$[Pt(InCl_2)(SiPh_3)(PMe_2Ph)_2]$,[86] $[(Et_3P)_2(p\text{-MeOC}_6H_4NC)PtInCl_2][ClO_4]$, and $Ph_3PAuInCl_2$,[22] all prepared by the insertion of InCl into the corresponding metal–chlorine bond.

6. Transition Metal–Thallium Complexes

A number of transition metal derivatives of both thallium(I) and -(III) have been prepared (Table IV). The thallium(III) complexes are, in general, more stable than the corresponding highly air-sensitive thallium(I) derivatives. The colour and chemical properties of the thallium(I) species closely parallel those of the corresponding ionic alkali metal derivatives. Although the relatively larger thallium(I) ion does confer some covalent character on its linkage to the metal carbonyl

anion in less polar solvents such as benzene, such interaction between the two moieties which may occur through the carbonyl oxygen atom, cannot be taken as an indication for the existence of a metal–metal bond. That their solid state structures are strictly of the ionic lattice type has been substantiated by the crystallographic studies on $Tl[Co(CO)_4]$.[87] The nature of these thallium(I) complexes is less certain in solution, in which the formation of ion pairs and/or anionic complexes may well be a more decisive factor. Consistent with this contention is the observation of solvent dependence in the carbonyl stretching absorption of some thallium(I) complexes.

No Group IVA organometallic derivatives of thallium have been reported.

A. Complexes of Group VA Metals

Redox reaction between metallic thallium and $V(CO)_6$ results in the formation of $Tl[V(CO)_6]$,[79] which is also prepared from the metathetical reaction between $[Na(diglyme)_2][V(CO)_6]$ and $TlNO_3$ in water.[12] The latter reaction has also been applied in the synthesis of the organothallium(III), complexes $[R_2Tl][V(CO)_6]$ (R = Me or Ph).[12]

B. Complexes of Group VIA Metals

Sodium borohydride reduction of the complex, $(\eta^5\text{-}Ph_2CC_5H_4)Cr(CO)_3$, obtained from the reaction of 6,6-diphenylfulvene with $Cr(CO)_6$, gives a yellow anion solution. Treatment of this solution with an aqueous solution of $TlNO_3$ produces an orange precipitate of the thallium(I) complex, $[(\eta^5\text{-}Ph_2CHC_5H_4)Cr(CO)_3]Tl$, which is formally a substituted cyclopentadienyl complex.[88]

Metathetical reactions between $[\eta^5\text{-}C_5H_5(CO)_3M]Na$ and thallium(I) salts in water afford the corresponding yellow thallium(I) complexes, $[\eta^5\text{-}C_5H_5(CO)_3M]Tl$ (M = Cr,[14] Mo, or W[14,15]). These highly air-sensitive and thermally rather unstable complexes which can be crystallized unchanged from degassed 10% aqueous NaOH solution, have been characterized by their infrared spectra. The more thermally stable tungsten complex $[\eta^5\text{-}C_5H_5(CO)_3W]Tl$ shows the parent ion in its mass spectrum and reacts with $Co_2(CO)_8$ oxidatively to form the mixed metal complex, $[\eta^5\text{-}C_5H_5(CO)_3W]Tl[Co(CO)_4]_2$, which is also the product of the redistribution reaction:[14]

$$[\eta^5\text{-}C_5H_5(CO)_3W]_3Tl + 2Tl[Co(CO)_4]_3 \rightarrow [\eta^5\text{-}C_5H_5(CO)_3W]Tl[Co(CO)_4]_2 \quad (38)$$
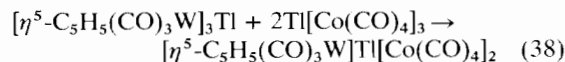
Although the complexes, $[\eta^5\text{-}C_5H_5(CO)_3M]Tl$ (M = Mo or W), have been successfully used in the synthesis of metal–metal bonded species such as $\eta^5\text{-}C_5H_5(CO)_3MoW(CO)_3(\eta^5\text{-}C_5H_5)$, $\eta^5\text{-}C_5H_5(CO)_3MMn(CO)_5$, and $\eta^5\text{-}C_5H_5(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$,[15] they have no apparent advantage over the less exotic alkali metal derivatives. In toluene, the thallium(I) complexes

TABLE IV. Transition Metal–Thallium Complexes.

Complex	Colour	Method of Preparation[a]	Physical Data[a]
Tl[V(CO)$_6$]	pale yellow	A,[12 b]	IR
Me$_2$Tl[V(CO)$_6$]	yellow	A[12]	IR
Ph$_2$Tl[V(CO)$_6$]	yellow	A[12]	IR
[(η^5-Ph$_2$CHC$_5$H$_4$)(CO)$_3$Cr]Tl	orange	A[88]	IR, NMR
[η^5-C$_5$H$_5$(CO)$_3$Cr]Tl	orange	A[14]	IR[14, 103] MS[103]
[η^5-C$_5$H$_5$(CO)$_3$Cr]$_3$Tl	deep red	A[14]	IR[14, 103] MS[103]
[η^5-C$_5$H$_5$(CO)$_3$Mo]Tl	yellow	A[14, 15]	IR
[η^5-C$_5$H$_5$(CO)$_3$Mo]TlMe$_2$	red brown	D[32]	IR, NMR, MS
[η^5-C$_5$H$_5$(CO)$_3$Mo]$_3$Tl	deep red–green	A[14, 15] B,[14] E(iii)[40]	IR,[14, 15] NMR,[15, 40] X-ray
[η^5-C$_5$H$_5$(CO)$_2$(Ph$_3$P)Mo]$_3$Tl	red	E(iii)[41, c]	
[η^5-C$_5$H$_5$(CO)$_3$W]Tl	yellow	A[14, 15, 90]	IR[14, 15]
[η^5-C$_5$H$_5$(CO)$_3$W]TlMe$_2$		D[32]	NMR
[η^5-C$_5$H$_5$(CO)$_3$W]$_3$Tl	deep red–green	A[14, 15]	IR[14, 15] NMR[15]
[η^5-C$_5$H$_5$(CO)$_3$W]Tl[Co(CO)$_4$]$_2$	deep red	B, C(ii)[14]	IR
Tl[Mn(CO)$_5$][d]	yellow	D[14]	IR
Ph$_2$Tl[Mn(CO)$_5$]	yellow	A[20]	IR
ClTl[Mn(CO)$_5$]$_2$	yellow	A[20]	IR
Tl[Mn(CO)$_5$]$_3$	dark red–black	A,[11] B,[14] D,[28] E(iv)[42–44]	IR,[11, 14] FIR, MS[11]
Tl[Fe(CO)$_3$NO]	yellow	A[93, 94]	
Tl[Fe(CO)$_4$CH$_2$CN]		A[94]	
Tl[Fe(CO)$_4$COPh]		A[94]	
Tl[Fe(CO$_4$SnPh$_3$]		A[94]	
[η^5-C$_5$H$_5$(CO)$_2$Fe]$_2$TlCl	scarlet	A[18]	IR
[η^5-C$_5$H$_5$(CO)$_2$Fe]$_2$Tl$^+$		e	
[η^5-C$_5$H$_5$(CO)$_2$Fe]$_3$Tl[d]	red	A, E(iv)[14]	IR
Tl[Co(CO)$_4$]	yellow	A, B, C(i),[14, 87] C(ii),[14] E(ii)[37]	IR,[14] X-ray[87]
Tl[Co(CO)$_3$PPh$_3$][d]		A[14]	IR
Tl[Co(CO)$_3$P(OPh)$_3$]		f, g	
Tl[Co(CO)$_3$P(p-OC$_6$H$_4$Cl)$_3$]		f, g	
[Ph$_3$PCH$_2$Ph] {Tl[Co(CO)$_4$]$_2$}	black	E(i)[87]	IR
Tl[Co(CO)$_4$]$_3$	dark red	A,[10] B,[10, 14, 87] E(ii)[37]	IR[10, 14]
Tl[Co(CO)$_3$PPh$_3$]$_3$	dark red	E(iv)[14, f, h]	IR
Tl[Co(CO)$_3$PBu^n$_3$]$_3$		E(iv)[94]	
Tl[Co(CO)$_3$siphos]$_3$	dark red	E(iv),[100 f, i]	IR, NMR
Tl[Co(CO)$_3$P(OMe)$_3$]$_3$		E(iv)[94]	
Tl[Co(CO)$_3$P(OEt)$_3$]$_3$		E(iv)[94]	
Tl[Co(CO)$_3$AsPh$_3$]$_3$		E(iv)[94]	
Tl[Co(CO)$_3$SbPh$_3$]$_3$		E(iv)[94]	
Ph$_3$POTl[Co(CO)$_4$]$_3$[d]		E(i)[79]	IR
[Ph$_4$As] {Tl[Co(CO)$_4$]$_4$}	black	E(i)[83]	IR, FIR
Me$_2$Tl[Co(dmgH)$_2$py]	deep yellow	A[101]	IR
Ph$_2$Tl[Co(dmgH)$_2$py]	deep yellow	A[101]	IR
Br(C$_6$F$_5$)TlPt(C$_6$F$_5$)Br$_2$(PPh$_3$)$_2$		j	

[a]See footnotes of Table I. [b]See text and ref. 79. [c]Not isolated pure. [d]Not isolated; infrared evidence only. [e]See text and ref. 19. [f]Prepared by carbonyl substitution. [g]See text and ref. 94. [h]See text and ref. 99. [i]See text and ref. 100. [j]See text and ref. 102.

[η^5-C$_5$H$_5$(CO)$_3$M]Tl (M = Cr, Mo, or W), dispro-portionate slowly at room temperature and more rapidly when warmed yielding the corresponding thallium(III) derivatives along with metallic thallium.[14, 15]

The dark red–green dichroic thallium(III) complexes [η^5-C$_5$H$_5$(CO)$_3$M]$_3$Tl (M = Cr, Mo, or W) have been prepared from the metathetical reaction between [η^5-C$_5$H$_5$(CO)$_3$M]Na and TlCl$_3$ in tetrahydrofuran[14] or TlCl$_3 \cdot$4H$_2$O in water.[15] The less pure molybdenum complexes [η^5-C$_5$H$_5$(CO)$_2$LMo]$_3$Tl (L = CO[40] and PPh$_3$[41]) have also been obtained from oxidative elimination reactions between C$_5$H$_5$Tl and L$_3$Mo(CO)$_3$. The

large number of peaks appearing in the $\nu(CO)$ region of their infrared spectra suggests considerable lowering of symmetry from the idealized C_{3h} or C_{3v} structure.[14, 15] The crystal structure of the complex $[\eta^5\text{-}C_5H_5(CO)_3Mo]_3Tl$ contains a trigonal pyramidally coordinated thallium atom which is 58.6 pm out of the plane of the three molybdenum atoms, with an average Mo–Tl bond distance of 296.5 ± 0.3 pm.[89] In chloroform solution, the appearance of additional peaks in the NMR spectrum of this complex has been attributed to reductive elimination of the type:[40]

$$[\eta^5\text{-}C_5H_5(CO)_3Mo]_3Tl \rightleftharpoons [\eta^5\text{-}C_5H_5Mo(CO)_3]_2 + [\eta^5\text{-}C_5H_5(CO)_3Mo]Tl \quad (39)$$
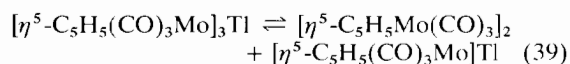
That this is indeed a reversible equilibrium has been proved by the formation of the thallium(III) complex in greater than 80% yield from the insertion reaction [reverse of equation (39)] performed in tetrahydrofuran in the presence of light; no reaction occurred in the dark.

The dimethylthallium(III) derivatives, $[\eta^5\text{-}C_5H_5(CO)_3M]TlMe_2$ (M = Mo or W) have been obtained by protolysis of Me_3Tl with an equimolar amount of $\eta^5\text{-}C_5H_5M(CO)_3H$ at $-78°C$ in dichloromethane [equation (24)]. The mass spectrum of the molybdenum complex shows ions derived from $C_5H_5(CO)_3Mo^+$ and Me_2Tl^+ but lacks Mo–Tl species.[32]

C. Complexes of Group VIIA Metals

The dark red to almost black crystalline complex, $Tl[Mn(CO)_5]_3$, has been prepared by the metathesis between $Na[Mn(CO)_5]$ and anhydrous $TlCl_3$ in tetrahydrofuran [equation (2)],[11] and is also the product of the reaction between $HMn(CO)_5$ and Me_3Tl [equation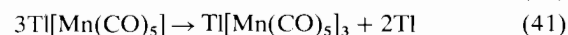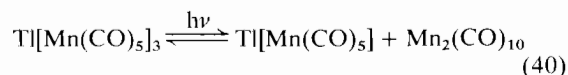 (22)].[28] A more convenient route to the complex is to react $Na[Mn(CO)_5]$ with thallium(I) salts in tetrahydrofuran[44] or in water[42, 43] at room temperature. The latter reaction is believed to involve the un-

stable thallium(I) complex, $Tl[Mn(CO)_5]$, which has been obtained by the protolysis of $[TlOEt]_4$ with $HMn(CO)_5$ at $-78°C$ but proved to be too unstable to be isolated. A tetrahydrofuran solution of this low-valent complex prepared *in situ* is stable at $-65°C$ for several days in the dark and reacts with $Mn_2(CO)_{10}$ and Ph_3SnCl to give respectively, the complexes $Tl[Mn(CO)_5]_3$ and $Ph_3SnMn(CO)_5$.[14]

The trisubstituted complex exhibits thermochromism, dissolves in polar solvents to furnish air-sensitive solutions, and is completely ionized in dimethylformamide generating the $[Mn(CO)_5]^-$ anion. The planar (D_{3h}) arrangement of the $TlMn_3$ moiety has been inferred from its infrared spectrum although the exact configuration of the $Mn(CO)_5$ groups could not be determined. The presence of Mn–Tl bonds in this complex is indicated by the intense far-infrared absorption at 139 cm^{-1} attributable in the main to the $\nu_{as}(TlMn_3)$ mode, and further substantiated by its mass spectrum which contains various metal–metal bonded species including $TlMn_2^+$ and $TlMn^+$.[11]

The photodecomposition of the thallium(III) complex in tetrahydrofuran is of particular interest [*cf.* $\eta^5\text{-}C_5H_5(CO)_3Mo$ derivatives]. This involves a light-promoted reductive elimination followed by a disproportionation reaction:[14]

$$Tl[Mn(CO)_5]_3 \xrightarrow{h\nu} Tl[Mn(CO)_5] + Mn_2(CO)_{10} \quad (40)$$

$$3Tl[Mn(CO)_5] \rightarrow Tl[Mn(CO)_5]_3 + 2Tl \quad (41)$$

The chemical reactivity of $Tl[Mn(CO)_5]_3$ has been investigated in some detail; the corresponding reactions with other transition metal complexes of thallium(III) would be expected to be fairly if not entirely analogous.

The Mn–Tl bonds in $Tl[Mn(CO)_5]_3$ are readily cleaved under mild conditions by halogens, hydrogen halides, and organic halides:

TlX + 3XMn(CO)$_5$

TlI + 2MeMn(CO)$_5$ + IMn(CO)$_5$ X$_2$ (X = Br or I)   TlCl$_3$ + 3ClMn(CO)$_5$

CCl$_4$

2MeI   excess Cl$_2$ MeCN

Tl[Mn(CO)$_5$]$_3$

RCOCl (R = Me or Ph)   3HX (X = Cl or I)

2BrC$_2$H$_4$Br

TlCl + 2RCOMn(CO)$_5$ + ClMn(CO)$_5$ TlX + H$_2$ + HMn(CO)$_5$ + 2XMn(CO)$_5$

TlBr + C$_2$H$_4$ + 3BrMn(CO)$_5$
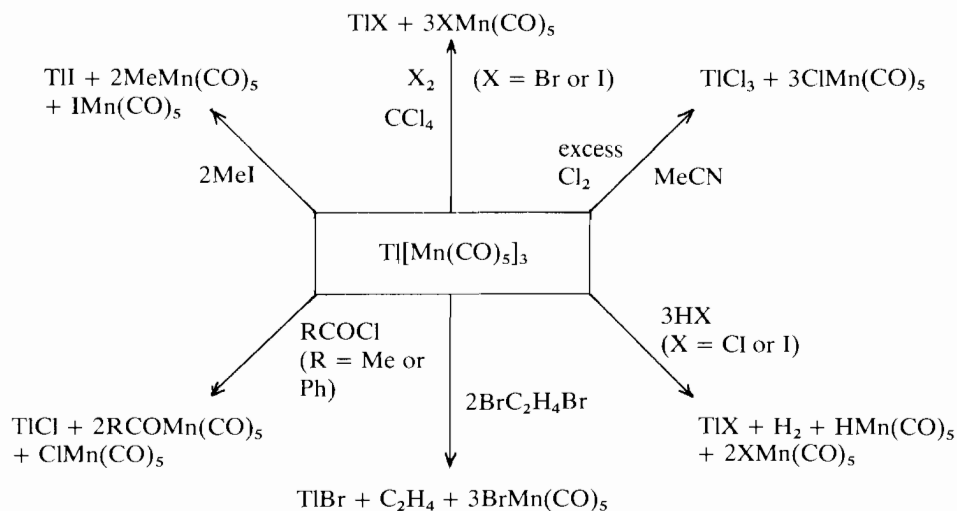
It does not form stable adducts with triphenylphosphine or pyridine;[11] this is consistent with the fact that the Lewis acidity of the tervalent Group IIIB metal diminishes with increasing atomic number.

It undergoes transmetallation reactions with a variety of substrates and is therefore a versatile synthetic intermediate. Thus, it reacts with other main group metals:[11, 12]

$$nTl[Mn(CO)_5]_3 + 3M' \rightarrow 3M'[Mn(CO)_5]_n + nTl \tag{42}$$
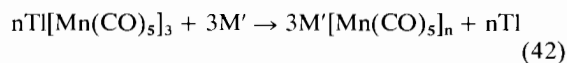
(M' = Zn, Cd, Hg, Se, or Te; n = 2; M' = Ga, In, or Bi; n = 3) and with low-valent metal halides:[12]

$$Tl[Mn(CO)_5]_3 + M'X_n \rightarrow X_{n-1}M'[Mn(CO)_5]_3 + TlX \tag{43}$$
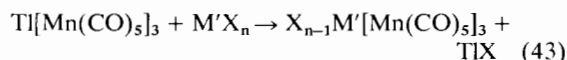
(M' = Ga or In, X = Cl or Br, n = 1; M' = Ge or Sn, X = Cl or Br, n = 2; M' = Sb, X = Cl, n = 3).

The reaction of $Na[Mn(CO)_5]$ with various organothallium(III) halides has been studied. While Ph_2TlCl gives the expected complex $Ph_2Tl[Mn(CO)_5]$, $PhTlCl_2$ affords $ClTl[Mn(CO)_5]_2$ under similar reaction conditions. The by-products in these reactions are, *inter alia*, Ph_2TlCl and the complex $Tl[Mn(CO)_5]_3$, which is also the sole metal–metal bonded product in the reaction of $Na[Mn(CO)_5]$ with R_2TlCl (R = Me or Pr).[20]

D. Complexes of Group VIII Metals
(i) The iron subgroup
Acidification of an aqueous methanol mixture containing $Fe(CO)_5$ or $[HFe(CO)_4]^-$ and Tl_2CO_3 or Tl_2O_3 in hydrochloric acid furnishes an extremely air-sensitive, red-brown crystalline solid which has been formulated as $Tl_2Fe_3(CO)_{12}$ on the basis of its elemental analysis.[91] Unlike $Fe_3(CO)_{12}$, this polymetallic complex has no bridging carbonyl group as evident from its infrared spectrum; otherwise its structure is unknown. Slow aerial oxidation gives a high yield of $Fe_3(CO)_{12}$.[12]

Treatment of TlOAc with $[\eta^5\text{-}C_5H_5(CO)_2Fe]Na$ in a methanol–tetrahydrofuran mixture yields, along with a deposition of thallium metal, a deep red solution believed to contain the complex, $[\eta^5\text{-}C_5H_5(CO)_2Fe]_3Tl$,[14] the infrared spectrum of which is similar to that of the isoelectronic anionic mercury complex, $[Bu^n_4N]\{[\eta^5\text{-}C_5H_5(CO)_2Fe]_3Hg\}$.[92] Metathesis between $TlCl_3$ and $[\eta^5\text{-}C_5H_5(CO)_2Fe]Na$ furnishes a similar red solution containing some $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. Attempts to isolate $[\eta^5\text{-}C_5H_5(CO)_2Fe]_3Tl$ from either of these solutions have been unsuccessful. This is not at all surprising in view of the plausible decomposition route analogous to that of $Tl[Mn(CO)_5]_3$ [equations (40) and (41)] in which a cyclic process begins by the reductive elimination of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ followed by the rapid disproportionation of the thallium(I) complex $[\eta^5\text{-}C_5H_5(CO)_2Fe]Tl$ to $[\eta^5\text{-}C_5H_5(CO)_2Fe]_3Tl$ and thallium metal.[14]

If the metathesis between $TlCl_3$ and $[\eta^5\text{-}C_5H_5(CO)_2Fe]Na$ is performed in a 1:2 molar ratio, a red solution is also obtained from which an impure scarlet powder can be isolated; its analytical data approximate to the formulation $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2TlCl$.[18] The cation $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2Tl^+$ has been briefly mentioned.[19]

The complex $Tl[Fe(CO)_3NO]$, first reported by Hieber and coworkers,[93] has been prepared from the reaction of a soluble thallium(I) salt with the anion $[Fe(CO)_3NO]^-$ in water[93] or in a tetrahydrofuran–water mixture.[94] This synthetic route has also been employed in the synthesis of the complexes $Tl[Fe(CO)_4R]$ (R = CH_2CN, COPh, and $SnPh_3$).[94]

Treatment of the complex, $K_2[Fe(CN)_2(C:CPh)_3NO]$ with Ph_2TlBr in liquid ammonia results in the formation of the complex, $K[Ph_2Tl][Fe(CN)_2(C:CPh)_3NO]\cdot NH_3$,[95] which shows little or no evidence for it being metal–metal bonded.

(ii) The cobalt subgroup
Perhaps the most stable of the thallium(I) derivatives of transition metal carbonyl is the complex, $Tl[Co(CO)_4]$, which was first synthesized by direct carbonylation of a mixture of cobalt and thallium metal in 1:1 atomic ratio.[37] The yellow, very air-sensitive complex has also been obtained from the metathetical reaction between $TlNO_3$ and $Na[Co(CO)_4]$ in water[14] or a tetrahydrofuran–water mixture,[87] from the interaction of thallium metal with $Hg[Co(CO)_4]_2$ in tetrahydrofuran[14, 87] or with $Co_2(CO)_8$ in tetrahydrofuran[14] or toluene,[81, 87] and from the redistribution reaction between $Tl[Co(CO)_4]_3$ and metallic thallium in dichloromethane.[14] The unusual stability of $Tl[Co(CO)_4]$ towards disproportionation is reflected in the last reaction.

The crystal structure of $Tl[Co(CO)_4]$ consists of discrete Tl^+ and $[Co(CO)_4]^-$ ions arranged in a NaCl-like lattice with three interpenetrating chains of alternate Tl^+ and $[Co(CO)_4]^-$. Both the cation and the anion are in six-fold coordination.[87] The nature of this complex in solution is more complicated and has been examined by infrared spectroscopy. In toluene or dichloromethane solution, the presence of a characteristic three-band pattern ($2a_1$ + e in C_{3v} symmetry) occurring at higher wave-numbers than that of the free $[Co(CO)_4]^-$ ion, is indicative of a charge transfer from the cobalt to the thallium atom through a covalent metal–metal bond. Ionization occurs in water generating the anion $[Co(CO)_4]^-$ which is also the predominant species in its methanol or acetonitrile solution.[14] Infrared band contour analysis has demonstrated that the vibration of the anion occurs in a number of different sites. While only a single site (*i.e.* ion-pair formation) is formed in dimethylformamide, dimethyl-sulphoxide, and dichloromethane, several including

two-site interactions (*e.g.* triple ions) with tight cation–anion association, are found in the tetrahydrofuran, acetonitrile, and nitromethane solutions. Unlike Na[Co(CO)$_4$] which has close Na$\cdots$O association in solution, a weak Co–Tl bond results from the close proximity of the two metal atoms in Tl[Co(CO)$_4$] in the latter solutions.[96]

The reactions of Tl[Co(CO)$_4$] resemble those of Na[Co(CO)$_4$] in many respects. Thus, the metal–metal bonded complexes, Hg[Co(CO)$_4$]$_2$, In[Co(CO)$_4$]$_3$, (OC)$_4$CoMn(CO)$_5$, and MeCCo$_3$(CO)$_9$ can be readily obtained from the reaction of Tl[Co(CO)$_4$] with respectively, Hg(CN)$_2$ in water, InCl$_3$ in tetrahydrofuran, BrMn(CO)$_5$ in dichloromethane, and MeCCl$_3$ in tetrahydrofuran.[81] Although the Co–Sn bonded complex Ph$_3$SnCo(CO)$_4$ is the product of its reaction with Ph$_3$SnCl in tetrahydrofuran, toluene,[14] or benzene,[81] the silicon analogue could not be isolated in any significant yield from Ph$_3$SiCl.[14] With [Ph$_3$PCH$_2$Ph][Co(CO)$_4$], it forms a black, air-sensitive 1:1 adduct which readily dissociates in solution:[87]

$$Tl[Co(CO)_4]_2^- \rightleftharpoons Tl[Co(CO)_4] + [Co(CO)_4]^- \quad (44)$$
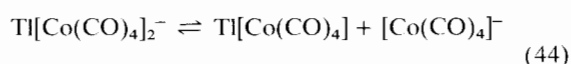
The instability of this adduct is similar to that of [TlX$_2$]$^-$ (X = halogen)[97] and of {Tl[Co(CN)$_5$]$_2$}$^{5-}$.[98]

The reaction of Tl[Co(CO)$_4$] with PPh$_3$ is solvent dependent; whereas no reaction occurs in dimethyl-sulphoxide, the thallium(III) complex, Tl[Co(CO)$_3$PPh$_3$]$_3$·2CH$_2$Cl$_2$ and metallic thallium are the isolable products from the dichloromethane solution.[87, 94] The substituted thallium(I) complexes, Tl[Co(CO)$_3$L] [L = P(OPh)$_3$ or P(*p*-OC$_6$H$_4$Cl)$_3$], have been prepared by direct carbonyl substitution with the corresponding phosphine ligand in dichloromethane, while other Lewis bases such as PBu$^n_3$, P(OMe)$_3$, P(OEt)$_3$, AsPh$_3$, and SbPh$_3$ afford thallium(III) derivatives.[94] There is infrared evidence for the formation of the unstable thallium(I) complex, Tl[Co(CO)$_3$PPh$_3$], in a tetrahydrofuran–methanol solution containing an equimolar quantity of TlOAc and Na[Co(CO)$_3$PPh$_3$]. The mixture slowly deposits thallium metal leaving a solution of Tl[Co(CO)$_3$PPh$_3$]$_3$; a similar aqueous mixture instantly generates the thallium(III) complex,[14] which has previously been obtained by a direct carbonyl substitution reaction with Tl[Co(CO)$_4$]$_3$.[99] The related tris(trimethylsilylmethyl)phosphine derivative, Tl[Co(CO)$_3$siphos]$_3$, has also been similarly prepared.[100]

In marked contrast to the insertion reaction of Tl[Co(CO)$_4$] with Co$_2$(CO)$_8$ giving Tl[Co(CO)$_4$]$_3$,[10, 14, 87] there is no indication of an analogous reaction with [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$,[14, 87] Mn$_2$(CO)$_{10}$, or [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$.[87]

The unsubstituted parent complex, Tl[Co(CO)$_4$]$_3$, has also been prepared by the metathetical reaction between TlCl$_3$ and Na[Co(CO)$_4$] in tetrahydrofuran,[10] and by direct carbonylation of a mixture of cobalt and

thallium metal [equation (25)].[37] Unlike the substitution reactions mentioned above, it forms a black crystalline 1:1 adduct with [Co(CO)$_4$]$^-$,[83] and a weak Ph$_3$PO adduct formulated on the basis of its infrared spectrum.[94] The reactions of Tl[Co(CO)$_4$]$_3$ with low-valent metal halides such as SnCl$_2$ are entirely analogous to those of Tl[Mn(CO)$_5$]$_3$ described above. Of particular interest is the reaction with [Rh(CO)$_2$Cl]$_2$:[12]

$$2Tl[Co(CO)_4]_3 + [Rh(CO)_2Cl]_2 \xrightarrow{\text{hexane}}$$
$$RhCo_3(CO)_{12} + 4CO + 2TlCl \quad (45)$$
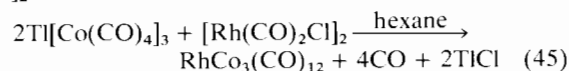
which may be extended to other cobalt-containing polynuclear carbonyl complexes.

The organothallium(III) derivatives, R$_2$Tl[Co(dmgH)$_2$py] (R = Me or Ph) have been obtained as insoluble yellow solids by treating the cobaloxime anion, [Co(dmgH)$_2$py]$^-$, with the corresponding R$_2$TlX (X = Cl or I).[101]

(iii) The nickel subgroup

The reaction of (Ph$_3$P)$_2$PtCl$_2$ with (C$_6$F$_5$)$_2$TlBr leads to the formation of a highly coloured compound which yields (Ph$_3$P)$_2$Pt(C$_6$F$_5$)Br$_3$ with bromine and, on reduction with hydrazine, affords the platinum(II) complex (Ph$_3$P)$_2$Pt(C$_6$F$_5$)Br. These reactions together with molecular weight and conductivity measurement are thought to be consistent with the structure (XIV).[102]

(XIV)

Acknowledgement

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