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PHOSPHORUS-BRIDGED DERIVATIVES OF MANGANESE AND RHENIUM CARBONYLS DERIVED FROM (TRIMETHYLSILYL)-DIPHENYLPHOSPHINE

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Clusters of manganese and rhenium atoms are becoming increasingly well known and among the atoms known to act as bridges in such clusters are chlorine[1], bromine[1], sulphur [2,3,4], selenium[5] and hydrogen[6]. In an effort to extend the range of bridging atoms for such clusters, we have investigated the reaction between (trimethylsilyl)diphenylphosphine, $(CH_3)_3SiP(C_6H_5)_2$, and the pentacarbonyl halides of manganese and rhenium. Similar reactions involving fission of organosulphur and organoselenium derivatives of tin[2a,2b,5] and silicon[7] having previously resulted in the direct or indirect formation of metal clusters.

Under mild conditions, the silylphosphine reacted with the pentacarbonyl halides to produce the known[8] dimeric species $[M(CO)_4P(C_6H_5)_2]_2$. The overall reaction may be represented by eqn. (1), and the structure of the product is believed to be as represented in Fig. 1.

$$2\,M(CO)_5Br + 2\,Me_3SiP(C_6H_5)_2 \rightarrow [M(CO)_4P(C_6H_5)_2]_2 + 2\,(CH_3)_3SiBr + 2\,CO \qquad (M = \text{Mn and Re}) \quad (1)$$

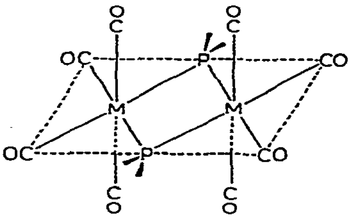

Fig. 1.

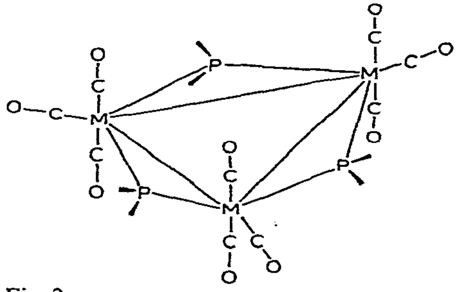

Fig. 2.

A repetition of this reaction under more vigorous conditions for prolonged periods resulted in the predominant formation of the tricarbonyl species $[M(CO)_3P(C_6H_5)_2]_n$. Osmometric solution molecular weight measurements in benzene indicated a trimeric formulation for these compounds, and the structure in Fig. 2 is suggested.

The mass spectra of the dimers $[M(CO)_4P(C_6H_5)_2]_2$ show the expected parent ion, and a cracking pattern characteristic of this formula. Unfortunately the tricarbonyl compounds were insufficiently volatile for us to obtain a spectrum, and on a heated probe decomposition took place.

In the corresponding bridged compounds of sulphur and selenium, originally characterised as trimers[2], solution molecular weight measurements appear to give anomalous results varying between trimer and tetramer[4] and furthermore trimeric and tetrameric species of $[M(CO)_3SR]_n$ have been observed in mass spectra[3,4,9]. The close similarity between the infrared spectra (in the metal carbonyl stretching region) of these anomalous sulphur-bridged compounds and the tricarbonyl phosphorus bridged species reported herein is striking. In this light, whilst a trimeric structure is proposed on the basis of the available evidence for these compounds, a similar anomaly and some alternative structure cannot be entirely eliminated.

In the formation of the tricarbonyl compounds the overall reaction may be represented by eqn. (2).

$$3\,M(CO)_5Br+3\,Me_3SiP(C_6H_5)_2 \rightarrow [M(CO)_3P(C_6H_5)_2]_3+3\,(CH_3)_3SiBr+6\,CO \quad (2)$$

The failure to observe a monomeric species $(C_6H_5)_2PM(CO)_5$ is in common with extensive observations that, with certain special exceptions[2c,2d], monomers of this general type are unstable and undergo rapid dimerization. Though eqns. (1) and (2) represent overall reactions for the formation of the dimers and trimers respectively, they give no indication as to the paths of the reactions. It is not possible to say if the products result from an initial substitution of carbonyl groups by the silylphosphine, followed by inter- or intramolecular elimination of organosilicon halide; or alternatively the fission followed by substitution. It is believed that both of these sequences have been observed in similar systems[2b,5].

The infrared spectra of the tetracarbonyl dimers and the tricarbonyl trimers in the carbonyl stretching region are shown in Fig. 3. Both types of spectrum conform to the expected patterns for these tetracarbonyl and tricarbonyl moieties. For the dimers four $(B_{1u}+B_{2u}+2B_{3u})$ infrared active modes are predicted and these are clearly distinguishable in both the manganese and rhenium compounds. The energy separations of the bands are greater for the rhenium dimer and the virtually overlapping central two peaks are better resolved. Theory predicts three $(2E^1+A_2)$ infrared active CO modes for the idealised trimer structure, but assuming that coupling between carbonyl groups on different metals is small, a simplified two band spectrum is to be expected from the local symmetry of the individual $M(CO)_3$ groups.

EXPERIMENTAL

(Trimethylsilyl)diphenylphosphine was obtained as a slightly viscous liquid from the interaction of chlorotrimethylsilane and sodium diphenylphosphide. Each batch was characterized by b.p. 90°/0.05 mm, n_D^{20} 1.600 and an integrated proton magnetic resonance spectrum.

(Diphenylphosphino)tetracarbonylmanganese dimer, $[Ph_2PMn(CO)_4]_2$

Manganese pentacarbonyl bromide (0.67 g) and (trimethylsilyl)diphenylphosphine (0.90 g) in 1,2-dimethoxyethane were heated at 45 to 50° under nitrogen. Reaction took place rapidly and after about ten minutes evolution of bromotrimethylsilane and carbon monoxide had ceased. On cooling brilliant yellow crystals of product

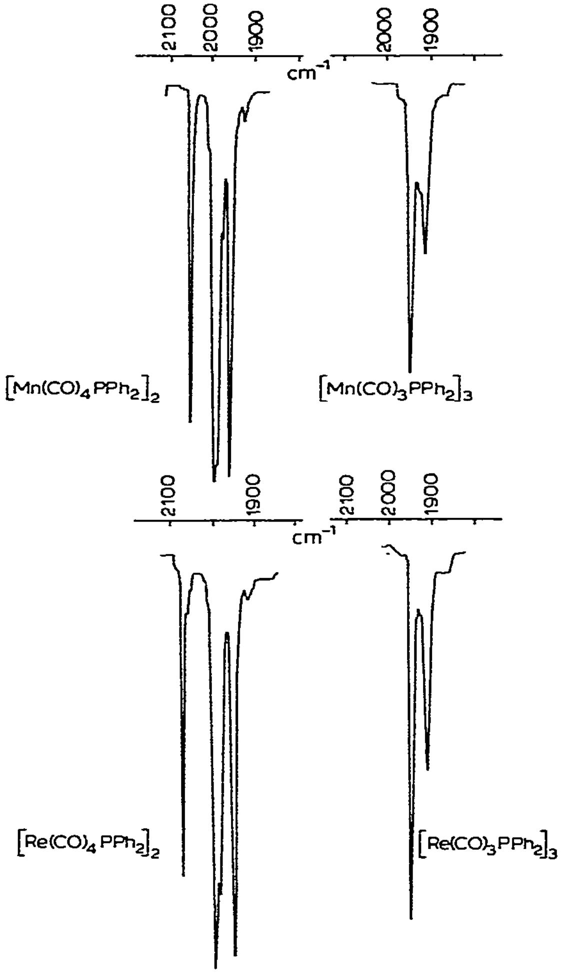

Fig. 3. Metal carbonyl stretching modes of the phosphorus-bridged dimers and trimers.

were deposited, and after decantation, washing with dimethoxyethane (2 × 1 ml) and cyclohexane (3 × 2 ml) left pure (diphenylphosphino)tetracarbonylmanganese dimer (80% yield). (Found: C, 54.1; H, 3.1; mol. wt., 693. $[C_{16}H_{10}MnO_4P]_2$ calcd.: C, 54.6; H, 2.9%; mol. wt., 704.)

(Diphenylphosphino)tetracarbonylrhenium dimer, $[Ph_2PRe(CO)_4]_2$

In an exactly analogous reaction between rhenium pentacarbonyl chloride and (trimethylsilyl)diphenylphosphine carried out at 65° for 30 min the product was (diphenylphosphino)tetracarbonylrhenium dimer (85% yield). (Found: C, 39.6; H, 2.3; O, 13.4; mol. wt., 941. $[C_{16}H_{10}O_4PRe]_2$ calcd.: C, 39.8, H, 2.1; O, 13.2%; mol. wt., 967.)

(Diphenylphosphino)tricarbonylmanganese trimer, $[Ph_2PMn(CO)_3]_3$

Manganese pentacarbonyl bromide (0.7 g) and (trimethylsilyl)diphenylphosphine (0.9 g) in "diglyme" (12 ml) were heated in nitrogen under reflux for 8 h. The resulting solution was reduced to about half of its volume by pumping at 60°, and cooled in the refrigerator to produce a crop of dimeric (diphenylphosphino)tetracarbonylmanganese (0.4 g). From the mother liquor the crude trimeric product (0.3 g) was precipitated by the addition of light petrol (40–60°). The pure (diphenylphosphino)-tricarbonylmanganese trimer (Found: C, 55.6; H, 4.0; O, 16.7; mol. wt., 981. $[C_{15}H_{10}MnO_3P]_3$ calcd.: C, 55.6; H, 3.1; O, 14.8%; mol. wt., 972.) was obtained by recrystallization from a 1:5 mixture of benzene and cyclohexane.

(Diphenylphosphino)tricarbonylrhenium trimer $[Ph_2PRe(CO)_3]_3$

In an analogous reaction between rhenium pentacarbonyl chloride and (trimethylsilyl)diphenylphosphine carried out for sixteen hours, the product was (diphenylphosphino)tricarbonylrhenium trimer (Found: C, 39.9; H, 2.4; O, 10.8; mol. wt., 1290. $[C_{15}H_{10}O_3PRe]_3$ calcd.: C, 39.6; H, 2.2; O, 10.5%; mol. wt., 1366.)

Strong absorptions in the C–O stretching region of the infrared spectrum were as follows. (See also Fig. 2).

$[Ph_2PMn(CO)_4]_2$	2053, 1992, 1983, 1958 cm^{-1}
$[Ph_2PMn(CO)_3]_3$	1945, 1912 cm^{-1}
$[Ph_2PRe(CO)_4]_2$	2078, 2001, 1988, 1953 cm^{-1}
$[Ph_2PRe(CO)_3]_3$	1955, 1913 cm^{-1}

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SUMMARY

(Trimethylsilyl)diphenylphosphine reacted with manganese and rhenium pentacarbonyl halides under different conditions to produce both the dimeric (diphenylphosphino)metaltetracarbonyl dimer $[Ph_2PM(CO)_4]_2$, and the (diphenylphosphino)metaltricarbonyl trimer $[Ph_2PM(CO)_3]_3$. The trimers are believed to consist of triangular clusters of metal atoms with phosphorus bridges.

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