

980. *Chemistry of the Metal Carbonyls. Part XXX.*<sup>1</sup>  
*trans-Bromotetracarbonyl(triphenylphosphine)rhenium*

By P. W. JOLLY and F. G. A. STONE

Ultraviolet irradiation of triphenylphosphine and decacarbonyldirhenium in cyclohexane gives dimeric  $[\text{Ph}_3\text{PRe}(\text{CO})_4]_2$ , which on bromination at 0° yields a mixture of *cis*- and *trans*- $\text{Ph}_3\text{PRe}(\text{CO})_4\text{Br}$ . The *cis*- and *trans*-isomers of  $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$  can be similarly prepared. The rhenium complex *trans*- $\text{Ph}_3\text{PRe}(\text{CO})_4\text{Br}$ , although stable in solution at room temperature, is converted into the *cis*-form at 40° in chloroform. The manganese compound *trans*- $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$  isomerises even more readily.

THE preferred substitution of a second ligand into the *cis*-position relative to the first in a substituted pentacarbonyl metal complex  $\text{LM}(\text{CO})_5$  is widely interpreted as being due to the *trans*-effect.<sup>2</sup> However, in certain cases involving relatively large ligands, the *trans*-isomer may also be formed and be quite stable.<sup>3</sup> Moreover, substitution of triphenylphosphine on to pentacarbonylmethylmanganese apparently proceeds through the initial formation of a *trans*-acyl complex.<sup>4</sup> We here describe the preparation of two additional *trans*-isomers, those of bromotetracarbonyl(triphenylphosphine)rhenium and its manganese analogue, and present some observations on the complex  $[\text{Ph}_3\text{PRe}(\text{CO})_4]_2$ .

It has been reported<sup>5</sup> that decacarbonyldirhenium and triphenylphosphine in refluxing xylene afford dimeric  $[\text{Ph}_3\text{PRe}(\text{CO})_4]_2$ , but no structure was assigned and subsequently others<sup>6</sup> obtained instead a paramagnetic complex  $(\text{Ph}_3\text{P})_2\text{Re}(\text{CO})_3$  from the same reactants. More recently Nyman<sup>7</sup> showed that one or the other rhenium complex can be formed by varying the reaction conditions. In confirmation of this we find that triphenylphosphine and decacarbonyldirhenium in cyclohexane, on irradiation with ultraviolet light, yield  $[\text{Ph}_3\text{PRe}(\text{CO})_4]_2$ . If the carbonyl and triphenylphosphine are refluxed in xylene the dimeric rhenium complex is first formed. The reaction can be conveniently followed since  $[\text{Ph}_3\text{PRe}(\text{CO})_4]_2$  shows only one strong and one weaker carbonyl stretching frequency (Table). This result, together with the molecular weight, establishes the structure as one containing a rhenium-rhenium bond, in which the triphenylphosphine groups are substituted on the four-fold axis. If the dimeric rhenium complex is heated for a prolonged period with more triphenylphosphine a second species  $(\text{Ph}_3\text{P})_2\text{Re}(\text{CO})_3$  is formed.

Carbonyl spectral bands of some triphenylphosphine complexes of manganese and rhenium

Compound	Symmetry point group	Number of i.r.-active carbonyl stretching frequencies predicted	Carbonyl stretching frequencies (cm. <sup>-1</sup> )
$[\text{Ph}_3\text{PRe}(\text{CO})_4]_2$ .....	$D_{4d}$ or $D_{4h}$	$2(B_2 + E_1)$ or $2(A_{2u} + E_u)$	1988w, 1965vs
<i>trans</i> - $\text{Ph}_3\text{PRe}(\text{CO})_4\text{Br}$ ...	$C_{4v}$	$2(A_1 + E)$	2105w, 1995vs
<i>cis</i> - $\text{Ph}_3\text{PRe}(\text{CO})_4\text{Br}$ .....	$C_s$	$4(3A' + A'')$	2100s, 2015s, 1998vs, 1940s
$[\text{Ph}_3\text{PMn}(\text{CO})_4]_2$ .....	$D_{4d}$ or $D_{4h}$	$2(B_2 + E_1)$ or $2(A_{2u} + E_u)$	1980vw, 1962vs
<i>trans</i> - $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$ ...	$C_{4v}$	$2(A_1 + E)$	2095w, 1995vs
<i>cis</i> - $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$ .....	$C_s$	$4(3A' + A'')$	2088s, 2020s, 2002vs, 1958s

Interestingly, in contrast to  $[\text{Ph}_3\text{PMn}(\text{CO})_4]_2$ , the metal-metal bond in the rhenium analogue is not cleaved with sodium amalgam.<sup>8</sup> Treatment with bromine in carbon tetrachloride at 0° affords a mixture of the *cis*- and *trans*-isomers of  $\text{Ph}_3\text{PRe}(\text{CO})_4\text{Br}$ , structure

<sup>1</sup> Part XXIX, J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 389.

<sup>2</sup> F. Basolo and R. G. Pearson, (a) *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 1; (b) *Progr. Inorg. Chem.*, 1962, **4**, 381.

<sup>3</sup> P. W. Jolly and F. G. A. Stone, *Chem. Comm.*, 1965, 85.

<sup>4</sup> R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 5043.

<sup>5</sup> W. Hieber and W. Freyer, *Chem. Ber.*, 1960, **93**, 462.

<sup>6</sup> M. Freni, D. Giusto, and V. Valenti, *J. Inorg. Nuclear Chem.*, 1965, **27**, 755.

<sup>7</sup> F. Nyman, *Chem. and Ind.*, 1965, 604.

<sup>8</sup> P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J.*, 1965, in the press.

assignments being made on the basis of their infrared spectra (Table). The *trans*-isomer, although stable in solution at room temperature, is isomerised to the *cis*-form in refluxing chloroform. The *cis*-complex can also be obtained by refluxing bromopentacarbonylrhenium and triphenylphosphine in chloroform, no reaction occurring below 40°. The analogous manganese complex was recently obtained by the same route.<sup>9</sup> Previous workers<sup>10</sup> showed that triphenylphosphine and bromopentacarbonylrhenium in light petroleum at 120° form  $(\text{Ph}_3\text{P})_2\text{Re}(\text{CO})_3\text{Br}$ .

Bromination of dimeric  $[\text{Ph}_3\text{PMn}(\text{CO})_4]_2$  has been reported to give exclusively *cis*- $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$  when carried out at room temperature in chloroform.<sup>11</sup> However, when reaction is carried out at 0° we find that the *trans*-isomer predominates over the *cis*-form. Nevertheless, *trans*- $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$ , although stable as a solid in air, rearranges rapidly at room temperature in solution to form the *cis*-compound. Bromination of  $[\text{Ph}_3\text{PMn}(\text{CO})_4]_2$  at 40° results exclusively in formation of *cis*- $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$ .

#### EXPERIMENTAL

Infrared spectra were measured with a grating spectrophotometer, for solutions in cyclohexane.

*Tetracarbonyl(triphenylphosphine)rhenium Dimer*.—(a) Decacarbonyldirhenium (1 g., 1.6 mmoles) and triphenylphosphine (1.2 g., 4.6 mmoles) in cyclohexane (50 ml.) were irradiated with a Hanovia 50 w mercury lamp for 4 hr. under nitrogen. In this manner crude tetracarbonyl-(triphenylphosphine)rhenium (1.5 g., 84%) was isolated, and purified by chromatography on Florisil with benzene–light petroleum (3 : 1) as eluant; it had m. p. 231° (lit.,<sup>7</sup> 228°) [Found: C, 47.1; H, 2.7; P, 5.5%; *M* (Mechrolab osmometer), 1164. Calc. for  $\text{C}_{44}\text{H}_{30}\text{O}_8\text{P}_2\text{Re}_2$ : C, 47.1; H, 2.7; P, 5.5%; *M*, 1123].

(b) Decacarbonyldirhenium (0.4 g., 0.64 mmole) and triphenylphosphine (0.6 g., 2.3 mmoles) were refluxed in xylene (50 ml.) under nitrogen. The reaction was followed by observing the carbonyl region of the infrared spectrum and was complete after 20 hr. Removal of solvent, followed by chromatography, afforded product (0.2 g., 28%) identical with that prepared above.

*Tricarbonylbis(triphenylphosphine)rhenium*.—Tetracarbonyl(triphenylphosphine)rhenium dimer (0.23 g., 0.20 mmole) and triphenylphosphine (0.13 g., 0.50 mmole) were refluxed (48 hr.) in xylene (50 ml.). After removal of solvent, recrystallisation (ether) afforded the product, m. p. 203–205° (0.1 g., 35%), identified spectroscopically as  $(\text{Ph}_3\text{P})_2\text{Re}(\text{CO})_3$ .<sup>7</sup>

*cis*-Bromotetracarbonyl(triphenylphosphine)rhenium. —Bromopentacarbonylrhenium (0.2 g., 0.50 mmole) and triphenylphosphine (0.13 g., 0.50 mmole) were refluxed in chloroform (30 ml.). Reaction was complete in 8 hr. (infrared spectroscopy). Solvent was removed, and the solid chromatographed [ether–light petroleum (2 : 3) as eluant], to give a white crystalline *solid*, m. p. 146° (Found: C, 41.4; H, 2.4%; *M*, 610.  $\text{C}_{22}\text{H}_{15}\text{BrO}_4\text{PRe}$  requires C, 41.35; H, 2.4%; *M*, 640).

*Bromination of Tetracarbonyl(triphenylphosphine)rhenium Dimer*.—A sample (0.224 g., 0.2 mmole) of  $[\text{Ph}_3\text{PRe}(\text{CO})_4]_2$  was suspended in carbon tetrachloride (20 ml.) at 0°. Bromine (40 mg., 0.25 mmole) in carbon tetrachloride (10 ml.) was added dropwise. The pale orange solution was evaporated (0°/20 mm.), and the resultant white solid chromatographed. The complex *cis*- $\text{Ph}_3\text{PRe}(\text{CO})_4\text{Br}$  (80 mg., 31%) (identified by m. p. and infrared spectrum) was eluted first with ether–light petroleum (3 : 7), and the white *compound trans*- $\text{Ph}_3\text{PRe}(\text{CO})_4\text{Br}$  (120 mg., 47%), m. p. 134° (Found: C, 41.3; H, 2.4.  $\text{C}_{22}\text{H}_{15}\text{BrO}_4\text{PRe}$  requires C, 41.35; H, 2.4%), eluted next with ether–light petroleum (3 : 1).

*trans*-Bromotetracarbonyl(triphenylphosphine)rhenium (60 mg., 0.09 mmole) was heated under reflux in chloroform (10 ml.) and isomerised to the *cis*-isomer in 2 hr., the reaction being followed spectroscopically. No isomerisation occurred in solution after 24 hr. at 40°.

*Bromination of Tetracarbonyl(triphenylphosphine)manganese Dimer*.—A sample (0.2 g., 0.24 mmole) of  $[\text{Ph}_3\text{PMn}(\text{CO})_4]_2$ , suspended in carbon tetrachloride (20 ml.) at 0°, was treated with bromine (45 mg., 0.3 mmole) in the same solvent (10 ml.). After removal of solvent (0°/20 mm.) and chromatography, *cis*- $\text{Ph}_3\text{PMn}(\text{CO})_4\text{Br}$  (60 mg., 26%) (Found: C, 52.2; H, 3.2. Calc. for  $\text{C}_{22}\text{H}_{15}\text{BrMnO}_4\text{P}$ : C, 51.9; H, 3.0%) was eluted with ether–light petroleum (2 : 3),

<sup>9</sup> R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 2495.

<sup>10</sup> E. W. Abel and G. Wilkinson, *J.*, 1959, 1501.

<sup>11</sup> A. G. Osborne and M. H. B. Stiddard, *J.*, 1964, 634.

and orange crystals of *trans*-Ph<sub>3</sub>PMn(CO)<sub>4</sub>Br (120 mg., 52%) (identified by its infrared spectrum and by analysis) (Found: C, 52.3; H, 3.3. C<sub>22</sub>H<sub>15</sub>BrMnO<sub>4</sub>P requires C, 51.9; H, 3.0%) were eluted with ether.

In carbon tetrachloride at room temperature *trans*-Ph<sub>3</sub>PMn(CO)<sub>4</sub>Br is converted into the *cis*-isomer after 48 hr. At 40° the conversion takes place in a few minutes.

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DEPARTMENT OF INORGANIC CHEMISTRY,  
THE UNIVERSITY, BRISTOL 8.

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