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Preliminary communication

THE REACTION OF $Re_2(CO)_{10}$ WITH CYCLOHEPTATRIENE

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Summary

The reaction of $Re_2(CO)_{10}$ and cycloheptatriene (CHT) under photochemical conditions has been shown to yield $(CHT)Re_2(CO)_n$ (n = 7 and 8) and (cyclo-C_7H_9)$Re(CO)_3$.

As part of a study of the reactivity of complexed olefins we have investigated the reaction of $Re_2(CO)_{10}$ with cycloheptatriene under photochemical conditions and in view of the recent interest in the bonding of olefins to manganese carbonyl moieties [1,2], we wish to communicate the following results.

Photolysis of $Re_2(CO)_{10}$ and excess cycloheptatriene in petroleum ether (b.p. 60-80°) under nitrogen by means of a 125 Watt Hanovia lamp during 9 h yielded an insoluble colourless product and a yellow solution. The former was identified by means of infrared and analytical data as the tetranuclear hydroxycarbonyl, $[Re(CO)_3OH]_4$ [3], presumably arising from the presence of small quantities of water in the solvent. Thin-layer chromatography of the petroleum soluble material showed the presence of three products, together with a small quantity of unreacted cycloheptatriene. Separation of this mixture was attempted on a silica column employing graded elution from petroleum ether (b.p. 60-80°) to toluene and yielded 66 ten ml fractions. Fractions 37 to 49 contained $(C_7H_8)Re_2(CO)_7$ (I) and fractions 20 to 35 yielded a mixture of $(C_7H_8)Re_2(CO)_8$ (II) and $(C_7H_9)Re(CO)_3$ (III). As yet, this mixture has not been separated on a preparative scale. I was recrystallised from isopropanol yielding bright yellow crystals (1%) and was characterised by mass spectrometry (M^+, $(M - nCO)^+$ (n = 1-7) observed), FT ^1H NMR (τ 4.6 ppm, multiplet, 3 protons; τ 5.3 ppm, multiplet, 3 protons; τ 6.2 ppm, triplet (8Hz), 2 protons), and infrared spectroscopy (2080w, 2010m, 1995s, 1962w, 1945m cm^{-1} (hexane solution)). Mass spectrometry of the mixture of II and

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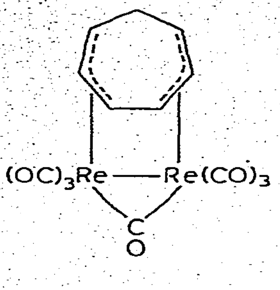
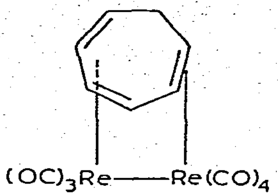
III showed clearly the molecular and fragment ions associated with these species and low voltage studies (12 eV) showed only the two molecular ions. The mixture showed infrared absorptions at 2108w, 2080m, 2014s, 1996m, 1980s, 1977(sh) and 1969m (hexane solution).

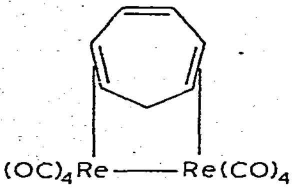


(Ia)



(Ib)

Two structures may be postulated for I (Ia and Ib), the 18-electron rule being satisfied in both cases. The bis-allyl structure Ia is discounted as there is no band attributable to a bridging carbonyl group in the infrared spectrum and the NMR spectrum is quite unlike that shown by the related compound, $(C_7H_8)Fe_2(CO)_6$ [4]. We suggest structure Ib for I and it is noteworthy in this context, that the related compound, (cyclo-C_8H_8)$Mn_2(CO)_6$ has been shown to adopt a bis-diene mode of coordination [2]. The NMR spectrum of I is somewhat surprising as it might be anticipated that the rigid mode of coordination suggested would lead to the observation of separate signals for the two C(7) protons. The reason for the equivalence of these protons is, at present, not clear.



(II)

Although II has, so far, only been identified by means of mass spectrometry, we suggest that it adopts the structure shown by analogy with I. The isolation of the cycloheptadienyl complex, III, is somewhat surprising; however, the manganese analogue has been reported from the reaction of cycloheptatriene and $H_3Mn_3(CO)_{12}$ [1] and as $H_3Re_3(CO)_{12}$ is formed as an intermediate in the production of $[Re(CO)_3OH]_4$ [3], the heptadienyl complex may arise via this route. Other sources of hydrogen are, of course, the solvent and cycloheptatriene, but as we have been unable to completely inhibit the formation of $[Re(CO)_3OH]_4$, despite rigorous attempts to exclude moisture, we are unable to eliminate any of the possible hydrogen sources.

Further studies are in progress on these and related reactions.

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