Synthesis and Reactions of Complexes of 1,3-Bis(diphenylphosphino)-2-methylallyl with Molybdenum or Tungsten Tetracarbonyls

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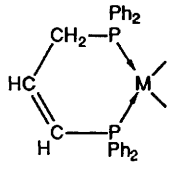
Treatment of molybdenum or tungsten hexacarbonyls with the diphosphine $CH_2{=}C(CH_2PPh_2)_2$ gives complexes $[M\{(Ph_2PCH_2)_2C{=}CH_2\}(CO)_4]$ (M = Mo, **3a**; or W, **3b**). Either of these complexes with sodium ethoxide in boiling ethanol exhibits prototropic rearrangement to give $[M\{Ph_2PCH{=}CMeCH_2PPh_2\}(CO)_4]$ (M = Mo, **4a**; or W, **4b**). Treatment of either complexes **3** or **4** with strong bases such as methyllithium, lithium 2,2,6,6-tetramethylpiperidide or lithium bis(trimethylsilyl)amide gave bright orange solutions of the symmetrical 1,3-bis(diphenylphosphino)-2-methylallylmetal tetracarbonyl anions $[M\{Ph_2PCHC(Me)CHPPh_2\}(CO)_4]^-$ **5**. The molybdenum complex **5a**, when treated with D_2O, gave $[Mo(Ph_2PCH{=}CMeCHDPPh_2)(CO)_4]$ **6**, which was shown to be a monodeuterio-complex by ^2H, ^1H and ^{13}C NMR spectroscopy. Both the $^{31}P\text{-}\{^1H\}$ and the $^{13}C\text{-}\{^1H\}$ NMR spectra of this compound showed secondary isotope effects and the $^{13}C\text{-}\{^1H\}$ spectrum showed that there was no plane of symmetry, whereas with the corresponding perhydro complex **4a**, there is such a plane (going through the Mo and the two P). The carbanions **5** react with electrophiles such as MeI, $SiMe_3Cl$, EtI, allyl bromide, $PhCH_2Br$ or PPh_2Cl to give substitution products $[M(Ph_2PCH{=}CMeCHR'PPh_2)(CO)_4]$ (R' = Me, **7**; $SiMe_3$, **8**; Et, **9**; $CH_2{=}CHCH_2$, **10**; CH_2Ph, **11**, or PPh_2, **13**); these complexes were fully characterised. Treatment of **7a** (M = Mo) with LiMe and then an equivalent amount of methanol, followed by more LiMe and methanol, gave the isomerised product $[Mo(Ph_2PCMe{=}CMeCH_2PPh_2)(CO)_4]$ **12**. When a solution of complex **13a** M = M) was heated in toluene the tricarbonyl $[Mo\{(Ph_2P)_2CHCMe{=}CHPPh_2\}(CO)_3]$ **14a**, in which all three phosphoruses are co-ordinated, was formed; similarly the corresponding tungsten complex **13b**, when heated in decane, gave $[W\{(Ph_2P)_2CHCMe{=}CHPPh_2\}(CO)_3]$ **14b**. Proton, ^2H, ^{13}C and ^{31}P NMR data, infrared [ν(C≡O)] and some mass spectral data are given and discussed.

Chelating ditertiary phosphines are very important in co-ordination and organometallic chemistry and in associated areas of catalysis.[1–4] Specific areas where ditertiary phosphines are useful include chiral hydrogenation using diphosphine-rhodium or -ruthenium complexes with diphosphines such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap), $Ph_2PCH\text{-}MeCHMePPh_2$ (chiraphos) or $Ph_2PCH_2CHOCHO(CMe_2)\text{-}PPh_2$ (diop) *etc.*[4,5] Other areas include reactions of co-ordinated dinitrogen *e.g.* with the complex $[W(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[6] and aryl coupling for which nickel or palladium complexes are effective.[4] Palladium–diphosphine complexes have also been used in the allylation reaction.[4,7]

It is well established that, on co-ordination of a tertiary phosphine, the hydrogen of a CH in the α position to co-ordinated phosphorus becomes much more acidic.[8] It occurred to us that a diphosphine, *Z*-$Ph_2PCH{=}CHCH_2PPh_2$, when complexed to a metal, as in **1**, might deprotonate readily to give a chelated bis(diphenylphosphino)allyl system, as in **2**. Such a ligand system is hitherto unknown but its complexes could have interesting properties. In this paper we describe a convenient strategy for producing a closely related system, which was to start with the known diphosphine $CH_2{=}C(CH_2PPh_2)_2$. The synthesis of this diphosphine has been described by two other groups of workers[9–11] and is readily made by treating the commercially available dichloride $CH_2{=}C(CH_2Cl)_2$ with $L_2(PPh_2)$. The base-promoted isomerisation of $CH_2{=}C(CH_2\text{-}PPh_2)_2$ to a mixture of *Z*- and *E*-$Ph_2PCH{=}C(Me)CH_2PPh_2$ has been reported very briefly without experimental details.[9] We considered that complexation of $CH_2{=}C(CH_2PPh_2)_2$ to a metal, followed by base-promoted isomerisation to give the co-ordinated $Ph_2PCH{=}C(Me)CH_2PPh_2$, which therefore must be the *Z* isomer *exclusively*, would be a better strategy and this is what we have done. The complex $[Cr\{PPh_2C(=CH_2)CH_2\text{-}$



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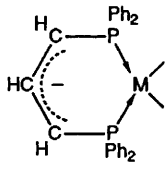

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$PPh_2)(CO)_4]$ has been shown to isomerise to $[Cr\{PPh_2\text{-}C(Me){=}CHPPh_2)(CO)_4]$ in the presence of $KOBu^t$.[12] We have gone on to study some reactions of carbanions analogous to those of type **2**.

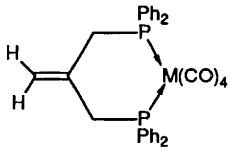
Results and Discussion

Treatment of $[Mo(CO)_6]$ with an equimolar amount of the diphosphine $CH_2{=}C(CH_2PPh_2)_2$ in boiling decane gave the tetracarbonyl complex **3a** in 89% yield. The corresponding tungsten complex **3b** was prepared similarly in 88% yield: details are in the Experimental section. These complexes were characterised by elemental analysis (C and H, Table 1), mass spectrometry and by NMR and IR spectroscopy. The $^{31}P\text{-}\{^1H\}$ spectrum of the molybdenum complex **3a** showeed a singlet (Table 2) and the $^1H\text{-}\{^{31}P\}$ NMR spectrum, two singlets, at δ 4.60 and 3.22 of relative intensities 1:2. Both of these resonances became second-order patterns in the ^1H NMR spectrum: that at δ 4.60 showed an *N*-doublet separation[13] $|^4J(PH)(cis) + {}^4J(PH)(trans)|$ of 5.7 Hz; that at δ 3.22 showed an *N*-doublet separation of 11.0 Hz (Table 2). The tungsten complex **3b** behaved similarly (see Table 2). The $^{13}C\text{-}\{^1H\}$ NMR spectrum of the molybdenum complex confirmed the assigned structure **3a**, with two resonance patterns due to the two types of carbonyl ligands. One pattern was a first-order 1:2:1 triplet at δ 210.1,

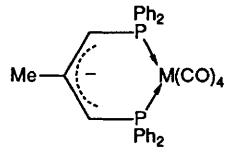
Table 1 Microanalytical data, infrared absorption maxima (cm^{-1}) and masses of the most intense peak in the molecular ion in the mass spectrum

Compound	Analysis[a] (%) C	H	ν(C≡O)[b]	M[c]
3a	60.45 (60.75)	4.1 (4.15)	2025, 1925 (sh), 1900	634 (634)
3b	53.0 (53.35)	3.55 (3.65)	2022, 1922, 1898	
4a	60.85 (60.75)	4.15 (4.15)	2020, 1922 (sh), 1910, 1898 (sh)	634 (634)
4b	53.35 (53.35)	3.55 (3.65)	2022, 1920 (sh), 1902, 1890 (sh)	
6	60.5 (60.7)	4.1 (4.3)	2020, 1920 (sh), 1900, 1890(sh)	635 (635)
7a	61.05 (61.3)	4.35 (4.35)	2028, 1925 (sh), 1918, 1892	648 (648)
7b	53.75 (53.95)	3.8 (3.85)	2025, 1922 (sh), 1905, 1890 (sh)	
8a	59.65 (59.65)	4.9 (4.85)	2030, 1930 (sh) 1915, 1890 (sh)	706 (706)
8b	52.85 (53.05)	4.25 (4.3)	2020, 1920, 1900, 1885 (sh)	
9	61.6 (61.85)	4.5 (4.6)	2025, 1920 (sh), 1915, 1885	662 (662)
10	55.15 (55.3)	3.95 (4.0)	2020, 1920 (sh), 1905, 1885	
11	64.75 (64.85)	4.5 (4.45)	2020, 1920 (sh), 1905, 1885 (sh)	724 (724)
12	61.0 (61.3)	4.2 (4.35)	2022, 1922 (sh), 1910, 1890 (sh)	648 (648)
13a	65.15 (64.7)	4.35 (4.3)	2025, 1922 (sh) 1915, 1895	
13b·C_6H_6	61.5 (61.15)	4.15 (4.2)	2022, 1920 (sh), 1905, 1890	
13b·CH_2Cl_2	54.8 (54.6)	3.7 (3.75)		
14a	63.35 (65.5)	4.65 (4.45)	1946, 1855 (br)	
14b	59.1 (58.9)	3.95 (4.0)	1940, 1845 (br)	

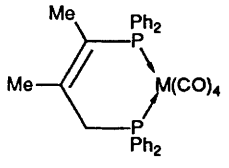
[a] Calculated values in parentheses. [b] Measured in CH_2Cl_2 solution; sh = shoulder, br = broad. All the peaks are very strong. [c] Calculated parent molecular ion mass for molybdenum-98 in parentheses. All the mass spectra showed ions corresponding to successive losses of one, two, three and four CO groups.



3a M = Mo
3b M = W



5a M = Mo
5b M = W



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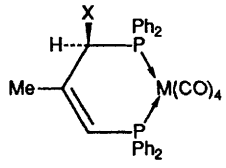
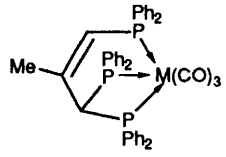


	M	X
4a	Mo	H
4b	W	H
6	Mo	D
7a	Mo	Me
7b	W	Me
8a	Mo	$SiMe_3$
8b	W	$SiMe_3$
9	Mo	Et
10	W	$CH_2CH{=}CH_2$
11	Mo	CH_2Ph
13a	Mo	PPh_2
13b	W	PPh_2



14a M = Mo
14b M = W

with $^2J(PC)$ = 8.7 Hz, clearly due to the mutually *trans* carbonyls. The other pattern was second order and typical of an AA'X spin system, with an intermediate value of $|J(AX) - J(A'X)|/J(AA')$.[14] The alkenyl carbon resonances were assigned (Table 3) by recording another ^{13}C NMR spectrum under conditions of low-power noise decoupling. The values of ν(C≡O) for these two complexes **3a** and **3b** are given in Table 1.

We have effected prototropic shift reactions on both complexes **3a** and **3b** by heating them in boiling ethanol, in the presence of NaOEt, for 16 h, giving the hoped-for rearranged complexes **4a** and **4b** in excellent (89%) isolated yields. Details of these preparations are in the Experimental section and microanalytical data are in Table 1. The ^{31}P-$\{^1H\}$ NMR spectrum of **4b** consisted of two doublet resonances, at δ −0.5 and 32.2, $^2J(PP)$ = 24 Hz, with satellites due to coupling to tungsten-183 (Table 2). The ^1H NMR spectrum showed three non-aromatic resonance patterns at δ 6.07, 3.18 and 1.80, of relative intensities 1:2:3, and assigned to the CH=, the CH_2 and the CH_3 protons, respectively. Broad-band and selective ^{31}P decoupling of the proton spectra indicated that the phosphorus absorbing at δ 32.2 was coupled to all three types of aliphatic proton and was assigned as the allylic phosphorus CCH_2P (see Table 2 for data); the other phosphorus resonance (at δ −0.5) was assigned to the alkenyl phosphorus C=CHP (data in Table 2). There was also a four-bond coupling of 1.4 Hz between the HC=C proton and the methyl group. The carbon-13 NMR spectrum (data in Table 3) was in agreement with the assigned structure **4b**. The carbonyl resonances were at δ 206.6, 206.2 and 202.1 (relative intensities 1:1:2). The resonance of the mutually *trans* carbonyls, absorbing at δ 202.1, consisted of a 1:2:1 triplet through coupling to the two P nuclei, whilst the other two carbons gave doublet of doublet patterns. The molybdenum complex **4a** was characterised in the same way as for the tungsten complex (data in Tables 1–3).

As already mentioned, Schmidbaur *et al.*[9,10] have reported that treatment of $CH_2{=}C(CH_2PPh_2)_2$ with sodium methoxide gives a mixture of the *cis* and *trans* isomers of $PPh_2CH{=}CMe{-}CH_2PPh_2$, in unspecified proportions and which were not separated. We have observed no products which could have arisen from *trans*-$PPh_2CH{=}CMeCH_2PPh_2$.

As discussed above, we anticipated that an allylic disphosphine complex of type **4** would be deprotonated by a strong base. We have therefore treated complexes of types **3** and **4** with strong bases: methyllithium, lithium 2,2,6,6-tetramethylpiperidide or lithium bis(trimethylsilyl)amide. Treatment of tetrahydrofuran solutions of complexes of types **3** or **4** with any of these strong bases caused an immediate colour change from pale yellow to bright orange. Thus treatment of a tetrahydrofuran solution of the molybdenum complex **3a** with methyllithium gave a bright orange solution. ^{31}P-$\{^1H\}$ NMR spectroscopy showed that none of the starting complex remained and that only one phosphorus-containing species, characterised by a singlet ^{31}P resonance at δ 14.6, was present. This species was longed-lived in solution in the absence of air or moisture but reacted rapidly with moisture or methanol to give **4a** (but no **3a**) and we assign to the deprotonated product a symmetrical allylic carbanion structure **5a**. The deprotonated product showed an invariant ^{31}P-$\{^1H\}$ NMR singlet resonance over the range −70 to +28 °C. Similar treatment of either of the tungsten complexes **3b** or **4b** gave the symmetrical allylic carbanion **5b**, characterised by a singlet ^{31}P resonance at δ 4.4 with satellites due to coupling to tungsten-183, $^1J(WP)$ = 206 Hz. We also found that complexes of type **5** could be generated from the unrearranged complexes of type **3** using 1 mol equivalent of lithium tetramethylpiperidide, but that, when an

Table 2 $^{31}P-\{^1H\}$[a] and ^1H[b] and $^1H-\{^{31}P\}$[b] NMR spectroscopic data

Complex	$^{31}P-\{^1H\}$ (δ)	^1H (δ)
3a	24.2 PCH_2[c]	4.60 [H_2C=, $A_2A'_2XX'$, *N* 5.7][d]
		3.22 [CH_2P, $A_2A'_2XX'$, *N* 11.0][d]
3b	4.9 (226) PCH_2[c]	4.63 [CH_2, $A_2A'_2XX'$, *N* 5.7][d]
		3.33 [CH_2P, $A_2A'_2XX'$, *N* 11.9][d]
4a	48.1 PCH_2, *J*(PP) 29	6.07 [CH=C, ^4J(PH) 3.6, ^2J(PH) 4.7, ^4J(HH) 1.5][e]
	18.5 PC=C	3.22 [CH_2, ^4J(PH) 1.7, ^2J(PH) 7.9][e]
		1.71 [CH_3, ^4J(PH) 1.7, ^4J(HH) 1.5][e]
4b	32.2 (244) PCH_2, *J*(PP) 24	6.07 [HC=C, ^2J(PH) 5.6, ^4J(PH) 4.7, ^4J(HH) 1.4][e]
	−0.5 (221) PC=C	3.18 [CH_2, ^4J(PH) 0.7, ^2J(PH) 8.6][e]
		1.80 [CH_3, ^4J(PH) 1.6, ^4J(HH) 1.4][e]
6	47.2 PCHD,[f] *J*(PP) 30	6.09 [HC=C, ^4J(PH) 4.2, ^2J(PH) 5.6, ^4J(HH) 1.4, 0.6][f]
	17.7 PC=C[f]	2.95 [CHD, ^4J(PH) 0.7, ^2J(PH) 8.6][f]
		1.74 [CH_3, ^4J(PH) 1.7, ^4J(HH) 1.4][f]
7a	54.8 PCHMe, *J*(PP) 26	6.31 [HC=C, ^4J(PH) 1.6, ^4J(HH) 1.3]
	12.8 PC=C	3.10 [C*H*Me, ^2J(PH) 13.0, ^3J(HH) 7.1]
		2.33 [CH_3C=C, ^4J(HH) 1.3]
		0.90 [CH_3CH, ^3J(PH) 15.9, ^3J(HH) 7.1]
7b	37.7 (234) PCHMe, *J*(PP) 19	6.27 [HC=C, ^4J(PH) 2.1, ^2J(PH) 1.1, ^4J(HH) 1.2][e]
	−7.2 (222) PC=C	3.14 [C*H*Me, ^3J(HH) 7.1, ^2J(PH) 13.2][e]
		2.33 [CH_3C=C, ^4J(HH) 1.2][e]
		0.88 [CH_3CH, ^3J(HH) 7.1, ^3J(PH) 13.2][e]
8a	45.0 PCHSi, *J*(PP) 27	6.46 [HC=C, ^4J(PH) 1.2, ^4J(HH) 1.0]
	12.4 PC=C	3.14 [CHSi, ^4J(PH) 1.5, ^2J(PH) 14.8, ^2J(SiH) 10.0]
		2.51 [CH_3, ^4J(HH) 1.0]
		−0.41 [$SiCH_3$, ^2J(SiH) 6.4]
8b	26.3 (238) PCHSi, *J*(PP) 20	6.44 [HC=C, ^4J(PH) 1.7, ^4J(HH) 1.2]
	−7.5 (226) PC=C	3.39 [CHSi, ^2J(PH) 15.3, ^4J(PH) 1.0]
		2.50 [CH_3, ^4J(HH) 1.1]
		−0.40 [$SiCH_3$, ^2J(SiH) 6.4]
9	See text	6.42 [HC=C, ^4J(PH) 2.8, ^2J(PH) 1.3, ^4J(HH) 1.3]
		3.06 [PC*H*Et, ^2J(PH) 12.9, ^3J(HH) + ^3J(HH) 14.8]
		2.26 [C=CCH_3, ^4J(HH) 1.3]
		1.28 [CH_2CH_3, ^3J(HH) 7.4, ^3J(PH) 7.4]
		0.68 [CH_2CH_3, ^3J(HH) 7.4]
10	See text	6.44 [HC=C, ^4J(PH) 2.7, ^2J(PH) 1.3, ^4J(HH) 1.2]
		5.50, 4.81, 4.40, 1.99 (CH$_2$CH=CH$_2$)
		3.26 [PC*H*(CH$_2$CH=CH$_2$), ^2J(PH) 13.6, ^3J(HH) + ^3J(HH) 14.5]
		2.28 [C=CH_3, ^4J(HH) 1.2]
11	See text	6.47 [HC=C, ^4J(PH) 2.4, ^4J(HH) 1.3]
		3.39 [PC*H*(CH_2Ph), ^2J(PH) 13.7, ^4J(PH) 0.4, ^3J(HH) 12.5, 2.4]
		1.73 [C=CCH_3, ^4J(HH) 1.5]
		2.38 [C*H*HPh, ^3J(PH) 4.7, ^2J(HH) 13.2, ^3J(HH) 12.5]
		2.54 [CH*H*Ph, ^3J(PH) 8.0, ^2J(HH) 13.2, ^3J(HH) 2.4]
12	48.3 PCH_2, *J*(PP) 31	3.04 [PCH_2, ^2J(PH) 6.8, ^4J(PH) 2.6]
	36.4 PC=C	1.56 [PC(CH_3)=C(CH_3), ^4J(PH) 1.3, ^4J(HH) 1.3]
		1.53 [PC(CH_3)=C, ^3J((PH) ≈9, ^5J(PH) ≈6]
13a	50.7, Mo*P*CHP,[g] ^2J(Mo*P*CH*P*) 173, ^2J(*P*Mo*P*) 26	6.28 [HC=C, ^4J(HH) 1.1][h]
	12.6 MoPCH=,[g] −8.1 MoPCH*P*,[g] ^4J(*P*MoPCH*P*) 8	4.24 [PCHP, ^2J(PH) 12.7, 1.2][h]
		1.82 [C=CCH_3, ^4J(HH) 1.1][h]
13b	32.7 (241), W*P*CHP,[g] ^2J(W*P*CH*P*) 167, ^2J(*P*W*P*) 19	6.50 [HC=C, ^4J(HH) 1.0]
	−7.2 (224), WPCH=[g]	4.69 [PCHP, ^2J(PH) 12.3, 1.1]
	−7.2 WPCH*P*,[g] ^4J(*P*WPCH*P*) 6	1.93 [C=CH_3, ^4J(HH) 1.0]
14a	20.0, PC=C,[g] ^2J(PP) 24	6.10 [HC=C, ^4J(PH) 3.7, ^4J(HH) 0.9]
	24.8 *P*CH*P*[g]	5.60 [PCHP, ^2J(PH) 6.1, ^4J(PH) 1.7]
		2.40 [C=CCH_3, ^4J(HH) 0.9]
14b	2.8 (213) PC=C,[g] ^2J(PP) 20	6.27 [PCHP, ^2J(PH) 6.5, ^4J(PH) 1.2]
	1.6 (200) *P*CH*P*[g]	6.13 [HC=C, ^4J(PH) 3.9, ^4J(HH) 1.3]
		2.39 [C=CCH_3, ^4J(PH), 2.3, ^4J(HH) 1.3]

[a] Recorded at 36.2 MHz in $CDCl_3$ solution at 28 °C unless stated otherwise, chemical shifts ±0.1 ppm, *J* values ±1 Hz. Values of $J(^{183}W-P)$ are shown in parentheses. [b] Recorded at 400.13 MHz in $CDCl_3$ at 25 °C, unless stated otherwise, chemical shifts ±0.1 ppm, *J* Values ±10 Hz. [c] In CH_2Cl_2. [d] At 89.5 MHz and 28 °C. [e] At 99.5 MHz and 22 °C. [f] At +40 °C. [g] In CH_2Cl_2 solution at 161 MHz. [h] In CD_2Cl_2 solution at 99.5 MHz and 22 °C.

equivalent amount of lithium bis(trimethylsilyl)amide was used, deprotonation of **3** or **4** to **5** was incomplete, as judged by the $^{31}P-\{^1H\}$ NMR spectra.

We have also studied the action of D_2O on the carbanion **5a** in an attempt to effect monodeuteriation at an allylic position, as in **6**. We added an equimolecular amount of D_2O to a tetrahydrofuran solution of this carbanion, generated by adding methyllithium to a solution of **3a**. The $^2D-\{^1H\}$ NMR spectrum of **6** was measured at +40 °C in order to sharpen the resonance by reducing the rate of quadrupole relaxation. The ^2D NMR

Table 3 Carbon-13 NMR data[a]

Compound	M–CO	HC=*C*	HC=*C*	PHCR	C=*C*CH$_3$	PC_6H_5 groups P–C_i	P–C_o	P–C_m	P–C_p
3a[b]	214.9 (t) (15.9[c]) 210.1 (t) (8.7[h])	137.2 (s)	118.8 (t) (8.2[d])	42.1 (t) (19.5[e])		137.8 (m) (34.8[e])	132.1 (t) (11.6[f])	128.2 (t) (9.2[g])	129.5 (s)
3b[b]	205.6 (t) (16.8[c]) 202.5 (t) (7.0[h])	137.3 (t) (8.7[h])	119.2 (t) (8.7[d])	42.3 (t) (23.5[e])		137.3 (m) (40.9[e])	132.1 (t) (11.4[f])	128.2 (t) (9.4[g])	129.8 (s)
4a[b]	215.5 (dd) (26.7,[h] 9.5[h]) 215.5 (dd) (23.2,[h] 7.7[h]) 209.7 (t) (8.5[h])	150.3 (dd) (10.4,[h] 1.2[h])	120.8 (dd) (34.2, 11.0[d])	36.1 (dd) (14.6, 12.9[d])	30.0 (dd) (11.0,[d] 2.5[d])	137.5 (dd) (36.0, 2.5[d]) 136.8 (dd) (29.9, 1.2[d])	131.9 (d) (12.8[h]) 131.8 (d) (12.2[h])	128.5 (d) (9.8[d]) 128.4 (d) (8.5[d])	129.8 (d) (1.8[i]) 129.5 (d) (1.8[i])
4b[b]	206.6 (dd) (25.7,[h] 7.2[h]) 206.2 (dd) (21.8,[h] 5.0[h]) 202.1 (t) (6.7[h])	150.9 (dd) (9.4,[h] 1.7[h])	120.3 (dd) (39.2, 10.2[d])	36.0 (dd) (18.6, 11.9[h])	30.3 (dd) (11.7,[d] 3.0[d])	137.0 (dd) (42.0, 3.0[d]) 136.4 (dd) (36.7, 1.7[d])	131.9 (d) (12.1[h]) 131.8 (d) (11.4[h])	128.5 (d) (9.8[d]) 128.4 (d) (9.1[d])	129.9 (d) (2.0[i]) 129.7 (d) (1.7[i])
6[j]	215.8 (dd) (27.1,[h] 9.5[h]) 215.4 (dd) (22.9,[h] 7.9[h]) 209.7 (t) (8.5[h]) 209.7 (t) (8.5[h])	150.2 (dd) (10.5,[h] 1.1[h])	120.9 (dd) (33.7, 10.8[d])	35.8 (br)	30.0 (dd) (11.2,[d] 2.7[d])	137.6 (dd) (36.2, 2.5[d]) 137.5 (dd) (36.5, 2.5[d]) 136.9 (dd) (30.5, 1.2[d]) 136.9 (dd) (30.2, 1.1[d])	131.9 (d) (12.8[h]) 131.9 (d) (12.8[h]) 131.8 (d) (11.9[h]) 131.8 (d) (11.8[h])	128.5 (d) (9.4[d]) 128.3 (d) (8.9[d])	129.7 (d) (1.2[i]) 129.7 (d) (1.2[i]) 129.4 (d) (1.3[i]) 129.4 (d) (1.4[i])
7a[k]	215.6 (dd) (21.6,[h] 9.5[h]) 215.5 (dd) (25.4,[h] 9.5[h]) 211.7 (t) (9.3[h]) 207.1 (t) (7.9[h])	158.6 (dd) (12.1,[h] 1.9[h])	119.6 (dd) (32.9, 8.0[d])	36.1 (dd) (16.7, 8.6[d])	31.2 (dd) (12.1,[d] 4.4[d])	140.8 (dd) (39.8, 2.8[d]) 140.2 (d) (13.3[h]) 137.0 (d) (35.5) 135.5 (dd) (30.4, 3.2[d])	134.2 (d) (13.3[h]) 132.6 (d) (13.3[h]) 130.6 (d) (10.2[h]) 130.4 (d) (12.1[h])	128.4 (d) (9.5[d]) 128.2 (d) (8.3[d])	129.9 (d) (1.9[i]) 128.9 (d) (1.3[i]) 128.7 (m)[l]
7b[m]	206.1 (dd) (23.8,[h] 7.6[h]) 205.9 (dd) (21.0,[h] 6.6[h]) 203.5 (t) (7.6[h]) 199.5 (t) (6.4[h])	159.3 (dd) (10.7,[h] 1.4[h])	118.3 (dd) (38.9, 7.4[c])	35.3 (dd) (11.1, 8.1[d])	31.4 (dd) (12.5,[d] 4.6[d])	140.3 (dd) (45.6, 3.6[d]) 139.8 (d) (38.1) 136.2 (dd) (40.6, 1.3[d]) 134.8 (dd) (36.5, 4.2[d])	134.3 (d) (12.4[h]) 132.6 (d) (12.3[h]) 130.4 (d) (10.2[h]) 130.3 (d) (11.4[h])	128.3 (d) (9.8[d]) 128.1 (d) (8.5[d]) 128.0 (d) (9.5[d])	130.4 (d) (2[i]) 129.9 (d) (2[i]) 129.0 (d) (1.5[i]) 128.7 (dd) (1.9[i])
							Others[n]		
8a	215.8 (dd) (22.3,[h] 8.9[h]) 215.4 (dd) (25.9,[h] 9.6[h]) 213.4 (t) (9.1[h]) 205.5 (t) (7.7[h])	157.3 (d) (13.0[h])	117.5 (dd) (35.3, 9.2[d])	34.8 (d)[o] (7.6)	33.2 (dd)[o] (12.1,[d] 5.3[d])		0.7 (d) (1.7[d]) $Si(CH_3)_3$		
8b	206.4 (dd) (20.9,[h] 6.8[h]) 205.8 (dd) (24.5,[h] 7.6[h]) 205.7 (t) (7.7[h]) 198.2 (t) (5.7[h])	157.8 (d) (11.7[h])	116.7 (dd) (40.5, 8.9[d])	34.4 (dd)[o] (7.2, 4.1[d])	35.5 (dd)[o] (12.6,[d] 5.6[d])		0.71 (d) (1.6[d]) $Si(CH_3)_3$		
9	215.7 (dd) (22.6,[h] 8.5[h]) 215.5 (dd) (26.2,[h] 9.8[h]) 211.2 (t) (9.2[h]) 207.7 (t) (8.2[h])	158.3 (d)[p] (11.9[h])	118.0 (dd)[p] (33.5, 8.9[d])	42.3 (dd)[p,q] (15.0, 8.7[d])	33.8 (dd)[p] (12.2,[d] 3.7[d])		26.7 (d)[p] (8.8[h]) $PCHCH_2$ 11.7 (d)[p] (14.0[d]) $PCHCH_2CH_3$		

Table 3 (*continued*)

10	206.0 (dd) (21.0,[h] 6.4[h]) 205.9 (dd) (24.8,[h] 7.5[h]) 203.5 (t) (7.5[h]) 199.7 (t) (6.2[h])	159.1 (d)[p] (10.0[h])	118.1 (dd)[p] (38.9, 7.2[h])	41.7 (dd) (17.7, 7.8[d])	34.6 (dd)[p] (12.5,[d] 3.8[d])	39.1 (d)[p] (9.1[h]) PCHCH_2CH=CH_2 134.8 (d) (13.9[d]) PCHCH_2CH=CH_2 117.2 (s) PCHCH_2CH=CH_2
11	215.7 (dd) (22.4,[h] 8.8[h]) 215.1 (dd) (26.0,[h] 10.0[h]) 212.1 (dd) (9.7,[h] 9.0[h]) 206.8 (t)[q] (8.6[h])	158.8 (dd)[p] (11.9,[h] 1.3[h])	119.2 (dd)[p] (33.6, 7.9[d])	44.6 (dd) (13.8, 8.4[d])	34.3 (dd)[p] (11.8[d] 3.8[d])	40.5 (d)[p] (9.3[h]) PCHPh 139.0 (d) (14.1[d]) PCHPh-C_i 128.4 (s) PCHPh-C_o 128.2 (s) PCHPh-C_m 126.4 (s) PCHPh-C_p
12	216.0 (dd) (22.7,[h] 7.8[h]) 216.0 (dd) (27.8,[h] 9.0[h]) 210.1 (t) (8.6[h])	140.3 (dd) (14.6,[h] 2.1[h])	125.3 (dd) (26.9, 11.0[d])	39.6 (dd) (16.7, 14.0[d])	24.7 (dd) (8.9,[d] 2.2[d])	19.6 (dd) (4.7,[h] 3.2[i]) PC(CH_3)=C
13a[r]	216.3 (dd) (22.9,[h] 9.3[h]) 216.0 (dd) (25.8,[h] 10.0[h]) 213.5 (dt) (12.3[h] 9.7[i]) 206.6 (dt) (7.6,[h] 1.2[i])	153.5 (d) (12.7[h])	121.7 (ddd) (33.2, 8.0,[d] 4.0[d])	41.5 (ddd) (38.4, 14.6, 6.3[d])	33.5 (dd) (11.9,[d] 5.2[d])	
13b	206.2 (dd) (21.5,[h] 7.3[h]) 205.8 (dd) (24.3,[h] 7.8[h]) 205.2 (dt) (11.3,[h] 8.1[i]) 198.2 (dt) (5.4,[h] 1.3[i])	153.3 (dd) (10.3,[h] 1.0[h])	120.5 (ddd) (38.1, 7.4,[d] 3.9[d])	40.7 (ddd) (39.5, 19.0, 5.9[d])	33.7 (dd) (12.3,[d] 5.6[d])	
14a	223.6 (dt) (18.8,[c] 9.7[h]) 222.2 (dt) (24.0,[h] 8.5[h])	152.7 (dt) (17.5,[h] 5.4[h])	115.3 (dt) (33.4, 7.5[h])	58.1 (dt) (12.7, 6.7[d])	32.6 (dt) (13.0,[d] 2.0[d])	
14b	216.2 (dt) (18.3,[c] 9.0[h]) 214.2 (dt) (22.5,[h] 7.0[h])	152.6 (dt) (10.0, 5.8[h])	114.7 (dt) (38.1, 7.3[d])	60.5 (dt) (16.3, 6.3[d])	32.7 (dt) (13.5,[d] 2.2[d])	

[a] Measured at 100.6 MHz and 27 °C in $CDCl_3$ solution, unless stated otherwise. Figures in parentheses are couplings to phosphorus (in Hz) and unless shown otherwise are ^1J(PC). s = Singlet, d = doublet, t = triplet, m = multiplet and br = broad. [b] At 22.5 MHz. [c] $|^2J(PC) + {}^2J(P'C)|$. [d] ^3J(PC). [e] $|^1J(PC) + {}^3J(P'C)|$. [f] $|^2J(PC) + {}^4J(P'C)|$. [g] $|^3J(PC) + {}^5J(P'C)|$. [h] ^2J(PC). [i] ^4J(PC). [j] Spectrum recorded at 40 °C. [k] Also: δ 18.3 (d), ^2J(PC) 8.2 Hz, PCHCH_3. [l] Obscured. [m] Also: δ 18.5 (d), ^2J(PC) 7.0 Hz, PCHCH_3. [n] The compounds **8a** to **11** and **13a** and **13b** all showed phenyl carbon resonances indicating no plane of symmetry through the molecule, as with compounds **6** to **7b**. The shifts and coupling constants are not quoted here for brevity. [o] Resonances distinguished by 90° distortionless enhancement by polarisation transfer (DEPT) pulse sequence. [p] Resonance broad at 25 °C but sharp at −40 °C. The values quoted are for −40 °C. [q] Resonances somewhat broad at 25 °C but sufficiently resolved to see couplings. [r] Spectrum recorded in CD_2Cl_2 solution.

spectrum of the product **6** consisted of a single, broad resonance at δ 3.0 ($w_{\frac{1}{2}}$ = 12 Hz at 61.4 MHz) indicating, as expected, that all the deuterium was present in the allylic position. The ^{31}P-{^{1}H} NMR spectrum of **6** was almost identical to that of **4a**, except that the resonance due to the allylic phosphine was shifted by *ca.* 0.2 ppm to lower frequency from the resonance of the undeuteriated complex **4a** (a small amount of this undeuteriated complex was present in the deuteriated sample so that this small difference in the phosphorus-31 chemical shifts, due to a secondary isotope effect, was measured accurately). The phosphorus-31 resonance of the deuteriated complex was slightly broader than that of the undeuteriated complex [since ^2J(PH) (allylic protons) is 7.9 Hz one would expect ^2J(PD) to be 1.2 Hz and unresolved]; the two values of $w_{\frac{1}{2}}$ were 1.1 (deuteriated) and 0.7 Hz (undeuteriated).

The ^{1}H NMR spectrum showed allylic and alkenyl resonances of equal intensity and, again, a small isotope shift was observed for the allylic resonance with respect to the CH_2 resonance of the small amount of the undeuteriated complex **4a** present in the deuteriated sample **6**. No H–D coupling was observed but the CHD resonance was slightly broader than the equivalent resonance of CH_2. Additionally, a long-range coupling, ^4J(HH), of 0.6 Hz was observed between the alkenyl and C*H*D protons (the expected triplet pattern for the alkenyl proton in **4a** was not resolved). The single deuterium in complex **6** was sufficient to destroy the symmetry to the extent that pairs of carbons related by the plane of symmetry present in **4a** showed different chemical shifts in the ^{13}C-{^{1}H} NMR spectrum of **6** (see Fig. 1 and Table 3). The CHD carbon resonance was broad with some fine structure but we were unable to resolve the ^1J(CD) coupling. A ^{13}C-{^{1}H} NMR spectrum recorded with an attached-proton test sequence demonstrated that the allylic carbon bore only one hydrogen and thus unequivocally established that **6** was a monodeuteriated species.

We have also methylated the carbanions of type **5**. A

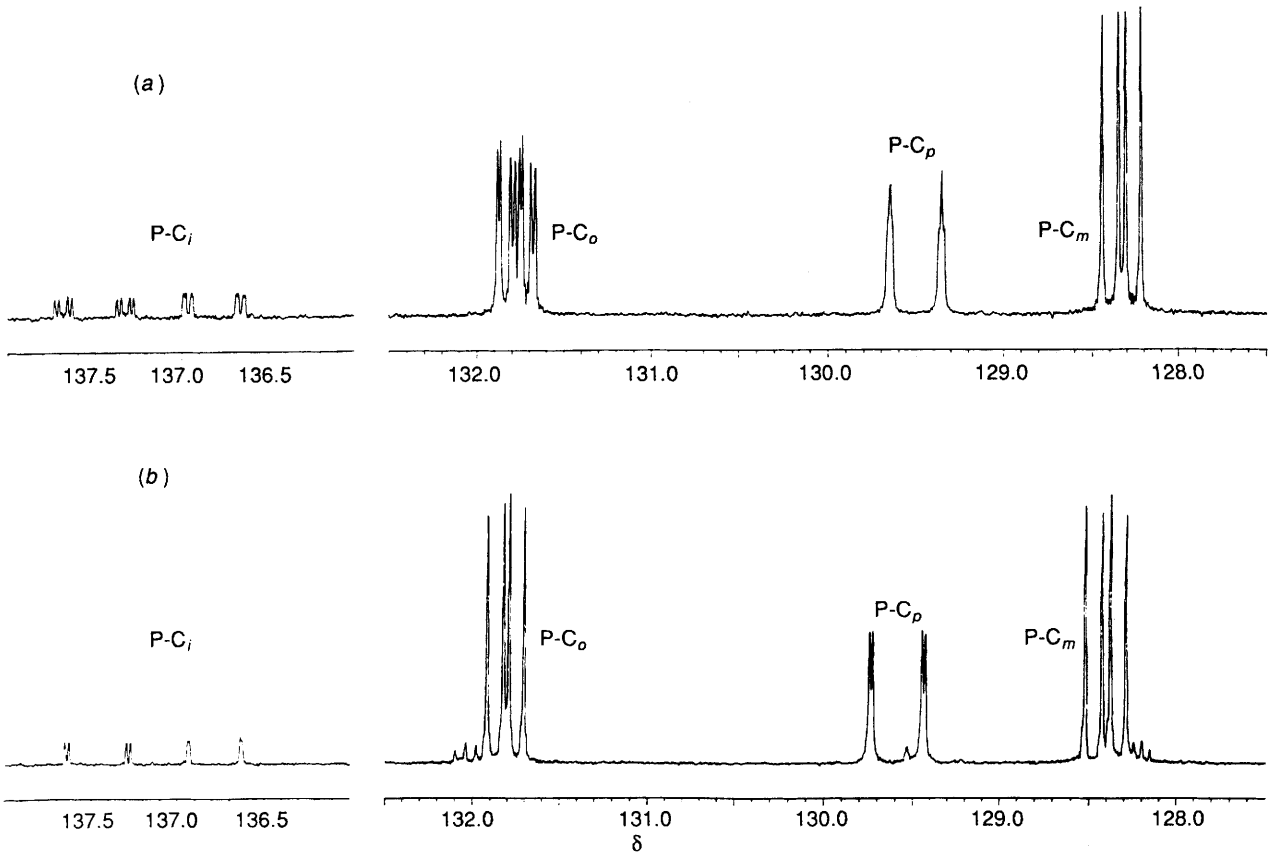


Fig. 1 ^{13}C-{^1H} NMR spectra, in the phenyl region, of (*a*) of the monodeuterio-complex **6** and (*b*) its perhydro analogue **4a**, showing the secondary isotope effect of the deuterium atom in making all four phenyl groups non-equivalent, as is shown particularly by the *ipso*- and *ortho*-carbon resonances. Spectra measured at 27 °C and 100.6 MHz in $CDCl_3$ solution

convenient method of doing this was to treat a solution of **4a** or **4b** with a five-fold excess of the commercially available lithium bis(trimethylsilyl)amide and then add a five-fold excess of methyl iodide. This produced the required methylated complex **7a** or **7b** in 69 and 73% yields, respectively. These complexes were fully characterised (Tables 1–3) in particular the ^1H NMR spectra established the position of the methyl group to be as shown. With smaller proportions of lithium bis(trimethylsilyl)-amide and methyl iodide the yields were lower but we also prepared the methyl derivative **7a** by deprotonating the molybdenum complex **4a** with lithium tetramethylpiperidide (1 equivalent) and adding 1 equivalent of methyl iodide to the resultant carbanion; the yield of **7a** was 82%. We also prepared the trimethylsilyl derivative **8a** by treating complex **4a** with lithium bis(trimethylsilyl)amide and adding trimethylsilyl chloride; similarly for the tungsten complex **8b**. Details of these preparations are in the Experimental section and characterising data in the Tables.

We have also made analogues of the methyl derivatives of type **7** by alkylating the carbanions of type **5** with (*i*) ethyl iodide, (*ii*) allyl bromide, or (*iii*) benzyl bromide, giving, respectively, the ethyl derivative **9** (Mo), the allyl **10** (W), or the benzyl **11** (Mo). Preparative details for these three complexes are in the Experimental section and characterising data are in Tables 1–3. When the carbanions of type **5** were treated with 2-bromopropane, diiodomethane or neopentyl chloride we were unable to isolate substitution products, some of the impure complex of type **4** being recovered in each case. For each of the complexes **9–11** the substituent is of the type CH_2R and the methylene protons are diastereotopic. For the ethyl derivative **9** the ^1H-{^{31}P} NMR spectrum (100 MHz) showed the CH_2 protons to give a single, broad resonance and the allylic proton gave a deceptively simple 1:2:1 triplet pattern resulting from a strongly coupled ABX spin system. At 400 MHz the resonance of this methine proton appeared as a six-line pattern, confirming the ABX spin system but the CH_2 resonances were not resolved. For the allyl derivative [W{PPh_2CH=$CMeCH(CH_2CH$=$CH_2)PPh_2$}$(CO)_4$] **10** the resonances of the diastereotopic methylene (CH_2CH) hydrogens remained coincident at 400 MHz and the methine hydrogen [$CH(CH_2CH$=$CH_2)$] gave a virtual triplet even at this high field. For the benzyl complex **11**, however, separate resonances were observed for the two CH_2Ph protons (ABX spectrum at 100 MHz) and the spectrum was approximately first order (AMX) at 400 MHz and −40 °C. The coupling constants between the three ($CHCH_2Ph$) protons established that of the two resonances for the benzylic methylene group the one at higher field (δ 2.38) was more strongly coupled to the vicinal methine proton. This was therefore assigned as being approximately antiperiplanar to the methine proton (H_a in the Newman projection shown in Fig. 2). At 25 °C and at 400 MHz the other benzylic proton absorbed as a broad resonance at δ 2.54 and this suggested fluxionality in the complex. The best evidence for fluxionality in complexes **9–11** came from the ^{31}P-{^1H} NMR spectra over a range of temperatures, in contrast to the spectra of complexes of types **3**, **4**, **7** and **8** which were invariant over the range +25 to −70 °C.

Thus the benzyl complex **11**, at −63 °C and 161 Mz, gave a low-temperature-limiting spectrum consisting of a major component with δ(P) 56.5 and 11.3 and ^2J(PP) = 26 Hz and a minor component (1–2% of the whole) with δ(P) 67.8 and 18.9 and ^2J(PP) = 26 Hz. At +27 °C and 161 MHz the resonances of the minor component had broadened and disappeared whilst those of the major component had broadened, $w_{\frac{1}{2}} \approx 150$ and ≈ 100 Hz, respectively. The fast-exchange limit was more readily seen at 36.2 MHz and at 28 °C, with δ 56.5 and 11.3 and J(PP) = 26 Hz.

Similar behaviours were shown by the tungsten complex **10** and the molybdenum complex **9**. For **10**, at −63 °C the major component had δ(P) 40.4, ^1J(WP) = 241 Hz and −8.9,

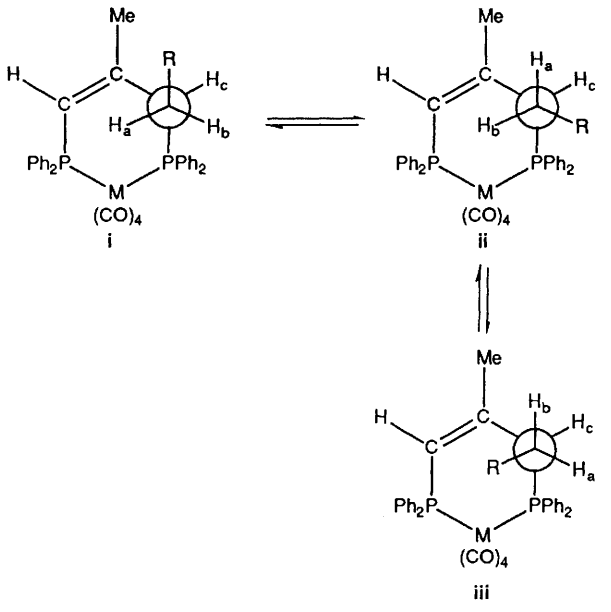


Fig. 2 Newman projections of the conformers **i**–**iii** of complexes of the type $[M\{Ph_2PCH{=}CMeCH(CH_2R)PPh_2\}(CO)_4]$ (R = Me, **9**; $CH{=}CH_2$, **10**; or Ph, **11**). We suggest that conformer **i** is the most stable and **iii** the least stable for steric reasons. Since only two conformers were observed in the low-temperature $^{31}P\text{-}\{^1H\}$ NMR spectra (see Discussion), we suggest that these are **i** (major) and **ii** (minor) and that the amount of conformer **iii** was too small for us to observe

$^1J(WP)$ = 222 Hz and $^2J(PP)$ = 21 Hz and the minor component (1–2% of the whole) showed δ(P) 56.5 and 12.3 and $^2J(PP)$ = 21 Hz. At +27 °C and at 161 MHz the resonances of the minor component had disappeared whilst those of the major component had broadened, $w_{\frac{1}{2}} \approx 200$ Hz. In the fast-exchange-limiting spectrum, at 36.2 MHz and at 28 °C, the two shifts were δ 40.3 and −8.0 and $J(PP)$ = 21 Hz. For **9**, at −63 °C, the major component had δ(P) 58.2 and 13.1 and $^2J(PP)$ = 28 Hz and the minor component (1–2% of the whole) showed δ(P) 70.6 and 21.3 and $^2J(PP)$ = 28 Hz. As before, at +27 °C and at 161 MHz the resonances of the minor component had disappeared whilst those of the major component had broadened, $w_{\frac{1}{2}} \approx 150$ and ≈ 100 Hz, respectively. In the fast-exchange limit, at 36.2 MHz and at 28 °C, the two shifts were δ 57.9 and 12.9 and $J(PP)$ = 29 Hz. We suggest that these effects of temperature are caused by the presence of the two conformers **i** (major) and **ii** (minor) in Fig. 2 and that the third conformer **iii** is present in amounts which we could not detect.

The $^{13}C\text{-}\{^1H\}$ NMR spectrum of complex **11** at 25 °C also showed that some of the resonances were broadened by exchange effects (Table 3). A series of ^1H nuclear Overhauser enhancement (n.O.e.) difference spectra indicated no unusually close interactions with the benzyl group.

We have also tried to effect a base-promoted 1,2-prototropic shift of the C=C bond in the chelated ring of complex **7a**. Treatment of **7a** in boiling ethanol–sodium ethoxide solution caused decomposition, but two successive treatments of **7a** with methyllithium, followed by methanol, gave the required product **12**, containing a tetrasubstituted C=C bond. The yield of this product was only 13% but it was fully characterised (see Tables 1–3).

We have treated solutions of the carbanions of type **5** with chlorodiphenylphosphine and thereby made the molybdenum **13a** and tungsten **13b** complexes of the triphosphine $(Ph_2P)_2CHCMe{=}CHPPh_2$ acting in a bidentate fashion. When complexes **13** were heated (at 100 °C for Mo or *ca.* 180 °C for W) the *fac*-tricarbonyl complexes **14a** or **14b** were formed containing the triphosphine $(Ph_2P)_2CHCMe{=}CHPPh_2$, acting in a tridentate fashion. See Experimental section and Tables 1–3 for preparative details and characterising data for all four complexes.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen or dry argon. Tetrahydrofuran was distilled from sodium and benzophenone under argon immediately before use. Infrared spectra were recorded using a Perkin-Elmer model 257 grating spectrometer with the sample contained in a cell with path length 0.1 mm. The NMR spectra were recorded using a JEOL FX-90Q (operating frequencies for ^1H, ^{31}P and ^{13}C of 89.5, 36.2 and 22.5 MHz, respectively), a JEOL FX-100 (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz, respectively) or a Bruker AM400 spectrometer (operating frequencies for ^1H, ^{31}P, ^{13}C and ^2H of 400.13, 161.9, 100.6 and 61.4 MHz, respectively); ^1H and ^{13}C shifts are relative to tetramethylsilane, ^2H shifts to $\delta(CDCl_3)$ 7.27 and ^{31}P shifts to 85% phosphoric acid. Mass spectra were recorded on an AEI MS30 mass spectrometer.

$[Mo\{(Ph_2PCH_2)_2C{=}CH_2\}(CO)_4]$ **3a**.—A mixture of $[Mo(CO)_6]$ (1.00 g, 3.8 mmol) and the diphosphine (1.62 g, 3.8 mmol) in decane (35 cm^3) was heated under reflux for 70 min. The mixture was allowed to cool, upon which the product separated as pale yellow microcrystals. These were collected and recrystallised from dichloromethane–ethanol to give the required product as pale yellow microcrystals. Yield 2.14 g, 89%. The corresponding tungsten complex **3b** was prepared similarly from $[W(CO)_6]$, with a reflux time of 2.5 h. Yield 88%.

$[Mo(Ph_2PCH{=}CMeCH_2PPh_2)(CO)_4]$ **4a**.—The tetracarbonyl complex **3a** (2.1 g, 3.34 mmol) was heated under reflux with ethanolic sodium ethoxide solution (40 cm^3, 0.65 mol dm^{-3}) for 16 h. The mixture was allowed to cool and the resultant solid collected and recrystallised from dichloromethane–ethanol, giving the required compound as pale yellow microcrystals (1.86 g, 89%). The corresponding tungsten complex **4b** was prepared similarly from **3b** in 89% yield.

$[Mo(Ph_2PCH{=}CMeCHDPPh_2)(CO)_4]$ **6**.—A solution of complex **3a** (0.27 g, 0.42 mmol) in tetrahydrofuran (8 cm^3) was treated with a solution of methyllithium in diethyl ether (0.4 cm^3, 1.4 mol dm^{-3}, 0.42 mmol). The mixture was stirred for 10 min, D_2O (0.07 cm^3) was then added and the product was isolated by evaporation and recrystallisation from dichloromethane–ethanol. Yield 0.22 g, 85%.

$[Mo(Ph_2PCH{=}CMeCHMePPh_2)(CO)_4]$ **7a**.—A solution of complex **3a** (0.13 g, 0.21 mmol) in tetrahydrofuran (5 cm^3) was treated with methyllithium (0.21 mmol), as above, and the resultant solution then treated with methyl iodide (0.02 cm^3, 0.31 mmol). The mixture was then stirred for 10 min and the product isolated by evaporation and extraction into dichloromethane. The product was recrystallised from dichloromethane–ethanol as yellow microcrystals. Yield 0.058 g, 43%.

The corresponding benzyl derivative **11** was prepared similarly using benzyl bromide as the alkylating agent, and isolated as white microcrystals. Yield 30%. The ethyl derivative **9** was prepared in an analogous fashion except that the rearranged species **4a** was deprotonated and the resulting carbanions ethylated with ethyl iodide. Yield 65%. The allyl tungsten derivative **10** was similarly prepared from **4b**, alkylating with allyl bromide. Yield 40%.

Using lithium 2,2,6,6-tetramethylpiperidide as strong base. A solution of lithium 2,2,6,6-tetramethylpiperidide was prepared from 2,2,6,6-tetramethylpiperidine (124 μl, 0.74 mmol) and butyllithium (0.48 cm^3, 1.55 mmol dm^{-3} solution in hexane, equivalent to 0.74 mmol). This solution was then mixed with a solution of complex **3a** (0.47 g, 0.74 mmol) in tetrahydrofuran (5 cm^3) and after 10 min methyl iodide (0.46 cm^3, 0.74 mmol) was added and the resultant solution stirred for 10 min. The product was isolated as before; yield 82%. A similar preparation, using 5 mol equivalents of lithium bis(trimethylsilyl)amide as deprotonating agent, gave **7a** in 69% yield.

[$W(Ph_2PCH{=}CMeCHMePPh_2)(CO)_4$] **7b**.—A solution of complex **4b** (0.29 g, 0.41 mmol) in tetrahydrofuran (2 cm^3) was treated with a tetrahydrofuran solution of lithium bis(trimethylsilyl)amide (2.5 mmol) and after 10 min the resultant solution was treated with methyl iodide (1 cm^3). The mixture was then stirred for 10 min and the product isolated by evaporation and extraction into dichloromethane. The product was recrystallised from dichloromethane–ethanol and formed pale yellow microcrystals. Yield 0.22 g, 73%.

The following compounds were similarly made by treating the molybdenum complex **4a** or the tungsten complex **4b** with lithium bis(trimethylsilyl)amide, followed by the appropriate alkylating agent. They were all recrystallised from dichloromethane–ethanol: **8a**, pale yellow microcrystals, yield 27%, using trimethylsilyl chloride; **8b**, off-white microcrystals, yield 26%, using trimethylsilyl chloride; **13a**, white microcrystals, yield 78%, using chlorodiphenylphosphine; and **13b**, white microcrystals, yield 42%, using chlorodiphenylphosphine.

[$Mo(Ph_2PCMe{=}CMeCH_2PPh_2)(CO)_4$] **12**.—A solution of methyllithium (0.3 cm^3, 1.4 mol dm^{-3}, 0.42 mmol) was added to a solution of complex **7a** (0.26 g, 0.40 mmol) in tetrahydrofuran (10 cm^3). The progress of the reaction was monitored by ^{31}P-$\{^1H\}$ NMR spectroscopy until no further change took place. After 0.5 h methanol (0.009 g) was added. Another portion of methyllithium (0.42 mmol) was added and the progress of the reaction again followed by NMR spectroscopy and methanol added. The solvent was evaporated and the product taken up in dichloromethane. A ^{31}P-$\{^1H\}$ NMR spectroscopic study showed that some of the starting complex **7a** was present in the mixture. The dichloromethane solution was passed through a short column of Fluorisil (*ca.* 0.6 g) and then evaporated to dryness and triturated with ethanol. This gave the required product as pale yellow microcrystals (0.035 g, 13%).

[$Mo\{(Ph_2P)_2CHMe{=}CHPPh_2\}(CO)_3$] **14a**.—A solution of complex **13a** (0.35 g, 0.43 mmol) in toluene (2 cm^3) was heated to 100 °C for 2 h, during which time it became yellow. The solution was then heated under reflux for 15 min and allowed to cool to 20 °C. This gave the required product as yellow prisms, which were filtered off, washed with pentane and dried. Yield 0.27 g, 76%.

[$W\{(Ph_2P)_2CHCMe{=}CHPPh_2\}(CO)_3$] **14b**.—A suspension of complex **13b** (0.094 g, 0.10 mmol) in decane (5 cm^3) was heated carefully to reflux and the suspension kept at reflux temperature for 3 h. The mixture was then allowed to cool and the yellow crystalline precipitate collected, washed with pentane and dried. This gave the required product as yellow microcrystals. Yield 0.077 g, 85%.

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