SOME NEW MIXED METAL CARBONYLS OF MANGANESE RHENIUM, RUTHENIUM, AND OSMIUM. E.W. Abel, R.A.N. McLean and S. Moorhouse. Department of Inorganic Chemistry, The University, Bristol BS8 ITS, England.

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The homolysis of metal carbonyls either thermally or under the action of radiation has been reported to produce a wide range of mixed metal carbonyls such as $MnRe(CO)_{10}^{1}$, $Mn_2Fe(CO)_{14}^{1}$, $Ru_2Os(CO)_{12}^{2}$, $RuOs_2(CO)_{12}^{2}$, Ru

We have found the thermally induced action of manganese and rhenium decacarbonyls upon other metal carbonyls and organometallic compounds to be extensive.

There has been discussion^{4,5} recently regarding the presence of manganese pentacarbonyl radicals in the reactions of manganese decacarbonyl, but there now appears to be no necessity⁵ to invoke $Mn(CO)_5$ radicals to explain the kinetics of substitution reactions of manganese decacarbonyl by Lewis bases. Thus the only unequivocal evidence for the existence of $Mn(CO)_5$ radicals to date is in the mass spectrometer⁶ above 210°, and in reactions following the neutron bombardment⁷ of manganese decacarbonyl. We believe the reactions below suggest that manganese decacarbonyl can undergo homolytic fission to produce radicals under normal reaction conditions. This accords with a bonding picture in which the A₁ metal-metal σ bonding orbital is considered to be the highest filled level in manganese decacarbonyl.

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to attack another metal carbonyl has provided a useful route to a number of mixed metal carbonyls A typical reaction involves manganese decacarbonyl and ruthenium dodecacarbonyl.

 $3Mn_2(CO)_{10} + Ru_3(CO)_{12} \longrightarrow 3(CO)_5 MnRu(CO)_4 Mn(CO)_5$

A mixture of ruthenium dodecacarbonyl (0.128g.), and $Mn_2(CO)_{10}$ (1.17g.) was heated in an evacuated sealed tube (205°C, 50hr.). Excess of manganese decacarbonyl was removed at 25°/0.001 mm., and the residue was sublimed at 90°/0.001 mm., to produce the yellow rutheniumdimangarese tetradecacarbonyl (0.127g., 35% based upon $Ru_3(CO)_{12}$). Calculated for $C_{14}Mn_2O_{14}Ru$: C, 27.9; H, O; Mn, 18.3; O, 37.2; Ru, 16.8%. M.W. 604. Found: C, 28.1; H, O; Mn, 18.1; O, 37.2; Ru, 16.9%. M.W. 614 (vapour pressure, acetone). The product was further characterised by mass spectrometry, and the accurate mass determinations of the ions $[Mn_2Ru(CO)_{14}]^+$ (Found: 603.710, Calculated 603.709) and $[Mn_2Ru]^+$ (Found: 211.782, Calculated: 211.780).

In the same way were prepared $(CO)_5 MnOs(CO)_4 Mn(CO)_5$; and $(CO)_5 ReOs(CO)_4 Re(CO)_5$ as outlined in Table 1. The structure of these new mixed metal carbonyls is believed to be that illustrated in Figure 1, by analogy with the X-ray structural determination of $(CO)_5 MnFe(CO)_4 Mn(CO)_5 = \frac{8}{5}$.



Figure 1. Structure of the Metal Carbonyls. $MM_2^1(CO)_{14}$ [M = Mn and Re; M = Ru and Os.].

TABLE 1.

Homolysis Reactions Between Metal Carbonyls.

Reactants.	Condition	Product	CO Stretching Frequency cm ⁻¹
$Mn_2(CO)_{10} + Ru_3(CO)_{12}$	205 ⁹ /40hr.	(CO) ₅ MnRu(CO) ₄ Mn(CO) ₅	2060 (5.6), 2026 (10), 1985 (5.4), 1981 (5.4).
$Mn_2(CO)_{10} + 0s_3(CO)_{12}$	205 ⁰ /50hr.	(CO) ₅ MnOs(CO) ₄ Mn(CO) ₅	2068 (3.5), 2020 (10), 1987 (3.1).
Re ₂ (CO) ₁₀ + Os ₃ (CO) ₁₂	250 ⁰ /50hr.	(CO) ₅ ReOs(CO) ₄ Re(CO) ₅	2094 (2.1), 2021 (10), 1982 (3.5).
$\text{Re}_{2}(\text{CO})_{10} + \text{Mn}_{2}(\text{CO})_{10}$	220 ⁰ /€0hr.	(CO) ₅ ReMn(CO) ₅	2055 (6), 2019 (10), 1980 (7).

Manganese decacarbonyl also reacts with $[(\pi-C_5H_5)Fe(CO)_2]_2$ and $[(\pi-C_5H_5)Mo(CO)_3]_2$ to produce small quantities of $(\pi-C_5H_5)Fe(CO)_2Mn(CO)_5$ and $(\pi-C_5H_5)Mo(CO)_3Mn(CO)_5$ respectively, but also extensive formation of $(\pi-C_5H_5)Mn(CO)_3$. The latter compound is the sole product of the reaction between manganese decacarbonyl and $[(\pi-C_5H_5)Ni(CO)]_2$; and further, $(\pi-C_5H_5)Mn(CO)_3$ is formed in low yield (5%) by the action of manganese decacarbonyl upon ferrocene.

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