Reaction of Transition-metal Carbonylate Anions and 1,1,1-Tris(halogenomethyl)ethane. *X*-Ray Crystal Structures† of Tricarbonyl(η^5-cyclopentadienyl)-(1-methylcyclopropylmethyl)tungsten(II), and Tetraethylammonium Enneacarbonyliododirhenate(0)

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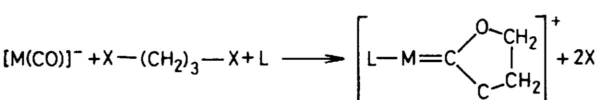
The interactions of 1,1,1-tris(halogenomethyl)ethanes, $MeC(CH_2X)_3$ (X = Br or I) with the carbonyl anions $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$, $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ (M = Mo or W), $[Ni(\eta^5\text{-}C_5H_5)(CO)]^-$, $[Mn(CO)_5]^-$, and $[Re(CO)_5]^-$ have been studied. All of the anions except $[Mn(CO)_5]^-$ react to give 1-methylcyclopropylmethyl (C_5H_9) derivatives; $[Mn(CO)_5]^-$ gives the acyl, $Mn(CO)_5(COC_5H_9)$. The structure of $W(\eta^5\text{-}C_5H_5)(CO)_3(C_5H_9)$ has been determined by *X*-ray diffraction; the other species are characterised spectroscopically. From the reactions other products have been characterised; in particular $[Re(CO)_5]^-$ gives the previously unknown anion $[Re_2I(CO)_9]^-$ whose structure in its $[NEt_4]^+$ salt has been determined by *X*-ray diffraction. The mechanisms of the various reactions involved are discussed.

The reaction between transition-metal nucleophiles and alkyl halides to form metal–alkyl bonds has long been known[1a] and studied in detail.[1b] The reaction between transition-metal nucleophiles and α,ω-dihalogenoalkanes has also been carried out using a number of different transition-metal systems, generally leading to the corresponding α,ω-dimetalla-alkanes [equation (1), ligands on M omitted]. Examples of this reaction are known for *n* = 1,[2] 3,[3–5] 4,[3,4,6] 5,[3] 6,[3] and 10;[7] for discussion and additional references see ref. 8. In the case of *n* = 3, the reaction sometimes follows a different pathway, leading to a carbene compound [equation (2)]. This particular path was first observed[9] with $[M(CO)]^- = L = [Mn(CO)_5]^-$ and the mechanism has been elucidated.[9b] Only recently has carbene formation been observed for other systems.[6,10,11]

$$2M^- + X\text{—}(CH_2)_n\text{—}X \longrightarrow M\text{—}(CH_2)_n\text{—}M + 2X^- \qquad (1)$$

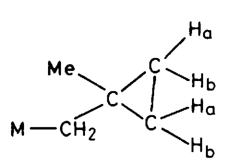


(2)

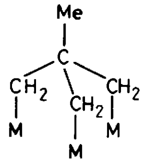
There appear to be no examples of reactions of transition-metal nucleophiles with an organic substrate containing more than two halogen atoms. We now report reactions between some selected metal carbonyl anions and 1,1,1-tris(halogenomethyl)ethane, $MeC(CH_2X)_3$, an organic molecule in which any pair of halogen atoms are separated by three carbon atoms, *i.e.* in 1,3-positions with respect to one another.

Results and Discussion

Interaction of $[M(cp)(CO)_n]^-$ (cp = η^5-C_5H_5; M = Mo or W, *n* = 3; M = Fe, *n* = 2; M = Ni, *n* = 1) and $[M(CO)_5]^-$ (M = Mn or Re) with $MeC(CH_2X)_3$ (X = Br or I) in tetrahydrofuran (thf) affords mononuclear alkyl complexes as a result of cyclization of part of the organic molecule to form a cyclopropane ring, (**I**). The reaction follows the stoicheiometry shown in equation (3) in the cases of the carbonyl(cyclopentadienyl)metal anions $[M(cp)(CO)_n]^-$, although in the case of M = Ni and *n* = 1 it goes further, as discussed later. We can formally consider this reaction as a metal nucleophile



(I)



(II)

$$3[M(cp)(CO)_n]^- + MeC(CH_2X)_3 \xrightarrow{\text{thf}} [M(cp)(CO)_n]_2 + (cp)(CO)_nM\text{—}(C_5H_9) + 3X^- \qquad (3)$$

(1a)—(1d)

	M	*n*	X
(1a)	Fe	2	Br
(1b)	Mo	3	I
(1c)	W	3	I
(1d)	Ni	1	I

displacing the three halogen atoms to give an hypothetical molecule (**II**), which undergoes a rearrangement with cleavage of two metal–carbon bonds and formation of a metal–metal and a carbon–carbon bond.

$[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$ also react to give cyclopropane–metal compounds, but the stoicheiometry is slightly different in these cases; different co-reaction products are formed, the nature of which provides evidence for the reaction mechanism (see below).

Cyclopropane ring formation seemed surprising, since the stable $(cp)(CO)_2Fe(CH_2)_3Fe(CO)_2(cp)$[3,4,12] had been isolated[3]

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† *Supplementary data available* (No. SUP 56162, 4 pp.): H-atom co-ordinates for (**1**), thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: eV ≈ 1.602×10^{-19}J; mmHg ≈ 133 Pa; atm = 101 325 Pa.

Table 1. Infrared spectra of the new complexes

Compound*	Solvent	ν_{CO}/cm^{-1}
(**1a**) $Fe(cp)(CO)_2(C_5H_9)$	Toluene	1 999m, 1 943s
(**1b**) $Mo(cp)(CO)_3(C_5H_9)$	n-Hexane	2 018m, 1 936s
(**1c**) $W(cp)(CO)_3(C_5H_9)$	n-Hexane	2 016m, 1 928s, 1 895vw
(**1d**) $Ni(cp)(CO)(C_5H_9)$	n-Hexane	2 031s
(**1e**) $Re(CO)_5(C_5H_9)$	n-Hexane	2 123w, 2 009vs, 1 983s, 1 940w
(**6**) $Mn(CO)_5(COC_5H_9)$	n-Hexane	2 112w, 2 049w, 2 005s, 1 669w
$[NEt_4][Re_2(CO)_9I]$	thf	2 090w, 2 029m, 1 980s,br, 1 935m,br, 1 895m

* C_5H_9 = 1-methylcyclopropylmethyl, cp = η^5-C_5H_5.

Table 2. Proton- and ^{13}C-n.m.r. (proton coupled and decoupled) spectra of $M{-}CH_2{-}C(CH_3){-}CH_2{-}CH_2$ compounds[a]

	^1H				^{13}C					
M	MCH_2	CH_3	CH_2CH_2	cp	MCH_2	CH_3	CH_2CH_2	C	CO	cp
(**1a**) $(cp)(CO)_2Fe^b$	1.63	1.16	0.54br, 0.49br	4.13	16.1 (130.6)	26.4 (126.1)	20.2 (160.9)	22.3	218.5	85.2 (177.4)
(**1b**) $(cp)(CO)_3Mo$	1.70	1.13	0.59br, 0.54br	4.53	14.0	26.1	20.3	22.2	241.3,[c] 229.1[d]	92.7
(**1c**) $(cp)(CO)_3W^b$	1.60	1.15	0.62br, 0.51br	4.47	2.0 (131.9)	26.4 (125.0)	19.8 (160.1)	21.1	230.3,[c] 219.1[d]	91.4 (178.8)
(**1e**) $(CO)_5Re$	1.55	1.04	0.55br, 0.38br		7.4	27.1	20.9	22.6	186.4,[e] 181.4[c]	
(**6**) $(CO)_5MnCO^b$	2.64	1.03	0.19		76.8 (128.8)	23.3 (125.4)	13.2 (161.1)	14.3	251.2,[f] 210.1[g]	

[a] Solvent C_6D_6. Spectra calibrated with internal C_6D_5H. Values given as δ/p.p.m. [b] Values in parentheses are J_{C-H}/Hz. [c] Intensity 1. [d] Intensity 2. [e] Intensity 4. [f] $(CO)_5Mn\mathit{C}OC_5H_9$, intensity 1. [g] $(\mathit{C}O)_5MnCOC_5H_9$, intensity 5, broad signal.

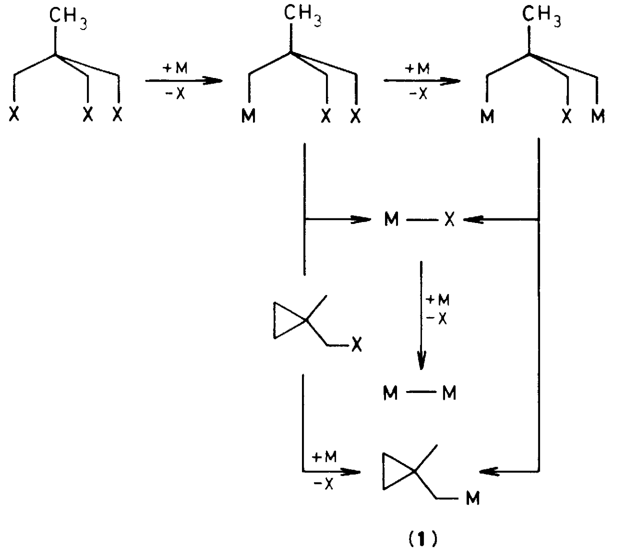
in 47% yield by interaction of $[Fe(cp)(CO)_2]^-$ and $Br(CH_2)_3Br$; this reaction probably proceeds *via* the formation of the intermediate, stable, monosubstituted $(cp)(CO)_2Fe(CH_2)_3Br$.[10] Other stable α:γ-μ-alkenyl compounds were prepared from metal nucleophiles and 1,3-dihalogenoalkanes; examples include $(cp)Co(\mu\text{-}CO)_2(\mu\text{-}CH_2CH_2CH_2)Co(cp)$ (Co–Co),[5] $(cp)(CO)_3W(CH_2)_3W(CO)_3(cp)$,[6] and $(CO)_5Mn(CF_2)_3Mn(CO)_5$.[9a] Another type of reaction between transition-metal carbonylate anions and 1,3-dihalogenoalkanes is the formation of a carbene complex [equation (2)]. Examples here include $[M(CO)]^- = L = [Mn(CO)_5]^-$;[9] $[M(CO)]^- = [Mo(cp)(CO)_3]^-$, $L = [M(cp)(CO)_3]^-$ (M = Mo or W)[6] or I^-;[11] $[M(CO)]^- = [W(cp)(CO)_3]^-$, $L = I^-$;[11] and $[M(CO)]^- = [Fe(cp)(CO)_2]^-$, $L = PPh_3$.[10] Also in these cases formation of the intermediate monosubstituted species $(CO)_5Mn(CH_2)_3Br$, $(cp)(CO)_3Mo(CH_2)_3Br$, and $(cp)(CO)_2Fe(CH_2)_3Br$ has been postulated,[9b] or demonstrated.[6,10,11] It seems therefore that the reactivity of these intermediates is highly sensitive to reaction conditions. In our case the presence of a third CH_2X group could be the factor responsible for the system following a path leading to the formation of the cyclopropane ring. Only one example appears to be known where a transition-metal nucleophile and a 1,3-dihalogenoalkane give a cyclopropane ring. This is in the thermal decomposition of the above mentioned $(cp)Co(\mu\text{-}CO)_2(\mu\text{-}CH_2CH_2CH_2)Co(cp)$ which gives rise to cyclopropane and propylene.[5a]

No alkyl was obtained on treating $Na[Co(CO)_4]$ with $MeC(CH_2X)_3$ under the same conditions used in other cases, presumably due to the very low nucleophilicity of the anion.[13]

1. *Iron*.—Reaction of the very nucleophilic[13] $[Fe(cp)(CO)_2]^-$ and $MeC(CH_2Br)_3$ in a 1.3:1 ratio proceeds rapidly and cleanly at −78 °C according to equation (3). No other compounds were detected in the reaction mixture, even when using an excess of the organic halide, which is not the case in other systems (see below).

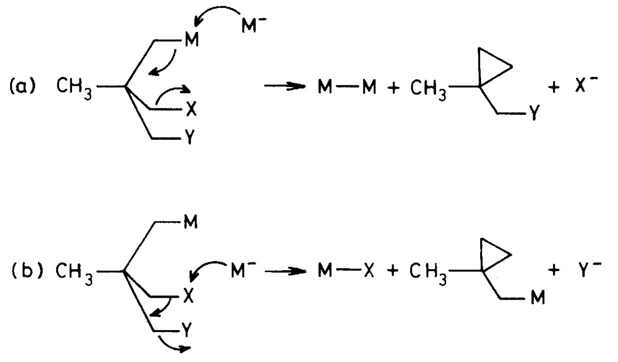
The i.r. spectrum of (**1a**) (Table 1) in the carbonyl stretching region shows the two bands for a bent OC–Fe–CO system. The ^1H and ^{13}C n.m.r. spectra (Table 2) are in agreement with the structure assigned. The ^1H n.m.r. shows two singlets for the CH_3 and MCH_2 protons, and two broad signals for the two sets of chemically but not magnetically equivalent protons H_a and H_b, see (**I**). The slight difference between H_a and H_b also appears in the proton-coupled ^{13}C n.m.r. spectrum, which exhibits a pattern close to a triplet for the two cyclopropane ring carbons, made slightly complex by the difference in coupling constant in the system $CH_aH_bH_{a'}H_{b'}$. The values of ^{13}C chemical shifts and J_{C-H} agree quite well with those reported for similar compounds.[14,15]

2. *Molybdenum and Tungsten*.—Interaction between $[M(cp)(CO)_3]^-$ (M = Mo or W) and $MeC(CH_2I)_3$ is much slower than that with $[Fe(cp)(CO)_2]^-$. Interaction with $MeC(CH_2Br)_3$ gave no product even after prolonged reflux. This behaviour is in line with the nucleophilicity order.[13] By contrast with the iron system, a third product, $MI(cp)(CO)_3$ (M = Mo or W), was formed. The iodide complex was present even after prolonged reflux in the presence of an excess of metal nucleophile. This suggests that the mechanism of reaction (3) involves the formation of M–I at some intermediate stage. This should be followed by interaction of M–I with M^- to produce the dimer M–M and I^-, a reaction known to be fast for $[Fe(cp)(CO)_2]^-$, but very slow for $[M(cp)(CO)_3]^-$ (M = Mo or W).[16a] There appears to be no information on the relative rates of reaction of different systems M–I + M^- to form the dimer M–M, although reports do exist on the formation of heterobimetallic species by the same reaction. Thus $[Mo(cp)(CO)_3]^-$ and $WI(cp)(CO)_3$ react only slowly on refluxing in thf to give $(cp)(CO)_3MoW(CO)_3(cp)$,[16b] thus supporting a slow molybdenum homonuclear reaction. Further, $MoI(cp)(CO)_3$ and $[Mo(cp)(CO)_3]^-$ produced simultaneously as products in a reaction persisted after 2 d in acetone at 25 °C.[16c]



(1)

Scheme 1.

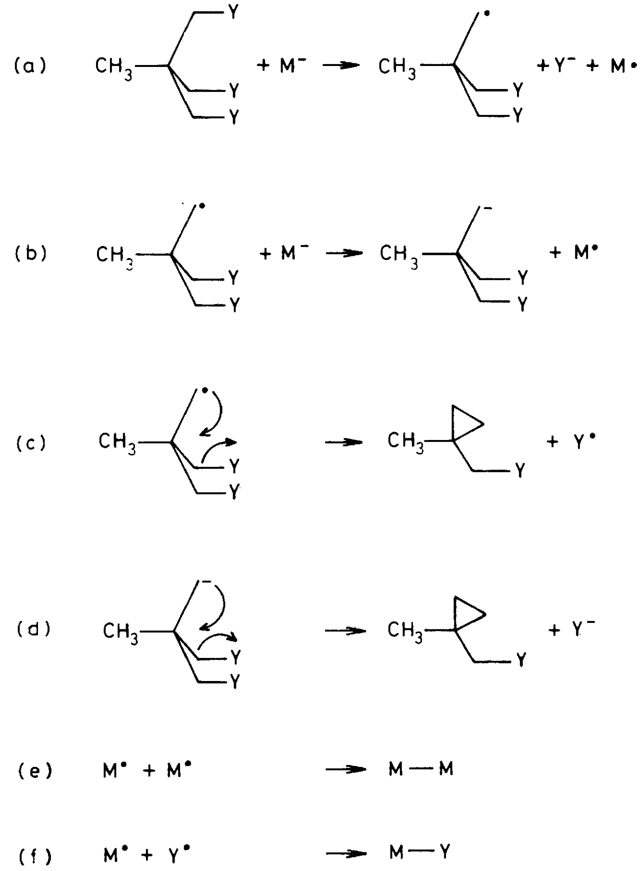


Scheme 2. Y = X or M

A possible mechanism for reaction (3) is shown in Scheme 1. The key step proposed for ring formation is a metathesis involving the metal, the halogen, and two carbon atoms.

Alternative pathways, such as those shown in Scheme 2, cannot, however be excluded; route (a), *i.e.* without formation of the intermediate M–X, could be followed in the iron reaction, whereas the Mo and W systems could prefer route (b). It is, however, not easy to explain why M$^-$ should attack M or X instead of giving the normal S_N2 substitution at carbon. It is worth noting that formation of cyclopropane rings from 1,3-dihalides is a well known phenomenon in organic chemistry[17] and methods of preparation include an electrochemical synthesis involving an electron-transfer mechanism.[18] It cannot be excluded therefore that M$^-$ acts simply as a reducing agent (see Scheme 3). There are indeed reports of a radical mechanism in interactions between cyclopentadienyl–iron nucleophiles and alkyl halides,[19a] but [Mo(cp)(CO)$_3$]$^-$ and [Mn(CO)$_5$]$^-$ are said not to produce radicals.[19b]

X-Ray Structure.—The tungsten compound (**1c**) has been studied crystallographically and the structure proposed on the basis of spectra confirmed. The structure of the molecule is shown in Figure 1; selected bond lengths and angles are given in Table 3. The geometry at tungsten is essentially that of a tetragonal pyramid with the base formed by the alkyl and three



Scheme 3. Y = X or M

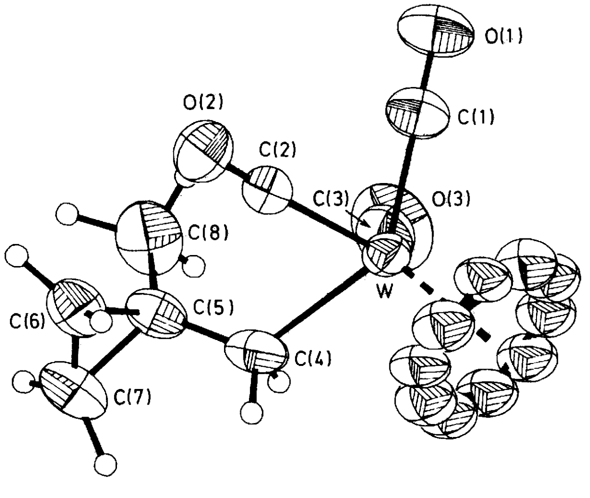
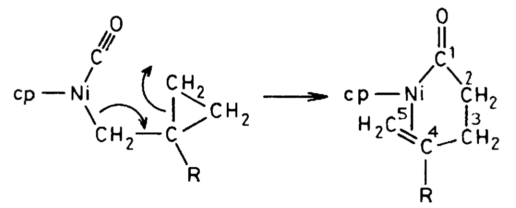


Figure 1. Molecular structure of W(cp)(CO)$_3$ (C$_5$H$_9$) (**1c**); note that the cp ring is disordered

carbonyl carbons, with *cis*-C–W–C angles in the narrow range 74.6(4)—77.5(4)°, capped by the almost symmetrically bonded η^5-cyclopentadienyl ring [W–C 2.32(1)—2.38(1) Å]. Not unexpectedly, the W–C(alkyl) bond is much longer than the W–C(carbonyl) bonds.

The solution i.r. spectra of (**1b**) and (**1c**) (carbonyl stretching region) show only two main bands. If we assume that the geometry in the solid state persists in solution, three strong



(1d) R = Me (4) R = Me
(3) R = H (5) R = H

Scheme 4.

bands ($2A' + A''$) are anticipated for the C_s symmetry of the structure observed for the tungsten compound. The third band observed at 1 895 cm^{-1} for (**1c**) is very weak and is most likely to be due to a ^{13}CO stretching mode; therefore an accidental degeneracy of two out of the three bands must be assumed. Proton and ^{13}C n.m.r. spectra are similar to those already discussed for the iron compound, including the second-order effect due to the inequivalency of the H_a and H_b protons of the cyclopropane ring.

3. *Nickel.*—The reaction between $[Ni(cp)(CO)]^-$ and $MeC(CH_2I)_3$ in thf is very fast at −78 °C and affords a solution which shows the characteristic carbonyl stretches of $[Ni(cp)(CO)]_2$ and of $Ni_3(cp)_3(CO)_2$, plus a sharp peak at *ca.* 2 010 cm^{-1} (*cf.* 2 031 cm^{-1} in hexane, Table 1) assigned to the unisolated complex (**1d**), and a weak band at 1 680 cm^{-1}, due to the complex (**4**) in Scheme 4. Very small amounts of $Ni(cp)_2$ were also found in the products, presumably due to impurity in the starting material.

Formation of the very stable $Ni_3(cp)_3(CO)_2$ is not surprising since this compound appears as a by-product in every reaction carried out with $[Ni(cp)(CO)]^-$.[20,21] Formation of (**4**) is rationalized by assuming the formation of complex (**1d**) [reaction (3)] which then rearranges according to Scheme 4.

This hypothesis is substantiated by an analogous reaction[22] on the closely related complex (**3**) of Scheme 4, prepared by interaction of $[Ni(cp)(CO)]^-$ with cyclopropylmethyl bromide. Although (**3**) was reported[22] to be stable and converted to complex (**5**) only by photolysis, the main product of our reaction was the acyl–η-alkene complex (**4**). This suggests that either this rearrangement is much faster for R = CH_3 or it is in some way catalysed in the reaction conditions employed. It is worth noting, as reported by Brown *et al.*,[22] that when cyclopropylmethyl iodide was used instead of the bromide, complex (**5**) was the only isolated product.

The ^{13}C n.m.r. spectrum of compound (**4**) exhibits a weak singlet at 241.9 p.p.m. due to the carbonyl group. Assignment of the other peaks was made by comparing the chemical shifts and the C–H coupling constants with the values reported in the literature for similar compounds;[15] in particular, the higher field of the two triplets at 49.8 and 48.8 p.p.m. was assigned to the vinylic group due to its typical J_{C-H} value (156.8 Hz). The other triplet had J_{C-H} = 130.4 Hz which is within the range commonly found[15] for α-functionalized aliphatic CH_2 groups and was therefore assigned to C^2.

4. *Manganese and Rhenium.*—In the reaction of $[Mn(CO)_5]^-$ with $MeC(CH_2I)_3$ one of the isolated compounds is not the expected $(CO)_5MnCH_2\overline{C(Me)CH_2CH_2}$, but rather the product of carbonyl insertion into the manganese–alkyl bond [compound (**6**), equation (4)]. Although $Mn_2(CO)_{10}$ was found also, the other main product of the reaction was the known anion $[Mn_3(CO)_{14}]^-$.[23] This reaction occurred using a Mn:I ratio of 4:1 which suggests the stoicheiometry of equation (4).

Table 3. Selected bond lengths and angles for $W(cp)(CO)_3(C_5H_9)$

Bond lengths (Å)			
C(1)–W	1.978(10)	C(2)–W	1.987(9)
C(3)–W	1.985(10)	C(4)–W	2.343(9)
C(91a)–W	2.365(13)	C(92a)–W	2.370(12)
C(93a)–W	2.371(12)	C(94a)–W	2.380(13)
C(95a)–W	2.373(12)	C(91b)–W	2.359(14)
C(93b)–W	2.325(13)	C(94b)–W	2.315(13)
C(1)–O(1)	1.154(10)	C(2)–O(2)	1.136(9)
C(3)–O(3)	1.139(10)	C(4)–C(5)	1.512(11)
C(6)–C(5)	1.517(12)	C(7)–C(5)	1.536(12)
C(8)–C(5)	1.498(11)	H(41)–C(4)	1.061(19)
H(42)–C(4)	0.961(18)	C(7)–C(6)	1.523(14)
H(61)–C(6)	1.015(16)	H(62)–C(6)	1.090(16)
H(71)–C(7)	1.079(16)	H(72)–C(7)	1.131(18)
H(81)–C(8)	0.913(18)	H(82)–C(8)	1.034(21)
H(83)–C(8)	1.180(16)	C(92a)–C(91a)	1.482(17)
C(94a)–C(91a)	1.453(17)	C(93a)–C(92a)	1.486(17)
C(95a)–C(93a)	1.428(18)	C(95a)–C(94a)	1.461(18)
C(93b)–C(91b)	1.388(18)	C(92b)–C(91b)	1.321(19)
C(94b)–C(93b)	1.366(19)	C(95b)–C(94b)	1.325(18)
C(95b)–C(92b)	1.532(21)		
Bond angles (°)			
C(2)–W–C(1)	77.2(4)	C(3)–W–C(1)	77.5(4)
C(3)–W–C(2)	108.5(4)	C(4)–W–C(1)	133.0(3)
C(4)–W–C(2)	76.8(4)	C(4)–W–C(3)	74.6(4)
O(1)–C(1)–W	179.3(8)	O(2)–C(2)–W	175.4(6)
O(3)–C(3)–W	174.3(7)	C(6)–C(5)–C(4)	117.7(7)
C(7)–C(5)–C(4)	114.7(7)	C(7)–C(5)–C(6)	59.9(6)
C(8)–C(5)–C(4)	119.3(7)	C(8)–C(5)–C(6)	115.4(7)
C(8)–C(5)–C(7)	116.0(7)	C(5)–C(4)–W	125.0(6)

$$4[Mn(CO)_5]^- + MeC(CH_2I)_3 \xrightarrow{thf} [Mn_3(CO)_{14}]^- + \underset{(\mathbf{6})}{Mn(CO)_5\text{–}C(O)\text{–}CH_2\text{–}\overline{C(Me)CH_2CH_2}} + 3I^- \quad (4)$$

Two other minor volatile products were found in the n-hexane extract which could not be fully characterized, but neither showed the expected spectroscopic properties of a C_5H_9 compound.

Spectroscopic data confirm the formulation of the acyl (**6**) having three ($2A_1 + E$) terminal CO stretching bands for the C_{4v} symmetry $Mn(CO)_5$ frame, and a low-frequency stretching mode at 1 669 cm^{-1} for the acyl carbonyl group (Table 1). The ^{1}H n.m.r. spectrum (Table 2) has three sharp singlets of relative intensity 2:3:4, suggesting that the four cyclopropane ring protons are essentially equivalent in this compound. This is confirmed in the proton-coupled ^{13}C n.m.r. spectrum (Table 2) where the two equivalent ring carbon atoms give rise to a normal triplet with J_{C-H} = 161.1 Hz. Terminal carbonyl (210.1 p.p.m.) and acyl carbonyl (251.2 p.p.m.) chemical shifts agree with those reported[24] for $(CO)_5Mn(COCH_3)$ (210.0 and 255.0 p.p.m., respectively), whereas the value for C^2 ($-CH_2-$ group) is unexpectedly high (76.8 p.p.m.) compared with the 35—50 p.p.m. generally observed for organic $-CH_2COX$ groups,[15] with 49.8 p.p.m. observed for the nickel compound (**4**) discussed above, and with 52.6 p.p.m. of the CH_3 group in $(CO)_5Mn(COCH_3)$.[24] The mass spectrum of compound (**6**), taken at 70 eV, showed $M^+ - CO$ (m/e = 264, 0.4%) as the heaviest fragment. The molecular peak became observable at 20 eV. In both spectra the most intense peak, at m/e = 223, is assigned to the very stable $[Mn(CO)_6]^+$ fragment.

The reaction with $[Re(CO)_5]^-$ produces the normal product of cyclopropane ring formation (**1e**); as in the manganese case,

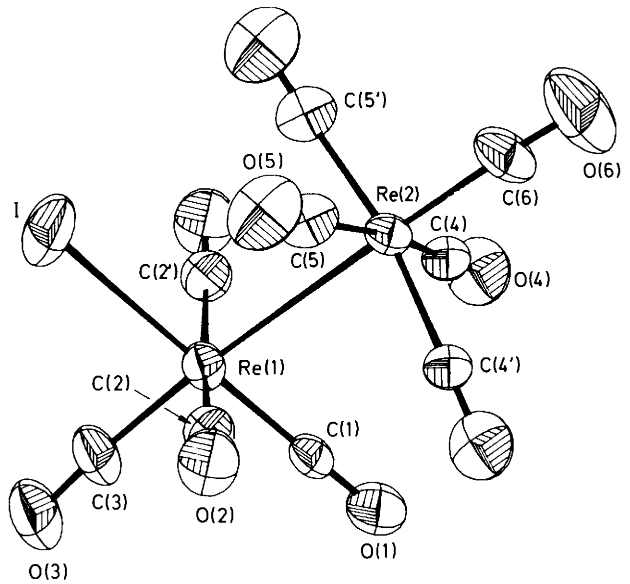


Figure 2. Molecular structure of the $[Re_2I(CO)_9]^-$ ion of (**2**)

some $M_2(CO)_{10}$ was found in the products, but the other major product was in this case the new anion, $[Re_2(CO)_9I]^-$, isolated as its $[NEt_4]^+$ salt and characterized by elemental analysis, i.r., and ^1H n.m.r. spectroscopy, and *X*-ray crystallography (see below). There was no evidence for the presence of an acyl insertion product or of the yet unknown[25] $[Re_3(CO)_{14}]^-$ even on using a Re:I ratio of >4:1. The rhenium reaction thus seems to follow the stoicheiometry of equation (5). The rhenium

$$3[Re(CO)_5]^- + MeC(CH_2I)_3 \xrightarrow{thf} \underset{(\mathbf{1e})}{Re(CO)_5(C_5H_9)} + [Re_2(CO)_9I]^- + 2I^- + CO \quad (5)$$

cyclopropyl (**1e**) shows ^1H and ^{13}C n.m.r. spectra similar to those of the related compounds (**1a**)—(**1c**) (Table 2).

The structure of $[NEt_4][Re_2(CO)_9I]$ (**2**) has been solved by *X*-ray methods. The structure of the anion is shown in Figure 2; selected bond lengths and angles are given in Table 4. The anion, in which the two rhenium atoms, the iodine and three carbonyl groups lie on a mirror plane, has a staggered L_4ReReL_4 conformation. The Re–Re distance is similar to that in $Re_2(CO)_{10}$, which is 3.041(1) Å.[26] The Re–C(carbonyl) distances show variations which are entirely consistent with their bonding positions. Thus, the two 'axial' (*i.e. trans* to the Re–Re bond) Re–C bonds [1.906(13), 1.910(13) Å] are shorter than those equatorial Re–C bonds which are *trans* to each other [1.981(10)—1.989(10) Å]. This feature also occurred in the neutral carbonyl and was explained in terms of availability of and competition for rhenium *d* electrons for back bonding.[26] Also consistent with this idea is the fact that the one Re–C bond *trans* to the iodide is also short, 1.919(13) Å.

Only five out of the possible nine ($6A' + 3A''$) carbonyl bands expected for the C_s symmetry of the anion are observed in thf solution, perhaps because of the poor resolving power of the solvent. Some of the bands are in fact quite broad, but we cannot rule out the possibility of an equilibrium with the axial isomer of symmetry C_{4v}, for which five i.r.-active bands ($3A_1 + 2E$) are expected. However, the similarity of the spectrum with that[27] of $[Re_2(CO)_9H]^-$ (2 078vw, 2 028m, 1 972s, 1 924mw, 1 888m cm^{-1}), for which an equatorial geometry in solution has been demonstrated by ^{13}C n.m.r., supports the assignment of equatorial geometry *in solution* for $[Re_2(CO)_9I]^-$.

Table 4. Bond lengths (Å) and angles (°) for $[NEt_4][Re_2I(CO)_9]$ (**2**)

Bond lengths			
Re(2)–Re(1)	3.052(4)	I(1)–Re(1)	2.833(4)
C(1)–Re(1)	1.919(13)	C(2)–Re(1)	1.982(10)
C(3)–Re(1)	1.906(13)	C(4)–Re(2)	1.981(10)
C(5)–Re(2)	1.989(10)	C(6)–Re(2)	1.910(13)
C(1)–O(1)	1.142(14)	C(2)–O(2)	1.124(10)
C(3)–O(3)	1.188(14)	C(4)–O(4)	1.137(10)
C(5)–O(5)	1.108(10)	C(6)–O(6)	1.132(15)
C(11a)–N(1)	1.481(17)	C(11b)–N(1)	1.454(16)
C(21a)–N(1)	1.583(17)	C(21b)–N(1)	1.620(17)
C(12)–C(11a)	1.583(21)	C(12)–C(11b)	1.614(22)
C(22)–C(21a)	1.709(20)	C(22)–C(21b)	1.651(22)
Bond angles (°)			
I(1)–Re(1)–Re(2)	95.3	C(1)–Re(1)–Re(2)	83.6(4)
C(1)–Re(1)–I(1)	178.9(3)	C(2)–Re(1)–Re(2)	85.4(3)
C(2)–Re(1)–I(1)	86.9(3)	C(2)–Re(1)–C(1)	93.0(3)
C(3)–Re(1)–Re(2)	175.9(4)	C(3)–Re(1)–I(1)	88.8(5)
C(3)–Re(1)–C(1)	92.3(6)	C(3)–Re(1)–C(2)	94.8(3)
C(4)–Re(2)–Re(1)	85.0(3)	C(5)–Re(2)–Re(1)	84.8(3)
C(5)–Re(2)–C(4)	169.8(3)	C(6)–Re(2)–Re(1)	178.3(4)
C(6)–Re(2)–C(4)	93.8(5)	C(6)–Re(2)–C(5)	96.4(5)
O(1)–C(1)–Re(1)	179.7(5)	O(2)–C(2)–Re(1)	176.2(8)
O(3)–C(3)–Re(1)	175.2(12)	O(4)–C(4)–Re(2)	178.7(6)
C(4)–Re(2)–C(4)	89.9(5)	O(5)–C(5)–Re(2)	177.4(8)
C(5)–Re(2)–C(5)	87.3(6)	O(6)–C(6)–Re(2)	178.2(14)

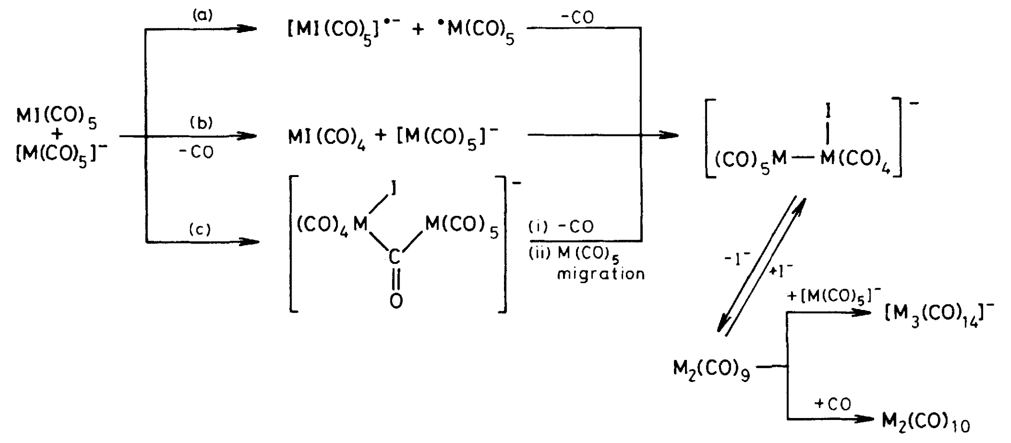
On the other hand, an axial geometry has been assigned to the anions $[Mn_2(CO)_9X]^-$ (X = F, Cl, Br, or I),[28] on the basis of the i.r. only; in view of the present results an *X*-ray structural study on these anions would be desirable.

No direct evidence of the presence of $MI(CO)_5$ (M = Mn or Re) in the reaction mixture could be obtained, but its involvement is nevertheless supported by the following observations.

(*a*) A reaction was carried out between $MnI(CO)_5$ and $[Mn(CO)_5]^-$ in a 1:2 ratio, $MnI(CO)_5$ being obtained *in situ* by iodine oxidation of $[Mn(CO)_5]^-$.[29] This experiment shows that $MnI(CO)_5$ and $[Mn(CO)_5]^-$ do not interact to an appreciable extent in thf within a few minutes at room temperature. After a few hours, however, $MnI(CO)_5$ had disappeared to produce a solution from which $[Mn_3(CO)_{14}]^-$ could be isolated as its $[NEt_4]^+$ salt in 31% yield.

(*b*) An analogous reaction was carried out between $ReI(CO)_5$ and $[Re(CO)_5]^-$ in a 1:1 ratio; again $ReI(CO)_5$ was obtained *in situ* by oxidizing part of the $[Re(CO)_5]^-$ with iodine. In this case a very fast reaction at room temperature took place to afford $[Re_2(CO)_9I]^-$ isolated in 75% yield as its $[NEt_4]^+$ salt.

On the basis of these results a mechanism such as that presented in Scheme 5 can be postulated. Thus $MI(CO)_5$ and $[M(CO)_5]^-$ give rise to $[M_2(CO)_9I]^-$, which is the actual main product for rhenium. Three routes are possible in principle: electron transfer [route (a)], preliminary CO dissociation followed by nucleophilic attack on the metal [route (b)], and nucleophilic attack on CO [route (c)]. The CO evolved in this step induces carbonyl insertion into the Mn–alkyl bond of an intermediate of type (**1**) to form the observed acyl complex (**6**). An analogous CO insertion into the Re–alkyl bond is not observed, in agreement with the known higher stability of this system.[30] $[M_2(CO)_9I]^-$ then reacts, by a dissociative mechanism, with substitution of I^- by either CO or $[M(CO)_5]^-$ to afford the observed products for manganese, $Mn_2(CO)_{10}$ and $[Mn_3(CO)_{14}]^-$.



Scheme 5.

The much higher reaction rate for rhenium suggests that this system follows route (a), in view of the known inertness of $ReX(CO)_5$ to CO dissociation with respect to $MnX(CO)_5$[31] ($k_{Mn} \approx 50\ k_{Re}$ for X = I[31a]). An electron-transfer mechanism has been demonstrated for the reaction between $[Re(CO)_5]^-$ and some $ReXL(CO)_3$ complexes (L = bidentate nitrogen ligand)[31] to form the dinuclear $(CO)_5Re{-}Re(CO)_3L$. What is striking in our reaction is that the supposed intermediate radical anion $[ReI(CO)_5]^{\bullet -}$ loses a CO and not I^-. Such a CO loss must be very fast since $Re_2(CO)_{10}$, which could arise by coupling of two $Re(CO)_5$ units, was found only in trivial amounts in the reaction mixture. The slower reaction for manganese if route (a) is followed is in line with the lower reducing power of $[Mn(CO)_5]^-$ with respect to $[Re(CO)_5]^-$.[32] It cannot, however, be excluded *a priori* that the manganese system follows route (b) or (c), in view of the fact that the reaction rate is enhanced by u.v. light. A nucleophilic attack on CO has been demonstrated for the reaction of $MX(CO)_5$ with LiMe.[33]

Experimental

Microanalyses were by the Imperial College Laboratory. Unless otherwise stated, all operations were carried out in an atmosphere of purified argon. Solvents were dried using conventional methods and distilled under nitrogen.

Spectrometers.—N.m.r.: JEOL FX 9Q [^1H (89.55 MHz) and ^{13}C (22.51 MHz)]. Mass spectra: VG 7070. I.r.: Perkin-Elmer 683; solution i.r. spectra in the carbonyl stretching region were recorded on expanded abscissa and calibrated with CO(g) and H_2O(g). I.r. and n.m.r. data are collected in Tables 1 and 2. $[Fe(cp)(CO)_2]_2$ (Alfa Inorganics), $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ (Strem Chemicals) were used as purchased. $[Mo(cp)(CO)_3]_2$,[34] $[W(cp)(CO)_3]_2$,[34] $[Ni(cp)(CO)]_2$,[35] $MeC(CH_2Br)_3$,[36] and $MeC(CH_2I)_3$[37] were prepared by standard methods.

Reaction between 1,1,1-*Tri*(*bromomethyl*)*ethane and Dicarbonyl*(η^5-*cyclopentadienyl*)*ferrate: Dicarbonyl*(η^5-*cyclopentadienyl*)(1-*methylcyclopropylmethyl*)*iron*(II), (**1a**).—$K[Fe(cp)(CO)_2]$ was prepared *in situ* by Na–K reduction[20] of $[Fe(cp)(CO)_2]_2$ (2.08 g, 6.98 mmol) in thf (150 cm^3), and treated at −78 °C with $MeC(CH_2Br)_3$ (0.50 cm^3, 1.04 g, 3.38 mmol) (Fe:Br = 1.3:1). A white solid was immediately formed; after warming to room temperature, the solution showed i.r. absorption in the carbonyl stretching region at 1 994s, 1 943s, 1 869m, and 1 783s cm^{-1}. The solvent was removed under reduced pressure and the residue sublimed directly at room temperature onto a dry-ice cooled finger. Complex (1a) was obtained as yellow-brown crystals which melted below room temperature to give a brown air-sensitive oil. Yield: 0.60 g, 72% based on $MeC(CH_2Br)_3$. *m/e* (120 °C, 70 eV): 246 (M^+, 5), 218 (M^+ − CO, 7.5), 190 (M^+ − 2CO, 100), 177 (M^+ − cp, 12), 149 (M^+ − cp − CO, 36), 121 [$Fe(cp)^+$, 80], 69 ($C_5H_9^+$, 32), 56 (Fe^+, 70).

The residue from the sublimation was dissolved in thf to give a deep red solution which showed only the i.r. carbonyl stretches of $[Fe(cp)(CO)_2]_2$ and $[Fe(cp)(CO)_2]^-$.

Reaction between 1,1,1-*Tri*(*iodomethyl*)*ethane and Tricarbonyl*(η^5-*cyclopentadienyl*)*tungstate: Tricarbonyl*(η^5-*cyclopentadienyl*)(1-*methylcyclopropylmethyl*)*tungsten*(II), (**1c**).—$K[W(cp)(CO)_3]$ was prepared *in situ* by Na–K reduction[20] of $[W(cp)(CO)_3]_2$ (2.04 g, 3.06 mmol) in thf (50 cm^3) and then treated with $MeC(CH_2I)_3$ (1.11 g, 2.47 mmol). The resulting solution was stirred overnight at room temperature and then refluxed for 1 h. The solvent was removed under vacuum and the residue extracted with n-hexane. Chromatography on Al_2O_3 (Grade 1, 15 × 1.5 cm) eluting with n-hexane–CH_2Cl_2 (1:1) gave an initial yellow band which was collected, the solvent removed under reduced pressure, and the residue recrystallized from n-hexane (*ca.* 5 cm^3) at −20 °C. Yield: 0.26 g, 31%; m.p. 59 °C (Found: C, 38.9; H, 3.4. $C_{13}H_{14}O_3W$ requires C, 38.8; H, 3.5%). *m/e* (120 °C, 70 eV): 400 (M^+, 42), 372 (M^+ − CO, 43), 344 (M^+ − 2CO, 33), 330 (M^+ − C_5H_9, 40), 316 (M^+ − 3CO, 53), 303 (M^+ − C_5H_9 − CO, 96), 275 (M^+ − C_5H_9 − 2CO, 69), 247 [$W(cp)^+$, 100], 182 (W^+, 1.5), 69 ($C_5H_9^+$, 60). The compound is air stable in the solid state but decomposes slowly in solution.

The residue from the n-hexane extraction was suspended in n-hexane (20 cm^3), heated to boiling and filtered hot to give red crystals on cooling. These were shown to be $WI(cp)(CO)_3$ by analysis and by spectroscopic properties. The residue from this last extraction was dissolved in thf to give a solution which showed the characteristic carbonyl stretches of $[W(cp)(CO)_3]_2$.

Reaction between 1,1,1-*Tri*(*iodomethyl*)*ethane and Tricarbonyl*(η^5-*cyclopentadienyl*)*molybdate*.—$K[Mo(cp)(CO)_3]$ was prepared *in situ* by Na–K reduction[20] of $[Mo(cp)(CO)_3]_2$ (2.68 g, 5.47 mmol) in thf (50 cm^3) and then refluxed for 1 h with $MeC(CH_2I)_3$ (0.72 g, 1.61 mmol). The solvent was removed under vacuum and the residue extracted with n-hexane (3 × 15 cm^3). This solution was evaporated and the residue sublimed at 70 °C (10^{-2} mmHg). The first fraction collected consisted mainly of tricarbonyl(η^5-cyclopentadienyl)(1-methylcyclopropylmethyl)molybdenum(II), (**1b**), by comparison of its spectroscopic properties (Tables 1 and 2) with those of the corresponding tungsten derivative. Further purification of this product failed because of rapid decomposition on an Al_2O_3 chromatographic column.

Sublimation was continued to give a red solid which, after recrystallization from hot n-hexane, was shown to be $MoI(cp)(CO)_3$ from its analytical and spectroscopic properties.

The residue from the n-hexane extraction contained $[Mo(cp)(CO)_3]_2$, determined by i.r. in the carbonyl stretching region.

Reaction between 1,1,1-*Tri*(*iodomethyl*)*ethane and Carbonyl*(η⁵-*cyclopentadienyl*)*nickelate:* η⁵-*Cyclopentadienyl*(1-σ:4—5-η-4-*methyl*-1-*oxopent*-4-*enyl*)*nickel*(II), (**4**).—$Na[Ni(cp)(CO)]$ was prepared *in situ* by sodium–naphthalene reduction[21] of $[Ni(cp)(CO)]_2$ (1.39 g, 4.58 mmol) and then treated at −78 °C with $MeC(CH_2I)_3$ (1.19 g, 2.64 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution i.r. spectrum in the carbonyl stretching region showed bands at 2 010m, 1 880m, 1 840s, 1 740m, and 1 680w cm^{-1}. After removal of the solvent under reduced pressure the residue was extracted with n-hexane (2 × 20 cm^3) and chromatographed on Al_2O_3 (Grade 1, 15 × 1.5 cm), eluting with n-hexane. The first eluted band was pale orange-red and showed an i.r. absorption at 2 031 cm^{-1}. This compound was not further characterized because it was obtained in insufficient amount and because its identity can be inferred from other data (see Discussion section). A green band, $Ni(cp)_2$, and a red band, $[Ni(cp)(CO)]_2$, followed whilst a yellow-brown band remained on the top of the column. This was then eluted with CH_2Cl_2 and the solvent removed under vacuum to leave a yellow-orange solid which after crystallization from n-hexane was shown to be compound (**4**). Yield: 0.27 g; m.p. 56—57 °C (Found: C, 59.7; H, 6.4. $C_{11}H_{14}NiO$ requires: C, 59.8; H, 6.4%). *m/e* (100 °C, 70 eV); 220 (M^+, 17), 192 ($M^+ - CO$, 70), 164 $[Ni(cp)C_3H_5^+$, 10], 150 $[Ni(cp)C_2H_3^+$, 5], 136 $[Ni(cp)CH^+$, 21], 124 $[Ni(cp)H^+$, 100], 123 $[Ni(cp)^+$, 38], 97 ($C_6H_9O^+$, 19), 58 (Ni^+, 53). I.r. (Nujol mull): 3 030w, 1 690vs, 1 665vs, 1 495w, 1 340w, 1 260m, 1 200m, 1 040w, 1 020w, 1 010w, 990w, 970m, 955(sh), 925w, 830m, 790s, 775m, 750w, 720w, 600w, 550m, 505w, and 480w cm^{-1}. N.m.r: ^1H (δ, C_6D_6), 5.09 (5 H, s, cp), 2.96 (1 H, s, *cis*-C^5H), 2.15 (1 H, s, *trans*-C^5H), 1.90 (3 H, s, br, CH_3), 1.58 (4 H, s, br $C^2H_2 + C^3H_2$); ^{13}C (δ, C_6D_6), 241.9 (s, C^1), 102.8 (s, C^4), 94.9 (d of m, $J_{C-H} = 174.4$, cp), 49.8 (t, $J_{C-H} = 130.4$, C^2), 48.8 (t, $J_{C-H} = 156.8$, C^5), 32.1 (t, $J_{C-H} = 123.1$, C^3), 29.8 (quartet, $J_{C-H} = 127.9$ Hz, CH_3).

Reaction between 1,1,1-*Tri*(*iodomethyl*)*ethane and Pentacarbonylrhenate: Pentacarbonyl*(1-*methylcyclopropylmethyl*)-*rhenium*(I), (**1e**), *and Tetraethylammonium Enneacarbonyliododirhenate*, (**2**).—$Na[Re(CO)_5]$ in thf (50 cm^3) obtained by Na–Hg reduction[38] of $Re_2(CO)_{10}$ (1.97 g, 30.2 mmol) was stirred overnight at room temperature with $MeC(CH_2I)_3$ (0.74 g, 1.64 mmol). The solvent was removed under vacuum and the yellow residue extracted with n-hexane (2 × 10 cm^3); after filtration, the solution was concentrated and cooled to −78 °C. The white crystals, shown by i.r. to be $Re_2(CO)_{10}$, were removed and the solution evaporated. The liquid residue was distilled at room temperature (10^{-2} mmHg) to a dry-ice cooled finger to give (**1e**) as a white solid which melted below room temperature. Yield: 0.18 g, 28% based on $Me(CH_2I)_3$. *m/e* (130 °C, 70 eV): 394 (M^+, 38), 366 ($M^+ - CO$, 30), 338 ($M^+ - 2CO$, 100), 325 ($M^+ - C_5H_9$, 66), 310 ($M^+ - 3CO$, 38), 297 ($M^+ - C_5H_9 - CO$, 95), 282 ($M^+ - 4CO$, 18), 269 ($M^+ - C_5H_9 - 2CO$, 64), 254 ($M^+ - 5CO$, 5), 241 $[Re(CO)_2^+$, 29], 213 $[Re(CO)^+$, 5], 185 (Re^+, 25), 69 ($C_5H_9^+$, 51).

The residue from the n-hexane extraction was dissolved in ethanol (10 cm^3), the solution filtered and treated with an excess of NEt_4Cl in ethanol. Subsequent addition of water caused the precipitation of a yellow solid which was collected and dried *in vacuo*. Yield: 1.24 g. The solid was washed with Et_2O (3 × 10 cm^3) and then crystallized from ethanol to give well formed crystals of $[NEt_4][Re_2I(CO)_9]$ (**2**) (Found: C, 23.1; H, 2.2; I, 14.6; N, 1.4. $C_{17}H_{20}INO_9Re_2$ requires C, 23.2; H, 2.3; I, 14.4; N, 1.6%). N.m.r: ^1H (δ, CD_3COCD_3), 3.47 (2 H, quartet, $J = 7.2$, CH_2), 1.38 (3 H, tt, $J = 7.2$, $J_{HN} = 1.9$ Hz, CH_3). The salt $[NEt_4][Re_2I(CO)_9]$ in thf showed no spectral change after 24 h exposure to CO (1 atm) at 25 °C.

Reaction between 1,1,1-*Tri*(*iodomethyl*)*ethane and Pentacarbonylmanganate.*—(*a*) *Pentacarbonyl*[2-(1′-*methylcyclopropyl*)-1-*oxoethyl*]*manganese*(I), (**6**)—$K[Mn(CO)_5]$ was obtained by Na–K reduction[20] of $Mn_2(CO)_{10}$ (2.36 g, 6.05 mmol) in thf (50 cm^3) and then stirred overnight at room temperature with $MeC(CH_2I)_3$ (1.79 g, 3.98 mmol). The solvent was removed under vacuum and the residue extracted with n-hexane (3 × 15 cm^3). The yellow solution was cooled to −78 °C to give a mixture of white and yellow crystals. The mother-liquor from this crystallization contained two minor volatile products which could not be fully characterized. The mixture of white and yellow crystals was dissolved in n-hexane. Chromatography on Al_2O_3 (10 × 1.5 cm), eluating with n-hexane, gave an initial band of $Mn_2(CO)_{10}$ (by i.r.); subsequent elution by CH_2Cl_2 (100 cm^3 of solution were collected) and evaporation of the eluate gave a white residue which was recrystallized from n-hexane to give pure (**6**). Yield: 0.12 g; m.p. 77—78 °C (Found: C, 45.1; H, 3.0. $C_{11}H_9MnO_6$ requires C, 45.2; H, 3.1%). *m/e* (90 °C, 20 eV): 292 (M^+, 3), 264 ($M^+ - CO$, 11), 236 ($M^+ - 2CO$, 6), 223 ($M^+ - C_5H_9$, 100), 208 ($M^+ - 3CO$, 8), 195 $[Mn(CO)_5^+$, 30], 180 ($M^+ - 4CO$, 7), 167 $[Mn(CO)_4^+$, 11], 152 ($M^+ - 5CO$, 12), 139 $[Mn(CO)_3^+$, 10], 124 ($M^+ - 6CO$, 38), 111 $[Mn(CO)_2^+$, 8], 96 ($MnC_3H_5^+$, 17), 83 ($MnCO^+$, 6), 69 ($C_5H_9^+$, 19), 55 (Mn^+, 7).

(*b*) *Formation of* $[Mn_3(CO)_{14}]^-$. An identical reaction as described above was carried out but with $Mn_2(CO)_{10}$ (1.06 g, 2.72 mmol) and $MeC(CH_2I)_3$ (0.66 g, 1.47 mmol). After the solvent had been removed from the reaction mixture and the residue extracted with n-hexane the remaining material was treated with Et_2O (30 cm^3) to give a dark red solution which was quickly filtered. From this solution an orange solid deposited on standing for a few hours. This was separated by filtration and dissolved in absolute ethanol. Treatment with an excess of NEt_4Cl gave a red precipitate which was shown to be $[NEt_4][Mn_3(CO)_{14}]$[23] from its analytical and spectroscopic properties. Yield 0.65 g.

Reaction between 1,1,1-*Tri*(*iodomethyl*)*ethane and Tetracarbonylcobaltate.*—$Na[Co(CO)_4]$ was prepared *in situ* from $Co_2(CO)_8$ and NaOH in thf[39] and then treated with $MeC(CH_2I)_3$ (ratio Co:I = 1.0:1). No reaction took place at room temperature after 24 h as evidenced by i.r. in the carbonyl stretching region. Further refluxing for 24 h caused the formation of a black precipitate, while the solution still showed (i.r.) $[Co(CO)_4]^-$ as the only CO-containing species.

Interaction between $[Mn(CO)_5]^-$ *and* I_2 (3:1): *Formation of* $[Mn_3(CO)_{14}]^-$.—$Na[Mn(CO)_5]$, prepared by Na–K reduction[20] of $Mn_2(CO)_{10}$ (0.63 g, 1.62 mmol) in thf (50 cm^3), was treated with I_2 (0.28 g, 1.12 mmol). An immediate formation of a white solid resulted, while the i.r. of the solution recorded a few minutes later showed the presence of $MnI(CO)_5$ and $[Mn(CO)_5]^-$ as the only CO-containing species. After stirring overnight, the i.r. of the solution showed $MnI(CO)_5$ to have reacted completely. The solvent was evaporated and the residue extracted with n-hexane (3 × 20 cm^3) to give a yellow solution from which $Mn_2(CO)_{10}$ (0.13 g) was recovered by evaporation of the solvent and sublimation. The residue was then extracted

Table 5. Fractional atomic co-ordinates (× 10^4) for $W(cp)(CO)_3(C_5H_9)$ (**1c**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	385(0.5)	2 373(0.5)	1 852(0.5)	C(8)	−4 124(11)	2 004(10)	5 052(10)
O(1)	−1 884(9)	2 655(9)	−240(7)	C(91a)	3 290(14)	3 310(13)	1 722(12)
O(2)	−2 120(9)	5 305(7)	2 591(7)	C(92a)	3 128(14)	3 394(13)	328(12)
O(3)	−1 963(10)	−460(8)	2 670(8)	C(93a)	3 095(14)	1 818(13)	11(13)
C(1)	−1 049(10)	2 561(9)	531(8)	C(94a)	3 329(14)	1 752(13)	2 227(12)
C(2)	−1 254(10)	4 209(9)	2 372(7)	C(95a)	3 197(14)	849(13)	1 157(13)
C(3)	−1 187(11)	617(10)	2 408(8)	C(91b)	3 359(15)	2 575(14)	2 117(13)
C(5)	−2 412(10)	2 658(8)	5 164(7)	C(93b)	3 234(15)	1 127(14)	1 799(13)
C(4)	−508(10)	2 167(8)	4 235(7)	C(94b)	3 107(15)	1 211(14)	507(13)
C(6)	−2 689(11)	4 249(9)	5 600(8)	C(92b)	3 240(15)	3 520(14)	1 092(14)
C(7)	−2 446(12)	2 970(10)	6 607(8)	C(95b)	3 050(15)	2 600(14)	−30(13)

Table 6. Fractional atomic co-ordinates (× 10^4) for $[NEt_4][Re_2I(CO)_9]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	−750	2 500	2 309(0.5)	C(3)	−1 450(14)	2 500	4 194(13)
Re(2)	595(0.5)	2 500	−616(0.5)	C(4)	1 927(8)	1 533(5)	198(8)
I(1)	−3 720(1)	2 500	1 242(1)	C(5)	−930(9)	3 449(5)	−1 110(8)
O(1)	2 481(9)	2 500	3 394(8)	C(6)	1 493(16)	2 500	−2 419(12)
O(2)	−897(8)	4 629(4)	1 927(7)	N(1)	5 000	0	5 000
O(3)	−1 782(12)	2 500	5 404(10)	C(11a)	3 551(18)	−472(13)	4 969(22)
O(4)	2 670(7)	967(4)	665(7)	C(11b)	3 811(18)	617(13)	4 530(18)
O(5)	−1 749(8)	3 987(5)	−1 428(8)	C(12)	2 181(9)	177(7)	4 606(10)
O(6)	2 062(17)	2 500	−3 469(12)	C(21a)	5 035(16)	−893(12)	4 030(15)
C(1)	1 275(12)	2 500	−2 993(10)	C(21b)	4 792(20)	−463(12)	6 549(17)
C(2)	−805(8)	3 862(5)	2 099(8)	C(22)	5 384(13)	−441(13)	2 398(11)

with Et_2O (2 × 20 cm^3) and filtered. Removal of the solvent and treatment with EtOH saturated with NEt_4Cl gave a red precipitate shown to be pure $[NEt_4][Mn_3(CO)_{14}]$ by comparison of its i.r. spectrum (Nujol mull) with that of an authentic sample. Yield 0.23 g, 31%.

A parallel experiment was carried out irradiating the suspension obtained after the addition of iodine. $MnI(CO)_5$ reacted completely within 20 min. Work-up as described above yielded 32% of $[NEt_4][Mn_3(CO)_{14}]$.

Interaction between $[Re(CO)_5]^-$ *and* I_2 (2:1): *Formation of* $[Re_2(CO)_9I]^-$.—$Na[Re(CO)_5]$ prepared by Na–Hg reduction of $Re_2(CO)_{10}$ (0.43 g, 0.66 mmol) in thf (50 cm^3) was added quickly to a stirred solution of I_2 (0.158 g, 0.62 mmol). At half addition the pale red solution showed the carbonyl stretches of $ReI(CO)_5$ only. Complete addition gave a bright yellow solution, the i.r. of which showed the carbonyl stretches of $[Re_2(CO)_9I]^-$ plus two weak bands in the region expected for $Re_2(CO)_{10}$. The mixture was evaporated, the residue thoroughly washed with n-hexane and dissolved in the minimum amount of EtOH. Treatment with EtOH saturated with NEt_4Cl, followed by addition of water, caused the precipitation of $[NEt_4][Re_2(CO)_9I]$, which was washed with water and dried *in vacuo*. Yield: 0.45 g (74.5%). The i.r. spectrum was identical to that of the specimen prepared as described above.

X-Ray Crystallographic Studies.—Crystals of both compounds were sealed under argon in thin-walled glass capillaries. All crystallographic measurements were made at 293 K using a CAD4 diffractometer, operating in the ω–2θ scan mode with graphite-monochromatized Mo-K_α radiation (λ = 0.710 69 Å) in a manner previously described in detail.[40] Both sets of data were corrected for absorption.[41]

The structures were solved and refined using routine procedures and standard computer programs. In the case of the rhenium complex, the tetramethylammonium cation occupies a centre of symmetry and is disordered. The N atom lies on the centre and the ethyl groups are oriented so that the four methyl carbons lie at the corners of an approximate square, with the four methylene carbons, half-occupying eight sites. The anion lies on a mirror plane. All atoms were refined anisotropically, and hydrogens were not included.

For the tungsten compound, the cyclopentadienyl group is also disordered, equally occupying two orientations separated by a twist angle of *ca.* 16°. Non-hydrogen atoms were refined anisotropically and hydrogens were freely refined with isotropic thermal parameters.

The weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o^2)]$ was used in each case, with the parameter *g* determined in the refinement so as to give acceptable agreement analyses.

Crystal data for compound (**1c**). $C_{13}H_{14}O_3W$, $M = 402.11$, triclinic, $a = 7.521(2)$, $b = 8.992(1)$, $c = 10.357(2)$ Å, $\alpha = 85.02(2)$, $\beta = 71.88(2)$, $\gamma = 85.41(2)°$, $U = 662.14$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 2.016$ g cm^{-3}, μ(Mo-K_α) = 83.48 cm^{-1}.

Data collection. Scan width $\omega = (0.8 + 0.35 \tan \theta)°$, $1.5 < \theta < 25.0°$, scan speeds 1.35—6.77° cm^{-1}. 2 326 Unique data, 2 101 observed $[I > 2\sigma(I)]$.

Structure refinement. No. of parameters 235, weighting factor $g = 0.0001$, $R = 0.026$, $R' = 0.0273$.

Crystal data for compound (**2**). $C_{17}H_{20}INO_9Re_2$, $M = 881.66$, monoclinic, $a = 9.069(3)$, $b = 14.474(2)$, $c = 9.389(2)$ Å, $\beta = 92.45(2)°$, $U = 1\,231.32$ Å^3, space group $P2_1/m$, $Z = 2$, $D_c = 2.38$ g cm^{-3}, μ(Mo-K_α) = 111.48 cm^{-1}.

Data collection. Parameters as above; 2 260 unique data, 1 853 observed $[I > 2\sigma(I)]$.

Structure refinement. No. of parameters 169, weighting factor $g = 0.0004$, $R = 0.0284$, $R' = 0.0295$.

Final atomic co-ordinates are given in Table 5 for (**1c**) and Table 6 for (**2**).

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