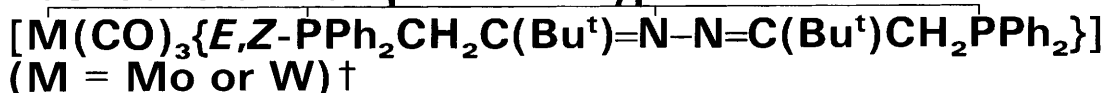


Highly Selective Mono- and Di-alkylation of the Backbone of Complexes of type *fac*-



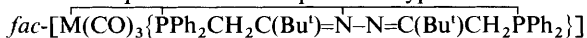
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Treatment of the tricarbonylmolybdenum(0) complex, $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **1a** with 1 equivalent of LiBu^n selectively deprotonated the backbone to give the carbanion $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CHC}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]^-$, which on addition of methyl iodide or allyl bromide gave the monoalkyl complexes $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{R})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ (R = Me **2a** or $\text{CH}_2\text{CH}=\text{CH}_2$ **3a**). The tungsten(0) analogues **2b** and **3b** were similarly prepared from $[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **1b**. Treatment of the tricarbonyltungsten(0) carbanion with deuterium oxide gave the monodeuterated complex $[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{D})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **4**. Treatment of **1b** with 4 equivalents of LiBu^n followed by methyl iodide gave the dimethyl complex $[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{Me})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}(\text{Me})\text{PPh}_2\}]$ **5a**, specifically as *R,R* and *S,S* isomers. Complex **5a** was also prepared by deprotonating and methylating **2b**. The analogous molybdenum complex **5b** was similarly prepared from **1a**. Proton, ^{13}C - $\{^1\text{H}\}$, ^{31}P - $\{^1\text{H}\}$ NMR and infrared data are reported. The crystal structures of **2a** and **5a** have been determined.

The proton on a carbon in α position to phosphorus in a tertiary phosphine is activated and can be removed by a strong base. However, the resultant carbanion is an ambidentate nucleophile and treatment with an alkylating agent frequently gives mixtures corresponding to attack on both carbon and phosphorus.^{1,2} Usually, one wants to attack the carbon in order to obtain substituted tertiary phosphines so that a synthesis *via* a 'carbanion' produced from the free tertiary phosphine is often not a good method.² However, we have shown that complexation of a tertiary phosphine (*e.g.* $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, dppm) to a metal followed by deprotonation and attack by an electrophile such as an alkyl halide constitutes a good method of synthesising substituted (and complexed) dppm derivatives. Chelation of dppm to a Group 6 metal carbonyl *e.g.* $[\text{W}(\text{CO})_4(\text{dppm-}P,P')]$ or to a platinum halide *i.e.* $[\text{PtX}_2(\text{dppm-}P,P')]$ is particularly suitable and deprotonation followed by alkylation gave derivatives of types $[\text{ML}_n(\text{Ph}_2\text{PCHRPPH}_2)]$ or $[\text{ML}_n(\text{Ph}_2\text{PCR}_2\text{PPh}_2)]$ [$\text{ML}_n = \text{W}(\text{CO})_4$ or PtI_2 ; R = alkyl such as Me].^{3,4}

In previous work we have shown that the azine diphosphine $\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2$ **1** in the *Z,E* form can act as a tridentate *P,N,P'* ligand with fused five- and six-membered rings in square-planar, octahedral or seven-co-ordinate complexes.^{5,6} Thus with Group 6 metal carbonyls we prepared and described complexes of the type *fac*- $[\text{M}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ (M = Mo **1a** or W **1b**) (Scheme 1).⁵ We also showed that in tridentate complexes of type $[\text{MCl}\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]\text{X}$ (X = Cl, picrate or formate) the CH_2 hydrogens underwent H/D exchange with acid catalysts, *i.e.* they were activated and

that on treatment with a base such as triethylamine the five-membered ring chelate in the cationic complex rapidly loses a proton to give a neutral complex of type $[\text{MCl}\{\text{PPh}_2\text{CH}=\text{C}(\text{Bu}^t)-\text{N}=\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ (M = Pd or Pt).⁶ A Group 6 tricarbonyl metal(0) moiety is much less electron-withdrawing than is PtX or PdX (X = halide), but we anticipated that when treated with a strong non-nucleophilic base a compound of type



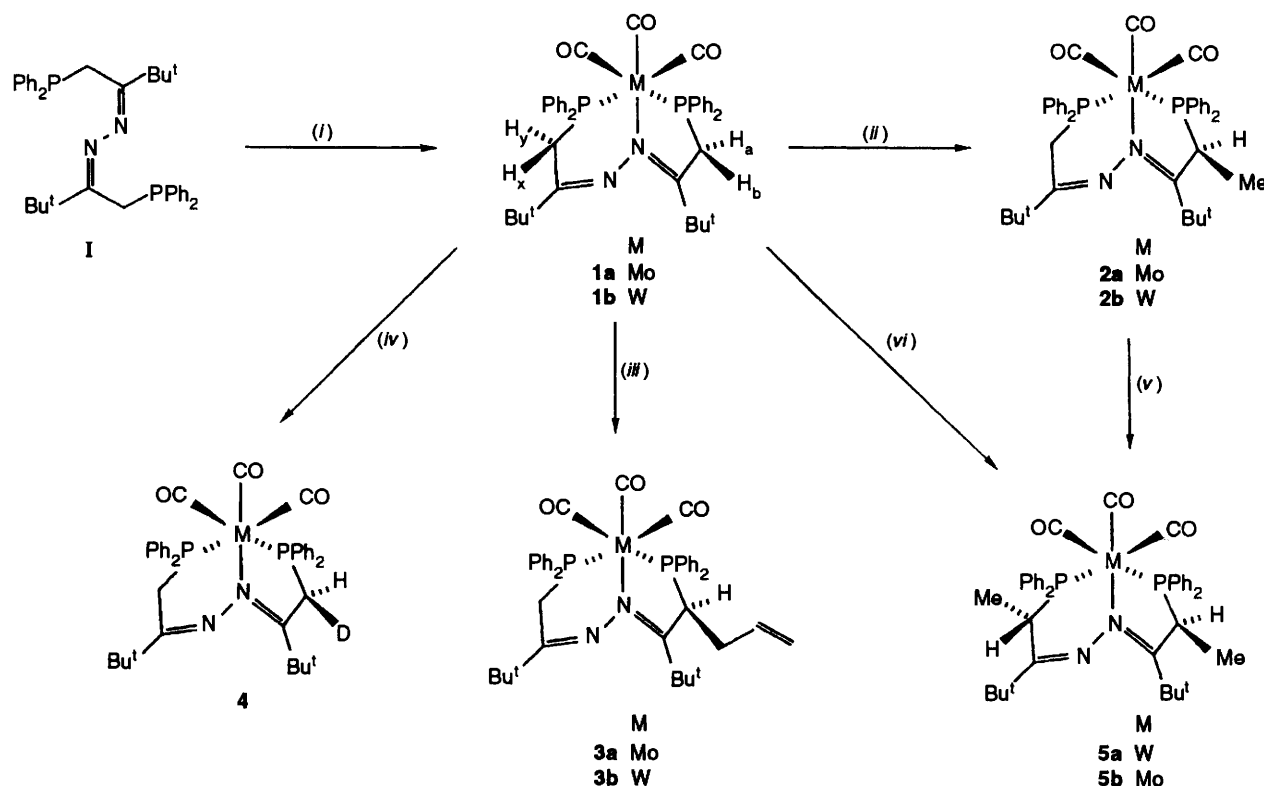
(M = Mo or W) would deprotonate in the five-membered ring and that it might be possible to alkylate the resultant carbanion to give a derivative

$[\text{M}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{R})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$. This we have found to be the case and in this paper we describe our results. Moreover, we also now show that the methylene in the six-membered ring can also be deprotonated and the carbon alkylated. The alkylations in both the five- and six-membered rings are stereospecific.

Results and Discussion

The various transformations and complexes are shown in Scheme 1. In a previous paper,⁵ we described the complexes *fac*- $[\text{M}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ (M = Mo **1a** or W **1b**) but did not assign the methylene carbons and hydrogens in the chelate rings. These we have now assigned by ^1H - ^{13}C correlation spectroscopy (COSY) experiments. The carbon of the methylene group in the six-membered ring in **1a** gives a doublet at δ 25.6⁵ whilst the doublet at δ 44.8⁵ is assigned to the methylene carbon in the five-membered ring. Similar NMR studies of azine diphosphine or phosphino-hydrazone complexes of metals such as Pd, Pt and Ir have shown that the methylene carbons in six-membered rings have lower δ_{C} values (δ 20–25) than the ones in five-membered rings (δ 40–45).^{6–8} For **1a** the two methylene protons absorbing at

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 For simplicity, only the complexes with *C* configuration at the metal centre are shown; some of the complexes with the *A* configuration are shown in Scheme 2. (i) $[\text{M}(\text{CO})_3(\eta^6\text{-cht})]$ (cht = cyclohexatriene); (ii) 1 equivalent LiBu^n , MeI; (iii) 1 equivalent LiBu^n , $\text{CH}_2=\text{CHCH}_2\text{Br}$; (iv) 1 equivalent LiBu^n , D_2O ; (v) 2 equivalents LiBu^n , MeI; (vi) 4 equivalents LiBu^n , MeI

δ 2.12 and 3.47 with $^2J(\text{HH}) = 12.3$ Hz are assigned to the six-membered ring while the resonances at δ 3.30 and 3.93, with $^2J(\text{HH}) = 17.1$ Hz, are assigned to the protons in the five-membered ring (Fig. 1). With the compounds of type *fac*- $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **1a** there is chirality at the metal centre and in Scheme 1 we have drawn the chirality as clockwise, using the chirality symbol *C* according to the skew-line convention.⁹ We have also drawn out the opposite chirality *A* (anticlockwise) in structures **1a'** and **1b'** (Scheme 2).

Treatment of *fac*-

$[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **1a** with 1 equivalent of LiBu^n at ca. 20 °C gave the carbanion, $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{Me})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]^-$, characterised by its $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum which showed two doublets centred at δ 38.7 and 26.9 with $^2J(\text{PP}) = 32$ Hz. When this carbanion was treated with an excess of methyl iodide a good yield (79%) of a monomethylated product

$[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{Me})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **2a** was isolated. Preparative details, mass spectral and elemental analytical data are in the Experimental section, phosphorus-31 NMR, infrared, proton and carbon-13 NMR data in Tables 1–3. From the $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum of the reaction mixture, only one methylated product, *i.e.* *fac*- $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{Me})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ had been formed as a mixture of two enantiomers. As discussed below, the less hindered of the two methylene hydrogens is replaced by methyl. The product **2a** was characterised by elemental analysis (C, H and N) and the mass spectrum (FAB) showed peaks corresponding to M^+ , $M - \text{CO}$, $M - 2\text{CO}$ and $M - 3\text{CO}$. The $^{31}\text{P}-\{^1\text{H}\}$ NMR spectrum (Table 1) showed $^2J(\text{PP}) = 24$ Hz, typical of mutually co-ordinated *cis*-phosphines,⁵ whilst the infrared spectrum showed three strong bands due to $\nu(\text{C}=\text{O})$. In the $^1\text{H}-\{^{31}\text{P}\}$ NMR spectrum the resonance of the *CHMe* proton appeared as a 1:3:3:1 quartet

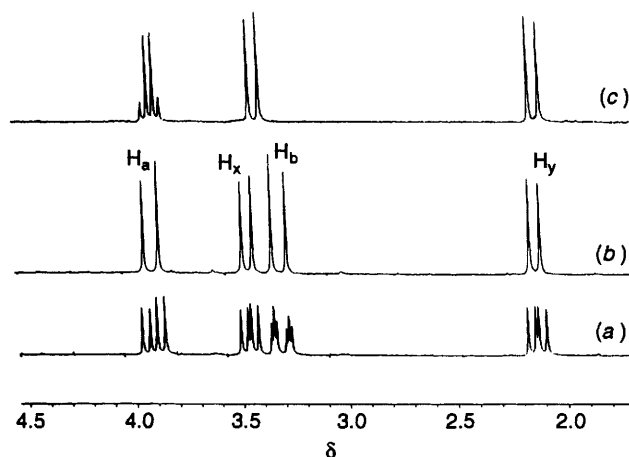
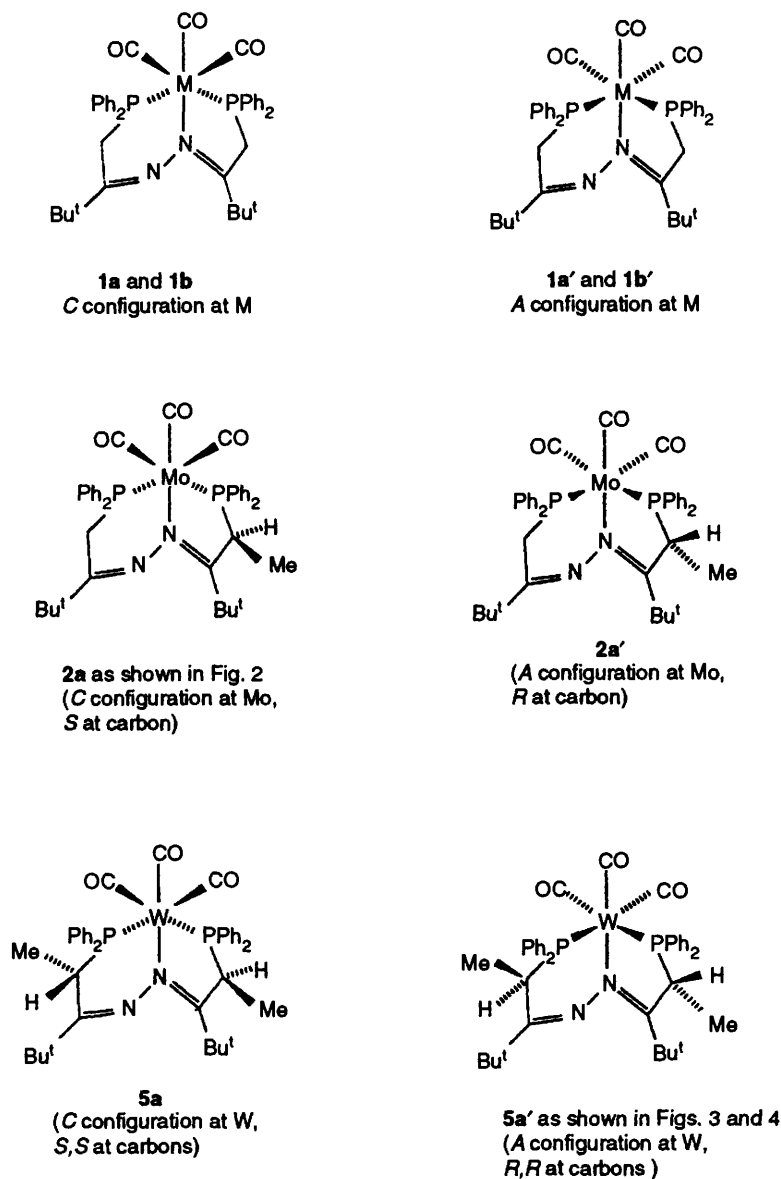


Fig. 1 Portions (between δ 1.7 and 4.5) of (a) the ^1H NMR spectrum of *fac*- $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **1a**, (b) the $^1\text{H}-\{^{31}\text{P}\}$ NMR spectrum of **1a** and (c) $^1\text{H}-\{^{31}\text{P}\}$ NMR spectrum of *fac*- $[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{Me})\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **2a**; all spectra were recorded in CDCl_3 at 250.13 MHz

at δ 3.90 with $^3J(\text{HH}) = 7.0$ Hz (see Fig. 1), whilst the *CHMe* protons gave a 1:1 doublet at δ 1.37. The carbon-13 NMR spectrum was fully assigned; noteworthy features include doublets at δ 15.6 with $^2J(\text{PC}) = 4.2$ Hz due to the methyl carbon *CHMe*, at δ 25.1 with $^1J(\text{PC}) = 3.5$ Hz for the methylene carbon CH_2 in the six-membered ring and at δ 47.6 with $^1J(\text{PC}) = 21.8$ Hz for the carbon *CHMe* in the five-membered ring.

Crystals of **2a**, suitable for X-ray diffraction analysis, were grown from dichloromethane-methanol. The molecular structure is shown in Fig. 2 with atomic coordinates in Table 4 and selected bond lengths and angles in Table 5. The main



Scheme 2 Chirality of the metal centre, *C* (clockwise) or *A* (anticlockwise) according to the skew-line convention for octahedral complexes

Table 1 Infrared and $^{31}\text{P}\{-^1\text{H}\}$ NMR data^a

Compound	$\nu(\text{C}=\text{N})^b$	$\nu(\text{C}=\text{O})^c$			$\delta(\text{P}_a)$	$\delta(\text{P}_b)$	$^2J(\text{PP})$	$^1J(\text{WP}_a)$	$^1J(\text{WP}_b)$
1	1620s				-14.4				
1a	1600w	1940	1840	1810	43.8	41.5	27		
1b	1600w	1935	1840	1810	37.9	32.7	23	264	231
2a	1610w	1930	1835	1805	59.1	42.4	24		
2b	1620w	1940	1840	1820	50.6	35.7	22	239	259
3a	1610w	1940	1845	1825	62.3	43.3	24		
3b	1610w	1935	1840	1820	53.7	36.5	20	239	257
4	1600w	1940	1840	1815	37.2	31.8	22	260	229
5a ^d	1605w	1940	1840	1820	46.5	45.8	26	241	246
5b	1610w	1935	1840	1820	46.7	45.7	26		

^a Recorded at 36.2 MHz, chemical shifts (δ) in ppm relative to 85% H_3PO_4 , solvent CDCl_3 ; J in Hz. ^b As KBr disc, w = weak, s = strong. ^c In CH_2Cl_2 , all carbonyl bands are strong. ^d At 161.9 MHz.

features are (i) the *fac* arrangement of tricarbonyls with one essentially planar five-membered chelate ring and one puckered six-membered chelate ring, (ii) the geometry around the metal is distorted octahedral and the tridentate ligand gives *C*

stereochemistry around the metal (Scheme 2), (iii) the bond angles $\text{P}(1)\text{--C}(2)\text{--C}(3)$ $108.72(13)$ and $\text{N}(4)\text{--Mo--P}(1)$ $71.53(5)^\circ$ in the five-membered ring are more acute than the corresponding ones [$111.8(3)$ and $73.2(2)^\circ$ respectively] in the

Table 2 Proton NMR data^a

	$\delta(\text{Bu}^1)$	$\delta(\text{CH}_2\text{P})$	Others
1	0.90 (18 H, s)	3.26 [4 H, d, $^2J(\text{PH})$ 3.9]	
1a^b	0.80 (9 H, s) 1.38 (9 H, s)	2.12 [1 H, dd, $^2J(\text{HH})$ 12.3, $^2J(\text{PH})$ 8.8, H ₂] 3.30 [1 H, dt, $^2J(\text{HH})$ 17.1, $^2J(\text{PH}) = ^4J(\text{PH})$ 3.2, H ₆] 3.47 [1 H, dd, $^2J(\text{HH})$ 12.3, $^2J(\text{PH})$ 8.5, H ₂] 3.93 [1 H, dd, $^2J(\text{HH})$ 17.1, $^2J(\text{PH})$ 8.9, H ₃]	
1b^b	0.90 (9 H, s) 1.40 (9 H, s)	2.20 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 9.8] 2.83 [1 H, ddd, $^2J(\text{HH})$ 17.1, $J(\text{PH})$ 3.0, 4.0] 3.55 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 8.9] 4.22 [1 H, dd, $^2J(\text{HH})$ 17.1, $^2J(\text{PH})$ 9.6]	
2a^c	0.88 (9 H, s) 1.42 (9 H, s)	2.11 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 8.7] 3.41 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 8.5]	1.37 [3 H, dd, $^3J(\text{HH})$ 7.0, $^3J(\text{PH})$ 12.3, CHMe] 3.90 [1 H, m, $^3J(\text{HH})$ 7.0, CHMe]
2b	0.89 (9 H, s) 1.40 (9 H, s)	2.19 [1 H, dd, $^2J(\text{HH})$ 12.3, $^2J(\text{PH})$ 9.8] 3.50 [1 H, dd, $^2J(\text{HH})$ 12.3, $^2J(\text{PH})$ 8.6]	1.37 [3 H, m, $^3J(\text{HH})$ 7.1, CHMe] ^d 4.08 [1 H, m, $^3J(\text{HH})$ 7.1, CHMe]
3a^b	0.81 (9 H, s) 1.49 (9 H, s)	1.96 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 9.1] 3.30 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 8.0]	2.30 [1 H, m, $J(\text{HH})$ 16.7, 8.2, 3.7, CHCH ₂] 3.06 (1 H, m, CHCH ₂) 3.72 [1 H, m, $^3J(\text{HH})$ 3.7, 4.5, CHP] 4.65 (2 H, m, CH ₂ =) 5.15 (1 H, m, CH=) 2.34 (1 H, m, CHCH ₂) 2.93 (1 H, m, CHCH ₂) 3.96 [1 H, m, $^3J(\text{HH})$ 3.7, 5.1, CHP] 4.75 (2 H, m, CH ₂ =) 5.20 (1 H, m, CH=)
3b	0.88 (9 H, s) 1.43 (9 H, s)	2.09 [1 H, dd, $^2J(\text{HH})$ 12.3, $^2J(\text{PH})$ 10.0] 3.45 [1 H, dd, $^2J(\text{HH})$ 12.3, $^2J(\text{PH})$ 8.7]	4.18 [1 H, d, $^2J(\text{PH})$ 9.5, CHD] 5.20 (1 H, m, CH=)
4	0.90 (9 H, s) 1.40 (9 H, s)	2.19 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 9.7] 3.55 [1 H, dd, $^2J(\text{HH})$ 12.2, $^2J(\text{PH})$ 9.6]	4.18 [1 H, d, $^2J(\text{PH})$ 9.5, CHD]
5a^c	0.98 (9 H, s) 1.47 (9 H, s)	— —	0.84 [3 H, dd, $^3J(\text{HH})$ 7.5, $^3J(\text{PH})$ 12.7, CHMe] 1.45 [3 H, dd, $^3J(\text{HH})$ 7.1, $^3J(\text{PH})$ 12.9, CHMe] 4.25 [1 H, m, $^3J(\text{HH})$ 7.1, CHMe] 4.61 [1 H, m, $^3J(\text{HH})$ 7.5, CHMe]
5b^b	0.98 (9 H, s) 1.47 (9 H, s)	— —	0.82 [3 H, dd, $^3J(\text{HH})$ 7.5, $^3J(\text{PH})$ 12.4, CHMe] 1.43 [3 H, dd, $^3J(\text{HH})$ 7.0, $^3J(\text{PH})$ 11.2, CHMe] 4.16 [1 H, m, $^3J(\text{HH})$ 7.5, CHMe] 4.25 [1 H, m, $^3J(\text{HH})$ 7.0, CHMe]

^a Recorded at 99.5 MHz, chemical shifts (δ) relative to SiMe₄, J in Hz, solvent CDCl₃ unless otherwise stated. In all cases ¹H and ¹H-³¹P NMR spectra were measured; multiplicities refer to ¹H NMR spectra. ^b At 250.13 MHz. ^c At 400.13 MHz. ^d Obscured by the resonance of a Bu¹ group.

Table 3 ¹³C-¹H NMR data*

Complex	δ_{C}
2a	15.6 [1 C, d, $^2J(\text{PC})$ 4.2, CHMe], 25.1 [1 C, d, $^1J(\text{PC})$ 3.5, CH ₂], 27.3 (3 C, s, CMe ₃), 28.2 (3 C, s, CMe ₃), 39.2 [1 C, d, $^3J(\text{PC})$ 1.8, CMe ₃], 39.7 [1 C, d, $^3J(\text{PC})$ 4.2, CMe ₃], 47.6 [1 C, d, $^1J(\text{PC})$ 21.8, CHMe], 167.3 (1 C, s, C=N), 177.1 [1 C, t, $^2J(\text{PC}) = ^3J(\text{PC})$ 5.1, C=N], 220.6 [1 C, dd, $^2J(\text{PC})$ 36.2, 10.2, C=O], 221.3 [1 C, dd, $^2J(\text{PC})$ 33.7, 11.7, C=O] and 228.7 [1 C, dd, $^2J(\text{PC})$ 9.3, 7.5, C=O <i>trans</i> to N]
2b	15.5 [1 C, d, $^2J(\text{PC})$ 3.8, CHMe], 24.9 [1 C, d, $^1J(\text{PC})$ 7.9, CH ₂], 27.4 (3 C, s, CMe ₃), 28.5 (3 C, s, CMe ₃), 39.4 [1 C, d, $^3J(\text{PC})$ 1.8, CMe ₃], 39.8 [1 C, d, $^3J(\text{PC})$ 3.5, CMe ₃], 45.5 [1 C, d, $^1J(\text{PC})$ 25.7, CHMe], 168.4 (1 C, s, C=N), 179.0 [1 C, d, $^2J(\text{PC})$ 5.1, C=N], 214.9 [1 C, dd, $^2J(\text{PC})$ 38.2, 7.6, C=O], 215.3 [1 C, dd, $^2J(\text{PC})$ 34.1, 9.6, C=O] and 220.1 [1 C, t, $^2J(\text{PC})$ 5.2, C=O <i>trans</i> to N]
3a	24.9 (1 C, s, CH ₂ P), 27.3 (3 C, s, CMe ₃), 28.6 (3 C, s, CMe ₃), 34.8 [1 C, d, $^2J(\text{PC})$ 6.2, CH ₂ CH=], 39.1 [1 C, d, $^3J(\text{PC})$ 1.6, CMe ₃], 39.6 [1 C, d, $^3J(\text{PC})$ 3.7, CMe ₃], 51.8 [1 C, d, $^1J(\text{PC})$ 19.8, CHP], 116.6 (1 C, s, =CH ₂), 127.9 (1 C, s, CH=), 167.1 (1 C, s, C=N), 177.5 [1 C, t, $^2J(\text{PC}) = ^3J(\text{PC})$ 5.1, C=N], 220.9 (2 C, m, 2C=O) and 228.7 [1 C, t, $^2J(\text{PC})$ 7.9, C=O <i>trans</i> to N]
3b	24.7 [1 C, d, $^1J(\text{PC})$ 6.7, CH ₂ P], 27.4 (3 C, s, CMe ₃), 28.8 (3 C, s, CMe ₃), 34.5 [1 C, d, $^2J(\text{PC})$ 5.5, CH ₂ CH=], 39.3 [1 C, d, $^3J(\text{PC})$ 1.8, CMe ₃], 39.6 [1 C, d, $^3J(\text{PC})$ 3.7, CMe ₃], 53.7 [1 C, d, $^1J(\text{PC})$ 23.7, CHP], 116.7 (1 C, s, =CH ₂), 128.1 (1 C, s, CH=), 168.2 (1 C, s, C=N), 179.5 [1 C, t, $^2J(\text{PC}) = ^3J(\text{PC})$ 5.1, C=N], 214.9 (2 C, m, 2C=O) and 220.0 [1 C, t, $^2J(\text{PC})$ 5.4, C=O <i>trans</i> to N]
4	25.0 [1 C, d, $^1J(\text{PC})$ 12.2, CH ₂ P], 27.4 (3 C, s, CMe ₃), 28.4 (3 C, s, CMe ₃), 39.3 [1 C, d, $^3J(\text{PC})$ 1.8, CMe ₃], 39.9 [1 C, d, $^3J(\text{PC})$ 3.4, CMe ₃], 46.3 (1 C, m, CHD), 168.7 (1 C, s, C=N), 176.4 [1 C, dd, $^2J(\text{PC})$ 4.4, $^3J(\text{PC})$ 2.4, C=N], 212.2 [1 C, dd, $^2J(\text{PC})$ 34.0, 5.4, C=O], 215.7 [1 C, dd, $^2J(\text{PC})$ 33.3, 8.9, C=O] and 221.0 [1 C, t, $^2J(\text{PC})$ 5.0, C=O <i>trans</i> to N]
5a	15.3 (1 C, s, CHMe), 15.7 [1 C, d, $^2J(\text{PC})$ 3.4, CHMe], 27.6 (3 C, s, CMe ₃), 29.2 (3 C, s, CMe ₃), 40.2 [1 C, d, $^3J(\text{PC})$ 3.3, CMe ₃], 41.4 [1 C, d, $^3J(\text{PC})$ 3.0, CMe ₃], 47.8 (1 C, s, CHMe), 48.1 (1 C, s, CHMe), 171.7 [1 C, d, $^2J(\text{PC})$ 4.4, C=N], 178.9 (1 C, s, C=N), 214.6 (2 C, m, 2C=O) and 220.4 [1 C, t, $^2J(\text{PC})$ 6.1, C=O <i>trans</i> to N]
5b	15.5 (1 C, s, CHMe), 15.9 [1 C, d, $^2J(\text{PC})$ 4.0, CHMe], 27.6 (3 C, s, CMe ₃), 29.1 (3 C, s, CMe ₃), 40.2 [1 C, d, $^3J(\text{PC})$ 3.8, CMe ₃], 40.9 [1 C, d, $^3J(\text{PC})$ 2.8, CMe ₃], 46.0 (1 C, s, CHMe), 46.2 (1 C, s, CHMe), 170.8 [1 C, d, $^2J(\text{PC})$ 5.2, C=N], 177.2 (1 C, s, C=N), 220.7 (2 C, m, 2C=O) and 228.9 [1 C, t, $^2J(\text{PC})$ 9.7, C=O <i>trans</i> to N]

* Recorded at 100.6 MHz, chemical shifts (δ) in ppm relative to SiMe₄, J values in Hz, solvent CDCl₃.

five-membered ring of **1a**⁵ and (iv) the methyl group on C(2) is on the same side as the three *fac*-tricarboxyls. Other bond angles and lengths are similar to those of **1a**. Interestingly, spontaneous resolution had occurred on crystallisation and the crystal we had selected had the *S* configuration at the substituted carbon with the *C* configuration at the metal. Therefore the *C* configuration at the metal centre promotes

substitution of one of the methylene hydrogens in the five-membered chelate ring to give the *S* configuration at carbon: clearly, therefore, the *A* configuration at the metal would give the *R* configuration at carbon, *i.e.* **2a**'.

A corresponding tungsten complex-

$$\text{fac-}\{\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{Me})\text{C}(\text{Bu}^1)=\text{N}-\text{N}=\text{C}(\text{Bu}^1)\text{CH}_2\text{PPh}_2\}$$
2b was similarly prepared in 70% yield by deprotonating

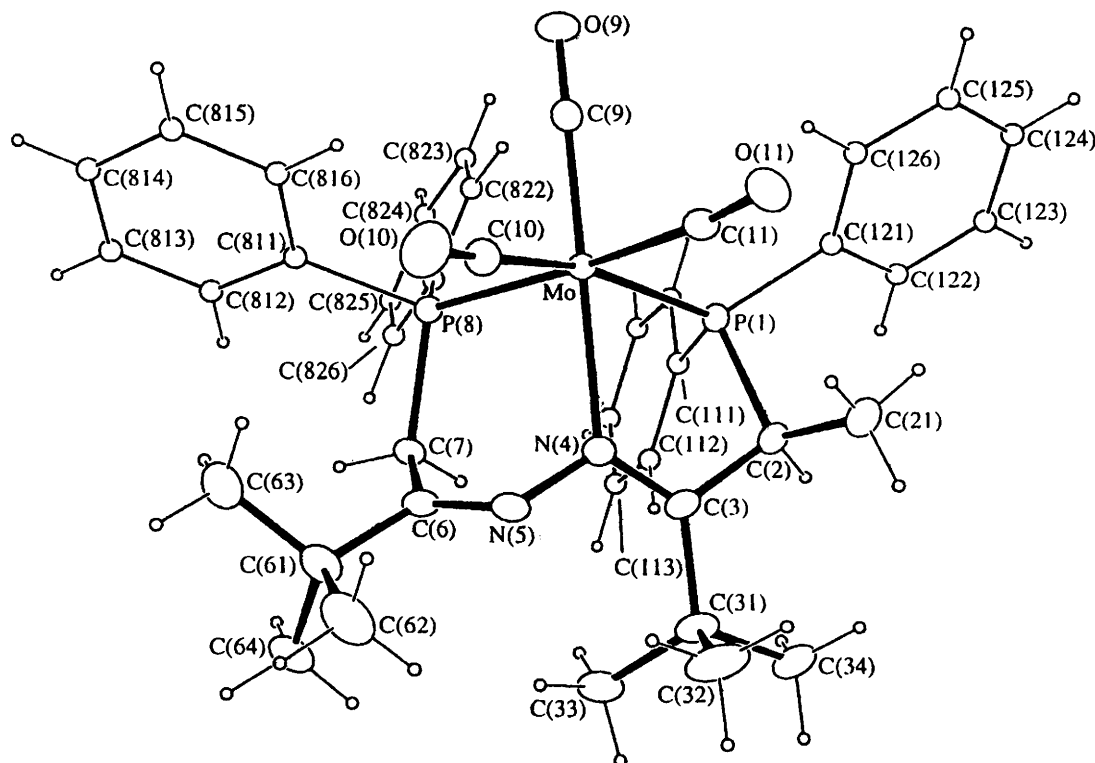


Fig. 2 An ORTEP diagram of the crystal structure of complex **2a**. Ellipses are drawn at the 50% probability level. For clarity, phenyl carbons and hydrogen atoms are drawn as small circles of arbitrary radius

Table 4 Fractional atom coordinates ($\times 10^4$) for compound **2a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Mo	1 803.5(2)	9 624.26(9)	1 155.04(7)	C(61)	4 693(3)	11 735.0(14)	518.8(11)
P(1)	3 125.4(6)	8 612.3(3)	1 699.8(2)	C(62)	4 801(4)	11 615(2)	-196.7(12)
C(111)	4 185(2)	8 809.3(11)	2 386.5(10)	C(63)	3 606(3)	12 322.1(15)	657.5(14)
C(112)	5 466(2)	9 118.9(12)	2 328.0(11)	C(64)	6 047(3)	12 038(2)	755.7(13)
C(113)	6 193(2)	9 328.5(13)	2 857.0(12)	C(7)	4 239(2)	10 982.1(12)	1 570.5(9)
C(114)	5 657(3)	9 232.8(14)	3 454.1(12)	P(8)	2 543.5(5)	10 692.7(3)	1 839.6(2)
C(115)	4 407(3)	8 919.8(14)	3 521.3(11)	C(811)	1 593(2)	11 589.7(11)	1 850.9(9)
C(116)	3 669(2)	8 711.1(12)	2 995.5(11)	C(812)	333(2)	11 628.3(12)	1 583.8(10)
C(121)	2 455(2)	7 669.5(12)	1 877.0(11)	C(813)	-398(2)	12 302.2(14)	1 611.3(11)
C(122)	1 172(2)	7 486.1(12)	1 681.5(10)	C(814)	123(3)	12 935.6(13)	1 908.3(13)
C(123)	676(2)	6 754.2(13)	1 767.5(11)	C(815)	1 364(2)	12 897.0(13)	2 185.5(13)
C(124)	1 449(2)	6 207.7(13)	2 055.9(13)	C(816)	2 092(2)	12 233.2(12)	2 161.8(11)
C(125)	2 713(3)	6 388.0(14)	2 268(2)	C(821)	2 704(2)	10 571.2(11)	2 698.8(9)
C(126)	3 218(3)	7 114.8(12)	2 177.8(13)	C(822)	1 685(2)	10 166.9(11)	2 992.2(9)
C(2)	4 396(2)	8 402.7(12)	1 082.4(11)	C(823)	1 618(2)	10 128.5(13)	3 646.0(10)
C(21)	3 863(3)	7 869.8(15)	557.0(13)	C(824)	2 566(3)	10 484(2)	4 011.5(10)
C(3)	4 870(2)	9 150.4(13)	798.1(9)	C(825)	3 601(3)	10 870(2)	3 725.7(11)
C(31)	6 274(2)	9 188.2(15)	493.9(11)	C(826)	3 673(2)	10 909.9(13)	3 069.4(10)
C(32)	6 066(3)	9 197(2)	-227.1(12)	C(9)	106(2)	9 549.8(12)	1 596.1(9)
C(33)	7 074(2)	9 897(2)	687.9(13)	O(9)	-886.5(15)	9 504.3(10)	1 879.9(7)
C(34)	7 121(2)	8 486(2)	664.8(14)	C(10)	1 103(2)	10 366.1(14)	533.4(9)
N(4)	3 995(2)	9 696.3(10)	808.1(7)	O(10)	676(2)	10 763.7(11)	150.6(9)
N(5)	4 315(2)	10 392.3(11)	507.9(8)	C(11)	1 100(2)	8 869.1(12)	549.8(10)
C(6)	4 379(2)	10 986.3(13)	855.8(10)	O(11)	577(2)	8 473.7(10)	192.5(8)

$[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **1b** and methylating the resultant carbanion. It was also fully characterised. Treatment of 1 equivalent of **1a** with 1 equivalent of LiBu^n followed by an excess of allyl bromide gave *fac*-

$[\text{Mo}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{CH}_2\text{CH}=\text{CH}_2)\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **3a**. Essentially, one product was formed and this was isolated in 81% yield. The elemental analytical, mass spectral, infrared and NMR data are in agreement with the assigned structure. The corresponding tungsten complex *fac*-

$[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{CH}_2\text{CH}=\text{CH}_2)\text{C}(\text{Bu}^t)=\text{N}-\text{N}=\text{C}(\text{Bu}^t)\text{CH}_2\text{PPh}_2\}]$ **3b** was made similarly in 56% yield and similarly characterised.

Thus deprotonation of the tungsten complex **1b** with 1 molar equivalent of LiBu^n gave essentially one product (carbanion) characterised by its $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum, which consisted of two doublets, at δ 31.2 and 21.0 with $^2J(\text{PP}) = 31$ Hz and satellites with $^1J(\text{WP}) = 224$ Hz and this on treatment with methyl iodide gave a methyl derivative **2b**, which we assume has the same structure as that of the molybdenum complex **2a**. We attempted to substitute just one methylene hydrogen in the five-membered chelate ring of **1b** by deuterium. The monocarbanion

characterised by its $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum, which consisted of two doublets, at δ 31.2 and 21.0 with $^2J(\text{PP}) = 31$ Hz and satellites with $^1J(\text{WP}) = 224$ Hz and this on treatment with methyl iodide gave a methyl derivative **2b**, which we assume has the same structure as that of the molybdenum complex **2a**. We attempted to substitute just one methylene hydrogen in the five-membered chelate ring of **1b** by deuterium. The monocarbanion

was generated as before and treated with an excess of deuterium oxide. The product was the hoped for monodeuterio derivative **4** and its mirror image. The proton spectrum showed a doublet of doublets for each of the methylene hydrogens in the six-membered chelate ring: one at δ 2.19 and the other at δ 3.55 each with $^2J(\text{HH}) = 12.2$ and $^2J(\text{PH}) \approx 9.6$ Hz. The single

Table 5 Selected bond lengths (pm) and angles ($^\circ$) for compound **2a** with e.s.d.s in parentheses

Mo–C(9)	1.947(2)	Mo–C(11)	1.976(2)
Mo–C(10)	1.982(2)	Mo–N(4)	2.321(2)
Mo–P(8)	2.486(1)	Mo–P(1)	2.501(1)
P(1)–C(121)	1.827(2)	P(1)–C(111)	1.835(2)
P(1)–C(2)	1.863(2)	C(2)–C(3)	1.522(3)
C(2)–C(21)	1.550(3)	C(3)–N(4)	1.301(3)
C(3)–C(31)	1.550(3)	N(4)–N(5)	1.416(3)
N(5)–C(6)	1.280(3)	C(6)–C(7)	1.521(3)
C(6)–C(61)	1.530(3)	C(7)–P(8)	1.864(2)
P(8)–C(821)	1.840(2)	P(8)–C(811)	1.843(2)
C(9)–O(9)	1.165(2)	C(10)–O(10)	1.153(3)
C(11)–O(11)	1.154(3)		
C(9)–Mo–C(11)	87.39(8)	C(9)–Mo–C(10)	93.07(9)
C(11)–Mo–C(10)	83.34(8)	C(9)–Mo–N(4)	169.73(7)
C(11)–Mo–N(4)	99.72(7)	C(10)–Mo–N(4)	95.10(8)
C(9)–Mo–P(8)	91.82(6)	C(11)–Mo–P(8)	173.05(7)
C(10)–Mo–P(8)	89.81(7)	N(4)–Mo–P(8)	82.01(4)
C(9)–Mo–P(1)	101.20(6)	C(11)–Mo–P(1)	90.63(7)
C(10)–Mo–P(1)	164.26(6)	N(4)–Mo–P(1)	71.53(5)
P(8)–Mo–P(1)	96.30(2)	C(2)–P(1)–Mo	100.31(7)
C(3)–C(2)–C(21)	110.2(2)	C(3)–C(2)–P(1)	108.72(13)
C(21)–C(2)–P(1)	112.8(2)	N(4)–C(3)–C(2)	114.8(2)
N(4)–C(3)–C(31)	126.0(2)	C(2)–C(3)–C(31)	119.0(2)
C(3)–N(4)–N(5)	118.5(2)	C(3)–N(4)–Mo	127.2(2)
N(5)–N(4)–Mo	113.84(12)	C(6)–N(5)–N(4)	117.2(2)
N(5)–C(6)–C(7)	124.4(2)	N(5)–C(6)–C(61)	116.3(2)
C(7)–C(6)–C(61)	119.2(2)	C(6)–C(7)–P(8)	112.94(14)
C(7)–P(8)–Mo	107.45(6)	O(9)–C(9)–Mo	177.6(2)
O(10)–C(10)–Mo	176.2(2)	O(11)–C(11)–Mo	173.1(2)

proton *CHDP* in the five-membered ring resonated at δ 4.18 with $^2J(\text{PH}) = 9.5$ Hz. In the carbon-13 NMR spectrum the methylene carbon in the six-membered ring resonated at δ 25.0 as a doublet with $^1J(\text{PC}) = 12.2$ Hz. The deuterated carbon in the five-membered ring resonated at δ 46.3 as a multiplet. The mass spectrum contained a profile at m/z 833 for the parent molecular ion and showed successive loss of one, two and three $\text{C}\equiv\text{O}$. Presumably, the deuterium atom in **4** occupies the corresponding position to that of the methyl substituent in **2b**. This result suggests that it is the deprotonation step which is stereospecific and that this is so in the methylation experiment, giving **2a** as described above.

Since monodeprotonations of the molybdenum or tungsten complex **1a** or **1b** respectively are so specific, we attempted to deprotonate twice and methylate the resultant dicarbanion. We reasoned that further deprotonation on **1b** would not occur on the same carbon atom in the five-membered ring but on the methylene carbon of the six-membered chelate ring. Treatment of **1b** with 4 equivalents of LiBu^n at *ca.* 20 $^\circ\text{C}$ gave essentially one species, identified by its $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum which consisted of two doublets at δ 5.0 and 20.5 with $^2J(\text{PP}) = 26$ Hz. On addition of an excess of methyl iodide to this dianion one product was obtained, the dimethyl complex *fac*- $[\text{W}(\text{CO})_3\{\text{PPh}_2\text{CH}(\text{Me})\text{C}(\text{Bu}')=\text{N}=\text{N}=\text{C}(\text{Bu}')\text{CH}(\text{Me})\text{PPh}_2\}]$ **5a**, and this was isolated in 71% yield. Complex **5a** was also obtained by treating **2b** with 2 equivalents of LiBu^n followed by an excess of methyl iodide, *i.e.* steric hindrance presumably prevented further attack on the carbon of the five-membered ring. The microanalytical, mass spectral, infrared, and $^{31}\text{P}\{-^1\text{H}\}$, proton and carbon-13 NMR data of **5a** showed that each methylene group in **1b** had been substituted to give two *CHMe* groups. Interestingly, the carbon-13 NMR spectrum showed a low-field shift of *ca.* 20 ppm for the methylene carbon in the six-membered ring on replacement of hydrogen by a methyl group. The $^1\text{H}\{-^{31}\text{P}\}$ NMR spectrum showed that each of the two *CHMe* protons gave a doublet: one at δ 0.84 with $^3J(\text{HH}) = 7.5$ Hz and the other at δ 1.45 with $^3J(\text{HH}) = 7.1$ Hz.

The crystal structure of complex **5a** was determined and is

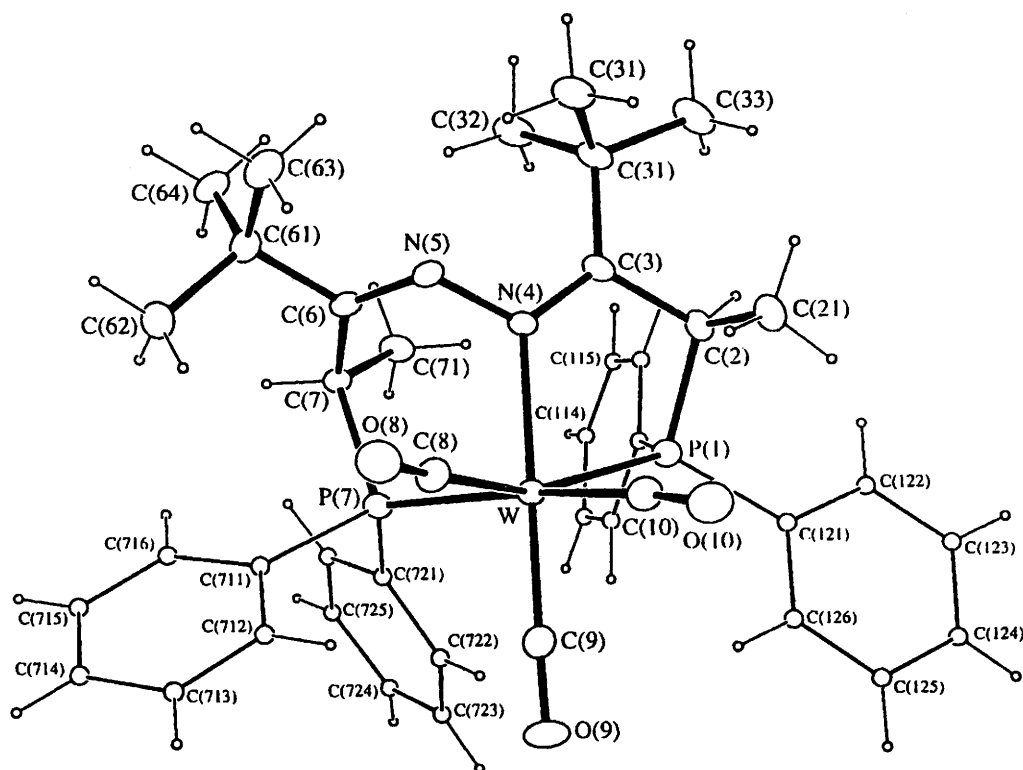


Fig. 3 An ORTEP diagram of the crystal structure of complex **5a**. Details as in Fig. 2

Table 6 Fractional atom coordinates ($\times 10^4$) for compound **5a'** with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
W	8 065.9(2)	9 583.03(10)	954.59(9)	C(62)	7 057(7)	12 537(3)	664(3)
P(1)	6 491.1(15)	8 573.8(7)	1 325.9(6)	C(63)	5 736(7)	11 985(3)	-188(2)
C(111)	5 394(5)	8 712(3)	1 994(2)	C(64)	4 600(6)	12 431(3)	759(3)
C(112)	5 995(6)	8 770(3)	2 565(2)	C(7)	6 146(5)	11 183(3)	1 509(2)
C(113)	5 286(7)	8 937(3)	3 097(3)	C(71)	4 955(6)	10 787(3)	1 814(2)
C(114)	3 923(7)	9 037(3)	3 064(3)	P(7)	7 727.3(13)	10 671.8(7)	1 701.0(6)
C(115)	3 315(6)	8 969(3)	2 506(3)	C(711)	9 001(5)	11 443(3)	1 712(2)
C(116)	4 028(6)	8 803(4)	1 967(2)	C(712)	1 0250(6)	11 285(3)	1 493(2)
C(121)	7 017(6)	7 566(3)	1 442(2)	C(713)	1 1255(6)	11 826(3)	1 536(3)
C(122)	8 351(6)	7 410(3)	1 538(3)	C(714)	1 1013(7)	12 542(3)	1 790(3)
C(123)	8 755(7)	6 657(3)	1 696(3)	C(715)	9 775(7)	12 711(3)	2 028(3)
C(124)	7 832(8)	6 081(3)	1 743(3)	C(716)	8 776(6)	12 158(3)	1 993(3)
C(125)	6 518(7)	6 222(3)	1 624(3)	C(721)	7 706(5)	10 514(3)	2 543(2)
C(126)	6 112(7)	6 971(3)	1 481(3)	C(722)	8 512(6)	9 932(3)	2 771(2)
C(2)	5 324(6)	8 567(3)	670(2)	C(723)	8 635(7)	9 801(3)	3 399(2)
C(21)	5 845(7)	8 155(3)	86(3)	C(724)	7 913(7)	10 256(4)	3 806(2)
C(3)	4 984(5)	9 412(3)	520(2)	C(725)	7 138(7)	10 856(4)	3 591(2)
C(31)	3 645(6)	9 616(3)	224(2)	C(726)	7 038(7)	10 983(3)	2 959(2)
C(32)	2 887(6)	10 245(3)	581(2)	C(8)	8 917(6)	10 336(3)	383(2)
C(33)	2 707(6)	8 908(4)	180(3)	O(8)	9 391(5)	10 730(2)	25(2)
C(34)	3 915(7)	9 900(4)	-437(2)	C(9)	9 729(6)	9 307(3)	1 337(2)
N(4)	5 956(5)	9 897(2)	631(2)	O(9)	10 729(4)	9 119(2)	1 573(2)
N(5)	5 805(5)	10 671(2)	433(2)	C(10)	8 629(6)	8 835(3)	322(2)
C(6)	5 966(5)	11 227(3)	809(2)	O(10)	9 095(5)	8 429(2)	-53(2)
C(61)	5 847(6)	12 045(3)	509(2)				

Table 7 Selected bond lengths (pm) and angles ($^\circ$) for compound **5a'** with e.s.d.s in parentheses

W-C(9)	1.933(6)	W-C(10)	1.968(6)
W-C(8)	1.991(5)	W-N(4)	2.308(5)
W-P(1)	2.492(1)	W-P(7)	2.503(1)
P(1)-C(121)	1.834(5)	P(1)-C(111)	1.841(5)
P(1)-C(2)	1.849(6)	C(2)-C(3)	1.532(7)
C(2)-C(21)	1.544(7)	C(3)-N(4)	1.312(7)
C(3)-C(31)	1.539(7)	N(4)-N(5)	1.410(6)
N(5)-C(6)	1.269(6)	C(6)-C(7)	1.533(6)
C(6)-C(61)	1.557(7)	C(7)-C(71)	1.534(7)
C(7)-P(7)	1.872(5)	P(7)-C(721)	1.848(5)
P(7)-C(711)	1.851(5)	C(711)-C(712)	1.376(7)
C(8)-O(8)	1.138(6)	C(9)-O(9)	1.179(7)
C(10)-O(10)	1.172(7)		
C(9)-W-C(10)	83.5(2)	C(9)-W-C(8)	93.0(2)
C(10)-W-C(8)	82.4(2)	C(9)-W-N(4)	172.2(2)
C(10)-W-N(4)	102.0(2)	C(8)-W-N(4)	93.2(2)
C(9)-W-P(1)	104.1(2)	C(10)-W-P(1)	87.3(2)
C(8)-W-P(1)	158.9(2)	N(4)-W-P(1)	70.90(11)
C(9)-W-P(7)	91.5(2)	C(10)-W-P(7)	169.3(2)
C(8)-W-P(7)	88.4(2)	N(4)-W-P(7)	83.96(10)
P(1)-W-P(7)	103.13(4)	C(2)-P(1)-W	99.4(2)
C(3)-C(2)-C(21)	109.9(4)	C(3)-C(2)-P(1)	107.5(3)
C(21)-C(2)-P(1)	114.7(4)	N(4)-C(3)-C(2)	113.6(5)
N(4)-C(3)-C(31)	126.1(5)	C(2)-C(3)-C(31)	120.2(5)
C(3)-N(4)-N(5)	117.8(4)	C(3)-N(4)-W	126.7(3)
N(5)-N(4)-W	114.5(3)	C(6)-N(5)-N(4)	120.4(4)
N(5)-C(6)-C(7)	128.0(4)	N(5)-C(6)-C(61)	114.0(4)
C(7)-C(6)-C(61)	117.9(4)	C(6)-C(7)-C(71)	110.9(4)
C(6)-C(7)-P(7)	110.2(3)	C(71)-C(7)-P(7)	111.3(3)
C(7)-P(7)-W	109.0(2)	O(8)-C(8)-W	175.2(5)
O(9)-C(9)-W	178.2(5)	O(10)-C(10)-W	172.8(5)

shown in Fig. 3. Spontaneous resolution had occurred on crystallisation and the crystal selected was that of **5a'**, i.e. the configuration at the metal centre is *A*. Atomic coordinates are in Table 6 and selected bond lengths and bond angles in Table 7. The molecule has a chiral centre at each of the two CHMe carbons and the configuration around both of these is *R*. The two methyl groups are on either side of the tricarbonyls. The bond lengths W-P(7) 2.503(3) Å and W-P(1) 2.491(1) Å are very similar to W-P bond lengths previously reported.^{10,11} There

were no significant changes in the other bond lengths and angles of **5a'** compared to **1a** or **2a**. The corresponding molybdenum complex **5b** was prepared similarly, in 56% yield, and fully characterised.

Thus substitution by methyl of one of the two methylene hydrogens in the five- and six-membered rings is essentially stereospecific. To explain this we reproduce the crystal structure of **5a'** in Fig. 4, drawn by the PLUTON program.¹² The stereochemistry at the metal is *A* (anticlockwise)⁹ and the four positions (methylene positions) available for deprotonation/methylation are a and b (five-membered chelate ring) and x and y (six-membered chelate ring). Inspection shows that the adjacent *tert*-butyl group and phenyl group hinder position a more than b; hence the methyl takes the b position. Similarly, in the six-membered ring the adjacent *tert*-butyl group and phenyl groups hinder the x more than the y position. A plot of the structure of **5a'** using van der Waals radii also shows that the a and x positions are the more sterically hindered. Our X-ray structural determination makes it possible to assign the chemical shifts of the four methylene hydrogen resonances in **1a**; the shifts are δ 3.93 (H_a), 3.30 (H_b), 3.47 (H_x) and 2.12 (H_y) (see Fig. 1 and Scheme 1).

Experimental

All the reactions were carried out in an atmosphere of dry nitrogen or dry argon. Tetrahydrofuran was distilled from sodium and benzophenone under nitrogen immediately before use. The tricarbonylmolybdenum(0) and -tungsten(0) complexes **1a** and **1b** were prepared according to our published procedure.⁵ Infrared spectra were recorded using a Perkin-Elmer model 257 grating spectrometer, NMR spectra using a JEOL FX-90 (operating frequencies for 1H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 (operating frequencies for 1H and ^{31}P of 99.5 and 40.25 MHz respectively), a Bruker ARX-250 (operating frequencies for 1H and ^{13}C of 250.13 and 62.9 MHz respectively) or a Bruker AM-400 spectrometer (operating frequencies for 1H , ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively); 1H and ^{13}C shifts are relative to tetramethylsilane and ^{31}P shifts to 85% phosphoric acid. Fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec with 8 kV acceleration. For the metal complexes, *m/z* values are quoted for ^{98}Mo and ^{184}W .

fac-[Mo(CO)₃{PPh₂CH(Me)C(Bu)^t=N=N=C(Bu)^tCH₂P-Ph_{2}}}] **2a**.—A solution of LiBu^t (0.13 cm³, 0.20 mmol) in hexane was added to a solution containing the tricarbonylmolybdenum(0) complex **1a** (0.15 g, 0.20 mmol) in dry tetrahydrofuran (3 cm³) at about 20 °C. After 15 min an excess of methyl iodide (0.1 cm³) was added. The resulting solution was then evaporated to dryness under reduced pressure and addition of methanol to the residue gave the required product **2a** as yellow microcrystals. Yield 0.12 g, 79% (Found: C, 63.1; H, 6.05; N, 3.8. C₄₀H₄₄MoN₂O₃P₂ requires C, 63.3; H, 5.85; N, 3.7%). Mass spectrum (FAB): *m/z* 760 (*M*⁺), 732 (*M* - CO), 704 (*M* - 2CO) and 676 (*M* - 3CO).

fac-[W(CO)₃{PPh₂CH(Me)C(Bu)^t=N=N=C(Bu)^tCH₂P-Ph_{2}}}] **2b**.—The preparation and isolation of the tungsten complex **2b** from **1b** was similar to that used for the analogous

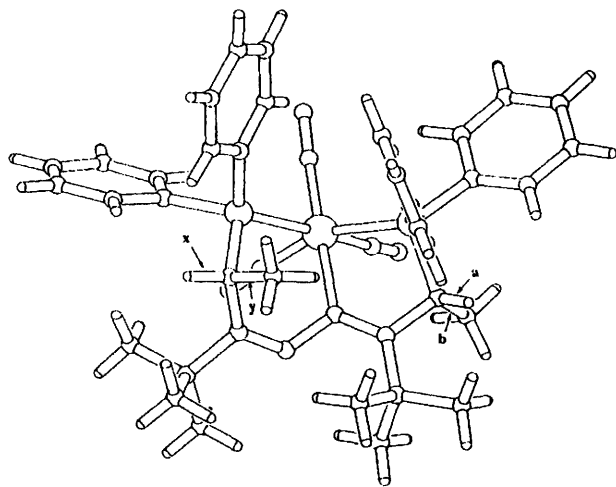


Fig. 4 The molecular structure of complex **5a'** drawn by the PLUTON program

molybdenum complex **2a**. It was isolated as yellow microcrystals in 70% yield (Found: C, 56.5; H, 5.15; N, 3.3. C₄₀H₄₄N₂O₃P₂W requires C, 56.7; H, 5.25; N, 3.3%). Mass spectrum (FAB): *m/z* 846 (*M*⁺), 790 (*M* - 2CO) and 762 (*M* - 3CO).

fac-[Mo(CO)₃{PPh₂CH(CH₂CH=CH₂)C(Bu)^t=N=N=C(Bu)^tCH₂P-Ph_{2}}}] **3a**.—A solution of LiBu^t (0.13 cm³, 0.20 mmol) in hexane was added to a solution containing complex **1a** (0.15 g, 0.20 mmol) in dry tetrahydrofuran (3 cm³) at ca. 20 °C. After 15 min an excess of allyl bromide (0.1 cm³) was added. The resulting solution was then evaporated to dryness under reduced pressure and the residue recrystallised from dichloromethane-methanol to give the required product **3a** as yellow microcrystals. Yield 0.13 g, 81% (Found: C, 59.55; H, 5.7; N, 2.95. C₄₂H₄₆MoN₂O₃P₂·CH₂Cl₂ requires C, 59.4; H, 5.5; N, 3.2%). Mass spectrum (FAB): *m/z* 786 (*M*⁺), 758 (*M* - CO), 730 (*M* - 2CO) and 702 (*M* - 3CO).

fac-[W(CO)₃{PPh₂CH(CH₂CH=CH₂)C(Bu)^t=N=N=C(Bu)^tCH₂P-Ph_{2}}}] **3b**.—This was prepared and isolated in a manner similar to that of the analogous molybdenum complex **3a**, as yellow microcrystals. Yield 56% (Found: C, 57.6; H, 5.35; N, 3.0. C₄₂H₄₆N₂O₃P₂W requires C, 57.85; H, 5.35; N, 3.25%). Mass spectrum (FAB): *m/z* 872 (*M*⁺), 844 (*M* - CO) and 788 (*M* - 3CO).

fac-[W(CO)₃{PPh₂CH(D)C(Bu)^t=N=N=C(Bu)^tCH₂PPh_{2}}}] **4**.—A solution of LiBu^t (0.075 cm³, 0.12 mmol) in hexane was added to a solution of complex **1b** (0.10 g, 0.12 mmol) in dry tetrahydrofuran (1 cm³) at ca. 20 °C. After 15 min an excess of D₂O (0.1 cm³) was added and the resulting solution evaporated under reduced pressure. Trituration with MeOD gave the required product **4** as yellow microcrystals. Yield 89 mg, 89%. Mass spectrum (FAB): *m/z* 833 (*M*⁺), 805 (*M* - CO), 777 (*M* - 2CO) and 749 (*M* - 3CO).

Table 8 Crystallographic data for compounds **2a** and **5a'**^a

	2a	5a'
Formula	C ₄₀ H ₄₄ MoN ₂ O ₃ P ₂	C ₄₁ H ₄₆ N ₂ O ₃ P ₂ W
<i>M</i>	758.689	860.615
Crystal dimensions/mm	0.61 × 0.61 × 0.38	0.76 × 0.38 × 0.38
<i>a</i> /Å	10.0282(7)	10.1021(5)
<i>b</i> /Å	17.5769(12)	17.2438(11)
<i>c</i> /Å	21.1919(15)	21.704(2)
<i>U</i> /Å ³	3735.4(5)	3780.8(5)
<i>D_c</i> /g cm ⁻³	1.349	1.512
<i>F</i> (000)	1576	1736
<i>μ</i> /mm ⁻¹	0.476	3.180
Scan widths/° + <i>α</i> -doublet splitting	<i>b</i>	1.05
No. of data collected	7915	5561
No. of unique data, <i>n</i>	6569	4819
No. of data observed ^c	6393	4419
<i>R</i> _{int} ^d	0.0155	0.0189
<i>R</i> _{sig} ^e	0.0185	0.0278
Minimum, maximum transmission factors	0.8885, 0.9992	0.4231, 0.5945
<i>ρ</i> _{max} , <i>ρ</i> _{min} /e Å ⁻³	0.22, -0.20	0.49, -1.249
<i>R</i> ₁ ^f	0.0198	0.0226
<i>wR</i> ₂ ^g	0.0518	0.0561
Weighting parameters <i>x</i> , <i>y</i> ^h	0.0269, 1.1012	0.0353, 1.6518
Flack parameter ⁱ	0.08(2)	-0.0009(7)
No. of parameters, <i>p</i>	404	450
Goodness of fit ^j	1.055	1.027

^a Common to both compounds: orthorhombic, space group *P*2₁2₁2₁; *Z* = 4; 4.0 < 2θ < 50.0°, data collection temperature 200 K; minimum, maximum scan speeds 1.5, 8.0° min⁻¹; Δ/σ_{max} 0.001. ^b Each scan divided into 30 steps; scan widths and step sizes from a learnt profile. ^c Criterion for observed reflections, |*F*_o| > 4.0σ(|*F*_o|). ^d Σ|*F*_o² - *F*_o²(mean)|/Σ(*F*_o²). ^e Σ[σ(*F*_o²)]/Σ(*F*_o²). ^f Σ(|*F*_o| - |*F*_c|)/Σ|*F*_o|. ^g Σw(|*F*_o| - |*F*_c|)²/Σw|*F*_o|². ^h Weighting scheme used *w* = [σ²(*F*_o²) + *xP*² + *yP*]⁻¹ where *P* = (*F*_o² + 2*F*_c²)/3. ⁱ See ref. 14. ^j *s* = [Σ[w(*F*_o² - *F*_c²)²]/(n - *p*)]^{1/2}.

fac-[W(CO)₃{PPh₂CH(Me)C(Bu^t)=N-N=C(Bu^t)CH(Me)P-Ph₂}] **5a**.—(i) *From complex 1b*. An excess of LiBuⁿ (0.9 cm³, 1.44 mmol) in hexane was added to a solution of complex **1b** (0.30 g, 0.36 mmol) in dry tetrahydrofuran (2 cm³). After 12 h an excess of methyl iodide (0.1 cm³) was added. The resulting solution was evaporated to dryness and the residue recrystallised from dichloromethane–methanol to give **5a** as a yellow microcrystalline solid. Yield 0.22 g, 71% (Found: C, 56.5; H, 5.4; N, 3.1. C₄₁H₄₆N₂O₃P₂W·0.25 CH₂Cl₂ requires C, 56.2; H, 5.35; N, 3.2%). Mass spectrum (FAB): *m/z* 860 (*M*⁺) and 776 (*M* – 3CO).

(ii) *From complex 2b*. An excess of LiBuⁿ (0.30 cm³, 0.47 mmol) was added to a solution of complex **2b** (0.20 g, 0.24 mmol) in dry tetrahydrofuran (2 cm³) and after 12 h an excess of methyl iodide (0.1 cm³) was added. The resulting solution was evaporated to dryness and the residue recrystallised from dichloromethane–methanol to give **5a** as yellow microcrystals. Yield 79 mg, 38%.

fac-[Mo(CO)₃{PPh₂CH(Me)C(Bu^t)=N-N=C(Bu^t)CH(Me)P-Ph₂}] **5b**.—The preparation and isolation of the molybdenum complex **5b** from **1a** was similar to that used for the analogous tungsten complex **5a**. It was isolated as yellow microcrystals in 56% yield (Found: C, 63.9; H, 6.05; N, 3.6. C₄₁H₄₆MoN₂O₃P₂ requires C, 63.85; H, 6.0; N, 3.65%). Mass spectrum (FAB): *m/z* 774 (*M*⁺), 718 (*M* – 2CO) and 690 (*M* – 3CO).

X-Ray Diffraction Analysis.—All diffraction measurements made at 200 K on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated Mo-K_α X-radiation (λ = 0.710 69 Å) and for compound **2a** an on-line profile-fitting method.¹³ Crystal data are listed in Table 8 together with details of data collection and structure refinement. Both data sets were corrected for absorption using azimuthal ψ scans.

Both structures were solved by standard heavy-atom techniques using SHELXS 86¹⁵ and were refined by full-matrix least squares using SHELXL 93.¹⁶ For both complexes all non-hydrogen atoms were refined with anisotropic thermal parameters. Restraints were applied to all phenyl groups such that they remained flat with overall C_{2v} symmetry. All hydrogen atoms were constrained to calculated positions (C–H 0.95, 0.98, 0.99 and 1.00 Å for phenyl, methyl, methylene and methine hydrogen atoms respectively) with fixed isotropic thermal parameters of *nU*_{eq} that of the parent carbon atom, where *n* was 1.5 for methyl hydrogens and 1.2 for all others. In both cases the complex crystallises in space group P2₁2₁2₁

implying that each crystal was chiral. We assume that, in both cases, the reactions produce a racemic mixture which crystallises separately in the *R* and *S* forms. The absolute structure of each crystal form is based on the refinement of a Flack enantiopole parameter¹⁴ which refined to 0.08(2) and –0.009(7) for **2a** and **5a'** respectively. The ORTEP¹⁷ diagrams of **2a** and **5a'** are shown in Figs. 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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