Studies in the Chemistry of Bonds Between Metals: Transition-metal Carbonyl Derivatives of Thallium

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Thallium(I) tetracarbonylcobaltate has been prepared by metathesis of Na[Co(CO)$_4$] with thallium(I) salts in water, by metal exchange between Hg[Co(CO)$_4$]$_2$ and thallium metal, by reaction of thallium metal with dicobalt octacarbonyl, and by reduction of Tl[Co(CO)$_4$]$_3$ with thallium metal. Also prepared by metathesis reactions and isolated were the new compounds Tl[M(CO)$_3$(cp)] (M = Cr, Mo, and W; cp = η-cyclopentadienyl). Spectroscopic evidence is presented for the existence of Tl[Co(CO)$_3$PPh$_3$] {*via* Na[Co(CO)$_3$PPh$_3$] and thallium(I) acetate} and of Tl[Mn(CO)$_5$] {from [HMn(CO)$_5$] and thallium(I) ethoxide}. The stability of the thallium(I) compounds toward disproportionation decreases in the order Co(CO)$_4$ $\gg$ M(CO)$_3$(cp) (W > Mo > Cr) > Co(CO)$_3$PPh$_3$ $\simeq$ Mn(CO)$_5$ $\gg$ Fe(CO)$_2$(cp). The corresponding thallium(III) compounds have been characterized, except for Tl[Fe(CO)$_2$(cp)]$_3$ which readily decomposed to [Fe(CO)$_2$(cp)]$_2$ and thallium metal. Some of these, particularly Tl[Mn(CO)$_5$]$_3$, readily undergo light-promoted, reductive elimination to the corresponding thallium(I) compound. The reverse of this process has been demonstrated in some cases.

ALTHOUGH the first metal carbonyl derivative of thallium(I) was reported by Hieber and Teller 30 years ago,[1] there apparently has not been any systematic attempt to synthesize and characterize compounds of this type before the present study. Very few examples of this class of compound, having the general formula TlX [X is a metal carbonyl group, *e.g.* Co(CO)$_4$, Fe(CO)$_2$(cp) (cp = η-cyclopentadienyl), *etc.*], have been described.

Thallium(I) tetracarbonylcobaltate was originally prepared through the reaction of a 1 : 1 mixture of thallium and cobalt metals with carbon monoxide at high pressure.[1] The volatile, air-sensitive product was characterized only by elemental analysis. More recently this compound has been used as a source of [Co(CO)$_4$]$^-$ for synthetic applications.[2] Cooper *et al.*[3] suggested that the product obtained on sodium tetrahydroborate reduction of (diphenylfulvene)chromium tricarbonyl followed by treatment with thallium(I) nitrate was the thallium(I) salt of the anion [(C$_5$H$_4$CHPh$_2$)Cr(CO)$_3$]$^-$. This highly air-sensitive compound was stable under an atmosphere of nitrogen and was characterized by analysis and by ^{1}H n.m.r. and i.r. spectroscopy. While the chemistry of its anionic precursor was compared to that of [(cp)Cr(CO)$_3$]$^-$, little information concerning the chemical properties or structural features of the Tl^I derivative was discussed.

The apparent ease of isolation of the two Tl^I derivatives described above contrasts with the reported instability of thallium(I) tricarbonyl(η-cyclopentadienyl)molybdate; attempts to prepare this compound from either thallium(I) cyclopentadienide and molybdenum hexacarbonyl or from Na[Mo(CO)$_3$(cp)] and thallium(I) sulphate resulted in formation of the corresponding thallium(III) derivative and led King to conclude that Tl[Mo(CO)$_3$(cp)] was unstable to disproportionation.[4] A similar interpretation was invoked by Haupt and Neumann [5] and by Hsieh and Mays [6] to explain the formation of Tl[Mn(CO)$_5$]$_3$ when a thallium(I) salt was treated with Na[Mn(CO)$_5$].

We have studied a series of transition-metal carbonyl derivatives of thallium(I) to explore the questions of stability, mode of bonding, and potential synthetic utility. This paper describes our observations on the TlX systems which may be classified according to their *stability* with respect to disproportionation to TlX$_3$ and Tl^0 as follows: Co(CO)$_4$ $\gg$ M(CO)$_3$(cp) (M = W > Mo > Cr) > Co(CO)$_3$PPh$_3$ $\simeq$ Mn(CO)$_5$ $\gg$ Fe(CO)$_2$(cp). In the course of this work a number of thallium(III) derivatives were prepared, some of which have not been reported previously.

RESULTS AND DISCUSSION

Co(CO)$_4$ *System*.—Thallium(I) tetracarbonylcobaltate, Tl[Co(CO)$_4$], was prepared by several routes as outlined

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[1] W. Hieber and U. Teller, *Z. anorg. Chem.*, 1943, **249**, 48.

[2] S. E. Pedersen, W. R. Robinson, and D. P. Schussler, *J. Organometallic Chem.*, 1972, **43**, C44.

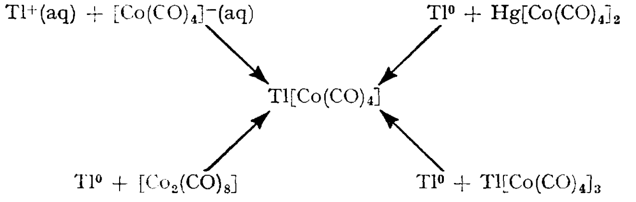
[3] R. L. Cooper, E. O. Fischer, and W. Semmlinger, *J. Organometallic Chem.*, 1967, **9**, 333.

[4] R. B. King, *Inorg. Chem.*, 1970, **9**, 1936.

[5] H.-J. Haupt and F. Neumann, *J. Organometallic Chem.*, 1971, **33**, C56.

[6] A. T. T. Hsieh and M. J. Mays, *J. Organometallic Chem.*, 1972, **38**, 243.

in the Scheme. The principal synthetic method used in this work was the metathesis reaction of Na[Co(CO)$_4$] with a water-soluble thallium(I) salt. Another route employed the reaction of thallium metal



SCHEME

with dicobalt octacarbonyl, also independently observed by Robinson and his co-workers;[2] in tetrahydrofuran (thf) this reaction was complete in 30 min. The reaction of thallium metal with Hg[Co(CO)$_4$]$_2$ was much slower, although i.r. spectroscopic analysis showed that equilibrium (1) lay far to the right and could be only partially reversed by treating Tl[Co(CO)$_4$] with a large excess of mercury.

TABLE 1

Physical properties and analytical data (%)

Compound	Colour	M.p. (t/°C)	Calc. C	Calc. H	Calc. Tl	Calc. M	Found C	Found H	Found Tl	Found M
Tl[Co(CO)$_4$]	Yellow	120—130 (decomp.)	12·8	0·00	54·5	15·7	11·8	0·00	54·5	15·7
Tl[Cr(CO)$_3$(cp)]	Orange	220—230 (decomp.)	23·7	1·25	50·4	12·8	21·6	1·30	51·9	10·5
Tl[Mo(CO)$_3$(cp)]	Yellow	230 (decomp.)	21·4	1·10	45·5	21·3	20·8	1·25	47·0	19·5
Tl[W(CO)$_3$(cp)]	Yellow	275 (decomp.)	17·9	0·95	38·1	34·2	17·7	0·95	38·2	34·0
Tl[Co(CO)$_4$]$_3$	Deep red	72—75	20·1	0·00			20·1	0·00		
Tl[Co(CO)$_3$PPh$_3$]$_3$	Deep red	192—195 (decomp.)	53·2	3·15			52·6	3·40		
Tl[Cr(CO)$_3$(cp)]$_3$	Deep red	205—210 (decomp.)	35·7	1·90			36·1	2·00		
Tl[Mo(CO)$_3$(cp)]$_3$	Deep red	225—230 (decomp.)	30·7	1·60			31·5	1·85		
Tl[W(CO)$_3$(cp)]$_3$	Red	275—285 (decomp.)	23·9	1·25			24·5	1·20		
Tl[Co(CO)$_4$]$_2$[W(CO)$_3$(cp)]	Deep red	74—76	21·8	0·55			22·2	0·60		

TABLE 2

I.r. spectra (cm^{-1}) of thallium(I) compounds in solution

Compound	Solvent	ν(CO)
Tl[Co(CO)$_4$]	Water	1 917vs
	Acetonitrile	2 027w, 1 927s, 1 898vs
	Methanol	2 023w, 1 953w(sh), 1 906vs
	thf	2 031m, 1 985w(sh), 1 944m(sh), 1 930vs
	Diethylether	2 034m, 1 960m, 1 926vs
	Toluene	2 031m, 1 954m, 1 921vs
	Dichloromethane	2 043s, 1 972m, 1 937vs
Tl[Cr(CO)$_3$(cp)]	thf	1 921vs, 1 833s, 1 800vs
Tl[Mo(CO)$_3$(cp)]	thf	1 932vs, 1 840s, 1 812vs
Tl[W(CO)$_3$(cp)]	thf	1 925vs, 1 836s, 1 803vs
Tl[Mn(CO)$_5$] [a]	thf	2 029m, 1 921vs
Tl[Co(CO)$_3$PPh$_3$] [a]	Tetrahydrofuran–Methanol (3 : 2)	1 892vs

[a] Not isolated, but the spectrum was obtained from the reaction mixture.

$$\mathrm{Hg[Co(CO)_4]_2} + 2\mathrm{Tl}^0 \rightleftharpoons 2\mathrm{Tl[Co(CO)_4]} + \mathrm{Hg}^0 \quad (1)$$

The fourth method of synthesis of Tl[Co(CO)$_4$] illustrates the unusual stability of this derivative toward disproportionation. When a solution of Tl[Co(CO)$_4$]$_3$ in dichloromethane was stirred with thallium metal, the conversion to Tl[Co(CO)$_4$] was complete in 1—2 h [equation (2)]. The compound Tl[Co(CO)$_4$] is soluble in a wide variety of organic solvents forming light yellow, highly air-sensitive solutions. In benzene, cryoscopic molecular-weight measurements showed it to be monomeric. Although a parent ion was not observed in the 70 eV mass spectrum, fragment ions corresponding to TlCo(CO)$^+$ and TlCo$^+$ were identified.

$$\mathrm{Tl[Co(CO)_4]_3} + 2\mathrm{Tl}^0 \longrightarrow 3\mathrm{Tl[Co(CO)_4]} \quad (2)$$

The i.r. spectrum of Tl[Co(CO)$_4$] in non-donor solvents contains three principal absorption bands in the carbonyl-stretching region (Table 2). This pattern ($2A_1 + E$) is consistent with the structures (I) and (II) of C_{3v} symmetry. An analysis of the positions of the i.r. absorption bands indicates (I) to be the predominant structure type in solutions of non-polar solvents. All three i.r.-active modes have frequencies higher than that of [Co(CO)$_4$]$^-$ {1 887 cm^{-1} for the F_2 mode of [Co(CO)$_4$]$^-$ from (Ph$_3$P)$_2$N[Co(CO)$_4$] in dichloromethane[7]} indicating that transfer of charge from cobalt to thallium occurs *via* a metal–metal covalent bond. Structure (II) would be expected to give rise to at least one C–O stretching frequency lower than that of [Co(CO)$_4$]$^-$, as indicated by recent structural studies on metal carbonyl anions *O*-co-ordinated to aluminium[8] and magnesium[9] and detailed spectroscopic investigations of

Tl–Co(CO)$_4$ Tl–OC–Co(CO)$_3$
(I) (II)

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[7] J. M. Burlitch and R. B. Petersen, unpublished work.

[8] R. B. Petersen, J. J. Stezowski, C. Wan, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1971, **93**, 3532.

[9] S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1973, **95**, 4469.

$Na[Co(CO)_4]$.[10] The i.r. spectrum of $Tl[Co(CO)_4]$ in water is that of tetrahedral $[Co(CO)_4]^-$. This anion also is the predominant species in acetonitrile and in methanol as indicated by i.r. spectra and molar conductivities of 8×10^3 and 1×10^2 Ω^{-1} cm^2 mol^{-1}, respectively.

When treated with triphenyltin chloride in thf or toluene $Tl[Co(CO)_4]$ produces $Ph_3SnCo(CO)_4$ rapidly and essentially quantitatively. This reaction was independently observed in benzene solution by Robinson and his co-workers.[2] Since $Tl[Co(CO)_4]$ is soluble in a variety of non-polar solvents it was of interest to determine whether it could be used for synthesis of analogous organosilicon derivatives from organosilicon halides, a transformation that is not usually successful with anionic metal carbonyls.[11] Very little reaction was observed with triphenyl- or triethylchlorosilane and $Tl[Co(CO)_4]$ in toluene at room temperature. In somewhat more polar solvents such as dichloromethane or diethyl ether, some thallium(I) halide formed but no evidence for significant amounts of the desired $R_3SiCo(CO)_4$ derivatives was obtained by i.r. analysis.

A more useful reaction of $Tl[Co(CO)_4]$ is that with dicobalt octacarbonyl to form $Tl[Co(CO)_4]_3$ [12] [equation (3)]. In hexane equilibrium (3) lies essentially

$$[Co_2(CO)_8] + Tl[Co(CO)_4] \rightleftharpoons Tl[Co(CO)_4]_3 \quad (3)$$

to the right and pure $Tl[Co(CO)_4]_3$ was isolated in 87% yield from the reaction mixture. In contrast, $[Mo(CO)_3(cp)]_2$ did not react with $Tl[Co(CO)_4]$ in thf. Equilibrium (3) favours the thallium(III) derivatives in many solvents but, curiously, in toluene it lies almost completely to the left as shown by the near identity of i.r. spectra of solutions of 1 : 1 $Tl[Co(CO)_4]$: $[Co_2(CO)_8]$ and of $Tl[Co(CO)_4]_3$ [Figure 1(*b*)]. The apparent stabilization of the thallium(I) species may occur through formation of a π-complex with the aromatic solvent. Two examples of such complexes are known for thallium(I) salts.[13] This possibility suggests that an electron-rich aromatic compound might form a π-complex with $Tl[Co(CO)_4]$ of sufficient stability to permit characterization. The i.r. spectrum of $Tl[Co(CO)_4]_3$ in hexane [Figure 1(*a*)] or in dichloromethane indicates that reductive elimination occurs to a much lesser extent in these solvents.*

(cp)$M(CO)_3$ *Systems* (M = Cr, Mo, *or* W).—The only other thallium(I) derivatives which were isolated in this study were those of the Group VI metals. These were prepared by metathetical reactions of $Na[M(CO)_3(cp)]$ and thallium(I) nitrate or sulphate in water. If the resulting highly air-sensitive, microcrystalline, yellow precipitates were promptly isolated and thoroughly dried, the products were sufficiently stable to be stored under an atmosphere of argon without decomposition for a few days at room temperature, or indefinitely at −65 °C. Of the many solvent systems tried, the only one found suitable for recrystallization of the molybdenum and tungsten derivatives was deaerated, 10% aqueous, sodium hydroxide.† Unlike the behaviour of $Hg[Co(CO)_4]_2$, no reaction was observed when a thf solution of $Hg[Mo(CO)_3(cp)]_2$ was stirred with thallium metal for 3 days at room temperature. That the equilibrium position favours the mercury(II) derivative was shown by rapid formation of $Hg[Mo(CO)_3(cp)]_2$ as the only product when $Tl[Mo(CO)_3(cp)]$ in thf was treated with excess of metallic mercury.

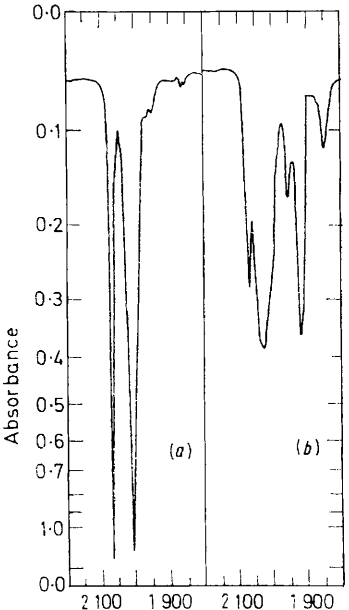

FIGURE 1 I.r. spectra of $Tl[Co(CO)_4]_3$ in hexane (*a*) and toluene (*b*)

All three $Tl[M(CO)_3(cp)]$ compounds were soluble and sufficiently stable in thf under an argon atmosphere to permit i.r. spectra to be obtained. Solutions in less-polar solvents, such as toluene, deteriorated rapidly with precipitation of thallium metal and formation of the corresponding thallium(III) derivative. The mass spectrum of $Tl[W(CO)_3(cp)]$, the most thermally stable member of the series, contained the parent ion in moderate intensity, but complete analysis of the spectrum was precluded by overlapping of polyisotopic

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* *Note added at proof:* A recent *X*-ray crystal-structure determination (D. P. Schussler, W. R. Robinson, and W. F. Edgell, *Inorg. Chem.*, 1974, **13**, 153) shows solid $Tl[Co(CO)_4]$ to consist of Tl^+ and $[Co(CO)_4]^-$ ions. Chemical properties also described for this compound, and conclusions from an unpublished spectroscopic study, are consistent with those reported here.

† King [4] reported substantial decomposition of the precipitate obtained from $Na[Mo(CO)_3(cp)]$ and thallium(I) sulphate in 5% aqueous base and was unable to isolate the thallium(I) derivative.

[10] W. F. Edgell, J. Lyford, IV, A. Barbetta, and C. I. Jose, *J. Amer. Chem. Soc.*, 1971, **93**, 6403; W. F. Edgell and J. Lyford, IV, *ibid.*, p. 6407.

[11] M. D. Curtis, *Inorg. Chem.*, 1972, **11**, 802.

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

[13] T. Avel and E. L. Amma, *J. Amer. Chem. Soc.*, 1968, **90**, 5941.

species (containing two tungsten atoms) presumably formed from thermal decomposition in the source.

I.r. spectra of the Tl[M(CO)$_3$(cp)] compounds in thf solution (Table 2) contain three carbonyl-stretching absorption bands ($2A' + A''$) consistent with C_s symmetry and are similar to spectra of R$_3$M'M(CO)$_3$(cp) (M' = Ge, Sn, or Pb) compounds.[14] All three bands are shifted to higher frequency {relative to those of the [M(CO)$_3$(cp)]$^-$} consistent with the presence of a metal–thallium bond. As with Tl[Co(CO)$_4$], the relatively small increase in frequency compared with that observed in the tin(IV) [14] or mercury(II) [15] covalent derivatives indicates substantial polarity in the metal–metal bond, *i.e.*, $\overset{\delta+}{\mathrm{Tl}}\text{–}\overset{\delta-}{\mathrm{M}}(\mathrm{CO})_3(\mathrm{cp})$.

Table 3

I.r. spectra (cm^{-1}) of thallium(III) compounds in solution

Compound	Solvent	ν(CO)
Tl[Co(CO)$_4$]$_3$	Hexane	2 068s, 2 025m, 2 007s
	Toluene	2 068m, 2 027s, 2 009m(sh), 1 955wm, 1 917s, 1 849wm
	Dichloromethane	2 070vs, 2 052w(sh), 2 041m, 2 006s, 2 025w(sh), 1 931wm, 1 855w
Tl[Cr(CO)$_3$(cp)]$_3$	thf [a]	2 006w, 1 988w, 1 947vs, 1 917vw, 1 895vs
Tl[Mo(CO)$_3$(cp)]$_3$	Toluene	2 000vw, 1 959s, 1 899s
	Dichloromethane [a]	1 994vw(sh), 1 957s, 1 892s, 1888s, 1 867vw(sh)
	thf [a]	2 011vw, 1 993w, 1 955s, 1 891s, 1 886s
Tl[W(CO)$_3$(cp)]$_3$	thf	2 007vw, 1 992w, 1 958vs, 1 893s
Tl[Co(CO)$_3$PPh$_3$]$_3$	thf	1 987m, 1 954s, 1 922w(sh)
Tl[Mn(CO)$_5$]$_3$	thf	2 052s, 1 996s, 1 979m
Tl[Fe(CO)$_2$(cp)]$_3$ [b]	thf	1 985m, 1 956vs, 1 918s
Tl[Co(CO)$_4$]$_2$[W(CO)$_3$(cp)]	thf	2 075m, 2 053s, 2 037m, 1 944vs, 1 975vs, 1 955w(sh), 1 933w(sh), 1 901m, 1 859w

[a] The spectrum was obtained on a Perkin-Elmer model 521 spectrometer with wavelength scale expansion. [b] Not isolated; spectrum is from the reaction mixture.

In thf, [Co$_2$(CO)$_8$] undergoes oxidative addition with Tl[W(CO)$_3$(cp)] to form the mixed-metal complex Tl[Co(CO)$_4$]$_2$[W(CO)$_3$(cp)] which was characterized by elemental analysis and shown by i.r. spectroscopy to be identical to the product of the redistribution reaction of Tl[Co(CO)$_4$]$_3$ and Tl[W(CO)$_3$(cp)]$_3$ in a 2 : 1 mol ratio.

The thallium(III) derivatives Tl[M(CO)$_3$(cp)]$_3$ (M = Cr, Mo, or W) were isolated as very dark red crystals from the reaction of thallium(III) chloride and Na[M(CO)$_3$(cp)] in thf and were characterized by elemental analysis (Table 1). The preparation of Tl[Mo(CO)$_3$(cp)]$_3$ has been reported by King.[4] Its structure, has been determined by single-crystal *X*-ray diffraction methods.[16] I.r. spectra of all three Tl[M(CO)$_3$(cp)]$_3$ compounds are similar (Table 3). The principal features are two or three strong bands, consistent with C_{3v} or C_s local symmetry. The spectrum of Tl[Mo(CO)$_3$(cp)]$_3$ in thf contains a very weak band at 2 011 cm^{-1} attributed to [Mo(CO)$_3$(cp)]$_2$. While this band was absent in spectra of toluene or dichloromethane solutions, irradiation of the thf solution in the cell with visible or u.v. light failed to increase its intensity significantly and did not generate any bands of Tl[Mo(CO)$_3$(cp)]. King has attributed extra peaks in the ^{1}H n.m.r. spectrum of Tl[Mo(CO)$_3$(cp)]$_3$ in chloroform solution to [Mo(CO)$_3$(cp)]$_2$ and Tl[Mo(CO)$_3$(cp)].[4] The indications of the compound [Mo(CO)$_3$(cp)]$_2$ suggested that the reverse reaction might be possible. Thus when [Mo(CO)$_3$(cp)]$_2$ was stirred with a thf solution of Tl[Mo(CO)$_3$(cp)] in the light for 12 h, i.r. analysis of the solution showed that conversion to Tl[Mo(CO)$_3$(cp)]$_3$ was greater than 80% complete. Under comparable conditions of concentration, temperature, and time, no reaction occurred in the dark. These observations point to a light-promoted redox equilibrium in thf that lies well to the side of Tl[Mo(CO)$_3$(cp)]$_3$.

[Co(CO)$_3$PPh$_3$] *System.*—Addition of thallium(I) acetate to a tetrahydrofuran–methanol solution of Na[Co(CO)$_3$PPh$_3$] resulted in formation of an unstable species containing a single carbonyl-stretching absorption band in the i.r. spectrum at 1 893 cm^{-1}. Within a few hours at room temperature a considerable amount of thallium metal had precipitated and the i.r. spectrum contained only the absorption bands characteristic of Tl[Co(CO)$_3$PPh$_3$]$_3$ [17] (Table 3). This thallium(III) derivative precipitated immediately when the metathesis reaction was carried out in water and was the only product isolated from the reaction in tetrahydrofuran–methanol.

The single absorption band in the spectrum of the unstable Tl[Co(CO)$_3$PPh$_3$] indicates axial substitution of thallium and triphenylphosphine. Although two i.r. bands (A_1 and E) are expected for the *trans*-arrangement of C_{3v} symmetry, Patmore and Graham [18] have observed that the A_1 equatorial stretching mode of Br$_3$SnCo(CO)$_3$(PPh$_3$) is very weak in the i.r. spectrum. It is probable that this is also the case with the thallium(I) derivative and is responsible for our failure to observe it.

Mn(CO)$_5$ *System.*—Hsieh and Mays [6] recently reported the preparation of Tl[Mn(CO)$_5$]$_3$ from the reaction

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[14] H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1401.

[15] R. D. Fischer and K. Noack, *J. Organometallic Chem.*, 1969, **16**, 125.

[16] J. Rajaram and J. A. Ibers, *Inorg. Chem.*, 1973, **12**, 1313.

[17] W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1259.

[18] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 771.

of thallium(I) nitrate and sodium pentacarbonylmanganate(—I) in water. A similar reaction, starting from thallium(I) chloride and Na[Mn(CO)$_5$] in thf, has been described by Haupt and Neumann.[5] The thallium(III) product was believed to be formed *via* rapid disproportionation of Tl[Mn(CO)$_5$], although no evidence for this thallium(I) compound was obtained. We have examined this reaction sequence in considerable detail and present evidence for the existence of Tl[Mn(CO)$_5$] and its disproportionation. This study was complicated by the unreported light sensitivity of the compound Tl[Mn(CO)$_5$]$_3$, particularly in thf solution; recrystallization of the crude compound from acetone, following the reported procedure,[6,19] produced substantial quantities of [Mn$_2$(CO)$_{10}$]. With suitable precautions to protect solutions from fluorescent laboratory light, however, pure Tl[Mn(CO)$_5$]$_3$ could be isolated.

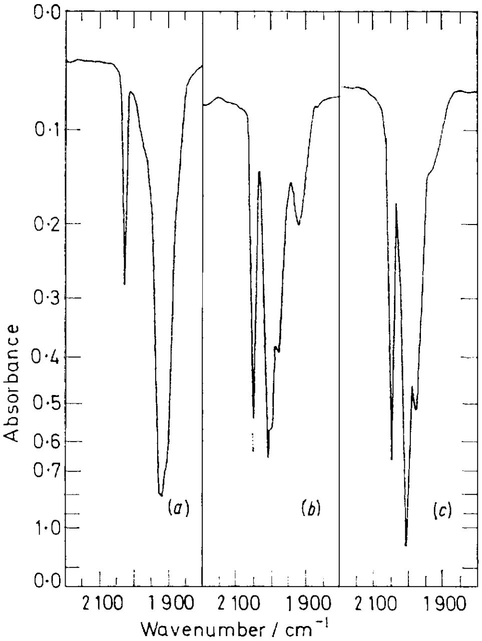

FIGURE 2 I.r. spectrum of Tl[Mn(CO)$_5$] in thf (*a*) and of the products of its decomposition at 25 °C in the dark after 45 min (*b*) and 6 h (*c*). The shoulder at *ca.* 1 970 cm^{-1} in (*a*) is due to the solvent

The most successful route to Tl[Mn(CO)$_5$] was through the reaction of thallium(I) ethoxide with hydridopentacarbonylmanganese in thf at low temperature [equation (4)]. The product was stable in solution at —65 °C for several days and proved too

$$[\mathrm{Tl(OEt)}]_4 + 4\mathrm{HMn(CO)}_5 \longrightarrow 4\mathrm{Tl[Mn(CO)}_5] + 4\mathrm{EtOH} \quad (4)$$

unstable to be isolated. If the i.r. spectrum of the cold solution was recorded rapidly, a simple two-band pattern was obtained [Figure 2(*a*)]. For Tl[Mn(CO)$_5$], of C_{4v} symmetry, three i.r.-active modes are expected ($2A_1 + E$). That only two were observed is probably the result of solvent broadening which merges the strong E mode with the weaker A_1 (equatorial symmetric stretching) mode. Similar effects have been noticed for Ph$_3$SnMn(CO)$_5$ in thf.[20] The relatively low frequencies of the bands of the compound Tl[Mn(CO)$_5$] indicate the existence of a polar, covalent thallium–manganese bond. Although very thermally unstable, Tl[Mn(CO)$_5$] reacted rapidly with triphenyltin chloride at low temperature to form Ph$_3$SnMn(CO)$_5$ in good yield.

When a thf solution of Tl[Mn(CO)$_5$] was permitted to stand in the dark at room temperature for 45 min the carbonyl absorption bands of the thallium(I) compound were almost entirely replaced by bands characteristic of Tl[Mn(CO)$_5$]$_3$ (2 053, 1 996, and 1 979 cm^{-1}) and a 2 008 cm^{-1} band attributed to [Mn$_2$(CO)$_{10}$] [Figure 2(*b*)]. The former compound probably arises from disproportionation of Tl[Mn(CO)$_5$] [equation 5(a)] as previously suggested,[5,6] while the latter results from decomposition

$$3\mathrm{Tl[Mn(CO)}_5] \longrightarrow \mathrm{Tl[Mn(CO)}_5]_3 + 2\mathrm{Tl}^0 \qquad (5a)$$

$$\mathrm{Tl[Mn(CO)}_5]_3 \longrightarrow \mathrm{Mn}_2(\mathrm{CO})_{10} + \mathrm{Tl[Mn(CO)}_5] \qquad (5b)$$

of the former [equation 5(b)]. A freshly prepared, saturated solution of Tl[Mn(CO)$_5$]$_3$ in dry, deaerated thf exhibited three strong carbonyl absorption bands if the sample was handled in the dark [Figure 3(*a*) and Table 3]. Little change was observed over 2 h. On exposure of the solution to laboratory light, however, absorption bands characteristic of Tl[Mn(CO)$_5$] and [Mn$_2$(CO)$_{10}$] grew in at the expense of those due to Tl[Mn(CO)$_5$]$_3$ [Figure 3(*b*—*d*)]. This occurred within minutes in the thin section of the i.r. cell but somewhat more slowly in the Schlenk tube in

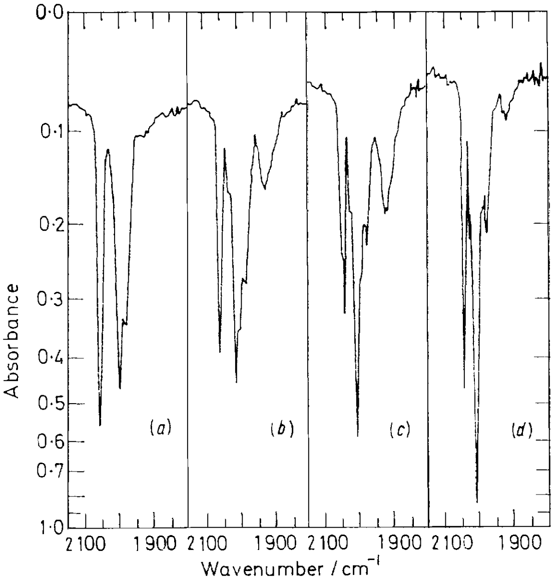

FIGURE 3 I.r. spectrum of Tl[Mn(CO)$_5$]$_3$ in thf (*a*) and of the products of its light-induced decomposition after 3 min (*b*), 10 min (*c*), and 8 h (*d*)

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

[20] J. M. Burlitch and S. W. Ulmer, unpublished work.

which conversion to $[Mn_2(CO)_{10}]$ and thallium metal was essentially complete in 8 h [Figure 3(*d*)]. Thus, decomposition of $Tl[Mn(CO)_5]_3$ in thf occurs in two steps: light-promoted reductive elimination, followed by disproportionation [equations (6) and (7)].

$$Tl[Mn(CO)_5]_3 \overset{h\nu}{\rightleftharpoons} Tl[Mn(CO)_5] + [Mn_2(CO)_{10}] \qquad (6)$$

$$3Tl[Mn(CO)_5] \longrightarrow Tl[Mn(CO)_5]_3 + 2Tl^0 \qquad (7)$$

The reversible nature of process (6) was demonstrated. At −78 °C an equimolar mixture of $Tl[Mn(CO)_5]$ and $[Mn_2(CO)_{10}]$ underwent no appreciable reaction (i.r. analysis) during 1 h in the dark. After exposure of the mixture at −78 °C to light for 6 h, however, bands characteristic of $Tl[Mn(CO)_5]_3$ were present at low to moderate intensity along with those of the starting compounds. Since $Tl[Mn(CO)_5]$ is stable to disproportionation at −78 °C, $Tl[Mn(CO)_5]_3$ must result from oxidative addition of $[Mn_2(CO)_{10}]$ to $Tl[Mn(CO)_5]$. This process was postulated by Haupt and Neumann to account for formation of $Tl[Mn(CO)_5]_3$ from equimolar quantities of TlCl, $Na[Mn(CO)_5]$, and $[Mn_2(CO)_{10}]$.[5]

In dichloromethane decomposition of $Tl[Mn(CO)_5]_3$ was somewhat slower and no evidence of the intermediate $Tl[Mn(CO)_5]$ was obtained from the i.r. spectra. Saturated solutions of $Tl[Mn(CO)_5]_3$ in acetonitrile kept in the dark showed only minor changes in the i.r. spectra with time [ν(CO) 2 056s, 1 998ms, and 1 969m cm^{-1}] but exposure to light for a few hours caused bands of $[Mn_2(CO)_{10}]$ to appear along with weaker bands at 2 027 and 1 937 cm^{-1} possibly due to $Tl[Mn(CO)_5]$. These observations demonstrate the general instability of $Tl[Mn(CO)_5]_3$ in solution, particularly on exposure to light.

$(cp)Fe(CO)_2$ *System*.—Addition of a tetrahydrofuran–methanol solution of thallium(I) acetate to the compound $Na[Fe(CO)_2(cp)]$ in thf caused immediate precipitation of thallium metal and formation of a deep red solution that had i.r. absorption bands at 1 985m, 1 955vs, and 1 918s cm^{-1}. A spectrum containing these bands, and also those of $[Fe(CO)_2(cp)]_2$, was obtained from the deep red solution produced when thallium(III) chloride was treated with $Na[Fe(CO)_2(cp)]$ in thf. All attempts to isolate a dimer-free product from either of these reactions failed. The similarity of the above spectrum with that of $(n\text{-}C_4H_9)_4N[Hg\{Fe(CO)_2(cp)\}_3]$ [ν(CO) in thf: 1 944m, 1 916vs, 1 873s, and 1 860m (sh) cm^{-1}],[21] together with the method of preparation, strongly suggest that the product of both reactions is $Tl[Fe(CO)_2(cp)]_3$. This neutral species would be expected to have carbonyl-stretching bands 40—50 cm^{-1} higher than those of $Hg[Fe(CO)_2(cp)]_3^-$. It is noteworthy that the latter compound has a tendency to decompose to $[Fe(CO)_2(cp)]_2$ and metallic mercury.[21] In view of the behaviour of the other system studied it seems reasonable to expect that decomposition of $Tl[Fe(CO)_2(cp)]_3$ occurs in a cyclic process that begins by reductive elimination of $Fe(CO)_2(cp)]_2$ followed by rapid disproportionation of the resulting $Tl[Fe(CO)_2(cp)]$ to $Tl[Fe(CO)_2(cp)]_3$ and thallium metal.

In summary, we conclude that the disproportionation reaction [equation (8)] is a major factor in the chemistry of thallium(I) compounds, except for $Tl[Co(CO)_4]$ which has unusual stability in this respect. The reductive-elimination process [equation (9)] occurs to a greater or lesser degree for all thallium(III) compounds depending on the reaction conditions and the stability of the corresponding thallium(I) derivative.

$$3TlX \longrightarrow TlX_3 + 2Tl^0 \qquad (8)$$

$$TlX_3 \rightleftharpoons TlX + X{-}X \qquad (9)$$

EXPERIMENTAL

All reactions were carried out under a purified argon atmosphere in modified (two-necked) Schlenk tubes (m.s.t.) that had been flame-dried under vacuum. Argon was purified by passage over B.A.S.F. Catalyst ' BTS ' and phosphorus pentoxide (Mallinckrodt Aquasorb). Except where noted, all solvents were distilled directly into the reaction vessels under an argon atmosphere and all filtrations were carried out using a Schlenk-type filter tube equipped with a fine porosity frit (10 to 20 μm) that contained Celite filter aid (Johns Manville, analytical grade). Magnetic stirring was employed. Trap-to-trap and rotary evaporations were undertaken under vacuum at ambient temperatures after first degassing the solution at −78 °C.

All melting and decomposition points were determined under an atmosphere of argon in sealed capillaries using a Büchi m.p. apparatus and are corrected. Most i.r. spectra were obtained using a Perkin-Elmer model 337 spectrometer; the 1 944 cm^{-1} band of polystyrene was used for calibration. In a few cases a model 521 instrument was employed and calibrated with DCl. Solution spectra were obtained with an International Crystal Laboratories demountable cell (model B-3S) which employed calcium fluoride windows and Teflon spacers. The most commonly employed path length was *ca.* 0·025 mm. One part of the cell was equipped with a Kel-F valve (Hamilton Co. type 3MMM2, connected to the aspirator for flushing) and the other with a septum-capped syringe barrel (0·25 cm^3) that served as an inlet-reservoir. The cell was dried by evacuation to <0·01 Torr before use. Solutions were transferred to the cell in a gas-tight syringe. Nujol mulls and KBr pellets of solid samples were prepared in a Vacuum/Atmospheres Co. nitrogen-filled dry-box; spectra are given in Table 4. Low-resolution mass spectra were obtained with an A.E.I. MS 902 instrument using a solid-probe inlet. Elemental analyses were carried out by the Pascher Microanalytical Laboratory, Bonn, Germany.

Solvents and Starting Materials.—Tetrahydrofuran (thf) and hexane (Fisher, mixed isomers) were distilled from potassium and benzophenone. Octane was twice distilled from sodium. Methanol was distilled from a solution of magnesium methoxide that was twice degassed at −78 °C. Distilled water and 10% w/w aqueous sodium hydroxide solutions were deaerated by bubbling argon through the boiling solution, followed by cooling under an atmosphere of argon.

When 1% sodium amalgam was used, a ten-fold excess

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[21] J. M. Burlitch and R. B. Petersen, *Abstr. C.I.C./A.C.S. Conference*, Toronto, Canada, May 1970, No. 25 (Inorg.).

was employed. Thallium metal (Alfa Inorganics) in the form of 1·3 cm diameter rods was cut into small pieces just prior to use. The following compounds were used as obtained: $TlNO_3$ and $TlCl_3,4H_2O$ (Alfa); Tl_2SO_4 (Research Organic/Inorganic Chemical Corp.); $[TlOEt]_4$ (Eastman Organic Chemicals); $[Co_2(CO)_8]$ (Strem Chemicals); and Ph_3SiCl (PCR, Inc.). Triphenyltin chloride (M and T Chemical Corp.) and triphenylphosphine (Eastman) were recrystallized from ether and ethyl alcohol, respectively. The compound $[Fe(CO)_2(cp)]_2$ (cp = η-cyclopentadienyl) (Strem) was sublimed at 120 °C/0·001 Torr. The following compounds were prepared by literature methods and stored at 5 °C under an atmosphere of argon: $Hg[Co(CO)_4]_2$;[22] $Hg[M(CO)_3(cp)]_2$ (M = Cr, Mo, or W);[22] $[(cp)Mo(CO)_3]_2$;[23] $[Mn_2(CO)_{10}]$;[24] $Hg[Co(CO)_3PPh_3]_2$;[17] and $[HMn(CO)_5]$.[25]

TABLE 4

I.r. spectra (cm^{-1}) of thallium(I) and thallium(III) derivatives in the solid state [a]

Compound	ν(CO)
$Tl[Co(CO)_4]$	2 020m, 1 931vs(br), 1 900w
$Tl[Cr(CO)_3(cp)]$	1 909s, 1 794s(sh), 1 742s(br)
$Tl[Mo(CO)_3(cp)]$	1 913s, 1 904s, 1 822m, 1 788m, 1 710s(br)
$Tl[W(CO)_3(cp)]$	1 920s, 1 909s, 1 790m, 1 720s(br)
$Tl[Co(CO)_4]_3$	2 079m, 2 060s, 2 025m, 2 010w, 1 980s(sh), 1 968vs, 1 943s
$Tl[Co(CO)_3PPh_3]_3$	2 026w, 1 985m, 1 938vs
$Tl[Mn(CO)_5]_3$	2 068m(sh), 2 057m, 2 027m, 2 007w, 1 957vs, 1 938m
$Tl[Cr(CO)_3(cp)]_3$	1 947s(sh), 1 930vs, 1 885vs, 1 771m, 1 711m
$Tl[Mo(CO)_3(cp)]_3$	1 960s(sh), 1 942vs, 1 876vs
$Tl[W(CO)_3(cp)]_3$	1 956s(sh), 1 937vs, 1 893m(sh), 1 865vs

[a] Thallium(I) compounds were observed in Nujol mulls, thallium(III) compounds in KBr pellets.

Preparation of $Tl[Co(CO)_4]$.—(a) *From* $Na[Co(CO)_4]$ *and thallium*(I) *nitrate*. Into a m.s.t. (60 cm^3), equipped with a magnetic stirrer, was placed $Hg[Co(CO)_4]_2$ (2·71 g, 5·0 mmol) and excess of sodium amalgam. thf (25 cm^3) Was added and the mixture was stirred at room temperature until a colourless solution was obtained (*ca.* 1 h). After filtering, the solvent was removed by trap-to-trap distillation, leaving $Na[Co(CO)_4]$ as a yellow-white solid. With the addition of a solution of $TlNO_3$ (2·66 g, 10·0 mmol) dissolved in deaerated water (30 cm^3), the $Na[Co(CO)_4]$ immediately dissolved and a flocculent, yellow precipitate was produced.* On warming the solution to 45 °C, the solid dissolved giving a bright yellow solution which was filtered while still warm. Slow cooling to −5 °C produced large yellow crystals which were isolated and washed with several aliquot portions (1 cm^3) of cold water. On drying under vacuum, 1·9 g {51% yield based on $Hg[Co(CO)_4]_2$} of $Tl[Co(CO)_4]$ was obtained as a bright yellow crystalline solid, m.p. 120—130 °C (decomp.). Analytical data for this compound are given in Table 1. A low-intensity 70 eV mass spectrum of $Tl[Co(CO)_4]$, recorded with a source temperature of 120 °C, contained peaks at *m/e* 205(100) Tl^+, 233(10) $TlCO^+$, 264(25) $TlCo^+$, and 292(10) $TlCo(CO)^+$, where relative intensities are given in parentheses and only the peaks containing Tl^{205} are listed.

(b) *From* $[Co_2(CO)_8]$ *and thallium metal*. A solution of $[Co_2(CO)_8]$ (0·331 g, 0·97 mmol) in thf (18 cm^3) was stirred with thallium metal (1·50 g) for 1·5 h during which time the colour of the solution changed from red- to yellow-brown. Filtration and removal of the solvent by trap-to-trap distillation yielded a yellow solid. Recrystallization from deaerated water (6 cm^3) as in (*a*) afforded 0·38 g {52% based on $[Co_2(CO)_8]$} of $Tl[Co(CO)_4]$ identified by comparison of its i.r. spectrum with that from (*a*).

(c) *From* $Hg[Co(CO)_4]_2$ *and thallium metal*. Into a m.s.t. (60 cm^3) equipped with a magnetic stirrer, was placed $Hg[Co(CO)_4]_2$ (0·542 g, 1·0 mmol) and thallium metal (2·0 g). thf (20 cm^3) Was distilled in and the mixture was stirred for 20 h. During this time the colour of the solution first turned dark red-brown, possibly due to the complex ion $Hg[Co(CO)_4]_3^-$,[26] then became light yellow-brown. Filtration and removal of the solvent by trap-to-trap distillation yielded a yellow-brown residue that was recrystallized from deaerated water (6 cm^3) as in (*a*). In this way 0·43 g {57% based on $Hg[Co(CO)_4]_2$} of $Tl[Co(CO)_4]$ was obtained.

(d) *From* $Tl[Co(CO)_4]_3$ *and thallium metal*. A mixture of $Tl[Co(CO)_4]_3$ (0·325 g, 0·45 mmol) and thallium metal (0·52 g) in dichloromethane (15 cm^3) was stirred for 4 h. During this time the colour of the solution changed from red to yellow and a yellow crystalline precipitate formed. I.r. spectra, recorded during the course of the reaction, showed gradual replacement of bands due to $Tl[Co(CO)_4]_3$ with those of $Tl[Co(CO)_4]$. The yellow solid was dissolved with added dichloromethane (15 cm^3). Slow cooling of the filtered solution to −65 °C produced yellow crystals that were isolated by decantation of the mother liquor, washed with dichloromethane (1 cm^3), and dried under vacuum. The yield of $Tl[Co(CO)_4]$ was 0·36 g (70%).

Reactions of $Tl[Co(CO)_4]$.—(a) *With mercury*. A solution of $Tl[Co(CO)_4]$ (0·0903 g, 0·240 mmol) in toluene (5 cm^3) was stirred with mercury (0·71 g) for 20 h. The i.r. spectrum of the yellow solution indicated that 30—40% of $Tl[Co(CO)_4]$ remained and that the compound $Hg[Co(CO)_4]_2$ [ν(CO) at 2 070s, 2 016m(sh), and 2 004s cm^{-1}] had formed. The origin of a weak band at 2 054 cm^{-1} is unknown.

(b) *With* $[Co_2(CO)_8]$. Hexane (35 cm^3) was distilled onto $Tl[Co(CO)_4]$ (1·050 g, 2·80 mmol) and $[Co_2(CO)_8]$ (0·950 g, 2·80 mmol) and the mixture was stirred for 3 h during which time the $Tl[Co(CO)_4]$ dissolved completely. The dark red mixture was warmed to 40 °C (water-bath) to ensure complete dissolution of the product and then filtered. Slow cooling of the filtrate to −65 °C over 24 h afforded black needle-like crystals which were washed with cold hexane (2 cm^3) and dried under vacuum. The product (1·75 g, 87% yield) was identified as $Tl[Co(CO)_4]_3$ by analysis (Table 1) and by comparison of its i.r. spectrum with that of an authentic sample prepared by the procedure of Patmore and Graham.[12] Their method generally gave substantially lower yields of the product which was contaminated with small amounts of $[Co_4(CO)_{12}]$.

(c) *With triphenyltin chloride*. To a solution of $Tl[Co(CO)_4]$ (0·521 g, 1·38 mmol) in thf (20 cm^3) was

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* At this point, a yellow oil, rather than a solid, was obtained in some preparations. Attempts to crystallize the oil failed. The supernatant liquid was removed with a syringe and the oil was dissolved in thf. On removal of this solvent by trap-to-trap distillation, a solid was produced which could be recrystallized from water.

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

[23] R. B. King, *Organometallic Synth.*, 1965, **1**, 109.

[24] R. B. King, J. C. Stockes, and T. F. Korenowski, *J. Organometallic Chem.*, 1968, **11**, 641.

[25] Ref. 23, p. 158.

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

added Ph_3SnCl (0·530 g, 1·38 mmol). A white precipitate formed immediately and the colour of the solution changed to a somewhat lighter yellow. After stirring the solution for 20 min, filtering, and removing the solvent by trap-to-trap distillation, the resulting light yellow residue was dissolved in a minimum amount of warm (45 °C) hexane. Filtering and slowly cooling the solution to -78 °C produced yellow crystals which were collected, washed with several aliquot portions (1 cm^3) of cold hexane, and dried under vacuum. The product, $Ph_3SnCo(CO)_4$ {0·666 g, 92% yield based on $Tl[Co(CO)_4]$} was identified by its m.p. of 122—123 °C (lit.,[27] 123 °C) and i.r. spectrum.

(d) *With triphenylchlorosilane.* A solution containing 1 mmol each of $Tl[Co(CO)_4]$ (0·375 g) and Ph_3SiCl (0·294 g) in toluene (20 cm^3) was stirred at room temperature and analysed periodically by i.r. spectroscopy. After 48 h the colour of the solution had changed from yellow to red and a small quantity of white solid had formed. The spectrum of the solution revealed that over 90% of $Tl[Co(CO)_4]$ had not reacted; the only new feature in the spectrum was a sharp band of moderate intensity at 2 049 cm^{-1} that had gradually increased during the 48 h interval. No evidence for $Ph_3SiCo(CO)_4$ [ν(CO) in toluene at 2 097m, 2 037m, and 2 007s cm^{-1}] was observed in this or similar reactions under more forcing conditions.

Molecular-weight and Conductivity Measurements on $Tl[Co(CO)_4]$.—The molecular weight of the compound $Tl[Co(CO)_4]$ was determined cryoscopically in benzene solution, using an instrument similar to that described by Knight *et al.*[28] Measurements on a solution of the compound (0·103 g solute in 5·650 g solvent) gave a molecular weight of 367 g/mol (calc. 375·3 g/mol). The molar conductivity of $Tl[Co(CO)_4]$ in solution was determined in dry degassed methanol and acetonitrile.* The measurements were made on 0·010M-solutions at 1 kHz and 25 °C with an Industrial Instruments Conductivity Bridge, model R.C. 16B2.

Preparation of $Tl[M(CO)_3(cp)]$ (M = Cr, Mo, *or* W) *from* $Na[M(CO)_3(cp)]$ *and Thallium*(I) *Nitrate.*—All three members of this series were prepared in the same manner, the synthesis of $Tl[Mo(CO)_3(cp)]$ is described as an example.

A solution of $Na[Mo(CO)_3(cp)]$ (2·0 mmol) in thf (20 cm^3) was prepared by stirring a solution of $Hg[Mo(CO)_3(cp)]_2$ (0·690 g, 1·0 mmol) with excess of sodium amalgam for 1 h. Filtration of the light yellow solution and removal of thf by trap-to-trap distillation gave a yellowish white solid which was dissolved in deaerated water (10 cm^3). To the resulting light yellow solution of $Na[Mo(CO)_3(cp)]$ was added thallium(I) nitrate (0·533 g, 2·0 mmol). On stirring for several min, a flocculent yellow precipitate was formed which was collected on a Celite-free 'medium' porosity frit, washed with deaerated water, and dried (P_4O_{10}) under vacuum. The yield of crude $Tl[Mo(CO)_3(cp)]$ was 0·603 g {67% based on $Hg[Mo(CO)_3(cp)]_2$}. A portion of this product, 0·352 g (0·78 mmol), was recrystallized from 10% aqueous sodium hydroxide [15 cm^3, prepared by dissolving solid sodium hydroxide (1·5 g) in deaerated water (15 cm^3)] over a temperature range of 70 to -10 °C. The yellow needle-like *crystals* which formed were isolated and washed with several aliquot portions (1 cm^3) of cold deaerated water and dried (P_4O_{10}) under vacuum. The yield of light yellow crystalline $Tl[Mo(CO)_3(cp)]$ was 0·27 g (77%).

By an identical procedure crude $Tl[W(CO)_3(cp)]$ was obtained as a light yellow powder (69% yield). Recrystallization afforded light yellow, needle-like crystals of the pure *product* in 73% yield. Crude $Tl[Cr(CO)_3(cp)]$ was isolated as an orange *powder* in 63% yield. All attempts to recrystallize this material failed due to extensive decomposition. Analytical data (Table 1) were obtained on the thoroughly washed and dried crude product.

Attempted Reaction of $Hg[Mo(CO)_3(cp)]_2$ *with Thallium Metal.*—A solution of $Hg[Mo(CO)_3(cp)]_2$ (0·69 g, 1·0 mmol) in thf (20 cm^3) was stirred with thallium metal (0·8 g) for 3 days at room temperature. After this time i.r. analysis of the solution showed only the bands of the starting mercury compound. Similar results were obtained with $Hg[W(CO)_3(cp)]_2$ (0·236 g, 0·272 mmol) and thallium metal (1·0 g) in thf (20 cm^3) over 3 days.

Reaction of $Tl[Mo(CO)_3(cp)]$ *and Mercury Metal.*—On stirring a solution of $Tl[Mo(CO)_3(cp)]$ (0·114 g, 0·253 mmol) in thf (8 cm^3) with mercury (0·30 g) i.r. analysis showed that $Tl[Mo(CO)_3(cp)]$ [ν(CO) at 1 929s, 1 840m, and 1 810s cm^{-1}] was completely converted to $Hg[Mo(CO)_3C_5H_5]_2$ [ν(CO) at 1 995w, 1 965s, 1 901w(sh), and 1 889m cm^{-1}] within 3 h. The product was not isolated.

Reaction of $Tl[Mo(CO)_3(cp)]$ *with* $[Mo(CO)_3(cp)]_2$.—To a solution of $Tl[Mo(CO)_3(cp)]$ (0·104 g, 0·23 mmol) in thf (10 cm^3), cooled to 0 °C, was added $[Mo(CO)_3(cp)]_2$ (0·113 g, 0·23 mmol). The solution was stirred at 0 °C in the normal laboratory light and aliquot portions (*ca.* 0·2 cm^3) were withdrawn periodically for immediate i.r. analysis. The progress of the reaction was monitored by following the simultaneous disappearance of the bands due to the starting materials. For this purpose the 1 840 and 1 812 cm^{-1} bands of $Tl[Mo(CO)_3(cp)]$ were easily observed and were well separated from the 2 011 cm^{-1} band of $[Mo(CO)_3(cp)]_2$ and bands due to the product. After 1·5 h *ca.* 50% of the reactants remained and most of the starting dimer had dissolved. Stirring was continued for a total of 12 h after which the i.r. spectrum of the deep red reaction solution showed mainly $Tl[Mo(CO)_3(cp)]_3$ [ν(CO) at 1 999w, 1 959vs, and 1 899s cm^{-1}] with small quantities (est. 10—15%) of the starting compounds. At this point the reaction mixture contained a very small quantity of grey-white solid, presumed to be thallium metal from slow disproportionation of $Tl[Mo(CO)_3(cp)]$. A similar experiment carried out in the dark showed little or no reaction.

Reaction of $Tl[W(CO)_3(cp)]$ *with* $[Co_2(CO)_8]$.—A m.s.t. (30 cm^3) was charged with $Tl[W(CO)_3(cp)]$ (0·584 g, 1·08 mmol) and $[Co_2(CO)_8]$ (0·342 g, 1·00 mmol). thf (10 cm^3) Was distilled into the vessel and the dark red solution which formed was stirred for 1 h. thf Was removed by rotary evaporation and the red-brown residue was extracted with warm octane (20 cm^3, 60 °C). On filtering and slowly cooling the filtrate to -40 °C, dark red, small, needle-like crystals were produced. These were isolated, washed with cold octane (1 cm^3), and dried under vacuum. The resulting solid (0·32 g, 36% yield) was identified as $Tl[W(CO)_3(cp)][Co(CO)_4]_2$ by elemental analysis (Table 1) and by the close similarity of its i.r. spectrum (in thf solution) with that of the redistribution product of a mixture of $Tl[Co(CO)_4]_3$ and $Tl[W(CO)_3(cp)]_3$ in 2 : 1 mol ratio in thf.

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* We are indebted to Dr. T. Blackmore for assistance with these measurements.

[27] F. Hein and W. Jehn, *Annalen*, 1965, **684**, 4.

[28] J. A. Knight, B. Wilkens, jun., D. K. Davis, and F. Sicilian, *Analyt. Chim. Acta*, 1961, **25**, 317.

Decomposition of $Tl[Mo(CO)_3(cp)]$ *in Toluene*.—A slurry of $Tl[Mo(CO)_3(cp)]$ (0·480 g, 1·07 mmol) in toluene (15 cm^3) was stirred for 1 h during which time the solid gradually dissolved with formation of a deep red solution and a metallic precipitate. After stirring for an additional 3 h, toluene (10 cm^3) was added to ensure complete dissolution of the product and the mixture was filtered. Concentration of the filtrate to *ca.* 5 cm^3 by rotary evaporation produced deep red crystals which were isolated by removal of the supernatant liquid with a syringe, washed with hexane (2 cm^3), and dried under vacuum. The product was identified as $Tl[Mo(CO)_3(cp)]_3$ by the identity of its i.r. spectrum with that of an authentic sample prepared as described below. The yield was 0·25 g (76%).

Preparation of $Tl[M(CO)_3(cp)]_3$ (M = Cr, Mo, *or* W).—All compounds were prepared by the procedure described below.

Into a m.s.t. (60 cm^3) were placed $Hg[W(CO)_3(cp)]_2$ (1·30 g, 1·50 mmol) and excess of sodium amalgam. thf (35 cm^3) Was added and the resulting mixture was stirred for 1 h and filtered to give a light yellow solution of $Na[W(CO)_3(cp)]$. With the addition of $TlCl_3,4H_2O$ (0·362 g, 0·95 mmol), the solution became deep red and a white precipitate was produced. The solution was filtered and the red-brown solid, obtained on removal of the solvent by rotary evaporation, was extracted with warm (36 cm^3, 45 °C) toluene. After filtration, the volume of the extract was slowly reduced to 8 cm^3 by rotary evaporation. A quantity of small, dark red, crystals was isolated, washed with several aliquot portions (1 cm^3) of toluene, and dried under vacuum. The yield of $Tl[W(CO)_3(cp)]_3$ was 0·59 g (49%). By similar procedures $Tl[Cr(CO)_3(cp)]_3$ and $Tl[Mo(CO)_3(cp)]_3$ were obtained as small, dark red, crystals in yields of 37 and 80% respectively.

Reaction of $Na[Co(CO)_3PPh_3]$ *and Thallium*(I) *Acetate*.—(a) *In tetrahydrofuran–methanol.* Into a m.s.t. (40 cm^3) was placed $Hg[Co(CO)_3PPh_3]_2$ (0·334 g, 0·333 mmol) and excess of sodium amalgam. thf (15 cm^3) Was added and the resulting mixture was stirred for 6 h at which point the reduction was complete as indicated by disappearance of the relatively insoluble $Hg[Co(CO)_3PPh_3]_2$. Methanol (10 cm^3) was added with a syringe to the filtered solution of $Na[Co(CO)_3PPh_3]$. The addition of thallium(I) acetate (0·175 g, 0·66 mmol) changed the colour of the solution from yellow to orange and the i.r. spectrum from that of the ion $[Co(CO)_3PPh_3]^-$ [ν(CO) at 1 932s, 1 857vs, and 1 815s cm^{-1}] to a single strong band at 1 893 cm^{-1} attributed to $Tl[Co(CO)_3PPh_3]$. On being set aside at room temperature, the solution turned deep red and a grey precipitate formed. After 12 h, i.r. analysis showed that the 1 893 cm^{-1} band had been almost completely replaced by bands at 1 984m, 1 972w(sh), 1 948s, and 1 926w(sh) cm^{-1} quite similar to the spectrum of $Tl[Co(CO)_3PPh_3]_3$ in thf (Table 3).

(b) *In Water* {*Isolation of* $Tl[Co(CO)_3PPh_3]_3$}. A solution of $Na[Co(CO)_3PPh_3]$ (2·0 mmol) was prepared as in the previous experiment and filtered. After removal of thf from the filtrate by trap-to-trap distillation, the solid yellow $Na[Co(CO)_3PPh_3]$ was dissolved in a mixture of water (30 cm^3) and thf (10 cm^3). On filtration and addition of thallium(I) acetate (0·527 g, 2·0 mmol) a deep red precipitate was formed. This solid was isolated in a Celite-free ' medium ' porosity frit, washed with several portions of water, and dried under vacuum. Extraction of the solid with warm toluene (40 cm^3) gave a deep red solution and a metallic grey residue. After filtration, small, deep red, crystals were produced by slow rotary evaporation to a volume of 7 cm^3. The crystals were isolated, washed with octane (2 cm^3), and dried under vacuum. The product was identified as $Tl[Co(CO)_3PPh_3]_3$ by comparison of its i.r. spectrum to that of an authentic sample.[17] A small sample was recrystallized from thf for elemental and spectroscopic analysis.

Preparation of $Tl[Mn(CO)_5]$ *from* $[HMn(CO)_5]$ *and Thallium*(I) *Ethoxide*.—(a) *At* −78 °C *in the light.* To 1 cm^3 of a 0·098M-solution of $[HMn(CO)_5]$ in thf at −78 °C was added 0·3 cm^3 of a 0·089M-solution of $[Tl(OEt)]_4$ in thf. The colour of the solution changed from light to dark yellow. An i.r. spectrum of the solution, obtained as rapidly as possible (*ca.* 3 min), showed that all the hydride had reacted (as indicated by complete disappearance of the very strong band at 2 015 cm^{-1}) and that a new compound had formed with ν(CO) at 2 029m and 1 921s cm^{-1} [Figure 2(*a*)]. After 48 h at −65 °C in the dark, the solution's i.r. spectrum was unchanged. When the solution was set aside at room temperature in the normal fluorescent laboratory light for 1·5 h a grey precipitate formed and the i.r. spectrum of the yellow supernatant liquid consisted of bands at 2 044s, 2 008vs, and 1 980 cm^{-1}, characteristic of $[Mn_2(CO)_{10}]$, and a shoulder at 1 930w cm^{-1} attributed to residual $Tl[Mn(CO)_5]$.

(b) *At* 25 °C *in the dark.* The following procedure was carried out under dim red light. To 2·5 cm^3 of 0·10M-$[HMn(CO)_5]$ (0·25 mmol) in thf was added 0·40 cm^3 of 0·063M-$[Tl(OEt)]_4$ (0·252 mmol) and the solution was stirred for 30 min at room temperature. The i.r. spectrum of the red solution was very similar to that shown in Figure 2(*b*) with bands at 2 053s, 2 027w(sh), 2 010s, 1 999s(sh), 1 979ms, and 1 923m cm^{-1}. After 6 h at room temperature in the dark a substantial quantity of metal had formed and an i.r. spectrum of the light yellow supernatant liquid consisted of ν(CO) at 2 049s, 2 028vw(sh), 2 010vs, 1 998s(sh), 1 980ms, and 1 924w(sh) cm^{-1}.

Reaction of $Tl[Mn(CO)_5]$ *with* $[Mn_2(CO)_{10}]$.—To a solution of $Tl[Mn(CO)_5]$ in thf, prepared at −78 °C as in part (*a*) of the previous experiment, was added $[Mn_2(CO)_{10}]$ (0·098 g, 0·25 mmol). After 1 h in the dark at −78 °C, i.r. analysis indicated only the presence of the starting materials [ν(CO) at 2 046s, 2 031ms, 2 010vs, 1 980m, and 1 925s cm^{-1}]. The solution at −78 °C was exposed to laboratory light for 6 h during which the colour darkened appreciably. I.r. spectroscopic analysis showed a substantial decrease in intensity of the bands of $Tl[Mn(CO)_5]$ [1 925ms and 2 027m(sh) cm^{-1}]; the presence of $Tl[Mn(CO)_5]_3$ was indicated by a strong band at 2 052 cm^{-1} which was just resolved from the 2 045 cm^{-1} band of $[Mn_2(CO)_{10}]$ of comparable intensity. Other bands appeared at 2 006vs and 1 980ms cm^{-1}.

Reaction of $Tl[Mn(CO)_5]$ *with Triphenyltin Chloride*.—To a thf solution of $Tl[Mn(CO)_5]$ (0·50 mmol), prepared as described in experiment (*a*) above and maintained at −78 °C, was added Ph_3SnCl (0·190 g, 0·50 mmol). On warming to room temperature a white precipitate formed. An i.r. spectrum of the pale yellow supernatant liquid contained only ν(CO) at 2 092s, 2 029w(sh), and 1 996vs cm^{-1} which indicated that all the $Tl[Mn(CO)_5]$ had reacted with formation of a single product, $Ph_3SnMn(CO)_5$, subsequently isolated in 62% yield, m.p. 146—148 °C (lit.,[29] 148—150 °C).

Light-induced Decomposition of $Tl[Mn(CO)_5]_3$ *in thf*.—Except where noted, this experiment was carried out under

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[29] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.

dim red, incandescent, light. A m.s.t. (40 cm^3), equipped with a magnetic stirrer and with a second m.s.t. attached to the side arm, was charged with Tl[Mn(CO)$_5$]$_3$ (0·25 g, 0·32 mmol).[6] thf (15 cm^3) Was distilled into the vessel and the mixture was stirred for several minutes to saturate the solvent with Tl[Mn(CO)$_5$]$_3$. The resulting solution was decanted into the second m.s.t. (*ca.* 2 cm in diameter) to remove it from any undissolved solid. An i.r. spectrum of the solution was recorded using great care to protect the solution from light [Figure 3(*a*)]. The sample in the reaction vessel was then exposed to normal fluorescent laboratory light for short periods of time (3, 10 min) and the i.r. spectrum was carefully recorded after each exposure [Figures 3(*b*) and 3(*c*) respectively]. After the last exposure, the solution was stirred for 8 h at room temperature and in the light before a final i.r. spectrum was taken [Figure 3(*d*)]. By this time the solution, which was originally red, had turned yellow and there was considerable metallic precipitate produced. This series of i.r. spectra revealed the rapid conversion of Tl[Mn(CO)$_5$]$_3$ [ν(CO) at 2 053s, 1 996s and 1 979m cm^{-1}] to [Mn$_2$(CO)$_{10}$] (1 945s, 2 009vs, and 1 982m cm^{-1}) and Tl[Mn(CO)$_5$] (2 031w and 1 923m cm^{-1}). The final spectrum [ν(CO) at 2 046(51), 2 011(100), and 1 982(20) cm^{-1}, Figure 3(*d*)] * was essentially that of [Mn$_2$(CO)$_{10}$] [ν(CO) in thf at 2 044(49), 2 009(100), and 1 980(17) cm^{-1}].

In another experiment, a solution of Tl[Mn(CO)$_5$]$_3$, prepared in a similar manner, was stored in the dark for several hours at room temperature without significant change in its i.r. spectrum.

Reaction of Na[Fe(CO)$_2$(cp)] *with Thallium*(I) *Acetate.*—To a filtered, light red, solution of Na[Fe(CO)$_2$(cp)], prepared by sodium-amalgam reduction of [Fe(CO)$_2$(cp)]$_2$ (0·226 g, 0·64 mmol) in thf (15 cm^3), was added a solution of thallium(I) acetate (1·15 mmol) in 1 : 2 tetrahydrofuran–methanol (8 cm^3). A deep red solution and a grey metallic precipitate formed immediately. The i.r. spectrum of the supernatant liquid showed ν(CO) at 1 986m, 1 956s, and 1 918ms cm^{-1}, attributed to Tl[Fe(CO)$_2$(cp)]$_3$, and a weak band at 1 782 cm^{-1} from [Fe(CO)$_2$(cp)]$_2$ [ν(CO) in thf at 1 992s, 1 953m, and 1 782s cm^{-1}]. Several attempts to isolate the product resulted in formation of inseparable mixtures of the desired compound and the iron dimer.

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* Relative absorbances are given in parentheses.