Dinitrogen, Hydrido-, and Carbonyl Complexes of Tungsten

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The reduction of *trans*-$[WCl_4(PR_3)_2]$ (PR_3 = tertiary phosphine) by sodium amalgam in tetrahydrofuran solution at *ca.* 20° under argon, dinitrogen, dihydrogen or carbon monoxide is discussed. The syntheses of hydrido-, dinitrogen, and carbonyl complexes are achieved by these routes. The interconversions and isomerisations of pentacarbonyl-, tetracarbonyl-, and tricarbonyl-tungsten complexes containing tertiary phosphines are described.

COMPLEXES of the type *trans*-$[WCl_4(PR_3)_2]$ (PR_3 = tertiary phosphine) have been prepared by the reduction of $[WCl_6]$ by zinc in dichloromethane solution in the presence of a tertiary phosphine.[1] In order to obtain halogeno-complexes in lower oxidation states, we have studied the reduction of $[WCl_4(PR_3)_2]$ by agents such as sodium amalgam under various conditions.[2] The products are only rarely halogeno-complexes, and depend upon the gas over the reaction mixture.

Reduction under Dinitrogen.—When $[WCl_4(PMe_2Ph)_2]$ (or $[WCl_4(PMe_2Ph)_3]$) is reduced at 20° by sodium amalgam in tetrahydrofuran (thf) solution in the presence of an excess of the phosphine, $[W(N_2)_2(PMe_2Ph)_4]$ is formed. The reaction is complete in *ca.* 1 h at room temperature, and for maximum yields the reaction mixture must be saturated with dinitrogen. The reduction of $[WCl_4(Ph_2PCH_2CH_2PPh_2)]$ in the presence of the diphosphine likewise yields $[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ but of the other phosphine derivatives investigated, only $[WCl_4(PEt_2Ph)_2]$ yielded a dinitrogen complex, and this was never obtained pure. Reduction of a mixture of dimethylphenylphosphine and commercial tungsten(VI) chloride with sodium amalgam under these conditions yields no dinitrogen complexes, but a small amount of $[WCl_2(PMe_2Ph)_4]$.

The i.r. spectrum of $[W(N_2)_2(PMe_2Ph)_4]$ in benzene solution has two bands (1931 and 1998 cm^{-1}) assignable to $\nu(N_2)$. The ^1H n.m.r. spectrum of the methyl protons consists of a doublet at τ 8·33, separation 5·2 Hz, and a triplet τ 8·43, for which the separation of the outer lines, $|^2J(PCH) + ^4J(PWPCH)|$, is 4·8 Hz. The data are consistent with a *cis*-configuration in solution. The i.r. spectrum of $[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ in benzene solution shows the single band (1953 cm^{-1}) to be expected of a *trans*-configuration.

cis-$[W(N_2)_2(PMe_2Ph)_4]$ Reacts with carbon tetrachloride at reflux, or with dichlorine in carbon tetrachloride, to reform $[WCl_4(PMe_2Ph)_2]$. The reaction of *trans*-$[W(N_2)_2(PPh_2CH_2CH_2PPh_2)_2]$ with dichlorine in carbon tetrachloride produces dinitrogen quantitatively during 5 h at 60°. *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ Reacts with $[VCl_3(thf)_3]$ to give dark green crystals which still contain nitrogen but do not have absorptions assignable to $\nu(N_2)$ in their i.r. spectra. These solids are probably adducts similar to those of $[ReCl(N_2)(PMe_2Ph)_4]$.[3]

Reduction under Argon.—The reduction of a mixture of *trans*-$[WCl_4(PMe_2Ph)_2]$ and dimethylphenylphosphine by sodium amalgam in thf at 20° under argon leads to $[WCl_2(PMe_2Ph)_4]$. This complex has a magnetic moment in the solid state of 2·30 B.M. at 20°, but it dissociates in solution. Its ^1H n.m.r. spectrum has no sharp resonances, although temperature-independent paramagnetism and a sharp n.m.r. spectrum would be expected because it is a d^4-system.[4] Its far-i.r. spectrum has a single strong band (280 cm^{-1}) assignable to $\nu(W-Cl)$ and is very similar to those of *trans*-$[OsCl_2(PMe_2Ph)_4]$ [5] and *trans*-$[ReCl_2(PMe_2Ph)_4]$.[6] It therefore probably has a *trans*-configuration.

The complex dissociates in solution, and reacts with neutral ligands such as carbon monoxide (giving $[WCl_2(CO)_2(PMe_2Ph)_3]$) and with nitric oxide (giving green, unstable nitrosyls). Methyl cyanide, dihydrogen, dinitrogen and olefins do not react with it under ambient conditions. The tungsten(II) chloride is not of itself a catalyst for olefin dismutation or polymerisation. It is not reduced by sodium amalgam in thf at room temperature under dinitrogen.

Reduction under Dihydrogen.—The reduction of *trans*-$[WCl_4(PMe_2Ph)_2]$ or of $[WCl_4(PMe_2Ph)_3]$ as above but under dihydrogen was not completely reproducible. Yields of $[WH_6(PMe_2Ph)_3]$ [7] were 10—25%, and the product was often strongly coloured by impurities. *trans*-$[WCl_4(PEt_2Ph)_3]$ Gave small amounts of $[WH_6(PEt_2Ph)_3]$ but $[WCl_4(Ph_2PCH_2CH_2PPh_2)]$ and *trans*-$[WCl_4(PMePh_2)_2]$ failed to yield hydrido-species. The major product from the reduction of tungsten(VI) chloride in the presence of dimethylphenylphosphine was, as always, *trans*-$[WCl_2(PMe_2Ph)_4]$.

Reduction under Carbon Monoxide.—The reduction of *trans*-$[WCl_4(PR_3)_2]$ by sodium amalgam in thf at 20° in the presence of a tertiary phosphine (PR_3) under carbon monoxide leads to mixtures of polycarbonyl complexes. These included the somewhat rare *meridional* isomers, but the mixtures could not always be separated owing to complications by light-catalysed isomerisations and disproportionations. As many as five different species were recognised in some solutions from their i.r. spectra in the carbonyl region. These may be quite distinctive, as shown in Table 1, and were used to analyse the mixtures qualitatively. We found that the phosphine influences the number of

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[1] A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J.C.S. Dalton*, 1972, 1064.

[2] B. Bell, J. Chatt, and G. J. Leigh, *Chem. Comm.*, 1970, 842.

[3] J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *Chem. Comm.*, 1970, 955.

[4] H. P. Gunz and G. J. Leigh, *J. Chem. Soc.* (*A*), 1971, 2229.

[5] B. Bell, J. Chatt, and G. J. Leigh, to be published.

[6] H. P. Gunz and G. J. Leigh, unpublished work.

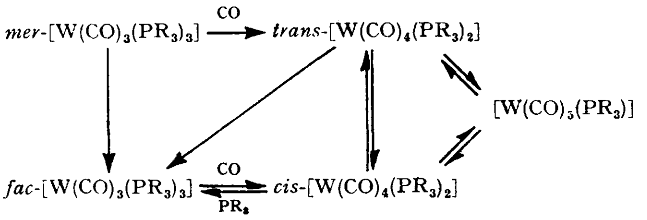
J. R. Moss and B. L. Shaw, *Chem. Comm.*, 1968, 632.

phosphine molecules complexed (*e.g.*, PEt_2Ph yielded *fac*- and *mer*-$[W(CO)_3(PEt_2Ph)_3]$ whereas PPh_3 form no tricarbonyls, and *trans*-$[W(CO)_4(PPh_3)_2]$ is the major product). The greater the relative concentration of the phosphine, the greater the degree of phosphine substitution in the resulting mixture. Finally, the mixtures reach equilibrium only slowly. The tungsten(0) carbonyls interconvert over a long period after reduction has ceased. We therefore decided to isolate individual complexes, and to study their isomerisation, and reactions, with carbon monoxide and with PR_3 under the conditions used for the reduction reactions. The results are summarised in the Scheme.

TABLE 1

I.r. spectra of some tungsten(0) complexes

	ν(CO) cm^{-1}
$[W(CO)_5(Bu^nPh_2)]$	2064m, 1970vw, 1939s (thf)
cis-$[W(CO)_4(Bu^nPh_2)_2]$	2009m, 1908s, 1892s, 1872s (thf)
trans-$[W(CO)_4(Bu^nPh_2)_2]$	1890s (thf)
fac-$[W(CO)_3(Bu^nPh_2)_3]$	1926s, 1825s (thf)
mer-$[W(CO)_3(Bu^nPh_2)_3]$	1959w, 1856s, 1830s (Nujol)



SCHEME

Using trisdimethylaminoarsine and trisdimethylaminophosphine as ligands, in systems derived from chromium, molybdenum, and tungsten carbonyls, King and Korenowski deduced that the principal driving force for the transformations is the reduction of the number of *cis*-interactions between like ligands.[8] However, it is apparent that, in our systems, *mer*-$[W(CO)_3(PR_3)_3]$ is less stable than its *fac*-isomer, and that the reduction of the number of *cis*-interactions cannot be the determining factor for the course of the reactions.

The incorporation of carbon monoxide into the reduction product of $[WCl_4(PR_3)_2]$ can occur at almost any stage. *trans*-$[WCl_4(PR_3)_2]$ Is itself co-ordinatively unsaturated, and for $PR_3 = PMe_2Ph$ can incorporate a further molecule of PMe_2Ph, or alkyl cyanides.[1] Carbon monoxide also reacts directly with $[WCl_4(PMe_2Ph)_2]$ in solution in tetrahydrofuran over 95 h as shown by the appearance of carbonyl bands at 2013, 1932, and 1843 cm^{-1} but no solid carbonyls were isolated. Compounds such as $[WCl_2(CO)_3(PR_3)_2]$ and $[WCl_2(CO)_2(PR_3)_2]$[9] are also plausible reaction intermediates, but we have no evidence that they are formed in detectable quantities.

Of the carbonyls synthesised, only the *mer*-$[W(CO)_3(PR_3)_3]$ are novel.[8,10] The stereochemistries were unequivocally determined by the ^{31}P n.m.r. spectra which are shown in Table 2. The intensities and coupling constants are consistent with the *meridional* arrangement.

TABLE 2

^{31}P N.m.r. spectra of some tungsten(0) carbonyls in benzene solution

	Resonance relative to P_4O_6 (p.p.m.) (relative intensities in parentheses)	
mer-$[W(CO)_3(PMePh_2)_3]$	+112·7(2)	+118·6(1)
mer-$[W(CO)_3(PEtPh_2)_3]$	+97·2(2) [a]	+102·8(1) [b]
mer-$[W(CO)_3(PBu^nPh_2)_3]$	+99·4(2)	+104·7(1)
cis-$[W(CO)_4(PBu^nPh_2)_2]$ [d]	+104·8 [c]	
trans-$[W(CO)_4(PBu^nPh_2)_2]$ [d]	+99·4	

$|^1J(^{183}W-^{31}P)| =$ (*a*), 284·0; (*b*), 234·5; (*c*), 238·0 Hz. [d] These complexes are mentioned in ref. 14; $|^1J(^{183}W-^{31}P)|$ quoted as 275 ± 10 Hz (*trans*-isomer) and 230 ± 10 Hz (*cis*-isomer).

We conclude that sodium amalgam reduction is useful for preparing tungsten(0) complexes in only a limited number of cases. The dinitrogen complexes cannot be obtained in any other fundamentally different manner. Reduction using sodium borohydride[7] is the best method for synthesising polyhydrido-complexes of tungsten.

EXPERIMENTAL

C, H, Cl, N, and P analyses were carried out by Mr. A. G. Olney, University of Sussex, and by Dr. A. Bernhardt, Germany. M.p.s were determined *in vacuo* on an Electrothermal m.p. apparatus. Conductivities were measured in nitromethane or nitrobenzene solutions, using a Portland Electronics conductivity bridge. Spectra were obtained as follows: i.r., 4000—400 cm^{-1}, Perkin-Elmer 337 and Pye-Unicam SP 1200 spectrometers; i.r., 400—40 cm^{-1}, R.I.I.C. F.S. 620 interferometer; i.r., 500—200 cm^{-1}, Grubb-Parsons DM4 spectrometer; ^1H n.m.r., Varian HA-100 or T-60 spectrometers, using tetramethylsilane as internal standard, temperature variation and ^{31}P decoupling carried out on a JEOL C60-HL spectrometer; ^{31}P n.m.r., Perkin-Elmer R10, P_4O_6 as internal standard; mass spectra, A.E.I. MS10 spectrometer. Magnetic susceptibilities were determined using a Faraday balance and molecular weights were measured on a Hitachi-Perkin-Elmer 115 apparatus.

Solvents were dried and distilled in an atmosphere of dry dinitrogen, and were then outgassed *in vacuo* before use. Tertiary phosphines were prepared by standard Grignard methods, and tungsten(VI) chloride was used as purchased. Complexes $[WCl_4(PR_3)_2]$ (PR_3 = tertiary phosphine) were synthesised by literature methods.[1]

(a) *Reductions under Dinitrogen*

cis-*Tetrakis*(*dimethylphenylphosphine*)*bis*(*dinitrogen*)*tungsten*(0).—Dinitrogen was bubbled through a stirred solution of *trans*-tetrachlorobis(dimethylphenylphosphine)tungsten(IV) (0·43 g) in thf (40 ml) at room temperature, and dimethylphenylphosphine (0·50 g) added, to give a purple solution. To this was added 0·4% sodium amalgam (40 g)

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[8] K. B. King and T. F. Korenowski, *Inorg. Chem.*, 1971, **10**, 1188.

[9] M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1967, **20**, 9.

[10] R. Mathieu, M. Lenzi, and R. Poilblanc, *Inorg. Chem.*, 1970, **9**, 2030; C. E. Jones and K. J. Coskran, *Inorg. Chem.*, 1971, **10**, 55.

and the stirring continued for 24 h to ensure completion of reduction. The yellow-brown thf solution was decanted from the mercury, centrifuged until clear and the solvent removed at 0·1 mmHg. The resulting oil was stirred with pentane (15 ml) for 3 h to give a yellow solid which was filtered off, washed with pentane (5 × 2 ml), and dried at 0·1 mmHg. The solid was then extracted with boiling pentane for 5 min, filtered off, washed with pentane (5 ml), and dried at room temperature and 0·1 mmHg, to give the product as a yellow *powder*, 0·15 g, 27%, m.p. 113—116 (decomp.) (Found: C, 48·35; H, 5·8; N, 6·9. $C_{32}H_{44}N_4P_4W$ requires C, 48·5; H, 5·6; N, 7·1%). When an attempt was made to determine the molecular weight in 1,2-dichloroethane solution, the compound decomposed with evolution of gas. The m.p. of the compound was 3° lower after exposure to air for 24 h.

Reduction using Grignard magnesium gave an N_2-containing tar.

trans-*Bis*[1,2,*bis*(*diphenylphosphino*)*ethane*]*bis*(*dinitrogen*)-*tungsten*(0).—Tetrahydrofuran (45 ml) and 0·5% sodium amalgam (40 g) were added to a mixture of 1,2-bis(diphenylphosphino)ethane (0·24 g) and tetrachloro[1,2-bis-(diphenylphosphino)ethane]tungsten(IV) (0·37 g). Dinitrogen was bubbled through the stirred mixture which became pale green in 5 min, then dirty brown in 10 min, and finally yellowish-brown in 2 h. After 16 h, the thf solution was syringed off and centrifuged until clear. The solution was evaporated to dryness and the residue was crystallised from a mixture of benzene (5 ml) and pentane (10 ml) to give an orange powder. This was recrystallised from a mixture of thf (5 ml) and ethanol (10 ml) to yield the product as orange *prisms* (0·19 g, 36%), m.p. 180—184° (decomp.) (Found: C, 60·0; H, 4·9; N, 5·1. $C_{52}H_{48}N_4P_4W$ requires C, 60·2; H, 4·7; N, 5·4%).

(b) *Reductions under Argon*

trans-*Dichlorotetrakis*(*dimethylphenylphosphine*)*tungsten*(II).—*trans*-Tetrachlorobis(dimethylphenylphosphine)tungsten(IV) (1·5 g), dimethylphenylphosphine (1·0 g), and 0·5% sodium amalgam (100 g) were stirred in thf (60 ml) for 4 h at room temperature to give a yellow solution. The thf solution was evaporated to dryness at 0·1 mmHg and the residue was extracted with benzene (60 ml). The extract was washed with water (20 ml), dried over sodium sulphate, and evaporated to dryness at 0·1 mmHg. The residue was stirred with methanol (10 ml) for 4 h to give the product as a yellow *powder* (1·3 g, 66%), m.p. 186—188° (decomp.) (Found: C, 47·65; H, 5·6; Cl, 8·9; P, 14·5. *M* (cryoscopic in benzene) 486. $C_{32}H_{44}Cl_2P_4W$ requires C, 47·6; H, 5·5; Cl, 8·8; P, 15·3%. *M* 807).

Reduction with Grignard magnesium in a similar experiment gave a crude product which was not purified.

(c) *Reduction under Dihydrogen*

tris(*Dimethylphenylphosphine*)*hexahydridotungsten*(VI).—Dihydrogen was bubbled through a stirred thf solution (65 ml) of *trans*-tetrachlorobis(dimethylphenylphosphine)-tungsten(IV) (1·0 g) and dimethylphenylphosphine (0·47 g) for 5 min and then 0·7% sodium amalgam (100 g) was added. After 24 h in the pale yellow solution was syringed off and evaporated to dryness at 0·1 mmHg. The residue was extracted with hexane (5 × 30 ml), and the extracts were combined and evaporated to 30 ml at 0·1 mmHg. On cooling to −20°, the product crystallised from the solution as white needles (0·10 g, 10%). The i.r. spectrum and m.p. of the product are identical to those of an authentic sample prepared by reduction with sodium borohydride.[7]

A similar experiment with tungstem hexachloride (2·4 g) and dimethylphenylphosphine (4·2 g) yielded *trans*-dichlorotetrakis(dimethylphenylphosphine)tungsten(II) (0·93 g, 19·3%).

tris(*Diethylphenylphosphine*)*hexahydridotungsten*(VI).—Under 130 atmospheres of dihydrogen, *trans*-tetrachlorobis-(diethylphenylphosphine)tungsten(IV) (0·60 g) was allowed to react with diethylphenylphosphine (0·40 g) and sodium amalgam (80 g, 0·8%) in thf (45 ml) for 93 h at room temperature. The solution was evaporated to dryness at 0·1 mmHg and the resulting brown oil was washed with methanol (2 × 5 ml) at 0° to leave as a pale yellow oil tris(diethylphenylphosphine)hexahydridotungsten(VI) (0·07 g, 11%). The i.r. spectrum shows ν(W–H) at 1783 and δ(W–H) at 843 cm^{-1}, identical with that of an authentic sample prepared by sodium borohydride reduction.[7]

(d) *Reduction under Carbon Monoxide*

In a typical experiment, *trans*-$[WCl_4(PR_3)_2]$, in thf at room temperature, was stirred with an excess of tertiary phosphine and sodium amalgam whilst carbon monoxide was bubbled through the solution. When the solution became yellow-orange, it was removed from the solids with a syringe and evaporated to dryness at 0·1 mmHg. The residue was extracted with benzene (4 × 25 ml), each extract washed with water (30 ml), and then the combined extracts were dried over sodium sulphate. The extract was evaporated to dryness at 0·1 mmHg and the residue, generally an oil, was worked-up as detailed below.

Reduction of trans-*Tetrachlorobis*(*dimethylphenylphosphine*)*tungsten*(IV).— *trans*-Tetrachlorobis(dimethylphenylphosphino)tungsten(IV) (0·63 g) with dimethylphenylphosphine (0·50 g) and 0·8% sodium amalgam (100 g) in thf (50 ml) reacted with carbon monoxide during 20 min to give a yellow oil. This was stirred with ethanol (5 ml) to yield *fac*-tricarbonyltris(dimethylphenylphosphine)tungsten(0) as a white *powder* (0·35 g, 50%).

Reduction of trans-*Tetrachlorobis*(*diethylphenylphosphine*)-*tungsten*(IV).— *trans*-Tetrachlorobis(diethylphenylphosphine)tungsten(IV) (1·7 g) with diethylphenylphosphine (0·82 g) and 0·5% sodium amalgam (150 g) in thf (40 ml) reacted with carbon monoxide during 15 h to give a yellow oil. This was loaded on to a 30 × 2 cm 60—100 mesh Florisil column and eluted with 10% benzene in hexane. The fractions (a—d) were worked-up and products isolated as follows: (a) trans-*tetracarbonylbis*(*diethylphenylphosphine*)*tungsten*(0), recrystallised from benzene–pentane 1 : 2 (3 ml) to yield the more stable cis-*tetracarbonylbis*(*diethylphenylphosphine*)*tungsten*(0) as white prisms (0·07 g, 5%), m.p. 105—107° (Found: C, 46·4; H, 5·0. $C_{24}H_{30}O_4P_2W$ requires C, 45·9; H, 4·8%); (b) *cis*-tetracarbonylbis(diethylphenylphosphine)tungsten(0) (a trace); (c) mer-*tricarbonyltris*(*diethylphenylphosphine*)*tungsten*(0) (a trace); and (d) *fac*-tricarbonyltris(diethylphenylphosphine)tungsten(0) [12] (a trace).

Reduction of trans-*Tetrachlorobis*(*methyldiphenylphosphine*)*tungsten*(IV).— *trans*-Tetrachlorobis(methyldiphenyl-

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[11] J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2796.

[12] F. Canziani, F. Zingales, and N. Sartorelli, *Gazzetta*, 1964, **94**, 841.

phosphine)tungsten(IV) (1·3 g) with methyldiphenylphosphine (0·38 g) and 0·5% sodium amalgam (130 g) in thf (50 ml) reacted with carbon monoxide during 3·5 h to give an orange oil. This was stirred with ethanol (22 ml) to give fac-*tricarbonyltris(methyldiphenylphosphine)tungsten*(0) as a white powder (0·30 g, 19%) m.p. 195—205° (Found: C, 57·2; H, 4·5. $C_{42}H_{39}O_3P_3W$ requires C, 58·1; H, 4·5%). The mother liquors were evaporated to dryness at 0·1 mmHg and the residue was crystallised from a hot mixture of benzene (2 ml) and ethanol (5 ml) to give mer-*tricarbonyltris(methyldiphenylphosphine)tungsten*(0) as yellow prisms (0·40 g, 26%), m.p. 178—181° (Found: C, 58·1; H, 4·6. $C_{42}H_{39}O_3P_3W$ requires C, 58·1; H, 4·5%).

Reduction of trans-*Tetrachlorobis(ethyldiphenylphosphine)-tungsten*(IV).—(a) *trans*-Tetrachlorobis(ethyldiphenylphosphine)tungsten(IV) (2·4 g) with ethyldiphenylphosphine (0·92 g) and 0·5% sodium amalgam (200 g) in thf (70 ml) reacted with carbon monoxide during 10 h to give an orange oil. The oil was stirred with ethanol (30 ml) to give an orange powder. This was filtered off and dissolved in benzene (15 ml). Ethanol (25 ml) was added, and the resultant solution was cooled to −20° to deposit fac-*tricarbonyltris(ethyldiphenylphosphine)tungsten*(0) as pale yellow prisms (0·60 g, 21%), m.p. 198—202° (Found: C, 59·5; H, 5·15. $C_{45}H_{45}O_3P_3W$ requires C, 59·3; H, 4·95%). The mother liquors were evaporated to 20 ml at 0·1 mmHg and ethanol (10 ml) was added. Yellow prisms crystallised when the solution was cooled to −20°. These were recrystallised from a mixture of benzene (2 ml) and hexane (20 ml) to yield mer-*tricarbonyltris(ethyldiphenylphosphine)tungsten*(0) as a yellow *powder* (0·50 g, 17%), m.p. 155—158° (Found: C, 59·25; H, 5·0. $C_{45}H_{45}O_3P_3W$ requires C, 59·3; H, 4·95%).

In a similar experiment with a reaction time of only 3 h, the *meridional* and *facial* isomers were isolated in a ratio of 2 : 1. Work-up using column chromatography allowed the isolation of mixtures of *cis*- and *trans*-[13] tetracarbonylbis(ethyldiphenylphosphine)tungsten(0).

Reduction of trans-*Tetrachlorobis(n-butyldiphenylphosphine)tungsten*(IV).— *trans*-Tetrachlorobis(n-butyldiphenylphosphine)tungsten(IV) (2·34 g) with n-butyldiphenylphosphine (1·54 g) and 0·7% sodium amalgam (150 g) in thf (50 ml) reacted with carbon monoxide during 1 h to give a yellow oil. To this was added benzene–ethanol 1 : 1 (20 ml) and the resultant solution cooled to −20° to deposit a mixture of carbonyl complexes (0·97 g) which was not further treated. The mother liquors were evaporated to dryness at 0·1 mmHg. The residue was loaded on to a 12 × 2 cm column filled with Whatman Column Chromedia CC31, and a single fraction eluted with cyclohexane. This was evaporated to dryness at 0·1 mmHg, and crystallised by adding methanol (5 ml) yielding yellow prisms of mer-*tricarbonyltris(n-butyldiphenylphosphine)tungsten*(0) (0·41 g, 22%), m.p. 156—158° (Found: C, 60·4; H, 4·6. $C_{51}H_{57}O_3P_3W$ requires C, 60·6; H, 5·7%).

Another experiment using tungsten(IV) complex (2·96 g), tertiary phosphine (1·30 g), and 0·6% sodium amalgam (180 g) gave, after 4 h, a pale yellow oil. This was loaded on to a 60—100 mesh Florisil column (30 × 2 cm) and eluted with 10% benzene in cyclohexane. The following fractions were eluted. (a) n-Butyldiphenylphosphine plus various carbonyl complexes (0·3 g); (b) *trans*-tetracarbonylbis(n-butyldiphenylphosphine)tungsten(0) [13,14] (0·16 g, 7%); (c) *cis*-tetracarbonylbis(di-n-butyldiphenylphosphine)-tungsten(0) [14] (a trace); and (d) fac-*tricarbonyltris(n-butyldiphenylphosphine)tungsten*(0), which was recrystallised from benzene and pentane (3 ml) as white *prisms* (0·18 g, 7%), m.p. 190—202° (Found: C, 60·8; H, 5·7. $C_{51}H_{50}O_3P_3W$ requires C, 60·6; H, 5·7%).

Reduction of trans-*Tetrachlorobis(triphenylphosphine)-tungsten*(IV).— *trans*-Tetrachlorobis(triphenylphosphine)-tungsten(IV) (1·81 g) with triphenylphosphine (0·87 g) and 0·5% sodium amalgam (200 g) in thf (130 ml) reacted with carbon monoxide during 16 h to give a pale yellow oil. This was stirred with ethanol (15 ml) to give a solid which was recrystallised from a hot mixture of benzene (10 ml) and ethanol (20 ml) to yield *trans*-tetracarbonylbis(triphenylphosphine)tungsten(0) [15] as yellow *prisms* (0·5 g, 29%).

Isomerisation and Substitution Reactions of Tungsten(0) *Carbonyls*.—The reactions were usually carried out at room temperature, in thf solution, and were followed by observing the changes in the carbonyl region of the i.r. spectrum. Concentrations of tungsten(0) carbonyls present in solution were not accurately determined, and are only quoted to give an indication of the rates of reactions. Unless stated otherwise, the reactions were carried out in daylight.

Reaction of Pentacarbonyl(n-butyldiphenylphosphine)tungsten(0) *with n-Butyldiphenylphosphine*.—n-Butyldiphenylphosphine (0·2 ml) was added to a solution of pentacarbonyl(n-butyldiphenylphosphine)tungsten(0),[16] (0·095 g) in thf (12 ml). There was a steady change in the composition of the solution and after 92 h it contained pentacarbonyl(n-butyldiphenylphosphine)tungsten(0) (5%), *fac*-tricarbonyltris(n-butyldiphenylphosphine)tungsten(0), and *cis*- and *trans*-tetracarbonylbis(n-butyldiphenylphosphine)-tungsten(0), the *trans*-isomer in higher concentration than the *cis*-isomer.

Isomerisation of trans-*Tetracarbonylbis(ethyldiphenylphosphine)tungsten*(0).— *trans*-Tetracarbonylbis(ethyldiphenylphosphine)tungsten(0) (0·065 g), in thf (8 ml) during 8 days at 20°, yielded an equilibrium mixture of *cis*- and *trans*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0) in which the latter isomer was predominant. Similarly, *cis*-tetracarbonylbis(n-butyldiphenylphosphine)tungsten(0) gave an equilibrium mixture in which the *trans*-isomer predominated.

Reaction of trans-*Tetracarbonylbis(ethyldiphenylphosphine)-tungsten*(0) *with Ethyldiphenylphosphine*.—Ethyldiphenylphosphine (0·4 ml) was added to a solution of *trans*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0) (0·04 g) in thf (5 ml). After 120 h, the solution contained *fac*-tricarbonyltris(ethyldiphenylphosphine)tungsten(0) (65%) and a mixture of *cis*- and *trans*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0) in equilibrium proportions.

The behaviour of a mixture of *cis*-tetracarbonylbis(n-butyldiphenylphosphine)tungsten(0) and n-butyldiphenylphosphine in thf was essentially similar.

Reaction of cis-*Tetracarbonylbis(n-butyldiphenylphosphine)-tungsten*(0) *with Carbon Monoxide*.—Carbon monoxide was

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bubbled slowly through a solution of *cis*-tetracarbonylbis-(n-butyldiphenylphosphine)tungsten(0) (0·11 g) in thf (15 ml). After 25 h at 20°, the solution contained 30% of pentacarbonyl(n-butyldiphenylphosphine)tungsten(0) and traces of *trans*-tetracarbonylbis(*n*-butyldiphenylphosphine)-tungsten(0). After 47 h, pentacarbonyl(n-butyldiphenyl phosphine)tungsten(0) (50%) was present together with an equilibrium mixture of *cis*- and *trans*-tetracarbonylbis (n-butyldiphenylphosphine)tungsten(0). After 160 h, pentacarbonyl(n-butyldiphenylphosphine)tungsten(0) was the only carbonyl species present.

Isomerisation of mer-*Tricarbonyltris*(*ethyldiphenylphosphine*)*tungsten*(0).—*mer*-Tricarbonyltris(ethyldiphenylphosphine)tungsten(0) (0·044 g) was dissolved in thf (10 ml). After 4·5 h at 27° *fac*-tricarbonyltris(ethyldiphenylphosphine)tungsten(0) (2%) was present. The solution was boiled for 1 h after which the concentration of *fac*-tricarbonyltris(ethyldiphenylphosphine)tungsten(0) was 3%. Ethyldiphenylphosphine (0·2 ml) was added, and the concentration of *fac*-tricarbonyltris(ethyldiphenylphosphine)tungsten(0) increased to 6% after 4 h.

A solution of *mer*-tricarbonyltris(ethyldiphenylphosphine)tungsten(0) after 5 days in the absence of light contained only traces of the *fac*-isomer.

Similar experiments with *fac*-tricarbonyltris(ethyldiphenylphosphine)tungsten(0) failed to yield the *mer*-isomer.

Reaction of mer-*Tricarbonyltris*(*ethyldiphenylphosphine*)-*tungsten*(0) *with Carbon Monoxide*.—Carbon monoxide was bubbled slowly through a solution of *mer*-tricarbonyltris-(ethyldiphenylphosphine)tungsten(0) (0·044 g) in thf (5 ml). After 1·5 h, half of the starting material had reacted to yield *trans*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0). After 6 h, 90% of the tungsten was present as *trans*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0), although *fac*-tricarbonyltris(ethyldiphenylphosphine)tungsten(0), *cis*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0), and a trace of pentacarbonyl(ethyldiphenylphosphine)tungsten(0) were also detected.

Reaction of fac-*Tricarbonyltris*(*ethyldiphenylphosphine*) *tungsten*(0) *with Carbon Monoxide*.—Carbon monoxide was bubbled slowly through a solution of *fac*-tricarbonyltris-(ethyldiphenylphosphine)tungsten(0) (0·072 g) in thf (10 ml). After 14·5 h, half of the starting material had reacted to yield a mixture of *cis*- and *trans*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0) which was predominantly the former isomer. After 19 h, traces of pentacarbonyl-(ethyldiphenylphosphine)tungsten(0) were present, but 70% of the tungsten was contained in a mixture of *cis*- and *trans*-tetracarbonylbis(ethyldiphenylphosphine)tungsten(0). After 40 h, this had risen to 90%. After 77 h, the solution contained 50% pentacarbonyl(ethyldiphenylphosphine)tungsten(0), and equilibrium proportions of tetracarbonyls.

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