

Photochemistry of $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$: Preparation and X-Ray Crystal Structure of $(\eta\text{-C}_5\text{Me}_5)_2\text{Re}_2(\mu\text{-CO})_3$

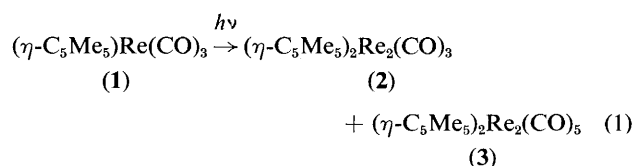
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Ultraviolet irradiation of $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ forms the stable complexes $(\eta\text{-C}_5\text{Me}_5)_2\text{Re}_2(\mu\text{-CO})(\text{CO})_4$ and $(\eta\text{-C}_5\text{Me}_5)_2\text{Re}_2(\mu\text{-CO})_3$; the length of the formal Re–Re triple bond in the latter is determined by X-ray diffraction to be 2.411(1) Å.

Several dinuclear metal carbonyls are known to which a metal–metal triple bond may formally be assigned. Their reactivity is of great interest, although investigations have hitherto been limited to the compounds $(\eta\text{-C}_5\text{R}_5)_2\text{M}_2(\text{CO})_4$ (R = H, Me; M = Mo, W).¹ We report here the synthesis of a new rhenium derivative of this class which, in view of its stability and ease of synthesis, promises to be a valuable model compound.

When $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ (1)² is irradiated with u.v. light (20 °C, cyclohexane, N₂ purge), two dinuclear rhenium compounds form [equation (1)].



Compound (2) is isolated (*ca.* 30% on the basis of unrecovered starting material) as air-stable, orange–red crystals decomposing above 175 °C. Its spectroscopic properties are as follows: i.r. (hexane), ν_{CO} 1748 cm⁻¹; ¹H n.m.r. (CD₂Cl₂)

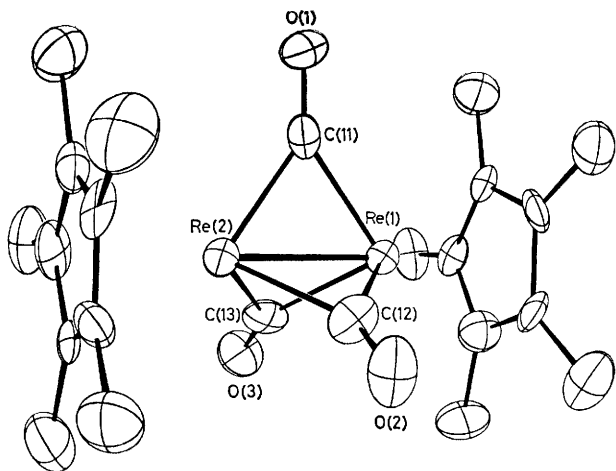


Figure 1. The structure of $(\eta\text{-C}_5\text{Me}_5)_2\text{Re}_2(\mu\text{-CO})_3$ (**2**). Selected bond lengths (Å): Re(1)–Re(2) 2.411(1), Re(1)–C(11) 2.040(10), Re(1)–C(12) 2.069(10), Re(1)–C(13) 2.078(10), Re(2)–C(11) 2.048(10), Re(2)–C(12) 2.072(10), Re(2)–C(13) 2.108(10). Selected bond angles ($^\circ$): Re(1)–C(11)–Re(2) 71.3(3), Re(1)–C(12)–Re(2) 71.4(3), Re(1)–C(13)–Re(2) 70.7(3).

δ 2.03 (s); ^{13}C n.m.r. (CD_2Cl_2) δ 10.2 (CH_3), 100.6 ($\eta\text{-C}_5$ ring), and 231.3 ($\mu\text{-CO}$) p.p.m.; mass spectrum (16 eV, 135°) M^+ and $(M - \text{CO})^+$. A highly symmetrical structure was indicated and the formulation as $(\eta\text{-C}_5\text{Me}_5)_2\text{Re}(\mu\text{-CO})_3\text{Re}(\eta\text{-C}_5\text{Me}_5)$ was confirmed by X-ray methods.†

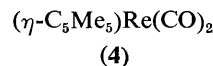
Crystal data for (2): $\text{C}_{25}\text{H}_{30}\text{O}_3\text{Re}_2$, $M = 726.89$, triclinic, space group $P\bar{1}$, $a = 10.151(2)$, $b = 13.498(3)$, $c = 8.806(3)$ Å, $\alpha = 94.20(2)$, $\beta = 101.77(2)$, $\gamma = 70.89(2)^\circ$, $U = 1116.04$ Å 3 , $D_c = 2.163$ g cm $^{-3}$, $Z = 2$, $\mu = 114.71$ cm $^{-1}$. Diffraction data were collected with an Enraf–Nonius CAD4 automated diffractometer using Mo- K_α radiation and an ω – 2θ scan technique. The structure was solved by a combination of Patterson and difference Fourier methods. In the final cycle 254 parameters were refined using 1773 observations having $I > 3.0 \sigma(I)$; final R and R_w values were 0.036 and 0.044, respectively.‡

The molecular structure of (**2**) (Figure 1) is indeed highly symmetrical, approximately D_{3h} , if only the metal atoms and carbonyl groups are considered. The planes formed by the five-membered rings are parallel to within one degree. The Re–Re separation is 2.411(1) Å, a short value consistent with the triple bond implied by the 18-electron formalism. It is intermediate in length between the formal double bond in $(\mu\text{-H})_2\text{Re}_2(\text{CO})_8$ [2.896(3) Å]³ and the quadruple bond in $[\text{Re}_2\text{Cl}_8]^{2-}$ [2.241(7) Å],⁴ although shorter than the formal triple bond in $\text{H}_4(\mu\text{-H})_4\text{Re}_2(\text{PET}_2\text{Ph})_4$ [2.538(4) Å].⁵

The invocation of a triple Re–Re bond in (**2**), while of undeniable heuristic value, does not facilitate a realistic discussion of bonding. The molecular orbital treatment of Hoffmann *et al.*⁶ provides a suitable framework, and those authors in fact predicted the existence of $(\eta\text{-C}_5\text{H}_5)_2\text{Mn}_2(\mu\text{-CO})_3$.§ The

orbital pattern in (**2**) (a 30-electron complex) would be similar to that in $\text{Fe}_2(\text{CO})_9$ (a 34-electron complex); the empty levels in (**2**) are antibonding between the metals, thus accounting for the short Re–Re distance. Compound (**2**) is also a homologue of the isoelectronic series exemplified by $(\eta\text{-C}_4\text{R}_4)_2\text{Fe}_2(\mu\text{-CO})_8$ ⁷ and $(\eta\text{-C}_5\text{H}_6)_2\text{Cr}_2(\mu\text{-CO})_8$.⁸

Compound (**3**), the other product from reaction (1), forms yellow crystals, m.p. 158–160 °C. Spectroscopic properties: i.r. (hexane), ν_{CO} 1971 w, 1930 s, 1901 s, 1877 w, and 1714 m cm $^{-1}$; ^1H n.m.r. (CD_2Cl_2) δ 2.00 (s); ^{13}C n.m.r. (CD_2Cl_2) δ 10.3 (CH_3), 100.2 ($\eta\text{-C}_5$), and 214.7 (CO) p.p.m. These data establish that (**3**) is similar structurally to $(\eta\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$,⁹ which it also resembles in its fluxional behaviour.¹⁰ Compound (**3**) arises (as suggested for the $\eta\text{-C}_5\text{H}_5$ reaction⁹) from reaction of (**1**) with the photochemically generated 16-electron intermediate $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2$ (**4**). Irradiation of (**3**) in the presence of L (L = PPh $_3$, MeCN) forms (**1**) and $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\text{L}$, suggesting that (**3**) is a further source of the crucial intermediate (**4**). We presume that dimerization of (**4**) with rapid loss of CO produces (**2**); the putative dimer $(\eta\text{-C}_5\text{Me}_5)_2\text{Re}_2(\text{CO})_4$ is not observed.



Preliminary investigation shows that (**2**) is less reactive than $(\eta\text{-C}_5\text{R}_5)_2\text{M}_2(\text{CO})_4$ ¹ or the double bonded complexes $\text{H}_2\text{Os}_5(\text{CO})_{10}$ ¹¹ and $(\eta\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\text{CO})_2$.¹² Compound (**2**) did not react with acetylene, diazomethane, or phosphines under conditions similar to those reported.^{1,12} At 100 °C and 200 atm of CO for 15 h, (**2**) was converted in good yield into (**1**). With I_2 , the only isolable product was $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\text{I}_2$.

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† The structure determination was carried out in the Structure Determination Laboratory of this department by Dr. Richard Ball.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ We have obtained i.r. (ν_{CO} 1781 cm $^{-1}$) and mass spectrometric evidence for $(\eta\text{-C}_5\text{Me}_5)_2\text{Mn}_2(\text{CO})_3$ but characterization is not yet complete. The dark green manganese analogue is much less stable than (**2**).