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Preliminary communication

Synthesis and X-ray structure of bis(π-cyclopentadienyl)pentacarbonyldirhenium

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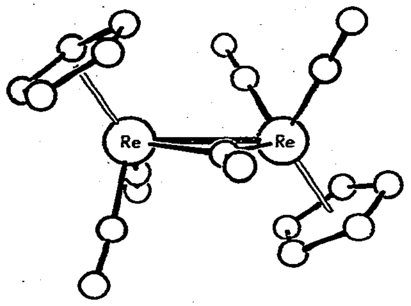
We wish to report the synthesis and structure of the title compound, $(h^5\text{-}C_5H_5)_2\text{-}Re_2(CO)_5$ (I), which is closely related to, but much more stable than, diosmium enneacarbonyl[1].

Ultraviolet irradiation of a cyclohexane solution (0.80 g in 100 ml, nitrogen atmosphere) of $\pi\text{-}C_5H_5Re(CO)_3$ for 2.5 h resulted in a yellow solution. Solvent was removed at reduced pressure and the solid sublimed to yield 0.60 g of starting material. Recrystallization of the residue from dichloromethane afforded yellow needles of I (0.08 g, m.p. 138–140° with decomposition). The mass spectrum of the compound exhibits the molecular ion, with the most intense peak of this multiplet at m/e 642. A satisfactory elemental analysis has also been obtained. The NMR spectrum showed a single sharp peak at τ 4.65, and carbonyl stretching bands were observed in the infrared spectrum at 1992 (0.7), 1956 (10.0), 1923 (9.0), 1904 (1.2) and 1740 (4.5) cm^{-1} (cyclohexane, relative intensities on a transmittance scale in parentheses).

Compound I crystallizes in the monoclinic system, space group $P2_1/n$, with a, 9.529 (1); b, 13.934 (2); c, 11.521 (2); β, 97.290 (4). Intensity data were collected on a Picker manual four-circle diffractometer with crystal monochromatized Mo-Kα radiation for $2\theta \leqslant 45°$. Of the 2034 reflections measured in the asymmetric unit, 1390 with $F \geqslant 5\sigma(F)$ were treated for Lorenz, polarization, and absorption effects and employed in the subsequent calculations.

The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares with rhenium atoms anisotropic, cyclopentadienes as hindered rotors[2], all other atoms isotropic and anomalous dispersion included, to a conventional R factor of 4.8% with 77 parameters. A detailed report of the structure will be made later. Figure 1 shows the determined geometry of $(C_5H_5)_2Re_2(CO)_5$.

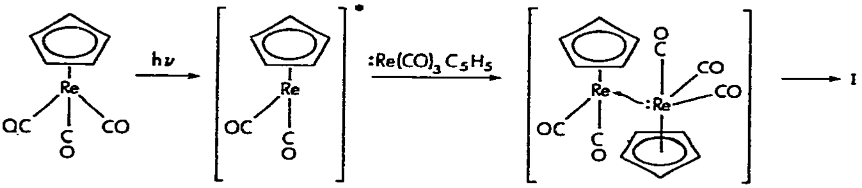
The principal stereochemical feature of I is the ketonic carbonyl group symmetrically bridging the 2.957 (1) Å Re–Re bond. This is the largest carbonyl-bridged metal–metal separation yet observed, and is distinctly greater than carbonyl-bridged metal–metal distances in the related compounds $(C_5H_5)_2Rh_2(CO)_3$ (Rh–Rh, 2.681Å)[3], $(C_5H_5)_2Ru_2(CO)_4$ (Ru–Ru, 2.735Å)[4], and $Pt_4(PPh_3)_4(CO)_5$ (Pt–Pt, 2.75–2.79Å)[5]. It is also distinctly longer than the bridged metal–metal distances in $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ (2.73Å)[6]. The *trans* arrangement of the cyclopentadienyl groups in I and resulting C_2 molecular symmetry are consistent with the solution infrared spectrum.



$(h^5\text{-}C_5H_5)_2Re_2(CO)_5$

Fig. 1. The molecular structure of bis(π-cyclopentadienyl)pentacarbonyldirhenium. Selected bond lengths (Å) are: Re–Re, 2.957 (1); Re–CO (bridging), 2.06 (2); Re–CO (terminal), 1.85 (2); Re–C (C_5H_5), 2.24–2.34 (1). Selected bond angles are Re–CO–Re, 91.7 (8)°; terminal CO–Re–terminal CO, 85 (1)°.

We postulate that I is formed in the following sequence of steps:



II

The basicity of the metal atom in $C_5H_5Re(CO)_3$ suggests that it may coordinate to the unsaturated intermediate II, followed by rearrangement of a terminal carbonyl to bridging to give I. This viewpoint is similar to the donor-acceptor interaction demonstrated by Deubzer and Kaesz[7], although subsequent rearrangement did not occur in the case they examined. We have found that I reacts with triphenylphosphine to give equimolar amounts of π-$C_5H_5Re(CO)_3$ and π-$C_5H_5Re(CO)_2P(C_6H_5)_3$, a process which can be regarded as a displacement of the donor π-$C_5H_5Re(CO)_3$ by the stronger donor $P(C_6H_5)_3$.

An exactly similar mechanism would account for the formation of $Os_2(CO)_9$ upon irradiation of $Os(CO)_5$ at low temperature. The $C_5H_5Re(CO)_2$ and $Os(CO)_4$ moieties are equivalent from the effective atomic number viewpoint, and the structure now established for I must be considered to lend support to the single-bridged structure inferred from infrared evidence for $Os_2(CO)_9$[1]

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