

Monomeric, Dimeric, and Trimeric Carbonyl(phenylthio)rhenium Complexes: A New Rhenium Atom Cluster

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MANY dimeric transition-metal complexes containing bridging RS groups have been prepared, *e.g.*, $[\text{RS}\cdot\text{Fe}(\text{CO})_2]_2$,¹ $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\cdot\text{SR}]_2$,² $[\pi\text{-C}_5\text{H}_5\text{Co}\cdot\text{SR}]_2$,² $[\pi\text{-C}_5\text{H}_5\text{V}(\text{SCH}_3)_2]_2$,³ $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{-SR}]_2$,⁴ $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{SCH}_3)_2]_2$,¹ and $[\text{RS}\cdot\text{Mn}(\text{CO})_4]_2$.⁴ In these complexes the RS group can formally be regarded as a three-electron donor, covalent metal-metal interactions being invoked in some instances to account for the magnetic properties.

Monomeric carbonyl complexes containing non-bridging RS groups were unknown until recently when a single example $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\cdot\text{SCH}_3]$ was described.⁵

In a search for mononuclear carbonyls containing RS groups it seemed certain that many such complexes could be stabilized if the group R was strongly electronegative. The electron-pair donor power⁶ of the sulphur atom would thereby be

¹ R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1584, 1587; and references cited therein.

² R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3600.

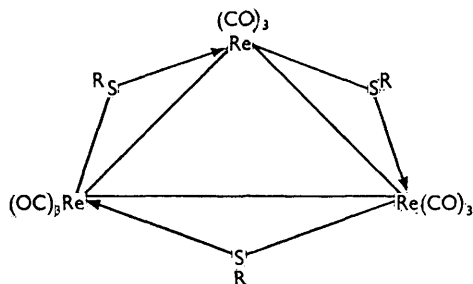
³ R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, 1963, **2**, 219.

⁴ P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 1963, 720.

⁵ R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1965, **4**, 482.

⁶ F. G. A. Stone, *Chem. Rev.*, 1958, **58**, 101.

reduced, hence further loss of CO and consequent dimerization would be inhibited. Experiments

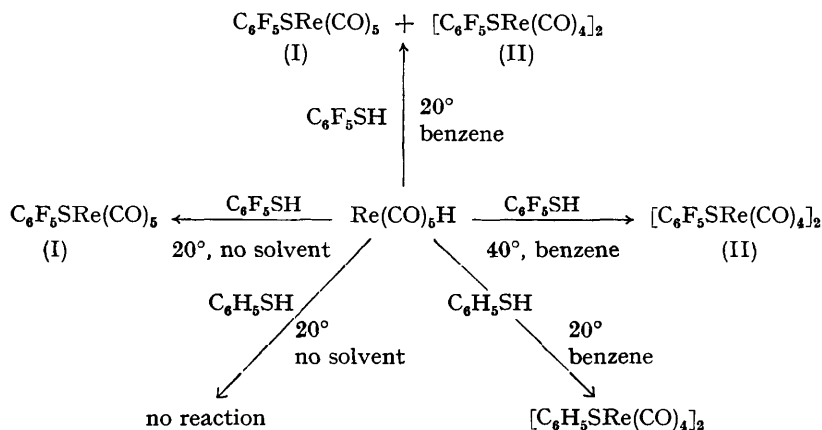


with pentafluorophenyl mercaptan and phenyl mercaptan gave the results shown on the accompanying chart.

$[\text{C}_6\text{F}_5\text{S}\cdot\text{Mn}(\text{CO})_4]_2$, while in benzene at 20° $\text{HMn}(\text{CO})_5$ and $\text{C}_6\text{F}_5\text{SH}$ yield only dimeric $[\text{C}_6\text{F}_5\text{S}\cdot\text{Mn}(\text{CO})_4]_2$.

The complex $[\text{C}_6\text{H}_5\text{S}\cdot\text{Re}(\text{CO})_4]_2$ has been previously prepared by treating $\text{ClRe}(\text{CO})_5$ with $\text{C}_6\text{H}_5\text{SH}$.⁷ We can confirm this result, but by using more vigorous conditions we have obtained a white complex (III) (m.p. 240° dec.) for which we suggest the structure shown, on the basis of analysis, molecular weight, diamagnetism, and the infrared spectrum. It is interesting to compare (I), (II), and (III) with the series $\text{ClRe}(\text{CO})_5$, $[\text{ClRe}(\text{CO})_4]_2$, and $[\text{Re}_3\text{Cl}_{12}]^{3-}$. The rhenium atoms in (III) would be essentially in the same kind of environment as those in $[\text{Re}_3\text{Cl}_{12}]^{3-}$.⁸

Several rhenium and manganese complexes $[\text{RS}\cdot\text{M}(\text{CO})_3]_3$ have been made by Abel, Brady, and Crosse⁹ by an entirely different route, and their



In solution, at room temperature, (I) (pale yellow, m.p. 158°) slowly releases CO affording (II) (pale yellow, m.p. 109°). In contrast monomeric $\text{C}_6\text{F}_5\text{S}\cdot\text{Mn}(\text{CO})_5$ is very rapidly converted into

work and ours suggests that RS groups will bind together metal-atom clusters in a manner analogous to that of halogen atoms.¹⁰

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⁷ W. Hieber and L. Schuster, *Z. anorg. Chem.*, 1956, **285**, 205.

⁸ (a) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 1963, 116; (b) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, 1963, **2**, 1166.

⁹ E. W. Abel, D. B. Brady, and B. C. Crosse, to be published.

¹⁰ J. Lewis, *Pure Appl. Chem.*, 1965, **10**, 11.