Pentacarbonylmanganese Complexes of Indium

By **A. T. T. Hsieh** and **M. J. Mays,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The preparation of $In[Mn(CO)_5]_3$, $XIn[Mn(CO)_5]_2$, and $X_2InMn(CO)_5$ (X = Cl or Br) is described and their i.r. and mass spectra are discussed. The In–Mn bonds are readily cleaved by halogens and hydrogen halides to form $XIn[Mn(CO)_5]_2$, $X_2InMn(CO)_5$, or InX_3 depending on the stoicheiometry of the reactants. In acetone or methanol solution the complexes $XIn[Mn(CO)_5]_2$ and $X_2InMn(CO)_5$ undergo redistribution reactions to give $In[Mn(CO)_5]_3$ and InX_3. In acetonitrile solution, however, all the complexes $X_{3-n}In[Mn(CO)_5]_n$ ionise to give the cation $[(MeCN)_2InMn_2(CO)_{10}]^+$ which has been isolated as its perchlorate salt. The interaction of halide ions with the indium complexes gives anionic halide derivatives such as $R_4N^+\{X_{4-n}In[Mn(CO)_5]_n\}^-$ (n = 1—3; R = Me, X = Cl; R = Et, X = Br) which also ionise in acetonitrile to yield the cation $[(MeCN)_2InMn_2(CO)_{10}]^+$.

WE have described the preparation, properties, and some reactions of the complex $Tl[Mn(CO)_5]_3$.[1] One of these reactions was the metal-exchange of this complex with metallic indium in tetrahydrofuran (THF) solution to give $In[Mn(CO)_5]_3$ and, for comparative purposes, we have now investigated the preparation, properties, and reactions of this latter complex in some detail. In the course of this work a number of other new cationic, neutral, and anionic complexes containing indium–manganese bonds have been prepared. Only two complexes, $BrIn[Mn(CO)_5]_2$ and $(acac)In[Mn(CO)_5]_2$,[2] containing indium–manganese bonds have been previously reported, although a number of complexes containing indium bound to other transition metals are known. These include the air-sensitive $In[Co(CO)_4]_3$,[3-6] $Br[InCo(CO)_4]_2,THF$,[4,5] $(acac)In[Co(CO)_4]_2$,[5] the polynuclear $Br_3In_3Co_4(CO)_{15}$,[4,5,7,8] and adducts such as $(Ph_3P)_2NCo(CO)_4InBr_3$,[9] and $[Bu_4N][C_5H_5(CO)_3WInPh_3]$.[10]

RESULTS AND DISCUSSION

Tris(pentacarbonylmanganese)indium.— Tris(pentacarbonylmanganese)thallium in THF solution exchanges readily with metallic indium at room temperature to give the corresponding indium complex in high yield.[1]

$$Tl[Mn(CO)_5]_3 + In \longrightarrow In[Mn(CO)_5]_3 + Tl \qquad (1)$$

It has been shown previously that the position of equilibrium in metal-exchange reactions involving Group IIB metals depends critically on the solvent, and that polar solvents favour the formation of zinc and cadmium complexes while non-polar solvents favour mercury complexes. It is thus often possible to reverse such reactions by changing the solvent.[11] For reaction (1), however, the equilibrium lies far to the right whether polar or non-polar solvents are used.

Tris(pentacarbonylmanganese)indium can also be prepared by metathesis between anhydrous indium(III) halides and sodium pentacarbonylmanganate(1—) either in THF or in aqueous solution. $In[Mn(CO)_5]_3$ is insoluble in water and precipitates out immediately if this solvent is used for the reaction.

$$InX_3 + 3NaMn(CO)_5 \longrightarrow In[Mn(CO)_5]_3 + 3NaX \qquad (2)$$

The solid complex is reasonably air-stable for short periods but deteriorates rapidly in solution. It may be obtained as orange crystals by slow sublimation at 120°, 0·001 mmHg. In contrast, the corresponding

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[1] A. T. T. Hsieh and M. J. Mays, *J. Organometallic Chem.*, 1970, **22**, 29.

[2] J. Hoyano, D. J. Patmore, and W. A. G. Graham, *Inorg. Nuclear Chem., Letters* 1968, **4**, 201.

[3] W. Hieber and U. Teller, *Z. anorg. Chem.*, 1942, **249**, 43.

[4] D. J. Patmore and W. A. G. Graham, *Chem. Comm.*, 1965, 591.

[5] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1586.

[6] G. N. Schrauzer, B. N. Bastein, and G. A. Fosselius, *J. Amer. Chem. Soc.*, 1966, **88**, 4890.

[7] P. D. Cradwick, W. A. G. Graham, D. Hall, and D. J. Patmore, *Chem. Comm.*, 1968, 872.

[8] P. D. Cradwick and D. Hall, *J. Organometallic Chem.*, 1970, **22**, 203.

[9] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1499.

[10] J. M. Burlitch and R. B. Petersen, *J. Organometallic Chem.*, 1970, **24**, C65.

[11] J. M. Burlitch and A. Ferrari, *Inorg. Chem.*, 1970, **9**, 563.

thallium complex decomposes to decacarbonyldimanganese and thallium metal on attempted sublimation.[1]

$In[Mn(CO)_5]_3$ is moderately soluble in polar solvents such as THF or dioxan but reacts slowly with halogenated solvents such as dichloromethane or chloroform to give pentacarbonylmanganese halides.

Although the molecular ion $InMn_3(CO)_{15}^+$ is absent in the mass spectrum of the complex, ions containing the $InMn_3$ system such as $InMn_3(CO)_n^+$ (n = 0—10) are observed, along with the abundant series $InMn_2(CO)_n^+$ (n = 0—10) and $InMn(CO)_n^+$ (n = 0—5). Ions such as $Mn_2(CO)_n^+$ (n = 0—10) and $Mn(CO)_n^+$ (n = 0—5) are also present but are of relatively low intensity.

TABLE 1

Infrared spectra of the complexes in the carbonyl stretching region

Complex	Phase	ν(C–O) (cm⁻¹)
$In[Mn(CO)_5]_3$	$CHCl_3$	2094w, 2068m, 1994vs, 1927mw
	CH_2Cl_2	2094w, 2071ms, 1992vs, 1929m
	THF	2090vw, 2082w,sh, 2064m,sh, 2056ms, 2045mw,sh, 1972vvs,br
	MeCN	2089w, 2061mw, 1988vs, 1960m,sh, 1899w, 1862m
$ClIn[Mn(CO)_5]_2$	$CHCl_3$	2097w, 2069m, 1996vs, 1931mw,sh
	THF	2091w, 2081w,sh, 2066m, 1976vs,br
	MeCN	2089w, 2060mw, 1987vs, 1960m,sh
$BrIn[Mn(CO)_5]_2$	$CHCl_3$	2096mw, 2069ms, 1999vs,br
	THF	2088w,sh, 2060s, 2002vs, 1930m,sh,br
	MeCN	2090w, 2061ms, 1986vs, 1961m,sh
$Cl_2InMn(CO)_5$	$CHCl_3$	2100w, 2069m, 2004vs
	THF	2090mw, 2061ms, 1973vvs,br
	MeCN	2089w, 2060mw, 1987vs, 1960m,sh
$Br_2InMn(CO)_5$	$CHCl_3$	2098m, 2070s, 2004vs,br
	THF	2088w, 2061ms, 1998vs, 1940m,sh,vbr
	MeCN	2090w, 2062ms, 1986vs, 1962m,sh
$[(MeCN)_2InMn_2(CO)_{10}][ClO_4]$	$CHCl_3$	*a*
	MeCN	2090w, 2060ms, 1988vs, 1960m,sh
$[Me_4N][ClInMn_3(CO)_{15}]$	THF	2085w, 2057s, *ca.* 1970vvs,br
	MeCN	2090w, 2060ms, 1987vs, 1960m,sh, 1897mw, 1859m
$[Et_4N][BrInMn_3(CO)_{15}]$	THF	2085w, 2059s, 2049ms,sh, *ca.* 1970vvs,br
	MeCN	2090w, 2062ms, 1988vs, 1962ms,sh, 1901ms, 1863s
$[Me_4N][Cl_2InMn_2(CO)_{10}]$	THF	2086w, 2058s, *ca.* 1970vvs,br
	MeCN	2089w, 2060s, 1986vs, 1960ms,sh
$[Et_4N][Br_2InMn_2(CO)_{10}]$	THF	2086w, 2059s, *ca.* 1969vvs,br
	MeCN	2090w, 2061s, 1988vs, 1962ms,sh
$[Et_4N]_2[Br_2InMn_2(CO)_{10}]$	THF	2087mw, 2059s, *ca.* 1972vvs,br
	MeCN	2090w, 2062s, 1988vs, 1962ms,sh
$[Me_4N][Cl_3InMn(CO)_5]$	THF	2087w, 2059ms, *ca.* 1969vs,br
	MeCN	2090w, 2061m, 1990vs, 1962ms,sh
$[Et_4N][Br_3InMn(CO)_5]$	THF	*b*
	MeCN	2089w, 2061ms, 1989vs, 1962m,sh
$(oxine)In[Mn(CO)_5]_2$	THF	2089w,br, 2065s, 2027mw,sh, 1974vs,br, 1931w,sh
	MeCN	2083w,br, 2052m, 2022w,sh, 1978vs, 1952w,sh, 1930w,sh

[a] Insoluble. [b] Insufficiently soluble.

The i.r. spectrum of $In[Mn(CO)_5]_3$ in THF, dichloromethane, or chloroform solution (Table 1) exhibits a total of five peaks in the carbonyl stretching region and is consistent with a trigonal planar arrangement of the manganese atoms around indium (*cf.* $Tl[Mn(CO)_5]_3$ [1]). In dimethylformamide (DMF), these peaks collapse into shoulders of low intensity and medium to strong absorptions at *ca.* 1900 and 1860 cm^{-1} appear. These low-frequency bands may be assigned to those of the anion,[12] $Mn(CO)_5^-$, formed by ionic dissociation. Such ionisation in DMF solution has been previously observed for other complexes containing transition metals bonded to Group IIB or IVB metals [13] or to thallium.[1]

Halogenobis(pentacarbonylmanganese)indium and Dihalogeno(pentacarbonylmanganese)indium.— Indium(III) halides react with sodium pentacarbonylmanganate in 1 : 2 or 1 : 1 molar ratio to give respectively the complexes $XIn[Mn(CO)_5]_2$ or $X_2InMn(CO)_5$ (X = Cl or Br):

$$InX_3 + 2NaMn(CO)_5 \longrightarrow XIn[Mn(CO)_5]_2 + 2NaX \quad (3)$$

$$InX_3 + NaMn(CO)_5 \longrightarrow X_2InMn(CO)_5 + NaX \quad (4)$$

An alternative and equally satisfactory route to these two complexes is *via* the insertion of the appropriate indium(I) halide into either the Mn–Mn bond of decacarbonyldimanganese [2,14] or the Mn–X bond of $XMn(CO)_5$ (X = Cl or Br).[14]

Analytical data on samples of $XIn[Mn(CO)_5]_2$ and $X_2InMn(CO)_5$ prepared by the first of these two routes and precipitated by evaporation of centrifuged THF solutions, show the presence of 1 mol of sodium halide per mol equivalent of complex. This is presumably due to the respective formation of the anionic complexes $Na\{X_2In[Mn(CO)_5]_2\}$ and $Na[X_3InMn(CO)_5]$ (*vide infra*). Repeated precipitation of these from saturated THF solution by addition of water results in gradual, but eventually complete, loss of the sodium halide.

The complexes $XIn[Mn(CO)_5]_2$ and $X_2InMn(CO)_5$ are pale to bright yellow and are reasonably stable over

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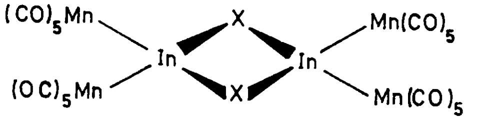
[12] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1962, **1**, 933.

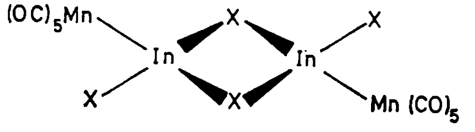
[13] J. M. Burlitch, *J. Amer. Chem. Soc.*, 1969, **91**, 4562.

[14] A. T. T. Hsieh and M. J. Mays, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 223.

long periods to air and light. They could not be sublimed at 160°, 0·001 mmHg indicating that they are associated to some extent in the solid state and structures such as (I) and (II) seem the most likely. Similar structures have previously been postulated for the related cobalt complexes, *e.g.* $BrIn[Co(CO)_4]_2$[4,5] is thought to have a structure analogous to (I).



(I)



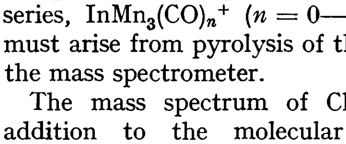
(II)

The mass spectrum of $ClIn[Mn(CO)_5]_2$ shows the ions $ClInMn_2(CO)_n^+$ (n = 0—5) formed by loss of carbonyl groups from the barely observed molecular ion, $ClInMn_2(CO)_{10}^+$. The absence of species containing two indium atoms suggests that the complex is monomeric in the gas phase. The four series of ions $InMn_2(CO)_n^+$ (n = 0—10), $ClInMn(CO)_n^+$ (n = 0—5), $InMn(CO)_n^+$ (n = 0—5), and $Mn(CO)_n^+$ (n = 0—5) are, as expected, also present in the spectrum but the presence of a further series, $InMn_3(CO)_n^+$ (n = 0—10), is less expected and must arise from pyrolysis of the sample on the probe of the mass spectrometer.

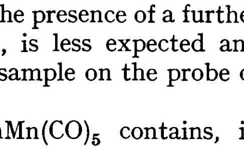
The mass spectrum of $Cl_2InMn(CO)_5$ contains, in addition to the molecular ion, such species as $Cl_4In_2Mn_2(CO)_n^+$ (n = 5 and 8) and $Cl_2In_2(CO)_n^+$ (n = 0, 3, and 7). This lends some support to the suggestion that the complex is dimeric in the solid state although it does not exclude the possibility of its being in a higher state of aggregation. Also present in the spectrum are the ions $M(CO)_n^+$, $InMn(CO)_n^+$, and $ClInMn(CO)_n^+$ (n = 0—5) and traces of $Mn_2(CO)_n^+$ (n = 0—5).

Both $ClIn[Mn(CO)_5]_2$ and $Cl_2InMn(CO)_5$ are, like $In[Mn(CO)_5]_3$, soluble in polar solvents and are unaffected by water. They are, however, slowly attacked by halogenated solvents such as dichloromethane.

The complexes are very soluble and indefinitely stable, in cyclic ethers such as THF or 1,4-dioxan and it is difficult to remove the last traces of these solvents from them, suggesting that adducts such as (III) and (IV) may



(III)



(IV)

be formed. We were, however, unable to isolate these adducts as solids although a THF adduct of $BrIn[Co(CO)_4]_2$ analogous to (IV) has been previously described.[5] In other polar solvents such as acetone or methanol slow redistribution reactions occur and the mixed complexes are converted into $In[Mn(CO)_5]_3$, indium(III) halides being precipitated from solution. These reactions can be reversed by dissolving the disproportionation products in THF and reprecipitating with water as described above. Despite the ease with which they disproportionate in some solvents, the fact that the complexes can be repeatedly recrystallised from THF solution in this way without any change in stoicheiometry suggests that the solid complexes $XInMn_2(CO)_{10}$ and $X_2InMn(CO)_5$ are discrete species. Confirmatory evidence that this is so comes from *X*-ray powder photography which shows for example that the complexes $In[Mn(CO)_5]_3$, $ClIn[Mn(CO)_5]_2$, and $Cl_2InMn(CO)_5$ each have entirely different powder patterns, and that the latter two species are not therefore merely mixtures of $In[Mn(CO)_5]_3$ and $InCl_3$ in different proportions.

Reactions of Tris(pentacarbonylmanganese)indium with Halogens and Hydrogen Halides.—The In–Mn bonds of $In[Mn(CO)_5]_3$ are cleaved by halogens to give the expected pentacarbonylmanganese halides. The other product depends upon the quantity of the halogen added, as represented by the equations:

$$In[Mn(CO)_5]_3 + 3X_2 \longrightarrow InX_3 + 3XMn(CO)_5 \qquad (7)$$

$$In[Mn(CO)_5]_3 + 2X_2 \longrightarrow X_2InMn(CO)_5 + 2XMn(CO)_5 \qquad (8)$$

$$In[Mn(CO)_5]_3 + X_2 \longrightarrow XIn[Mn(CO)_5]_2 + XMn(CO)_5]_2 \qquad (9)$$

(X = Cl or Br)

In each case, the pentacarbonylmanganese halide may be separated by vacuum sublimation.

Hydrogen halides behave similarly towards the In–Mn bonds of $In[Mn(CO)_5]_3$ forming one to three mol of hydridopentacarbonylmanganese according to the amount of the hydrogen halide present. It is noteworthy that these reactions differ considerably from those undergone by $Tl[Mn(CO)_5]_3$.[1]

Anomalous Behaviour of the Complexes $X_{3-n}In[Mn(CO)_5]_n$ (X = Cl *and* Br; n = 1—3) *in Acetonitrile.*—In DMF, the complexes $X_{3-n}In[Mn(CO)_5]_n$ (X = Cl and Br; n = 1—3) are extensively ionised to give the pentacarbonylmanganate anion, $Mn(CO)_5^-$ and no other carbonyl containing species (*vide supra*). In acetonitrile, however, all these complexes show similar and, within experimental error, superimposable i.r. spectra in the terminal carbonyl stretching region (Figure) which are not due to the $Mn(CO)_5^-$ anion.[15] In the case of $In[Mn(CO)_5]_3$, two additional peaks are observed at *ca.* 1900 and 1860 cm^{-1} which may be attributed to this anion. These strikingly similar spectra (Table 1) suggest that partial ionisation of the complexes occurs in acetonitrile and that the following equilibria are established:

$$In[Mn(CO)_5]_3 \rightleftharpoons In[Mn(CO)_5]_2^+ + Mn(CO)_5^- \qquad (10)$$

$$XIn[Mn(CO)_5]_2 \rightleftharpoons In[Mn(CO)_5]_2^+ + X^- \qquad (11)$$

$$2X_2InMn(CO)_5 \rightleftharpoons In[Mn(CO)_5]_2^+ + InX_4^- \qquad (12)$$

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[15] A. T. T. Hsieh and M. J. Mays, *Chem. Comm.*, 1971, 1234.

In accordance with these, the cation $In[Mn(CO)_5]_2^+$ has been isolated as an acetonitrile adduct, $[(MeCN)_2InMn_2(CO)_{10}]^+$, by treating the complexes $XIn[Mn(CO)_5]_2$ ($X = Cl$ or Br) with silver perchlorate:

$$XIn[Mn(CO)_5]_2 + AgClO_4 \xrightarrow{MeCN} [(MeCN)_2InMn_2(CO)_{10}]^+ClO_4^- + AgX \quad (13)$$

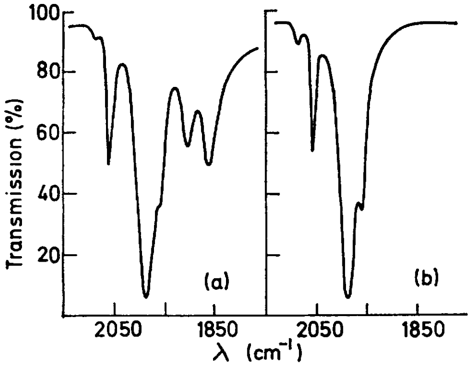
and also as a product of the metathetical reaction (14).

$$2X_2InMn(CO)_5 + Me_4N^+ClO_4^- \xrightarrow{MeCN} [(MeCN)_2InMn_2(CO)_{10}]^+ClO_4^- + Me_4N^+InX_4^- \quad (14)$$

However, attempts to isolate the cation by treating $In[Mn(CO)_5]_3$ with perchloric or hexafluorophosphoric acid according to reaction (15) was unsuccessful although

$$In[Mn(CO)_5]_3 + HClO_4 \xrightarrow{H_2O} In[Mn(CO)_5]_2^+ClO_4^- + HMn(CO)_5 \quad (15)$$

some hydridopentacarbonylmanganese was produced in the reaction.



I.r. spectrum of (a) $In[Mn(CO)_5]_3$ in acetonitrile solution; (b) (i) $ClIn[Mn(CO)_5]_2$, (ii) $Cl_2InMn(CO)_5$, or (iii) $(MeCN)_2In[Mn(CO)_5]_2^+$ in acetonitrile solution

Since the complex $[(MeCN)_2InMn_2(CO)_{10}]^+ClO_4^-$ in acetonitrile solution shows an i.r. spectrum in the carbonyl stretching region identical with that of any of the complexes $X_{3-n}In[Mn(CO)_5]_n$ ($X = Cl$ or Br) it is clear that all of these complexes give rise to the same cation in this solvent. The similarity between the i.r. spectrum of the cation and those of $L_2Cd[M(CO)_5]_2$ ($M = Mn$ [16] or Re [17]; L = amines) indicates that it probably possesses an analogous C_{2v} structure.

The above results show that not only does the extent of ionisation of metal–metal bonded complexes in solution depend upon the particular solvent employed [13] but that the mode of ionisation may also change. Any explanation in thermodynamic terms of this phenomenon is clearly difficult without a more detailed study of this and related reactions. However, the formation of a relatively stable acetonitrile adduct is certainly one important factor which favours the production of $In[Mn(CO)_5]_2^+$ in this solvent.

Addition of pyridine or 1,10-phenanthroline to $[(MeCN)_2InMn_2(CO)_{10}]^+ClO_4^-$ yields the crystalline adducts, $[(py)_2InMn_2(CO)_{10}]^+ClO_4^-$ and $[(phen)_2InMn_2(CO)_{10}]^+ClO_4^-$. The former is isoelectronic and probably isostructural with the cadmium complex $(py)_2Cd[Mn(CO)_5]_2$, while the latter may well contain a six-co-ordinate indium atom.

The extent and mode of ionisation of the complexes $X_{3-n}In[Mn(CO)_5]_n$ in polar solvents other than acetonitrile is less certain. $In[Mn(CO)_5]_3$ shows no peaks attributable to the $Mn(CO)_5^-$ ion in either THF or chloroform solution and ionisation as in (10) clearly does not take place to any significant extent. The spectra of $XIn[Mn(CO)_5]_2$ and $X_2InMn(CO)_5$ in these solvents are closely similar (but not identical) to those of $In[Mn(CO)_5]_3$, suggesting either that they disproportionate extensively to give this species, or that the CO stretching frequencies are remarkably insensitive to changes in the other ligands on indium.

Interaction of Halide Ions with $X_{3-n}In[Mn(CO)_5]_n$ ($X = Cl$ *and* Br; $n = 1$—3).—Tetra-alkylammonium halides react with $In[Mn(CO)_5]_3$ in methanol to form orange to bright yellow crystalline 1 : 1 adducts which may be formulated as $R_4N^+[XInMn_3(CO)_{15}]^-$ ($X = Cl$, $R = Me$; $X = Br$, $R = Et$). Similarly, addition of tetra-alkylammonium halides to the complexes $XIn[Mn(CO)_5]_2$ and $X_2InMn(CO)_5$ leads respectively to the formation of the bright yellow $R_4N^+[X_2InMn_2(CO)_{10}]^-$ and the pale yellow $R_4N^+[X_3InMn(CO)_5]^-$. For $BrIn[Mn(CO)_5]_2$ it was also possible to obtain a 2 : 1 adduct, $[Et_4N]_2^+[Br_3InMn_2(CO)_{10}]^-$. Other 2 : 1 adducts are possibly formed in solution but could not be isolated as crystalline solids.

The formulation of the 1 : 1 adducts as anionic complexes is supported by a crystal-structure determination on the closely related cobalt complex, $Et_4N^+[Br_2InCo_2(CO)_8]^-$, which reveals an essentially tetrahedral geometry about the indium atom, although the bond angles show considerable distortion from the ideal value of 109°.[18] Other anionic complexes containing indium–transition metal bonds which have been reported in the literature include $[(Ph_3P)_2N]_2^+[Fe(CO)_4InBr_3]^{2-}$,[9] $[(Ph_3P)_2N]^+[Fe(CO)_4InBr_2]^-$,[9] $[(Ph_3P)_2N]^+[Co(CO)_4InBr_3]^-$,[9] $In[Co(CO)_4]_4^-$,[19,20] and $Bu_4N^+[C_5H_5(CO)_3WInPh_3]^-$.[10]

The adducts described here are all relatively air-stable crystalline solids, insoluble in and unaffected by water. Their i.r. spectra in the carbonyl stretching region in acetonitrile and in THF solution are given in Table 1. Solid-state spectra in Nujol mulls were again very poorly resolved and are not recorded. In acetonitrile solution, the spectra are identical to those of the parent compounds $X_{3-n}In[Mn(CO)_5]_n$ indicating that the cation

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[16] A. T. T. Hsieh and M. J. Mays, *J. Chem. Soc.* (*A*), 1971, 729.

[17] A. T. T. Hsieh and M. J. Mays, *J. Chem. Soc.* (*A*), 1971, 2648.

[18] P. D. Cradwick, *J. Organometallic Chem.*, 1971, **27**, 151.

[19] J. M. Burlitch, R. B. Petersen, H. L. Conder, and W. R. Robinson, *J. Amer. Chem. Soc.*, 1970, **92**, 1783.

[20] W. R. Robinson and D. P. Schussler, *J. Organometallic Chem.*, 1971, **30**, C5.

$In[Mn(CO)_5]_2^+$ is once again formed, presumably as a result of ionisation schemes such as the following:

$$R_4N^+[XInMn_3(CO)_{15}]^- \rightleftharpoons In[Mn(CO)_5]_2^+ + Mn(CO)_5^- + R_4N^+ + X^- \quad (16)$$

$$R_4N^+[X_2InMn_2(CO)_{10}]^- \rightleftharpoons In[Mn(CO)_5]_2^+ + R_4N^+ + 2X^- \quad (17)$$

$$2R_4N^+[X_3InMn(CO)_5]^- \rightleftharpoons In[Mn(CO)_5]_2^+ + 2R_4N^+ + InX_6^{3-} \quad (18)$$

In THF solution the spectra of the adducts are also very similar to those of the parent complexes suggesting that reactions such as (19) may take place:

$$Et_4N^+[ClInMn_3(CO)_5]^- \rightleftharpoons Et_4N^+Cl^- + In[Mn(CO)_5]_3 \quad (19)$$

However there are some differences between the various spectra in THF solution and other equilibria may also be important.

Other Reactions of the Complexes $XIn[Mn(CO)_5]_2$ ($X = Cl$ *or* Br).—The reaction of thallium(I) acetylacetonate with the complex $BrIn[Mn(CO)_5]_2$ to yield the yellow crystalline complex $(acac)In[Mn(CO)_5]_2$ has previously been described.[2] The same product can be obtained by treating the complexes $XIn[Mn(CO)_5]_2$ ($X = Cl$ and Br) with sodium acetylacetonate or acetylacetone in the presence of a base.

TABLE 2

Analytical data

Complex	Colour	Found (%)				Calculated (%)			
		C	H	N	X	C	H	N	X
$In[Mn(CO)_5]_3$	Orange yellow	26·0				25·7			
$ClIn[Mn(CO)_5]_2$	Yellow	22·4			6·8	22·2			6·6
$Cl_2InMn(CO)_5$	Light yellow	15·5			19·0	15·8			18·6
$BrIn[Mn(CO)_5]_2$	Yellow	20·5			13·7	20·5			13·7
$Br_2InMn(CO)_5$	Lemon yellow	13·1			32·8	12·8			34·0
$[(MeCN)_2InMn_2(CO)_{10}][ClO_4]$	Colourless	24·7	0·9	4·2	5·0	24·5	0·9	4·1	5·2
$[(py)_2InMn_2(CO)_{10}][ClO_4]$	Colourless	31·0	1·5	3·7	4·1	31·5	1·3	3·7	4·7
$[(phen)_2InMn_2(CO)_{10}][ClO_4]$	Colourless	41·9	1·6	6·0	3·9	42·3	1·7	5·8	3·7
$[Me_4N][ClInMn_3(CO)_{15}]$	Bright yellow	28·3	1·6	1·8	4·2	28·2	1·5	1·7	4·4
$[Et_4N][BrInMn_3(CO)_{15}]$	Orange	30·8	2·1	1·8	8·6	30·3	2·2	1·5	8·8
$[Me_4N][Cl_2InMn_2(CO)_{10}]$	Yellow	25·8	1·9	2·5	10·0	25·8	1·9	2·2	10·9
$[Et_4N][Br_2InMn_2(CO)_{10}]$	Lemon yellow	27·3	2·8	2·2	19·7	27·2	2·5	1·8	20·1
$[Et_4N]_2[Br_3InMn_2(CO)_{10}]$	Yellow	30·9	4·1	2·7	24·5	31·1	4·0	2·8	23·9
$[Me_4N][Cl_3InMn(CO)_5]$	Pale yellow	22·4	2·5	2·8	21·0	22·0	2·5	2·9	21·7
$[Et_4N][Br_3InMn(CO)_5]$	Pale yellow	23·1	3·0	2·1	34·0	23·0	2·9	2·1	35·3
$(oxine)In[Mn(CO)_5]_2$	Bright yellow	35·1	1·3	2·1		35·1	0·9	2·2	

The bright yellow crystalline complex, $(oxine)In[Mn(CO)_5]_2$, may be prepared from the reaction of $XIn[Mn(CO)_5]_2$ ($X = Cl$ or Br) with an excess of 8-hydroxyquinoline. Its i.r. spectrum in the carbonyl stretching region (Table 1) is consistent with a C_s structure containing a tetrahedrally co-ordinated indium atom. There is no evidence from the i.r. spectrum that this complex is ionised in acetonitrile solution in the same way as are the halide complexes.

EXPERIMENTAL

All manipulations were performed under an atmosphere of dry nitrogen and solvents were dried and degassed before use.

I.r. spectra of the complexes in the carbonyl stretching region (2150—1800 cm^{-1}) were recorded on a Perkin-Elmer 257 grating spectrophotometer on ×2½ or ×10 scale expansion with a precision of ± 2 cm^{-1}. The spectra were taken in appropriate solvents using a pair of balanced NaCl (1·0 mm) or CaF_2 (0·5 mm) solution cells and calibrated against carbon monoxide.

Mass spectra were obtained on an A.E.I. MS9 or MS12 spectrometer and the details of the spectra will be described elsewhere.[21]

Analytical data for the new complexes are summarised in Table 2.

Preparation of Tris(pentacarbonylmanganese)indium.—(a) *In tetrahydrofuran.* A mixture of anhydrous $InCl_3$ (1·47 g, 6·65 mmol) and $NaMn(CO)_5$, prepared from $Mn_2(CO)_{10}$ (3·90 g, 10·0 mmol) by sodium amalgam reduction (15 ml, 1—2%) in THF (50 ml), was stirred at room temperature for 20 min. The deep yellow solution was filtered and evaporated *in vacuo*. The remaining crude product (*ca.* 95% yield) was purified either by recrystallisation from acetone–water or by slow sublimation at 120°, 0·001 mmHg.

(b) *In water.* An aqueous solution of $InCl_3,3H_2O$ (1·83 g, 6·65 mmol) was added to the solid $NaMn(CO)_5$, prepared as above from $Mn_2(CO)_{10}$ (3·90 g, 10·0 mmol). The yellow precipitate was centrifuged, washed well with water, and dried *in vacuo* over phosphoric oxide. The crude product, obtained in almost quantitative yield, was purified as described in (a).

Halogenobis(pentacarbonylmanganese)indium.—A mixture of anhydrous $InCl_3$ (1·55 g, 7·0 mmol) and $NaMn(CO)_5$, prepared by sodium amalgam (12 ml, 1—2%) reduction of $Mn_2(CO)_{10}$ (2·73 g, 7·0 mmol) in THF (45 ml), was stirred at room temperature for ½ h. The centrifuged solution was evaporated *in vacuo* leaving the complex, $ClIn[Mn(CO)_5]_2,NaCl$ as a yellow powder in 98% yield (Found: C, 20·3; 20·1; Cl, 12·1, 11·8. Calc. for $C_{10}Cl_2InMn_2NaO_{10}$: C, 20·05; Cl, 11·8%). The solid was then washed well with water and recrystallised from a mixture of THF–water. This complex could not be sublimed up to 160°, 0·001 mmHg.

The bromo-derivative was similarly prepared.

Dihalogeno(pentacarbonylmanganese)indium.—A mixture of anhydrous $InBr_3$ (1·77 g, 5·0 mmol) and $NaMn(CO)_5$, prepared from $Mn_2(CO)_{10}$ (0·98 g, 2·51 mmol) by sodium

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[21] A. T. T. Hsieh, to be published.

amalgam (8 ml, 1—2%) reduction in THF (30 ml), was vigorously stirred for ½ h at room temperature. The light yellow solution was evaporated *in vacuo* leaving the pale yellow complex, $Br_2InMn(CO)_5,NaBr$ in 98% yield (Found: C, 11·6; Br, 43·9. Calc. for $C_5Br_3InMnNaO_5$: C, 11·35; Br, 45·4%). Repeated washing with water or reprecipitating with water from a saturated THF solution gave the pure product as a pale yellow powder.

The chloro-complex was similarly prepared.

Reaction of Tris(pentacarbonylmanganese)indium with Halogens.—(a) *With chlorine*. An excess of chlorine gas was condensed (−196°) into an ampoule containing 231·0 mg (0·33 mmol) of $In[Mn(CO)_5]_3$ in $CHCl_3$ (5 ml). The reaction mixture was allowed to warm to room temperature and, after 5 min, the mixture was fractionated to give chlorine (1·00 mmol consumed), $CHCl_3$ (*ca.* 5 ml) and a yellow solid. Extraction of this residue with CH_2Cl_2 gave a yellow solution of $ClMn(CO)_5$ (identified by its i.r. spectrum), leaving a white powder of $InCl_3$ (identified by analysis).

The reaction of chlorine gas with $In[Mn(CO)_5]_3$ in 1 : 1 or 2 : 1 molar ratio was similarly performed and, in each case, the complex $ClMn(CO)_5$ was separated respectively from $ClIn[Mn(CO)_5]_2$ or $Cl_2InMn(CO)_5$ by sublimation at 50—65°, 0·001 mmHg. All the products were identified spectroscopically.

(b) *With bromine*. A solution of bromine in CCl_4 (50·0 ml; 0·0468M) was added dropwise to a vigorously stirred suspension of $In[Mn(CO)_5]_3$ (546 mg, 0·78 mmol) in the same solvent (10 ml). After 15 min, the solvent was removed under reduced pressure and extraction of the residue gave a yellow solution of the complex $BrMn(CO)_5$ (identified by its i.r. spectrum) leaving an off-white solid which analysed as $InBr_3$.

The reaction of bromine with $In[Mn(CO)_5]_3$ in 1 : 1 or 2 : 1 molar ratio was entirely analogous and the separation of the complex $BrMn(CO)_5$ respectively from $Br_2InMn(CO)_5$ and $BrIn[Mn(CO)_5]_2$ was effected by sublimation at 50—60°, 0·001 mmHg. All complexes were characterised by analysis and i.r. spectra.

Reaction of Tris(pentacarbonylmanganese)indium with Hydrogen Halides.—An excess of hydrogen chloride was condensed (−196°) into an ampoule containing 384 mg (0·55 mmol) of $In[Mn(CO)_5]_3$ and diethyl ether (10 ml). After 5—10 min at room temperature, the mixture was fractionated to give traces of a non-condensable gas (presumably hydrogen), hydrogen chloride (1·62 mmol consumed), diethyl ether (*ca.* 10 ml), $HMn(CO)_5$ (1·32 mmol, 80% yield) and a residual very pale yellow solid. After being washed with light petroleum (b.p. 30—40°), the remaining white solid was identified as $InCl_3$ by analysis.

The reaction of $In[Mn(CO)_5]_3$ with hydrogen chloride in 1 : 1 or 1 : 2 molar ratio was similarly carried out. The reaction of the complex with hydrogen bromide in 1 : 1, 1 : 2, 1 : 3, or excess was entirely analogous. All the products were identified spectroscopically.

Preparation of the Complexes $[(MeCN)_2InMn_2(CO)_{10}]^+ClO_4^-$.—(a) *From* $XIn[Mn(CO)_5]_2$ (X = Cl *or* Br). A saturated solution of $AgClO_4$ (414·6 mg, 2·0 mmol) in acetonitrile was added to $XIn[Mn(CO)_5]_2$ (X = Cl or Br; 2·0 mmol) in the same solvent. The greyish white precipitate of AgCl was centrifuged off leaving a very pale yellow solution which, when concentrated under a stream of nitrogen and cooled to −20°, deposited colourless prisms of the complex, $[(MeCN)_2InMn_2(CO)_{10}]^+ClO_4^-$, in 85% yield.

(b) *From* $X_2InMn(CO)_5$ (X = Cl *or* Br). A mixture of $Me_4N^+ClO_4^-$ (649·8 mg, 3·75 mmol) and $X_2InMn(CO)_5$ (X = Cl or Br; 3·75 mmol) in acetonitrile (50 ml) was vigorously agitated for ½ h. The resulting pale yellow solution was concentrated *in vacuo* to *ca.* 15 ml and the precipitated $Me_4N^+InCl_4^-$ was removed by centrifugation. On concentrating the solution further and cooling it to −20°, the crystalline product was obtained in 72% yield.

Preparation of the Adducts $[L_2InMn_2(CO)_{10}]^+ClO_4^-$ (L = *py and phen*).—An excess of the ligand was added either by itself (L = py) or as a saturated acetonitrile solution (L = phen) to the complex, $[(MeCN)_2InMn_2(CO)_{10}]^+ClO_4^-$, prepared *in situ* as described in the preceding section. The centrifuged solution was concentrated under a stream of nitrogen followed by cooling to −20°. The air-sensitive, colourless crystalline product (75—90%) deposited overnight was filtered off, washed once with a mixture of acetonitrile (1 ml) and light petroleum (b.p. 30—40°; 9 ml), and dried *in vacuo.*

Reaction of the Complexes $X_{3-n}In[Mn(CO)_5]_n$ (X = Cl *or* Br; n = 1—3) *with Tetra-alkylammonium Halides*.—A saturated solution of $R_4N^+X^-$ (X = Cl, R = Me; X = Br, R = Et; 1·5 mmol) in methanol was added to a solution of the complex $X_{3-n}In[Mn(CO)_5]_n$ (X = Cl or Br; n = 1, 2, or 3; 1·5 mmol) in the same solvent. The centrifuged solution was evaporated to a small volume followed by cooling to 0°. The crystalline product was filtered off, washed once with light petroleum (b.p. 30—40°, 5 ml) and dried *in vacuo*. Yield 85%.

Reactions of the complexes $X_{3-n}In[Mn(CO)_5]_n$ (X = Cl or Br; n = 1, 2, or 3) with $R_4N^+X^-$ in 2 : 1 or other molar ratio were entirely analogous.

Preparation of Acetylacetonatobis(pentacarbonylmanganese)-indium.—The complex $XIn[Mn(CO)_5]_2$ (X = Cl or Br; 1·75 mmol) in methanol was shaken vigorously with Na(acac) (220 mg, 1·80 mmol) for 15 min. The centrifuged yellow solution was then concentrated to give the microcrystalline product in 78% yield. Its i.r. spectrum is identical to that reported previously.[6]

Preparation of 8-Hydroxyquinolinatobis(pentacarbonylmanganese)indium.—A methanolic solution of 8-hydroxyquinoline (651 mg, 4·50 mmol) was added to the complex $XIn[Mn(CO)_5]_2$ (X = Cl or Br; 2·15 mmol) in the same solvent. On concentrating the filtered solution followed by cooling to −20°, the crystalline complex (oxine)-$In[Mn(CO)_5]_2$ was obtained in 64% yield.

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