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THE PREPARATION AND SOME REACTIONS OF TRIS(PENTACARBONYLMANGANESE)THALLIUM(III)

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SUMMARY

The new complex $Tl[Mn(CO)_5]_3$ is described and its reactions with certain metals, halogens, hydrogen halides, organic halides and Lewis bases are reported.

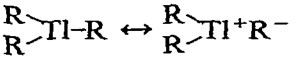
INTRODUCTION

Many complexes containing a transition metal bonded to metals of Groups IIB and IVB are known and the chemical reactivity of such complexes is currently receiving a good deal of attention[1,2]. In contrast, only a few complexes involving Group IIIB metals have been prepared and their chemical properties are almost unknown. Indeed for thallium the only complexes which have been prepared and are thought to contain thallium–transition metal bonds are $Tl_2Fe_3(CO)_{12}$[3] and $Tl[Co(CO)_4]_3$[4,5]. Other complexes such as $TlCo(CO)_4$[4] and $Tl[(C_5H_4CHPh_2)Cr(CO)_3]$[6] have also been reported but the existence of metal–metal bonds in these compounds appears rather doubtful.

In this paper we report the new complex tris(pentacarbonylmanganese)thallium(III) which we have prepared as a dark red crystalline material. It is very air-sensitive but, at least thermally, is probably the most stable complex containing a thallium–transition metal bond which has yet been reported. We have therefore carried out a number of reactions with this complex in order to provide a basis for a comparison of its properties with related complexes containing metals of Groups IIB or IVB such as mercury or tin.

RESULTS AND DISCUSSION

The complex was prepared by reacting anhydrous thallium(III) chloride with sodium pentacarbonylmanganate(−I) in dry tetrahydrofuran (THF) at room temperature. An alternative and equally satisfactory route is via the reaction of hydridopentacarbonylmanganese and trimethylthallium[7]. The complex is readily soluble in polar solvents such as THF or acetonitrile and these solutions are stable for long periods at room temperature in the absence of oxygen, but decompose rapidly on exposure to air. The complex is insoluble in, and is unaffected by, either water or alcohols at room temperature in contrast to the corresponding cobalt complex which disproportionates in these solvents giving the tetracarbonylcobaltate(−I) anion[8]. Both in the solid state and in solution, the complex undergoes thermochromic changes and tends to become a much lighter red colour on cooling. These changes have been observed for many other thallium compounds and it has been suggested that a charge transfer of the following type is involved[9]:



$$R_2Tl{-}R \leftrightarrow R_2Tl^+R^-$$

There is some evidence (*vide infra*) that tris(pentacarbonylmanganese)thallium is at least partially ionised in solution and it is likely that such ionisation would lead to the formation of the bis(pentacarbonylmanganese)thallium(III) cation, isoelectronic with the known bis(pentacarbonylmanganese)mercury. Attempts to precipitate this cation from solution with large anions, however, have failed although it is the most abundant ion in the mass spectrum of tris(pentacarbonylmanganese)thallium [in which the molecular ion, $TlMn_3(CO)_{15}^+$, is also observed]. This may reflect the relatively high stability of the cation in the vapour phase. The complex is decomposed completely on heating to 170–180° for an hour *in vacuo* giving a quantitative yield of dimanganese decacarbonyl and thallium metal.

The solution infrared spectrum of tris(pentacarbonylmanganese)thallium (in dichloromethane or acetonitrile) exhibits only three bands in the carbonyl stretching region (Table 1) and one strong band at 139 cm^{-1} [*cf.* 146 cm^{-1} for tris(tetracarbonylcobalt)thallium[8]] which can be assigned as being mainly due to a Tl–Mn stretching mode. This relatively simple spectrum is consistent with the molecule having D_{3h} symmetry with a planar metal-atom skeleton but does not distinguish between the two possible orientations of the $Mn(CO)_5$ groups with respect to the $TlMn_3$ plane (Table 2) for which group theory predicts respectively four or five C–O stretching modes. Attempts to obtain further information by recording the Raman spectrum of the complex were not successful since the sample decomposed rapidly in the He/Ne laser beam.

TABLE 1

INFRARED SPECTRA OF $Tl[Mn(CO)_5]_3$ IN VARIOUS SOLVENTS

Solvent	ν(C–O) (cm^{-1})				
CH_2Cl_2	2062 vs	2002 vs	1993 s,sh		
CH_3CN	2054 vs	1998 vs	1978 s,sh		
DMF				1889 s,sh	1852 vs

The chemical reactivity of tris(pentacarbonylmanganese)thallium resembles in many ways that of related compounds containing mercury–transition metal bonds. Where significant differences occur they can, in the main, be attributed to one of two factors. These are either (*i*) the presence of Tl^{III} which is much more strongly oxidising than Hg^{II} and often gives rise to a Tl^{I} compound as one of the reaction products, or (*ii*) the greater tendency of the Tl–Mn bond to ionise in polar solvents. The reactions we have carried out are best considered under several main headings as below.

TABLE 2

ACTIVE C–O STRETCHING MODES OF $Tl[Mn(CO)_5]_3$

Symmetry	Infrared	Raman
$D_{3h}{}^a$	A''_2+3E'	$2A'_1+3E'+2E''$
$D_{3h}{}^b$	A''_2+4E'	$3A'_1+4E'+E''$
$C_{3v}{}^c$	$4A_1+5E$	$4A_1+A_2$
$C_{3v}{}^d$	$3A_1+5E$	$3A_1+2A_2$

[a] Taking σ_h as the symmetry plane containing the $Tl[Mn(CO)]_3$ moiety. [b] Taking σ_h as the symmetry plane containing the $Tl[Mn(CO)_3]_3$ moiety. [c] The σ_v planes contain the $TlMn(CO)_3$ moiety. [d] The σ_v planes contain the TlMnCO moiety.

Metal exchange reactions

The ability to undergo metal exchange reactions is a common feature of complexes containing transition metal–main group metal bonds and, for example, bis(tetracarbonylcobalt)cadmium may be readily prepared from bis(tetracarbonylcobalt)mercury and metallic cadmium in hexane at room temperature[10]. Similarly, tris(pentacarbonylmanganese)thallium reacts both with metallic mercury and with metallic indium in THF at room temperature giving respectively bis(pentacarbonylmanganese)mercury and tris(pentacarbonylmanganese)indium together with metallic thallium. Burlitch[11] has recently shown that it is sometimes possible to alter the position of equilibrium in these exchange reactions to a significant degree by carrying them out in different solvents. Thus, while bis(π-cyclopentadienyltricarbonylmolybdenum)cadmium reacts completely with metallic mercury in benzene to give bis(π-cyclopentadienyltricarbonylmolybdenum)mercury and metallic cadmium[12], the reaction may be entirely reversed by use of THF instead of benzene as the solvent[11]. It seems that the cadmium complex, which forms stronger adducts than the mercury complex with Lewis bases such as 1,10-phenanthroline[12], must also be more strongly solvated in polar solvents such as THF and that this favours its formation. This is true also of indium as opposed to thallium complexes, but attempts to prepare tris(pentacarbonylmanganese)thallium from tris(pentacarbonylmanganese)indium and thallium metal were not successful even in non-polar solvents such as benzene. Neither could the complex be prepared from bis(pentacarbonylmanganese)mercury and thallium metal although in this case the barrier may well be kinetic rather than thermodynamic since, due to the different stoicheiometries of the two complexes, a simple bimolecular reaction is not possible.

Reaction with halogens

In the presence of a stoicheiometric quantity of bromine or iodine in carbon tetrachloride solution at room temperature, tris(pentacarbonylmanganese)thallium reacts to give the appropriate pentacarbonylmanganese halide and thallium(I) halide according to the scheme:

$$Tl[Mn(CO)_5]_3+2X_2 \rightarrow TlX+3XMn(CO)_5$$

The reaction with chlorine was carried out in acetonitrile using an excess and gave pentacarbonylmanganese chloride together with thallium(III) chloride.

This ready cleavage of the metal–metal bonds is typical also of complexes containing transition metals bound to mercury and has been reported *e.g.* for Mn–Hg[13], Ir–Hg[14] and Mo–Hg[15,16] bonds. For such complexes, however, it is often possible to isolate intermediate species which still contain transition metal–mercury bonds, such as in the reaction of bis(π-cyclopentadienyltricarbonylmolybdenum)-mercury with iodine in which iodo(π-cyclopentadienyltricarbonylmolybdenum)mercury may be isolated if a deficiency of iodine is used[16]. For thallium, on the other hand, only thallium(I) and pentacarbonylmanganese halides and unreacted complex were recovered when a deficiency of halogen was used. It seems, therefore, that either the remaining Tl–Mn bonds in $XTl[Mn(CO)_5]_2$ are much more reactive towards halogens than the complex itself or that, in contrast to mercury, the disproportionation reaction,

$$2\,XTl[Mn(CO)_5]_2 \rightarrow XMn(CO)_5 + TlX + Tl[Mn(CO)_5]_3$$

is thermodynamically favourable.

Reaction with hydrogen halides

Tris(pentacarbonylmanganese)thallium reacts with hydrogen chloride or iodide in THF according to the scheme:

$$Tl[Mn(CO)_5]_3 + 3\,HX \rightarrow TlX + H_2 + HMn(CO)_5 + 2\,XMn(CO)_5$$

Comparable reactions have not been studied for related mercury or tin complexes. The reaction is different in type, however, from the reactions of tris(trimethylsilyl)-thallium with hydrogen halides which have been studied in detail[9]. Here, the reaction differs according to whether X=Cl or X=I, CN or OMe:

$$Tl(SiMe_3)_3 + 2\,HCl \rightarrow Tl + \tfrac{1}{2}\,H_2 + 2\,ClSiMe_3 + HSiMe_3$$

$$Tl(SiMe_3)_3 + 2\,HI \rightarrow TlI + ISiMe_3 + 2\,HSiMe_3$$

This variation in the mode of reaction of different thallium complexes with different hydrogen halides suggests that the mechanism of the reaction is complex and that several reaction pathways may be possible. For tris(pentacarbonylmanganese)thallium, however, a plausible mechanism is that the Tl–Mn bonds are first cleaved by three moles of hydrogen halides giving thallium(III) halide and hydridopentacarbonylmanganese and that the thallium(III) halide so generated then reacts further with the hydridopentacarbonylmanganese:

$$TlX_3 + 2\,HMn(CO)_5 \rightarrow TlX + H_2 + 2\,XMn(CO)_5$$

We have shown in a separate experiment that this reaction does indeed take place for X=Cl.

Reaction with alkyl and acyl halides

Tris(pentacarbonylmanganese)thallium reacts with alkyl and acyl halides in THF at room temperature giving, respectively, alkyl and acyl manganese complexes together with the appropriate thallium(I) and pentacarbonylmanganese halides:

$$Tl[Mn(CO)_5]_3 + 2\,RX \rightarrow TlX + 2\,RMn(CO)_5 + XMn(CO)_5$$

$$R = Me,\ MeCO\ \text{or}\ PhCO$$

Although we have not studied the mechanism of this reaction in detail, the evidence suggests that the ease of reaction of complexes such as tris(pentacarbonylmanganese)thallium, which are apparently predominantly covalent compounds in in the solid state, may well depend upon their degree of ionisation in solution to furnish pentacarbonylmanganate anion. Burlitch has recently shown that both bis(pentacarbonylmanganese)-cadmium and -mercury are ionised in dimethylformamide (DMF) solution but that the cadmium complex is far more extensively ionised than the mercury complex[11,17]. This parallels the ease of their reaction with methyl iodide since reaction with bis(pentacarbonylmanganese)cadmium to give methylpentacarbonylmanganese and cadmium iodide in THF solution is complete after half an hour whereas reaction with the mercury complex is complete only after a day[18]. In agreement with this hypothesis we find that the thallium complex, for which reaction with methyl iodide is complete after half an hour, is extensively ionised in DMF solution and that bands which may be assigned to the pentacarbonylmanganate anion are by far the strongest peaks in the carbonyl region of the infrared spectrum of tris(pentacarbonylmanganese)thallium in this solvent.

The reaction of the complex with a dihalide, 1,2-dibromoethane, was also carried out. In this case no alkyl derivative was isolated but instead ethylene and a mixture of thallium(I) and pentacarbonylmanganese bromides were identified as the products of a reaction of the following stoicheiometry:

$$\mathrm{Tl[Mn(CO)_5]_3 + 2\ BrCH_2CH_2Br \rightarrow 2\ C_2H_4 + TlBr + 3\ BrMn(CO)_5}$$

This reaction is analogous to that of tris(triethylgermyl)thallium with 1,2-dibromoethane[19,20].

Reaction with Lewis bases

For complexes containing Group IIB–transition metal bonds, the tendency to form Lewis base adducts decreases from zinc to mercury and while several zinc and cadmium complexes form a number of well defined adducts with Lewis bases such as 1,10-phenanthroline and 2,2'-bipyridine, the corresponding mercury complexes do not react with these ligands[12,18]. Metal–metal bonded complexes containing metals of Group IIIB appear, in general, to be more weakly acidic than the related Group IIB complexes and, for example, while bromobis(tetracarbonylcobalt)indium(III) form a weak adduct with THF, no adducts were reported under the same conditions for either tris(tetracarbonylcobalt)-indium(III) or -thallium(III)[5]. Similarly, we find that tris(pentacarbonylmanganese)thallium exhibits virtually no tendency to react with Lewis bases and no adduct formation could be detected in reactions with *e.g.* THF, triphenylphosphine or pyridine at room temperature.

EXPERIMENTAL

General

All manipulations were performed under nitrogen or in a conventional Pyrex vacuum line. Reactions involving volatile materials were carried out in Rotaflo greaseless tap-ampoules.

Infrared spectra in the carbonyl region (2100–1800 cm^{-1}) were recorded on a Perkin–Elmer 257 grating instrument and were calibrated against carbon monoxide. The far-infrared spectrum (400–40 cm^{-1}) of tris(pentacarbonylmanganese)thallium was recorded in a polythene disc on a RIIC FS 720 interferometer with an on-line

FTC-100 Fourier Transform computer.

The mass spectrum of the complex was recorded on an A.E.I. MS9 mass spectrometer with an ionising energy of 70 eV and an ionising current of 100 mA at a source temperature of 140°.

Preparation of tris(pentacarbonylmanganese)thallium

A solution of $TlCl_3$ (3.5 mmoles) in dry THF (10 ml) was added to a vigorously stirred solution of $NaMn(CO)_5$ (10 mmoles) in THF (25 ml). Removal of the solvent *in vacuo* left a brown residue which was extracted with acetone (30 ml) to give a deep red solution. On addition of an equal volume of pentane and cooling to −32°, dark red to black crystals of the product were deposited. Yield 45%. (Found: C, 22.68; Tl, 25.5. $C_{15}Mn_3O_{15}Tl$ calcd.: C, 22.82; Tl, 25.9%.)

Metal exchange reactions

(*a*). *With mercury.* The complex (0.1 mmole) in THF (10 ml) was shaken with 1 ml of mercury at room temperature. After 3 h the deep red solution had lost its colour and, after separation from the metals, the solvent was evaporated to dryness. Extraction of the residue with boiling toluene gave a white powder identified spectroscopically as $Hg[Mn(CO)_5]_2$.

(*b*). *With indium.* The reaction was carried out as above but using excess powdered indium in place of mercury. After stirring 3 h at room temperature, the orange-red solution was decanted from the metals and the solvent was removed *in vacuo* to yield a red residue. Extraction of the residue with CH_2Cl_2 yielded an orange crystalline solid, the IR spectrum of which was identical with that of an authentic sample[8] of $In[Mn(CO)_5]_3$ prepared from $InCl_3$ and $NaMn(CO)_5$.

Reaction with halogens

(*a*). *Chlorine.* A solution of $Tl[Mn(CO)_5]_3$ (0.25 mmole) in acetonitrile (5 ml) was treated with chlorine in excess. The solution changed colour from red to yellow and, after 5 min, the solvent was evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 to give a solution of $ClMn(CO)_5$ (identified spectroscopically) leaving a white solid which, after being washed with pentane and dried, analysed as $TlCl_3$.

(*b*). *Bromine and iodine.* $Tl[Mn(CO)_5]_3$ (0.25 mmole) and iodine (0.5 mmole) in CCl_4 (10 ml) were agitated for $\frac{1}{2}$ h. Centrifugation of the solution gave a pale yellow solution which was identified spectroscopically as $IMn(CO)_5$ and a yellow solid which analysed as TlI.

The reaction with bromine was entirely analogous.

Reaction with hydrogen halides

(*a*). *Hydrogen chloride.* An excess of hydrogen chloride was condensed (−196°) into an ampoule containing 216 mg (0.275 mmole) of $Tl[Mn(CO)_5]_3$ dissolved in 3 ml of THF. The solution was allowed to warm up to room temperature and, after 1 h at room temperature, the pale yellow colour of the solution indicated that reaction was complete. A white precipitate was also present at this stage together with 0.29 mmole of a non-condensable gas (hydrogen). The reaction mixture was fractionated to give hydrogen chloride (0.85 mmole consumed), THF (*ca.* 3 ml) and $HMn(CO)_5$ (0.25 mmole) leaving a yellow residue (184.8 mg) (The calculated weight of a 1/2 mixture of TlCl and $ClMn(CO)_5$ is 192.3 mg). This residue was extracted with CH_2Cl_2 (30 ml) and the soluble portion identified spectroscopically as $ClMn(CO)_5$. The remaining solid was washed with pentane and dried to give a white powder which analysed as TlCl.

(*b*). *Hydrogen iodide.* The reaction with hydrogen iodide was entirely analogous to the reaction with hydrogen chloride. Starting with 102.4 mg (0.13 mmole) of the complex and an excess of hydrogen iodide, the following reaction products were obtained: hydrogen (0.15 mmole), hydrogen iodide (0.40 mmole consumed), $HMn(CO)_5$ (0.11 mmole) and a yellow residue (128.0 mg). (The calculated weight of residue for a 1/2 mixture of TlI and $IMn(CO)_5$ is 126.5 mg). Extraction of the residue with CH_2Cl_2 gave $IMn(CO)_5$ (identified by IR spectroscopy) and a yellow solid which, after washing with pentane, analysed as TlI.

Reaction with organic halides

(*a*). *Methyl iodide.* $Tl[Mn(CO)_5]_3$ (110.5 mg, 0.14 mmole) and an excess of methyl iodide in THF (1 ml) were allowed to react at room temperature in an evacuated ampoule. After $\frac{1}{2}$ h the reaction was complete as judged by the deep yellow colour of the solution and a yellow precipitate had been formed. Fractionation of the volatile reaction products gave 0.24 mmole of $MeMn(CO)_5$ (identified from the IR spectrum of a resublimed sample) and showed that 0.31 mmole of methyl iodide had been consumed. A bright yellow residue (90.0 mg) remained [calculated for a 1/1 mixture of TlI and $IMn(CO)_5$, 91.4 mg] and extraction of this with CH_2Cl_2 (30 ml) left a solid which, after washing with pentane, analysed as TlI. The presence of $IMn(CO)_5$ in the extract was indicated by its IR spectrum.

(*b*). *Other organic halides.* Analogous reactions were carried out using acetyl chloride and benzoyl chloride. In both cases, the corresponding acyl manganese complex was formed together with $ClMn(CO)_5$ and TlCl.

1,2-Dibromoethane reacted to give $BrMn(CO)_5$ (identified spectroscopically), TlBr (by analysis) and ethylene. From a reaction with 0.13 mmole of $Tl[Mn(CO)_5]_3$, 0.25 mmole of ethylene was recovered.

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