Complexes of 1,1,2-Tris(diphenylphosphino)ethane with Group 6 Metal Carbonyls

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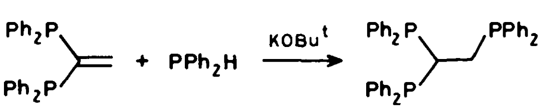
The preparation of $(Ph_2P)_2CHCH_2PPh_2$ (tppe) and its reactions with $[M(CO)_6]$ (M = Cr, Mo, or W) are described. In the 1 : 1 complexes $[M(CO)_n(tppe)]$ (n = 3—5) there are five possible modes of co-ordination, and all have been identified although indirect synthetic routes are required for several. The phosphorus-31 n.m.r. chemical shifts and coupling constants show consistent patterns of behaviour that are interpreted in terms of chelate ring formation and of through-the-metal and ligand backbone contributions. Molybdenum-95 and tungsten-183 n.m.r. data are also presented.

Bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) are well known as versatile ligands capable of chelating a wide range of metal substrates to give complexes with four- and five-membered rings respectively.[1,2] In addition, each ligand can co-ordinate in a monodentate mode,[3,4] and more interestingly dppm can act as a bridge between two proximate metal atoms to give 'A-frame' and related binuclear complexes.[1,5] We have previously reported[6,7] the synthesis of 1,1,2-tris(diphenylphosphino)ethane (tppe), which embodies features of both dppm and dppe in respect of its potential for forming complexes containing four- and five-membered chelate rings, and which also has the capability of exhibiting more complex modes of co-ordination. As part of a more comprehensive examination of the co-ordinative behaviour of tppe we have studied its ability to form complexes with chromium, molybdenum, and tungsten carbonyl moieties, and report here the preparation and n.m.r. spectral characteristics of 15 monometallic species in which a total of five different co-ordination modes are displayed.

Other ligands which can co-ordinate through three phosphorus atoms [*e.g.* bis(2-diphenylphosphinoethyl)phenylphosphine or tris(diphenylphosphino)methane] have been reported,[8] but none has a structure which so readily permits the study of competition between the formation of four- and five-membered chelate rings.

Results and Discussion

The ligand tppe was prepared in high yield, by the base-catalysed ($KOBu^t$) addition [equation (1)] of diphenylphosphine to the double bond of 1,1-bis(diphenylphosphino)ethene,[9] as an air-stable white solid soluble in covalent organic solvents. Its ^{31}P n.m.r. spectrum consists of a doublet (δ −3.6 p.p.m.) and a triplet (δ −19.6 p.p.m.) with $^3J(PP)$ = 24.4 Hz, thus confirming the chemical equivalence of the two geminally related phosphorus atoms.



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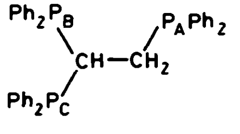

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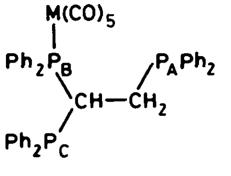

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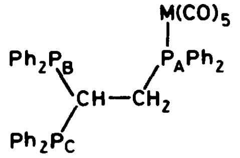

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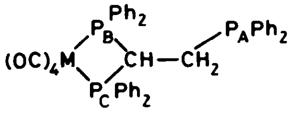

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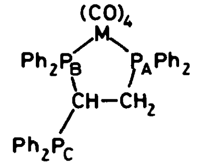

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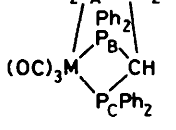

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In principle, tppe can co-ordinate to a single metal in any of the modes (1)—(5) in which for simplicity a Group 6 carbonyl moiety $M(CO)_n$ is assumed; and as we shall show, practical routes to each of these are available. It should be noted that there is expected to be substantially free rotation about the CH–CH_2 bond in tppe and (1)—(3) which will lead to equivalence of the geminally related phosphorus atoms in tppe, (2) and (3) on an n.m.r. time-scale, and this has been confirmed by variable-temperature experiments. Nevertheless, there may well be significant imbalances in conformer populations.

For the complexes of most metals, ring strain effects should be minimal in (4) in view of the presence of a five-membered ring, but they could be significant in (3) and substantial in (5). In fact, the existence of many chelate complexes of bidentate dppm suggests that this should not preclude the occurrence of mode (3), and molecular models indicate that ring strain should not be excessive even in mode (5). These predictions are borne out by the experimental results reported in this paper.

In many of the reactions leading to these complexes more than one product can be formed, and ^{31}P n.m.r. spectroscopy was found to be an ideal way of identifying the components of unseparated reaction mixtures. Thus, characteristic AX_2 patterns (triplet + doublet with possibly some second-order

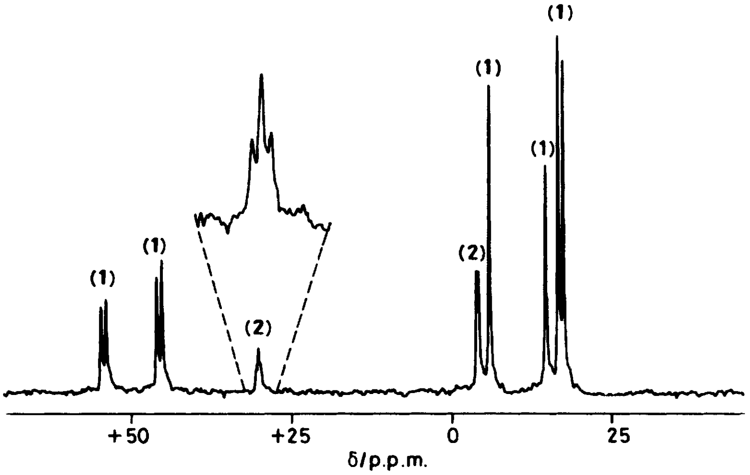
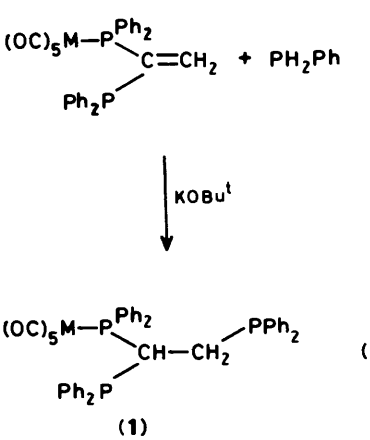


Figure 1. ^{31}P N.m.r. spectrum at 24.2 MHz of a mixture of (1) and (2) (M = Mo) resulting from the reaction between $(Ph_2P)_2CHCH_2PPh_2$ and $[Mo(CO)_5(thf)]$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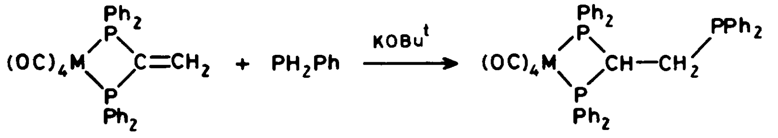
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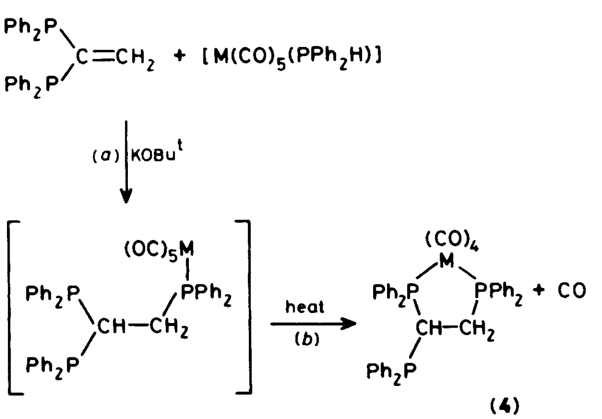
character) are given by the free ligand tppe, and by (2), (3), and (5), while (1) and (4) give AMX spectra. Further identification is provided by a knowledge of the non-overlapping chemical shift ranges for the different types of phosphorus site,[10] to the extent that in all cases it is possible to make an unequivocal assignment. Figure 1 shows the ^{31}P n.m.r. spectrum of a typical reaction mixture.

The direct high-temperature {refluxing diglyme [1,1′-oxybis-(2-methoxyethane)], 2 h} reaction between tppe and $[Cr(CO)_6]$ yielded predominantly (> 90%) the derivative (4) with M = Cr, and similar results were obtained using $[Mo(CO)_6]$ and $[W(CO)_6]$. However, for these last two, more prolonged refluxing led to the formation of (5) (M = Mo or W) in *ca.* 50% yield. In addition, small quantities (< 5%) of other, possibly bimetallic, components were also detected.

Thus the direct reaction between the ligand and $[M(CO)_6]$ is satisfactory as a preparative route to complexes of the type (4) by appropriate control of the reaction time, but for (5) it was found better (essential for M = Cr) to use tppe to displace[11] EtCN from *fac*-$[M(CO)_3(EtCN)_3]$. This reaction occurred rapidly in refluxing CH_2Cl_2, but at room temperature was slower, and what appear to be the intermediate species (3) and (4) with one CO replaced by EtCN have been detected in the reaction mixture, although they have not been isolated.

In none of the foregoing experiments was any significant amount of the monodentate species (1) or (2) observed. However, these were produced in a *ca.* 4:1 ratio by displacement of tetrahydrofuran (thf) from $[M(CO)_5(thf)]$ by tppe. It has not proved possible to obtain either (1) or (2) in pure form from this reaction mixture, which loses carbon monoxide at elevated temperatures to give a mixture of (3) and (4), but it was found possible to isolate (1) (M = Cr, Mo, or W) in pure form from the indirect reaction (2). In a similar way the reaction (3), which has also been reported by Shaw and co-workers[12] for M = W, was used as a preparative route to (3) (M = Cr, Mo, or W). Keiter *et al.*[13] have shown that co-ordinated secondary phosphines can undergo base-catalysed addition to double bonds, and therefore reaction (4)(*a*) was attempted as a route to (2). However, in cold thf solution no reaction was found to occur, while on heating to reflux rapid formation of (4) (M = Cr or W) or of a mixture of (3) and (4) (M = Mo), occurred. It is therefore suggested that reaction (4)(*b*) has an activation energy which is comparable with, or lower than that of (4)(*a*).

The complexes are white [(1), (2)], pale yellow [(4)], or bright yellow [(3), (5)], diamagnetic, air-stable crystalline solids for which melting points and analytical data are given in Table 1. Their mass spectra showed the molecular ion except for (1) (M = Cr, Mo, or W) and (3) (M = Mo). Ions corresponding to loss of one CO were observed for (1) (M = Cr or W), (3) (M = Cr, Mo, or W), and (4) (M = Cr or W); of two CO for (1) (M = Cr, Mo, or W) and (5) (M = Cr, Mo, or W); of three CO



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for (3) (M = Cr, Mo, or W), (4) (M = Cr or W), and (5) (M = Cr or Mo); of four CO for (1) (M = Cr, Mo, or W), (3) (M = Cr, Mo, or W), and (4) (M = Cr or W); and of five CO for (1) (M = Cr, Mo, or W). The complexes are readily soluble in chloroform and dichloromethane, only sparingly soluble in benzene and diethyl ether, and insoluble in methanol. Phosphorus-31 n.m.r. data are given in Table 2, and Table 3 gives the n.m.r. data for molybdenum-95 ($I = \frac{5}{2}$, natural abundance 16%) and tungsten-183 ($I = \frac{1}{2}$, natural abundance 14%). The tungsten-183 parameters were obtained indirectly by ^{31}P-{^{183}W} double-resonance experiments under conditions of broad-band proton decoupling,[14] and the presence of ^{183}W satellites in the phosphorus-31 n.m.r. spectra was a valuable additional aid to assignment.

As indicated above, the phosphorus chemical shifts lie in ranges which depend upon (*a*) chelate ring size and (*b*) type of co-ordinated metal. Superposed upon these effects is the inherent chemical shift difference (16.0 p.p.m.) between the two types of phosphorus in the free ligand itself, but this effect can be removed by considering the co-ordination chemical shifts Δ defined[15] as $\delta(^{31}P)_{complex} - \delta(^{31}P)_{ligand}$ which are also given in Table 2. In this context it is worth noting that the chemical shift of an unco-ordinated phosphorus can also be affected by complex formation. Thus, in complexes of type (1) $\delta(P_C)$ experiences a decrease of *ca.* 6 p.p.m. and $\delta(P_A)$ an increase of *ca.* 2 p.p.m., while in type (4) $\delta(P_C)$ experiences a decrease of *ca.* 12 p.p.m., these effects not being strongly metal-dependent.

Figure 2 displays the pattern of phosphorus co-ordination chemical shifts for complexes of types (1)—(4) as a function of ring size and of metal. It is similar to one which could be based on results for complexes of dppm and dppe,[16] and as expected the presence of one or more unco-ordinated diphenylphosphino groups has little or no effect. The origin of the ring-size effects upon co-ordination chemical shift is not understood,[10] but it appears to be unconnected with 'ring strain'.[17] This view is supported by our results for complexes of type (5) in which molecular models indicate that there is considerably greater strain than in complexes with just one four- or five-membered

Table 1. Elemental analyses for the complexes

Complex	M	Found (%)			Calc. (%)		
		C	H	P	C	H	P
(1)	Cr	66.6	4.3	11.9	66.7	4.3	12.0
	Mo	62.2	3.9	11.2	63.1	4.0	11.4
	W	56.6	3.6	10.1	56.9	3.6	10.2
(3)	Cr	66.9	4.4	12.1	67.6	4.4	12.4
	Mo	63.9	4.1	11.7	63.8	4.2	11.8
	W	57.2	3.7	10.7	57.4	3.8	10.6
(4)	Cr	67.5	4.4	12.2	67.6	4.4	12.4
	Mo				63.8	4.2	11.8
	W	57.1	3.7	10.5	57.4	3.8	10.6
(5)	Cr	68.5	4.6	12.7	68.5	4.6	12.9
	Mo	64.3	4.3	12.2	64.6	4.4	12.2
	W	57.4	3.8	10.7	57.9	3.9	10.9

Table 3. Molybdenum-95 and ^{183}W n.m.r. data for species (1)—(5)

Species	$\delta(^{95}Mo)^a$	$J(^{95}Mo-^{31}P)^b$	$\delta(^{183}W)^c$	$^1J(^{183}W-^{31}P)^d$
(1)	+149	127 ± 10	+239	249
(2)	*e*	*e*	*e*	237
(3)	+301	105 ± 10	+502	205
(4)	+144	132 ± 20,^{f} 132 ± 20^g	+286	230,^{f} 230^g
(5)	+352	120 ± 20,^{f} 120 ± 20^g	+558	178,^{f} 216^g

[a] In p.p.m. (±2 p.p.m.) to high frequency of [Mo(CO)$_6$] for which $\delta(^{95}Mo)$ −1 856 p.p.m. relative to $[MoO_4]^{2-}$. [b] In Hz. [c] In p.p.m. (±0.5 p.p.m.) to high frequency of [W(CO)$_6$] for which $\delta(^{183}W)$ −3 505 p.p.m. relative to $[WO_4]^{2-}$. [d] In Hz (±0.5 Hz). [e] Not determined owing to low concentration. [f] Coupling to P_B. [g] Coupling to P_A.

Table 2. Phosphorus-31 n.m.r. data for tppe and species (1)—(5)[a]

Species	Metal	$\delta(^{31}P_A)$	$\Delta_A{}^b$	$\delta(^{31}P_B)$	$\Delta_B{}^b$	$\delta(^{31}P_C)$	$\Delta_C{}^b$	$^3J(P_AP_B)$	$^3J(P_AP_C)$	$^2J(P_BP_C)$
tppe^c		−19.6		−3.6		−3.6		24.4	24.4	*d*
(1)	Cr	−17.3	*e*	+67.2	+70.8	−11.9	*e*	20.8	0.0	196.5
	Mo	−17.5	*e*	+50.0	+53.6	−10.5	*e*	19.5	0.0	213.6
	W	−17.5	*e*	+33.4	+37.0	−9.6	*e*	22.6	0.0	210.0
(2)	Cr	+49.6	+69.2	−3.7	*e*	−3.7	*e*	3.1	3.1	*d*
	Mo	+30.2	+49.8	−4.2	*e*	−4.2	*e*	8.5	8.5	*d*
	W	+12.0	+31.6	−3.9	*e*	−3.9	*e*	7.3	7.3	*d*
(3)	Cr	−19.3	*e*	+50.5	+54.1	+50.5	+54.1	7.3	7.3	*d*
	Mo	−19.5	*e*	+26.8	+30.4	+26.8	+30.4	7.3	7.3	*d*
	W	−20.0	*e*	+2.7	+6.3	+2.7	+6.3	8.5	8.5	*d*
(4)	Cr	+69.4	+89.0	+87.5	+91.1	−15.9	*e*	(−)20.8^f	1.8	25.9
	Mo	+47.4	+67.0	+64.8	+68.4	−14.8	*e*	(−)9.0^f	1.8	25.6
	W	+32.7	+52.3	+49.5	+53.1	−15.6	*e*	(−)1.5^f	2.4	29.5
(5)	Cr	+61.4	+81.0	+50.3	+53.9	+50.3	+53.9	(−)23.2^f	(−)23.2^f	*d*
	Mo	+40.6	+60.2	+29.2	+32.8	+29.2	+32.8	(−)12.2^f	(−)12.2^f	*d*
	W	+28.1	+47.7	+11.7	+15.3	+11.7	+15.3	(−)6.1^f	(−)6.1^f	*d*

[a] Chemical shifts in p.p.m. to high frequency of 85% H_3PO_4, ±0.1 p.p.m.; coupling constants in Hz, ±0.2 Hz. [b] $\Delta = \delta(^{31}P)_{complex} - \delta(^{31}P)_{ligand}$. [c] $P_B = P_C$. [d] Not determined owing to chemical equivalence of P_B and P_C. [e] Not applicable, see text. [f] See text for basis of signs of coupling constants.

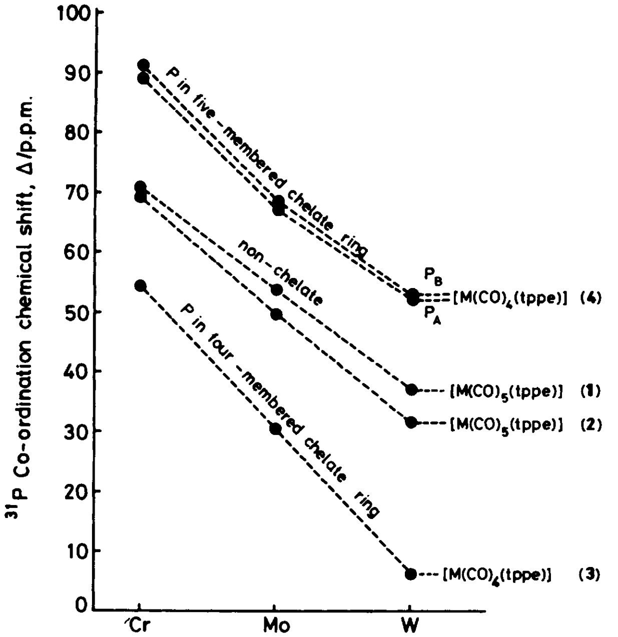

Figure 2. ^{31}P Co-ordination chemical shifts in chromium, molybdenum, and tungsten carbonyl complexes of $(Ph_2P)_2CHCH_2PPh_2$

ring. Even so, Δ for P_A which is incorporated in two five-membered rings is close to that for a phosphorus in a single five-membered ring, and Δ for P_B (one four- and one five-membered ring) is as expected for one four-membered ring only. Of course, phosphorus chemical shifts depend upon electronic excitation energies as well as hybridisation, and it is clear from the colours of the various complexes that there are significant differences here.

Coupling constants involving phosphorus are known to depend upon oxidation state, effective nuclear charge, hybridisation and especially conformational relationships. Unfortunately, the presence of symmetry has prevented the determination of $^2J(PP)$ in tppe, (**2**), (**3**), and (**5**), but comparison with related molecules[9] suggests a value of *ca.* 120 Hz for the free ligand itself. Thus, the results for (**1**) show that when one of the phosphorus atoms is co-ordinated there is a significant increase in this coupling, while the vicinal coupling is little changed. The relatively minor dependence upon the metal atom of these couplings probably reflects small differences in the electron density and/or interbond angles at P_B, the co-ordinated phosphorus atom. It is especially surprising that $^3J(P_AP_C)$ is accurately zero in all three species of (**1**), and also in the analogous monoselenide, $Ph_2PCH_2CH(PPh_2)PPh_2(Se)$.[6] This suggests that the same special conformational balance prevails in all the species of this type, and this presumably embraces both rotation about the CH_2–CH bond, and the orientation of the electron lone pairs on phosphorus.

For species (**2**) and (**3**) the small variations in the vicinal P–P couplings when the metal atom changes probably reflect corresponding changes in the hybridisation and effective nuclear charge of the co-ordinated phosphorus atom since conformational changes are unlikely to be important. The pattern of the P–P couplings in the species (**4**) provides strong support for the idea[18] of there being 'through-the-metal' and 'backbone' contributions of opposite sign in chelate metal complexes. Thus, $^3J(P_AP_C)$ and $^2J(P_BP_C)$, neither of which can incorporate a through-the-metal pathway, are essentially independent of the metal atom and therefore indicate relatively small variations in hybridisation and effective nuclear charge on phosphorus, whereas $^3J(P_AP_B)$ shows the expected[18] decrease in magnitude as the Group in the Periodic Table is descended. The observed values of $^3J(P_AP_B)$ in (**4**) can then be attributed to an approximately constant backbone contribution of +20 Hz (which is close to that in the free ligand), together with through-the-metal contributions of −41, −30, and −22 Hz for Cr, Mo, and W respectively, the signs being based upon those established[19] for the analogous complexes of dppe. Similar conclusions can be drawn from the values of $^3J(P_AP_B)$ in the complexes (**5**) in which the (strained) backbone contribution appears to be *ca.* +16 Hz, and we can further predict that in these species $^2J(P_BP_C)$ will show a similar systematic algebraic increase down the series Cr, Mo, W.

Although the usual references for molybdenum and tungsten chemical shifts are $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ respectively, it is convenient to use $[Mo(CO)_6]$ and $[W(CO)_6]$ respectively for carbonyl complexes. It is known[14] that there are close parallels between ^{95}Mo and ^{183}W chemical shifts in analogous compounds, the latter being *ca.* 1.7 times more sensitive to changes in chemical environment, and this pattern is repeated in the present complexes. In addition, the expected[14] effects of chelate ring formation are also observed, *viz.* a substantial increase in δ(M) for inclusion in a four-membered ring, and a decrease for a five-membered ring. In the case of the more highly strained (**5**) there is an even greater increase in δ(M). As with their chemical shifts, couplings involving ^{95}Mo and ^{183}W usually run parallel,[14] with $J(^{183}WX) \simeq 1.8\,J(^{95}MoX)$, and this tendency is repeated in the present complexes.

Experimental

Phosphorus-31 and ^{95}Mo n.m.r. spectra were recorded under conditions of broad-band proton decoupling on CH_2Cl_2 solutions contained in spinning tubes (10-mm outside diameter) on a JEOL FX 90Q multinuclear spectrometer at observing frequencies of 36.2 and 5.85 MHz respectively. $^{31}P\text{-}\{^{183}W\}$ Multiple resonance experiments with broad-band proton decoupling were performed as described previously[14] on a modified JEOL FX 60 n.m.r. spectrometer operating at an observing frequency of 24.2 MHz. Mass spectra were obtained on a JEOL DMX300 spectrometer using a electron-impact ionization at 70 eV (*ca.* 112 × 10^{-19} J).

All solvents were deaerated before use and manipulations were performed under an atmosphere of dry nitrogen.

1,1,2-Tris(diphenylphosphino)ethane.—1,1-Bis(diphenylphosphino)ethene[9] (5 g, 12.6 mmol) and diphenylphosphine (2.35 g, 12.6 mmol) were refluxed in dry thf (50 cm^3) for 0.1 h in the presence of potassium t-butoxide (catalytic amount). The solution was cooled and solvent was removed under vacuum to give an oily residue which yielded a white solid on addition of EtOH (40 cm^3). The solid was recrystallised from CH_2Cl_2–MeOH to give the product as a white powder, m.p. 107 °C, yield 6.9 g (94%) (Found: C, 78.4; H, 5.7; P, 15.7. $C_{38}H_{33}P_3$ requires C, 78.4; H, 5.7; P, 15.9%).

Species (**1**) (M = Cr).—Diphenylphosphine (0.3 g, 1.6 mmol) and [1,1-bis(diphenylphosphino)ethene-*P*]pentacarbonylchromium (0.94 g, 1.6 mmol) in dry thf (30 cm^3) were stirred at room temperature for 0.5 h in the presence of $KOBu^t$ (catalytic amount). The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (10 cm^3). Addition of MeOH to the filtered solution gave a green precipitate which was recrystallised from CH_2Cl_2–MeOH to give the product as white crystals (yield 0.8 g, 65%). The molybdenum (yield 65%) and tungsten (yield 56%) analogues were prepared similarly as white crystals in each case.

Species (**3**) (M = Cr).—A similar procedure to that for (**1**) starting from diphenylphosphine (0.5 g, 2.7 mmol) and [1,1-bis(diphenylphosphino)ethene-*PP′*]tetracarbonylchromium (1.5 g, 2.7 mmol) gave the product as bright yellow crystals (yield 1.25 g, 63%). The molybdenum and tungsten analogues were prepared similarly in yields of 58 and 53% respectively.

Species (**4**) (M = Cr).—1,1-Bis(diphenylphosphino)ethene (0.79 g, 2 mmol) in dry thf (25 cm^3) was added dropwise to pentacarbonyl(diphenylphosphine)chromium (0.74 g, 2 mmol) in refluxing dry thf (30 cm^3) containing $KOBu^t$ (catalytic amount). After cooling, the solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2 (10 cm^3). MeOH was added to the filtered solution to yield yellow-green crystals which were recrystallised from CH_2Cl_2–MeOH to give the product as pale yellow crystals (yield 0.66 g, 40%). The tungsten analogue was prepared similarly in 61% yield.

Species (**5**) (M = Cr).—Hexacarbonylchromium (0.4 g, 1.8 mmol) was refluxed in cyanoethane (30 cm^3) for 72 h as described by Kubas[11] to give a solution of *fac*-$[Cr(CO)_3(EtCN)_3]$. 1,1,2-Tris(diphenylphosphino)ethane (1.06 g, 1.8 mmol) in CH_2Cl_2 (10 cm^3) was added and the mixture refluxed for 1 h. Removal of solvent under vacuum and recrystallisation from CH_2Cl_2–MeOH gave the product as bright yellow crystals (yield 0.34 g, 26%). The molybdenum and tungsten analogues were prepared similarly in yields of 30 and 53% respectively.

Acknowledgements

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References

1 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99.
2 J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1961, 4980.
3 E. E. Isaacs and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 2560.
4 J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 1973, 347.
5 J. T. Mague, *Inorg. Chem.*, 1969, **8**, 1975.
6 I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 1982, 484.
7 J. L. Bookham, W. McFarlane, and I. J. Colquhoun, *J. Chem. Soc., Chem. Commun.*, 1986, 1041.
8 D. L. Berglund and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 2602; K. Issleib and H. P. Abicht, *J. Prakt. Chem.*, 1970, **312**, 456.
9 I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1982, 1915.
10 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
11 G. J. Kubas, *Inorg. Chem.*, 1983, **22**, 692.
12 G. R. Cooper, F. Hassan, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1985, 614.
13 R. L. Keiter, Y. Y. Sun, J. W. Brodack, and L. W. Cary, *J. Am. Chem. Soc.*, 1979, **101**, 2638.
14 G. T. Andrews, I. J. Colquhoun, W. McFarlane, and S. O. Grim, *J. Chem. Soc., Dalton Trans.*, 1982, 2353.
15 B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1972, 704.
16 S. O. Grim, R. Barth, W. Briggs, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.
17 S. Hietkamp, O. J. Stufflken, and K. Vrieze, *J. Organomet. Chem.*, 1979, **169**, 107.
18 S. O. Grim, R. C. Barth, J. D. Mitchell, and J. DelGaudio, *Inorg. Chem.*, 1977, **16**, 1776.
19 G. T. Andrews, I. J. Colquhoun, and W. McFarlane, *Polyhedron*, 1983, **2**, 783.

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