1188. *Reaction of* 1,2,5-*Triphenylphosphole and its Oxide with Metal Carbonyls*

By R. C. Cookson, G. W. A. Fowles, and D. K. Jenkins

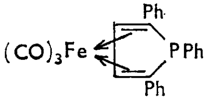
Triphenylphosphole ($C_{22}H_{17}P$) has been treated with several metal carbonyls. $Fe(CO)_5$ gave a π-complex $(C_{22}H_{17}P)Fe(CO)_3$, but $Fe_2(CO)_9$ yielded $(C_{22}H_{17}P)Fe(CO)_4$. $M(CO)_6$ (M = Cr, Mo, and W) yielded monosubstituted derivatives $(C_{22}H_{17}P)M(CO)_5$ only, but "mixed ligand" complexes $(C_4H_9NO)(C_{22}H_{17}P)M(CO)_4$ (M = Mo and W) were obtained from reactions with the bis-morpholine tetracarbonyls. The disubstituted product $(C_{22}H_{17}P)_2Mo(CO)_4$ was isolated from the reaction of the phosphole with π-toluene-molybdenum tricarbonyl. $Ni(CO)_4$ reacted to give $(C_{22}H_{17}P)Ni(CO)_3$.

A number of analogous reactions of the phosphole oxide were examined but only with $Fe(CO)_5$ was a complex isolated. $Cr(CO)_6$ and $W(CO)_6$ did not react, and $Mo(CO)_2(CH_2CHCN)_2$ gave a low yield of a Diels–Alder product.

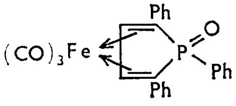
The infrared spectra of the complexes are recorded and their significance is discussed.

Braye and Hubel[1] described two kinds of complex of pentaphenylphosphole with iron carbonyls, one a monosubstituted product $[C_{34}H_{25}PFe(CO)_4]$ with the phosphorus atom co-ordinated to iron, and the second a π-complex $[C_{34}H_{25}PFe(CO)_3]$ in which the bonding to iron is through the conjugated π-bonds of the ring system. Using triphenylphosphole[2] we have isolated analogous complexes and extended the work to other carbonyls.

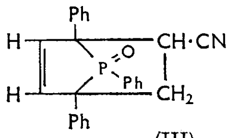
Reaction of iron pentacarbonyl with triphenylphosphole in a sealed tube at 140° gave a crystalline tricarbonyl complex (monomeric in benzene solution) formulated as (I), in which the bonding is similar to that in butadieneiron tricarbonyl and related diene complexes. The preparation, under similar conditions, of the analogous triphenylphosphole oxide[2] complex (II) provided further evidence for the diene type structure, since the quinquevalent phosphorus atom cannot σ-bond to iron, and bonding through oxygen is ruled out because there is no modification of the P=O stretching frequency (found at 1185 cm.$^{-1}$ in the phosphole oxide). The oxide and iron carbonyl groups are presumably on opposite sides of the phosphole ring. The infrared spectrum of the phosphole oxide complex showed the three expected CO stretching frequencies, but with the phosphole complex the three peaks appeared as doublets.



(I)



(II)



(III)

Triphenylphosphole reacted with iron nonacarbonyl under relatively mild conditions to give the P-bonded complex $C_{22}H_{17}PFe(CO)_4$. The analytical data would fit complex (I) equally well, but the two compounds differed in their melting points and infrared spectra. Comparison of the spectrum with that of Braye and Hubel's pentaphenylphosphole complex, $(C_{34}H_{25}P)Fe(CO)_4$, revealed a similar pattern of CO stretching frequencies, but with the frequencies some 25 cm.$^{-1}$ lower.

The hexacarbonyls of chromium, molybdenum, and tungsten all reacted with triphenylphosphole to give yellow, crystalline, monosubstituted products, $(C_{22}H_{17}P)M(CO)_5$, which were monomeric in benzene solution, and whose infrared spectra (cf. Table) showed

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[1] E. H. Braye and W. Hubel, *Chem. and Ind.*, **1959**, 1250; E. H. Braye, W. Hübel, and J. Caplier, *J. Amer. Chem. Soc.*, 1961, **83**, 4406.

[2] I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J.*, 1965, 2184.

Infrared spectra

Complex	ν_{CO} (cm.$^{-1}$)	δM–C–O (cm.$^{-1}$)
$(C_{22}H_{17}P)Cr(CO)_5$	2077m, 2000m, 1950s	670, 650br, 618
$(C_{22}H_{17}P)Mo(CO)_5$	2070m, 1980sh, 1943s	607, 585, 570
$(C_{22}H_{17}P)W(CO)_5$	2063m, 1980m, 1934s	594, 579, 572
$(C_{22}H_{17}P)Fe(CO)_4$	2038m, 1963m, 1940s, 1932s	
$(C_{22}H_{17}P)Fe(CO)_3$	2070, 2055, 2011, 1998, 1973, 1947	
$(C_{22}H_{17}P)_2Mo(CO)_4$	2035m, 1936s, 1925s, 1884s	615, 587, 575
$(C_{22}H_{17}P)_2W(CO)_4$	2029m, 1920s, 1880s	608, 590, 581
$(C_{22}H_{17}P)(C_4H_9NO)W(CO)_4$ *	2021m, 1920s, 1895s, 1840s	
$(C_{18}H_{15}P)(C_4H_9N)W(CO)_4$	2000m, 1890—1900vs, br, 1837s	
$(C_{22}H_{17}P)(C_4H_9N)W(CO)_4$	2019m, 1918s, 1895s, 1837s	
$(C_{22}H_{17}OP)Fe(CO)_3$	2072s, 2003s, 1990s	

* Also shows N–H at 3241 cm.$^{-1}$.

CO stretching frequencies typical of $-M(CO)_5$ groupings.[3] Attempts to effect further substitution of carbonyl groups were unsuccessful even with reaction temperatures up to 240°, but reaction of the bis-morpholine tetracarbonyls [4] (for molybdenum and tungsten) with triphenylphosphole resulted in the displacement of both morpholine groups. The products analysed for $(C_{22}H_{17}P)_3M(CO)_4$, however, and despite repeated recrystallisation the three molecules of phosphole were retained. It seems that one molecule of phosphole was not directly co-ordinated to the metal atoms (giving unexpected 7-co-ordination) since the CO stretching frequency patterns were typical of 6-co-ordinate $L_2M(CO)_4$ complexes and, moreover, in the molybdenum case identical with that of the $(C_{22}H_{17}P)_2Mo(CO)_4$ complex prepared by a different method. The latter complex was obtained in quite a good yield from the reaction of phosphole with π-toluenemolybdenum tricarbonyl, where it seems that the expected trisubstituted product must disproportionate under the experimental conditions.

Chromatographic separation of the phosphole-bis(morpholine) tetracarbonyl reaction mixtures also led to the isolation of orange crystalline "mixed ligand" complexes $(C_{22}H_{17}P)(C_4H_9NO)M(CO)_4$. An analogous complex $(C_4H_9N)(Ph_3P)W(CO)_4$ was obtained by the reaction of triphenylphosphine with bis-pyrrolidinetungsten tetracarbonyl.

The CO stretching frequencies showed the expected gradation along the series $(C_{22}H_{17}P)_2Mo(CO)_4$, $(C_{22}H_{17}P)(C_4H_9NO)Mo(CO)_4$, $(C_4H_9NO)_2Mo(CO)_4$, falling by 30—40 cm.$^{-1}$ in accordance with the inability of nitrogen to π-bond with molybdenum.[5]

Triphenylphosphole reacted with nickel carbonyl to give the simple monosubstituted product $(C_{22}H_{17}P)Ni(CO)_3$, but attempts to recrystallise this compound from benzene–methanol resulted in gradual decomposition. Thus, metallic nickel was deposited, and the infrared spectrum changed from that of the monosubstituted complex to that of a mixture containing $(C_{22}H_{17}P)_2Ni(CO)_2$, in accordance with the decomposition:

$$2(C_{22}H_{17}P)Ni(CO)_3 \longrightarrow (C_{22}H_{17}P)_2Ni(CO)_2 + Ni + 4CO$$

Triphenylphosphole oxide did not react with nickel carbonyl, or with chromium and tungsten hexacarbonyls, but a low yield of a crystalline yellow solid resulted from the reaction with molybdenum hexacarbonyl. Analytical data, together with the infrared spectrum (which showed two CO stretching frequencies at 2030 and 2005 cm.$^{-1}$), indicated that the product might be $(C_{22}H_{17}OP)_2Mo(CO)_2$, and hence analogous to the compound obtained by Hubel and Weiss [6] by the reaction of the hexacarbonyl with tetracyclone. Attempts to prepare the complex by reaction of the phosphole oxide with acrylonitrile-molybdenum dicarbonyl resulted in the formation of a crystalline, white, molybdenum-free compound containing both P=O and C≡N groups. The proton resonance spectrum was

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[3] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432; *Inorg. Chem.*, 1963, **2**, 533.

[4] G. W. A. Fowles and D. K. Jenkins, *Inorg. Chem.*, 1964, **3**, 257.

[5] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J.*, 1959, 2323.

[6] W. Hubel and E. Weiss, *J. Inorg. Nuclear Chem.*, 1959, **11**, 42.

consistent with Diels–Alder structure (III). This compound was then synthesised directly from acrylonitrile and triphenylphosphole oxide.

An examination of the infrared spectra of some of the phosphole complexes below 700 cm.$^{-1}$ shows correlations with peaks found for the parent carbonyls. These peaks are evidently [7] the δ M–C–O bending frequencies. The values found for the $(C_{22}H_{17}P)_2M(CO)_4$ compounds agree well with those observed for such complexes as $(Ph_2PCH_2CH_2PPh_2)Mo(CO)_4$, but δ M–C–O frequencies have not been reported previously for $LM(CO)_5$ complexes.

EXPERIMENTAL

1,2,5-Triphenylphosphole and 1,2,5-triphenylphosphole oxide were prepared as described recently.[2]

Reaction of Triphenylphosphole with $M(CO)_6$ (M = Cr, Mo, *and* W).—These reactions were carried out in benzene solution with excess of carbonyl in sealed tubes at 150—180°. The products were separated chromatographically and then recrystallised from benzene–methanol; the yellow-orange crystalline *solids* so obtained were diamagnetic and gave non-conducting solutions in nitrobenzene. (i) Found: C, 64·4; H, 3·2; P, 5·9%; *M*, 520 (1·0% in C_6H_6), m. p. 178—180° (decomp.). $C_{22}H_{17}PCr(CO)_5$ requires C, 64·3; H, 3·4; P, 6·1%; *M*, 504. (ii) Found: C, 60·0; H, 2·9; Mo, 17·2; P, 6·0%; *M*, 525 (0·95% in C_6H_6), m. p. 160—163° (decomp.). $C_{22}H_{17}PMo(CO)_5$ requires C, 59·2; H, 3·1; Mo, 17·5; P, 5·7%; *M*, 548. (iii) Found: C, 51·2; H, 2·6; P, 5·6; W, 29·4%; M, 642 (1·11% in C_6H_6), m. p. 185—186° (decomp.). $C_{22}H_{17}PW(CO)_5$ requires C, 51·0; H, 2·7; P, 4·9; W, 28·9%; *M*, 636.

Reaction of Triphenylphosphole with $Fe_2(CO)_9$ *and* $Fe(CO)_5$.—The $Fe_2(CO)_9$ reaction was carried out under reflux in light petroleum (b. p. 80—100°), and that of $Fe(CO)_5$ was carried out in benzene in a sealed tube at 140° for 12 hr. In each case the resulting solutions were chromatographed. $Fe_2(CO)_9$ yielded an orange *solid*, m. p. 107—110°, on evaporation of the appropriate portion of the chromatographed solution [Found: C, 66·5; H, 3·7; Fe, 12·4; P, 6·8. $C_{22}H_{17}PFe(CO)_4$ requires C, 65·0; H, 3·5; Fe, 11·6; P, 6·5%]. The product formed in the $Fe(CO)_5$ reaction was a red crystalline diamagnetic *solid*, m. p. 136—138° [Found: C, 66·8; H, 3·6; Fe, 12·5; P, 6·8%; *M*, 470 (0·91% in C_6H_6). $C_{22}H_{17}PFe(CO)_3$ requires C, 66·5; H, 3·8; Fe, 12·3; P, 6·9%; *M*, 452].

Reaction of Triphenylphosphole with $Ni(CO)_4$.—Reaction with excess of nickel carbonyl in a sealed tube at 60° for 3 hr. gave a lemon-yellow *solid* in 87% yield [Found: C, 67·6; H, 3·1; Ni, 13·1; P, 7·3%; *M*, 464 (0·8% in C_6H_6). $C_{22}H_{17}Ni(CO)_3$ requires C, 66·3; H, 3·8; Ni, 12·9; P, 6·9%; *M*, 454]. Attempts to recrystallise this product from benzene–light petroleum were unsuccessful, since the products became more orange in colour and had analyses approaching those required for $(C_{22}H_{17}P)_2Ni(CO)_2$. Repeated chromatographic separations gave an orange *powder* [Found: C, 76·8; H, 5·0. $(C_{22}H_{17}P)_2Ni(CO)_2$ requires C, 74·8; H, 4·6%].

Reaction of Triphenylphosphole with $(C_4H_9ON)_2M(CO)_4$ (M = Mo *and* W).—When the morpholine complexes were refluxed in benzene (under N_2) with two molar equivalents of the phosphole, the solutions rapidly became dark red. After 3 hr. reaction, the cooled solutions were chromatographed on an alumina column, and yielded two *compounds* (one yellow and one red) in each case. Found (for the molybdenum yellow product): C, 75·6; H, 4·9; P, 7·8. $(C_{22}H_{17}P)_2Mo(CO)_4,C_{22}H_{17}P$ requires C, 73·4; H, 4·5; P, 8·1%. Found (for W yellow product); C, 66·7; H, 4·3; P, 7·7. $(C_{22}H_{17}P)_2W(CO)_4,C_{22}H_{17}P$ requires C, 68·2; H, 4·2; P, 7·5%. Found (for W red product): C, 51·6; H, 3·9; N, 1·7. $(C_{22}H_{17}P)(C_4H_9ON)W(CO)_4$ requires C, 51·9; H, 3·6; N, 2·0%.

Reaction of Triphenylphosphole with $(C_7H_8)Mo(CO)_3$.—Reaction under reflux in nitrogen gave a 30% yield of $(C_{22}H_{17})_2Mo(CO)_4$ as yellow *crystals*, m. p. 172—174° (decomp.) [Found: C, 66·2; H, 4·3; Mo, 11·4; P, 7·5%; *M*, 815 (0·54% in C_6H_6). $(C_{22}H_{17})_2Mo(CO)_4$ requires C, 69·2; H, 4·1; Mo, 11·5; P, 7·5%; *M*, 770].

Reactions of Triphenylphosphole Oxide.—$Cr(CO)_6$, $W(CO)_6$, $Fe_2(CO)_9$, and $Ni(CO)_4$ did not appear to react with the phosphole oxide. $Fe(CO)_5$ in a sealed tube at 160° for 16 hr. reacted with the phosphole oxide (no solvent) to give a benzene-insoluble product that was recrystallised twice from ethanol to yield golden *needles*, m. p. 249—251° (decomp.) [Found: C, 63·5; H, 3·6; Fe, 10·7; P, 6·5. $(C_{22}H_{17}PO)Fe(CO)_3$ requires C, 64·1; H, 3·6; Fe, 12·0; P, 6·6%]. $Mo(CO)_6$

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[7] D. M. Adams, *J.*, 1964, 1771.

gave a very low yield (2%) of yellow *crystals* [Found: C, 67·9; H, 4·8. $(C_{22}H_{17}PO)_2Mo(CO)_2$ requires C, 68·3; H, 4·2%].

The reaction of acrylonitrilemolybdenum dicarbonyl with triphenylphosphole oxide in benzene under reflux (N_2 atmosphere) yielded a white *solid* of m. p. 178° in 35% yield (Found: C, 78·0; H, 5·5; N, 3·5; P, 8·2. $C_{25}H_{20}NOP$ requires C, 78·7; H, 5·2; N, 3·7; P, 8·1%). The infrared spectrum showed ν_{CN} 2246 cm.$^{-1}$ and P=O stretching frequencies at 1186, 1200, and 1215 cm.$^{-1}$. Infrared spectra were measured in chloroform solutions except where otherwise stated.

Analytical Procedures.—Phosphorus was determined volumetrically as the phosphomolybdate complex, after the sample had been decomposed by fusion with sucrose, potassium nitrate, and sodium peroxide in a Parr bomb; poor results were obtained in the presence of tungsten because of the formation of phosphotungstates. After the sample had been decomposed by fusion with sodium peroxide, chromium was determined by the standard bismuthate procedure, and molybdenum by mercury reduction to molybdenum(v) followed by titration with ceric sulphate; tungsten was determined colorimetrically at 400 mμ as the tungstovanadophosphate, iron [after separation as $Fe(OH)_3$] by dichromate titration, and nickel gravimetrically as the dimethylglyoxime complex.

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DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, SOUTHAMPTON.

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