Complexes of an Azine Diphosphine with Group 6 Metal Carbonyls: Crystal Structures of *Z,Z*-$PPh_2CH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$ and [$Mo(CO)_3$(*E,Z*-$PPh_2CH_2C(Bu^t)$=N–N=$(Bu^t)CCH_2PPh_2$)]†

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Treatment of the azine MeC(Bu^t)=NN=C(Bu^t)Me with 2 equivalents of $LiBu^n$, followed by 2 equivalents of PPh_2Cl, gives the azine diphosphine *Z,Z*-$PPh_2CH_2C(Bu^t)$=N–N=$(Bu^t)CCH_2PPh_2$ **1**. This new diphosphine was treated with H_2O_2 to give the corresponding diphosphine dioxide **2a** and with monoclinic sulfur to give the diphosphine disulfide **2b**. Treatment of [$M(CO)_3(\eta^6$-cht)] (cht = cyclohepta-2,4,6-triene) with **1** gave the metal tricarbonyl *fac*-[$M(CO)_3\{PPh_2CH_2C(Bu^t)$=NN=$(Bu^t)CCH_2PPh_2\}$] (M = Mo, **3a**; W, **3b**; or Cr, **3c**) in which the azine diphosphine is bonded in the *E,Z* configuration. Complexes **3a** and **3b** were also made by treating the corresponding metal hexacarbonyls with the azine diphosphine **1**. Treatment of [$M(CO)_4$(nbd)] (M = Mo, W, or Cr; nbd = norbornadiene) with **1** gave the tetracarbonyl complexes [$M(CO)_4\{PPh_2CH_2C(Bu^t)$=NN=$(Bu^t)CCH_2PPh_2\}$] **4** with the *E,Z*-azine diphosphine acting as a bidentate ligand. On heating, these tetracarbonyl complexes **4** were converted into the tricarbonyl complexes **3**. Treatment of either **3a** or **4a** with 1 mol equivalent of bromine gave the neutral molybdenum(II) complex [$MoBr_2(CO)_2\{PPh_2CH_2C(Bu^t)$=NN=$(Bu^t)CCH_2PPh_2\}$] **5**, whereas the tungsten complexes **3b** and **4b** with bromine gave the cation [$WBr(CO)_3\{PPh_2CH_2C(Bu^t)$=NN=$(Bu^t)CCH_2PPh_2\}$]$^+$ isolated as its BPh_4^- salt **6**. Proton, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR and infrared data are given. Crystals of **1** are monoclinic, space group $P2_1/n$, with a = 1667.2(2), b = 572.85(6), c = 1811.0(2)pm, β = 111.595(8)° and Z = 2; final R factor 0.0519 for 2049 observed reflections. Crystals of **3a** are monoclinic, space group $P2_1/n$, with a = 985.7(1), b = 1870.2(2), c = 2220.8(2) pm, β = 93.71(1)° and Z = 4, final R factor 0.0354 for 5219 observed reflections.

In a previous paper[1] we showed that (1*R*)-(+)-camphor dimethylhydrazone could be deprotonated at the 3 position by $LiBu^n$ and that the resultant carbanion when treated with PPh_2Cl gave the 3-*exo*-diphenylphosphino-derivative as a crystalline solid. We have generated an extensive chemistry of this new chelating monophosphine with chromium, molybdenum, tungsten, platinum or palladium[1–3] and have now extended this type of chemistry to azine diphosphines. It is known that a hydrogen on carbon α to an azine system is similarly activated and can be removed as a proton by a strong base such as $LiBu^n$ or lithium diisopropylamide. Some examples of such an activation include the acetophenone azine dianion, which was generated by treating acetophenone azine with 2 equivalents of $LiBu^n$; this dianion can be dibenzylated with benzyl chloride at 0 °C.[4] The acetophenone azine dianion can also rearrange to give pyrrole and tetrahydropyridazine derivatives at room temperature.[5] It has also been shown that the monoanions derived from azines containing a methyl or methylene group in the α position to one of the C=N bonds are oxidatively dimerised in the presence of copper(I) chloride to give bis-azines.[6]

In the present work MeC(Bu^t)=NN=C(Bu^t)Me was treated with 2 equivalents of $LiBu^n$ at −15 °C, followed by 2 equivalents of PPh_2Cl, reasoning that, because of the large steric requirements of the *tert*-butyl groups and the absence of α-hydrogens, one diphosphine only might be formed. As described below, this proved to be the case and herein is described the preparation and crystal structure of this diphosphine and its behaviour towards Group 6 metal carbonyls. To our knowledge this is the first example of such a diphosphine.

Results and Discussion

On treatment of MeC(Bu^t)=NN=C(Bu^t)Me[7] with 2 equivalents of $LiBu^n$ at −15 °C followed by 2 equivalents of PPh_2Cl, the azine diphosphine $Ph_2PCH_2C(Bu^t)$=N–N=$(Bu^t)CCH_2PPh_2$ **1** was obtained as a yellow crystalline solid in 54% yield. Proton NMR data are given in Table 1, ^{31}P-$\{^1H\}$ NMR data in Table 2, ^{13}C-$\{^1H\}$ NMR data are in Table 3, and infrared data in Table 4. The NMR data for this new azine diphosphine indicated that the two phosphorus nuclei, the *tert*-butyl groups and methylene groups are each equivalent and therefore it must have the *E,E* or *Z,Z* configuration. In order to establish the configuration, its crystal structure was determined by X-ray diffraction (Fig. 1), see below. This showed the configuration to be *Z,Z* as illustrated. Interestingly, in the ^{13}C-$\{^1H\}$ NMR spectrum of **1**, the resonance for the methylene carbons appears as a pseudo first-order doublet of doublets with long-range coupling ^6J(PC) = 3.7 Hz.

The diphosphine **1** could be converted into the corresponding diphosphine-dioxide **2a** or -disulfide **2b** by treating it respectively with H_2O_2 or monoclinic sulfur. The azine diphosphine dioxide is clearly symmetrical from the ^{31}P-$\{^1H\}$ and proton NMR data, and a *Z,Z* configuration is assigned; we similarly assign the same configuration to the disulfide. These conversions and other reactions of the azine diphosphine **1** are summarised in Scheme 1.

It is known that the energy barrier to rotation around a C=N

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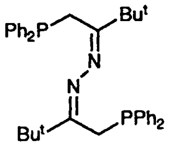
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Proton NMR data[a]

Complex	$\delta(Bu^t)$	$\delta(CH_2)$
1	0.90 (18 H, s)	3.26 [4 H, d, $^2J(PH)$ 3.9]
2a	0.98 (18 H, s)	3.82 [4 H, d, $^2J(PH)$ 15.9]
2b	0.76 (18 H, s)	4.15 [4 H, d, $^2J(PH)$ 15.4]
3a	0.89 (9 H, s), 1.38 (9 H, s)	2.12 [1 H, dd, $^2J(HH)$ 12.2, $^2J(PH)$ 8.8]
		3.38 [2 H, m, $^2J(HH)$ 12.4, $^2J(HH)$ 17.1][b]
		3.93 [1 H, dd, $^2J(HH)$ 17.1, $^2J(PH)$ 8.9]
3b	0.90 (9 H, s), 1.40 (9 H, s)	2.20 [1 H, dd, $^2J(HH)$ 12.2, $^2J(PH)$ 9.8]
		3.43 [2 H, m, $^2J(HH)$, 12.5, $^2J(HH)$ 17.3][b]
		4.22 [1 H, dd, $^2J(HH)$ 17.1, $^2J(PH)$ 9.6]
3c	0.90 (9 H, s), 1.36 (9 H, s)	1.95 [1 H, dd, $^2J(HH)$ 12.3, $^2J(PH)$ 8.4]
		3.37 [2 H, m, $^2J(HH)$ 12.0, $^2J(HH)$ 17.6][b]
		3.75 [1 H, dd, $^2J(HH)$ 17.6, $^2J(PH)$ 8.9]
4a	0.64 (9 H, s), 1.32 (9 H, s)	2.75 [2 H, d, $^2J(PH)$ 10.3]
		3.51 [2 H, d, $^2J(PH)$ 6.3]
4b	0.67 (9 H, s), 1.30 (9 H, s)	2.84 [2 H, d, $^2J(PH)$ 11.0]
		3.52 [2 H, d, $^2J(PH)$ 7.4]
4c	0.69 (9 H, s), 1.29 (9 H, s)	2.78 [2 H, d, $^2J(PH)$ 10.5]
		3.55 [2 H, d, $^2J(PH)$ 7.6]
5[c]	1.26 (9 H, s), 1.57 (9 H, s)	2.30 [1 H, dd, $^2J(HH)$ 14.2, $^2J(PH)$ 10.4]
		3.72 [1 H, dd, $^2J(HH)$ 14.2, $^2J(PH)$ 14.1]
		4.21 [1 H, dd, $^2J(HH)$ 18.5, $^2J(PH)$ 12.0]
		4.90 [1 H, ddd, $^2J(HH)$ 18.5, $^2J(PH)$ 8.5, $^4J(PH)$ 2.7]
6[c,d]	1.08 (9 H, s), 1.35 (9 H, s)	2.94 [1 H, dd, $^2J(HH)$ 12.3, $^2J(PH)$ 9.8]
		4.17 [2 H, m, $^2J(HH)$ 12.5, $^2J(HH)$ 18.9][b]
		4.98 [1 H, dd, $^2J(HH)$ 18.5, $^2J(PH)$ 5.6]

[a] Recorded at 100 MHz, chemical shifts (δ) are in ppm relative to $SiMe_4$, J values are in Hz, solvent $CDCl_3$ unless otherwise stated. [b] $J(PH)$ not resolved. [c] In CD_2Cl_2. [d] At 400 MHz.



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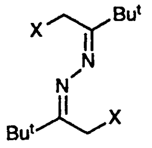
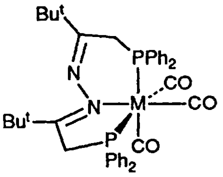
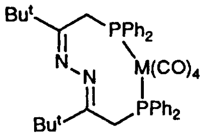


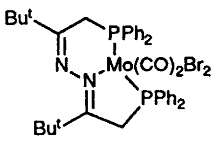
X
2a P(O)Ph₂
2b P(S)Ph₂



M
3a Mo
3b W
3c Cr



M
4a Mo
4b W
4c Cr



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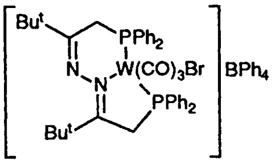

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bond in hydrazines lies between that of oximes (high) and Schiff bases (low).[8] One might expect the energy barrier to rotation in an azine to be similar to that of a hydrazone. Very few geometrical isomers of azines have been isolated but for *o*-nitroacetophenone azine all three isomers *E,E*, *E,Z* and *Z,Z* have been isolated.[9] In the case of the azine diphosphine **1** however no isomerisation to the *E,Z* or *Z,Z* forms was observed in solution (NMR evidence).

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

Complex	$\delta(P_A)$	$\delta(P_B)$	$^2J(PP)$	$^1J(WP_A)$	$^1J(WP_B)$
1	−14.4				
2a	25.1				
2b	37.0				
3a	43.8	41.5	27		
3b	37.3	32.1	23	264	231
3c	61.4	60.8	32		
4a	20.5	18.3	31		
4b	6.1	0.5	40	246	242
4c	39.8	37.3	42		
5[b]	64.7	55.8	20		
6[b]	45.4	42.0	149	171	185

[a] Recorded at 36.2 MHz, chemical shifts (δ) in ppm relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise stated. J Values are in Hz. [b] In CD_2Cl_2.

An attempt was made to displace cycloheptatriene (cht) from the well known molybdenum(0) complex $[Mo(CO)_3(\eta^6\text{-cht})]$ by the azine diphosphine **1**. After a reaction time of 16 h at 20 °C the azine diphosphine molybdenum(0) complex $[Mo(CO)_3\{PPh_2CH_2C(Bu^t){=}NN{=}(Bu^t)CCH_2PPh_2\}]$ **3a** was obtained in 88% yield. The NMR evidence and particularly the X-ray crystal structure (Fig. 2, see below) showed the configuration of the azine diphosphine had changed from *Z,Z* to *E,Z* upon co-ordination and that the complex was a *fac* isomer with *P,P,N* co-ordination of the azine diphosphine. The $^{31}P-\{^1H\}$ NMR spectrum of **3a** showed an AB pattern (data in Table 2); the small value of $^2J(PP)$ (27 Hz) is typical of a cisoid arrangement. In the ^1H NMR spectrum the *tert*-butyl groups are non-equivalent as are the four CH_2 protons. The $^{13}C-\{^1H\}$ NMR spectrum showed three resonances for the carbonyl ligands in a 1 : 1 : 1 ratio. The mass spectrum contained a profile at *m/z* 746 for the parent molecular ion which showed successive loss of one, two and three CO. This *fac*-tricarbonyl complex was also prepared by heating molybdenum hexacarbonyl with **1**.

The corresponding tungsten complex **3b** was prepared in a similar manner *i.e.* from either $[W(CO)_3(\eta^6\text{-cht})]$ or $[W(CO)_6]$

Table 3 ^{13}C-{^1H} NMR data[a]

Complex	δ_C
1	28.4 (6C, s, 2 CMe_3), 28.8 [2C, dd, ^1J(PC) 23.8, ^6J(PC) 3.7, 2 CH_2], 38.6 (2C, s, 2 CMe_3) and 168.1 [2C, t, ^2J(PC) = ^5J(PC) 3.3, 2 C=N]
3a	25.6 [1C, d, ^1J(PC) 5.2, CH_2], 27.5 (3C, s, CMe_3), 28.5 (3C, s, CMe_3), 39.5 [1C, d, ^3J(PC) 1.9, CMe_3], 40.4 [1C, d, ^3J(PC) 3.8, CMe_3], 44.8 [1C, d, ^1J(PC) 22.8, CH_2], 168.5 (1C, s, C=N), 175.6 [1C, t, ^2J(PC) = ^3J(PC) 4.0, C=N], 219.2 [1C, dd, ^2J(PC) 35.8, 9.2, C≡O], 222.3 [1C, dd, ^2J(PC) 33.8, 11.0, C≡O] and 229.6 [1C, t, ^2J(PC) 8.0, C≡O]
3b	25.0 [1C, d, ^1J(PC) 8.3 CH_2], 27.4 (3C, s, CMe_3), 28.4 (3C, s, CMe_3), 39.2 [1C, d, ^3J(PC) 1.9, CMe_3], 39.9 [1C, d, ^3J(PC) 3.6, CMe_3], 46.7 [1C, d, ^1J(PC) 27.7, CH_2], 168.7 (1C, s, C=N), 176.5 [1C, dd, ^1J(PC) 4.7, ^3J(PC) 2.6, C=N], 212.3 [1C, dd, ^2J(PC) 35.5, 5.7, C≡O], 215.6 [1C, dd, ^2J(PC) 33.4, 8.8, C≡O] and 221.1 [1C, t, ^2J(PC) 5.1, C≡O]
3c	25.3 [1C, d, ^1J(PC) 1.3, CH_2], 27.2 (3C, s, CMe_3), 28.3 (3C, s, CMe_3), 39.0 [1C, d, ^3J(PC) 2.0, CMe_3], 39.8 [1C, d, ^3J(PC) 3.5, CMe_3], 45.3 [1C, dd, ^1J(PC) 23.5, ^3J(PC) 2.1, CH_2], 168.3 (1C, s, C=N), 174.8 [1C, t, ^2J(PC) = ^3J(PC) 5.1, C=N], 228.5 [1C, dd, ^2J(PC) 15.6, 4.1, C≡O], 230.8 [1C, dd, ^2J(PC) 17.6, 4.1, C≡O] and 237.3 [1C, dd, ^2J(PC) 15.0, 11.7, C≡O]
4b	28.2 (3C, s, CMe_3), 28.5 (3C, s, CMe_3), 30.1 [1C, d, ^1J(PC) 10.2, CH_2], 36.8 [1C, d, ^1J(PC) 10.2, CH_2], 38.7 [1C, d, ^3J(PC) 2.0, CMe_3], 39.2 [1C, d, ^3J(PC) 3.2, CMe_3], 172.3 [1C, d, ^2J(PC) 4.1, C=N], 173.7 [1C, d, ^2J(PC) 7.4, C=N], 203.6 [2C, t, ^2J(PC) 7.4, 2 C≡O], 205.9 [1C, dd, ^2J(PC) 28.7, 6.6, C≡O] and 205.9 [1C, dd, ^2J(PC) 28.4, 7.3, C≡O]
4c	28.1 (3C, s, CMe_3), 28.4 (3C, s, CMe_3), 30.4 [1C, d, ^1J(PC) 5.0, CH_2], 36.2 [1C, d, ^1J(PC) 26.0, CH_2], 38.5 [1C, d, ^3J(PC) 1.6, CMe_3], 39.1 [1C, d, ^3J(PC) 3.2, CMe_3], 171.8 [1C, d, ^2J(PC) 3.6, C=N], 174.3 [1C, d, ^2J(PC) 7.5, C=N], 221.4 [2C, t, ^2J(PC) 16.0, 2 C≡O], 225.7 [1C, dd, ^2J(PC) 12.1, 2.8, C≡O] and 225.8 [1C, dd, ^2J(PC) 10.7, 2.9, C≡O]
5[b]	25.6 [1C, d, ^1J(PC) 10.8, CH_2], 28.4 (3C, s, CMe_3), 28.5 (3C, s, CMe_3), 40.5 [1C, d, ^3J(PC) 3.1, CMe_3], 41.3 [1C, d, ^3J(PC) 6.1, CMe_3], 41.8 [1C, d, ^1J(PC) 21.0, CH_2], 172.3 [1C, d, ^2J(PC) 1.9, C=N], 186.0 [1C, t, ^2J(PC) = ^3J(PC) 2.2, C=N], 235.8 [1C, t, ^2J(PC) 9.1, C≡O] and 259.3 [1C, dd, ^2J(PC) 45.6, 50.2, C≡O]

[a] Recorded at 100.6 MHz, chemical shifts (δ) in ppm relative to $SiMe_4$, J values are in Hz, solvent $CDCl_3$ unless otherwise stated. [b] In CD_2Cl_2.

Table 4 IR data in cm^{-1}

Complex	ν(C=N)[a]	ν(C≡O)[b]
1	1620s	
2a[c]	1615s	
2b	1625s	
3a	1600w	1940 1840 1810
3c	1600w	1935 1840 1810
3b	1600w	1930 1835 1805
4a	1605w	2020 1910 1870 (sh)
4b	1610w	2015 1895 1870 (sh)
4c	1610w	2010 1895 1870 (sh)
5	1610w	1975 1875
6	1600w	2045 1970 1945

[a] KBr disc, w = weak, s = strong. [b] In CH_2Cl_2, all carbonyl bands are strong, sh = shoulder. [c] 1215s, 1200s cm^{-1} ν(P=O).

and the chromium complex **3c** was prepared from [$Cr(CO)_3(\eta^6$-cht)]. Both the complexes **3b** and **3c** were fully characterised including by ^{13}C-{^1H} NMR spectroscopy.

The possibility of the azine diphosphine (as its *E,Z* isomer) acting as a bidentate ligand through only the two phosphorus

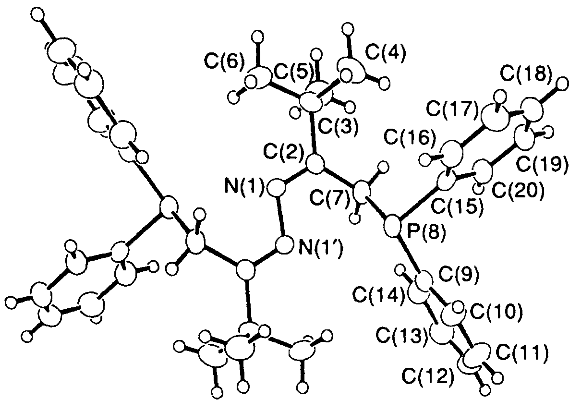
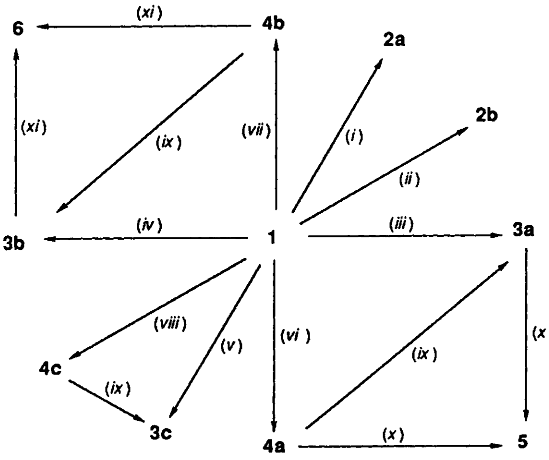


Fig. 1 ORTEP[10] drawing of the molecular structure of *Z,Z*-$PPh_2CH_2C(Bu^t)$=N–N=$(Bu^t)CCH_2PPh_2$ **1**



Scheme 1 (*i*) H_2O_2; (*ii*) monoclinic S; (*iii*) [$Mo(CO)_3(\eta^6$-cht)] or [$Mo(CO)_6$]; (*iv*) [$W(CO)_3(\eta^6$-cht)] or [$W(CO)_6$]; (*v*) [$Cr(CO)_3(\eta^6$-cht)]; (*vi*) [$Mo(CO)_4$(nbd)]; (*vii*) [$W(CO)_4$(nbd)]; (*viii*) [$Cr(CO)_4$(nbd)]; (*ix*) heat; (*x*) Br_2; (*xi*) Br_2–$NaBPh_4$

donor atoms was also investigated. Thus the norbornadiene (nbd) complex [$Mo(CO)_4$(nbd)] was treated with **1** in benzene at 20 °C for 5 h. This gave the hoped for tetracarbonyl complex **4a** which was characterised by elemental analysis, infrared, ^1H- and ^{31}P-{^1H} NMR spectroscopy. In particular the ^{31}P-{^1H} NMR spectrum showed an AB pattern with ^2J(PP) = 31 Hz, typical of two *cis*-related *P*-donor ligands and the proton NMR spectrum showed two non-equivalent *tert*-butyl groups and two non-equivalent methylene groups. However, the complex was thermally unstable in solution and at room temperature was converted within a day into the tricarbonyl complex **3a**. This prevented us from assigning resonances for the carbonyl ligands in the ^{13}C-{^1H} NMR spectrum. When a benzene solution of the tetracarbonyl complex **4a** was heated at *ca.* 75 °C for 20 min it was completely converted into the tricarbonyl complex **3a**.

The tungsten- and chromium-tetracarbonyl complexes **4b** and **4c** were also prepared from the corresponding norbornadiene complexes [$M(CO)_4$(nbd)] (M = W or Cr) except that more vigorous conditions were necessary to effect displacement of nbd (60 °C/5 h) than with [$Mo(CO)_4$(nbd)]. As would be expected, both the tungsten tetracarbonyl (**4b**) and the chromium tetracarbonyl (**4c**) were more stable than the molybdenum analogue and very good ^{13}C-{^1H} NMR spectra were obtained for both, each showing the presence of four carbonyl ligands in a (2 : 1 : 1) ratio. The two mutually equivalent carbonyl groups in the tungsten complex gave a 1 : 2 : 1 triplet with apparently equal coupling [^2J(PC) = 7.4 Hz] to both phosphorus nuclei. The other two, non-equivalent CO carbons coupled more strongly to one phosphorus than to the other, *viz.* 28.7, 6.6 Hz and 28.4, 7.3 Hz. One would, of course, expect the larger coupling to be with the mutually *trans* P-donor atom.

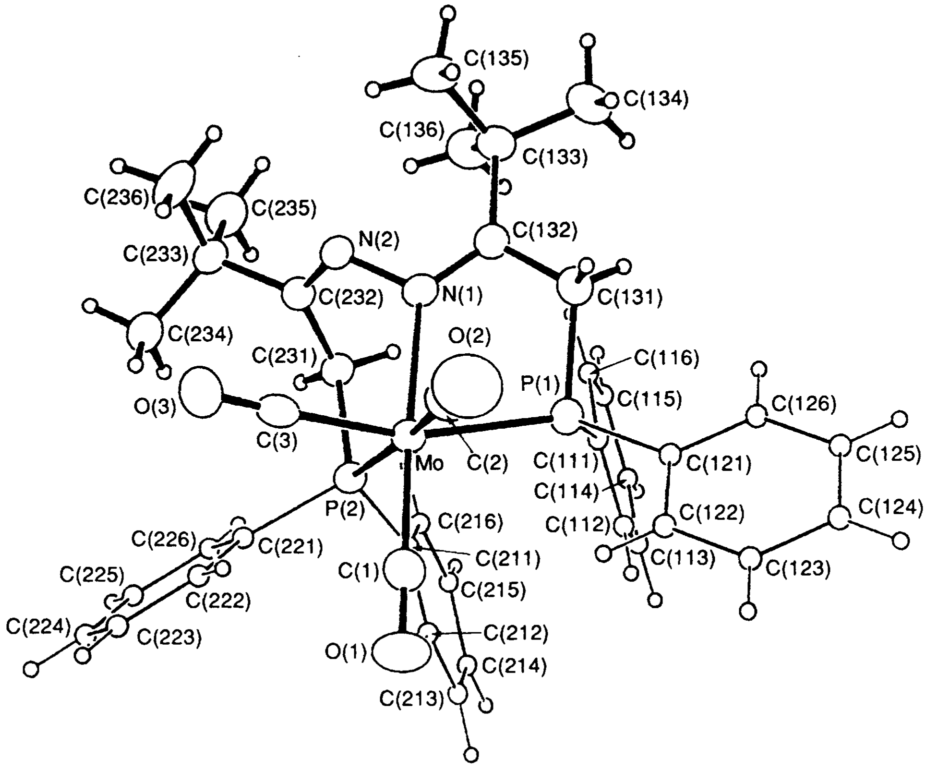


Fig. 2 ORTEP drawing of the molecular structure of *fac*-$[Mo(CO)_3(E,Z\text{-}\{PPh_2CH_2C(Bu^t){=}NN{=}(Bu^t)CCH_2PPh_2\}]$ **3a**

Table 5 Bond lengths (pm) and angles (°) for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

C(2)–N(1)	127.9(4)	N(1)–N(1′)	142.7(5)
C(3)–C(2)	152.5(6)	C(7)–C(2)	150.1(6)
C(4)–C(3)	153.0(6)	C(5)–C(3)	153.6(6)
C(6)–C(3)	152.3(6)	P(8)–C(7)	186.0(5)
C(9)–P(8)	185.2(3)	C(15)–P(8)	185.0(3)
C(2)–N(1)–N(1′)	112.4(3)	C(3)–C(2)–N(1)	117.6(3)
C(7)–C(2)–N(1)	123.2(3)	C(7)–C(2)–C(3)	119.2(3)
C(4)–C(3)–C(2)	109.6(3)	C(5)–C(3)–C(2)	107.9(3)
C(5)–C(3)–C(4)	109.4(4)	C(6)–C(3)–C(2)	111.3(3)
C(6)–C(3)–C(4)	110.1(4)	C(6)–C(3)–C(5)	108.5(4)
P(8)–C(7)–C(2)	113.4(3)	P(8)–C(7)–H(7a)	108.5(2)
P(8)–C(7)–H(7b)	108.4(2)	C(9)–P(8)–C(7)	101.7(2)
C(15)–P(8)–C(7)	102.0(2)	C(15)–P(8)–C(9)	99.0(2)
C(10)–C(9)–P(8)	114.0(2)	C(14)–C(9)–P(8)	125.9(2)
C(16)–C(15)–P(8)	116.5(2)	C(20)–C(15)–P(8)	123.4(2)

Atom N(1′) is related to atom N(1) by the symmetry operator 2.0 − x, −y, 1.0 − z.

Similar effects were observed for the $^{13}C\text{-}\{^1H\}$ NMR data of the chromium complex **4c**.

In $^{31}P\text{-}\{^1H\}$ NMR experiments it was found that the tungsten tetracarbonyl complex **4b** required heating at 75 °C for 60 h in benzene solution before conversion to the tricarbonyl complex **3b** was essentially complete; a similar conversion of the chromium tetracarbonyl complex **4c** to **3c** took 16 h.

A characteristic reaction of molybdenum(0) or tungsten(0) carbonyl–tertiary phosphine complexes is their oxidation by controlled amounts of halogen to give molybdenum(II) or tungsten(II) species.[11,12] On treatment of the molybdenum(0) tricarbonyl complex **3a** with 1 equivalent of bromine at 0 °C the molybdenum(II) complex **5** was obtained in excellent (78%) yield. Treatment of the azine diphosphine molybdenum tetracarbonyl complex **4a** with bromine also gave **5**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **5** showed a coupling of $^2J(PP)$ 20 Hz and the ^1H NMR spectrum (Table 1) showed all four methylene hydrogens to be non-equivalent. The $^{13}C\text{-}\{^1H\}$ NMR spectrum showed two carbonyl resonances and the IR spectrum only two bands due to ν(C≡O), as would be expected.

Treatment of the corresponding tungsten complexes **3b** or **4b** with one equivalent of bromine gave a monobromotricarbonyl $[WBr(CO)_3\{PPh_2CH_2C(Bu^t){=}NN{=}(Bu^t)CCH_2PPh_2\}]^+$ which was isolated as its tetraphenylborate salt **6**. This complex showed three bands due to ν(C≡O) in the infrared spectrum (Table 4). We have reported previously that treatment of *fac*-$[W(CO)_3(PMe_2Ph)_3]$ with iodine gives $[WI(CO)_3(PMe_2Ph)_3]^+$, also isolated as the tetraphenylborate salt.[11]

Crystal Structures of the Compounds $PPh_2CH_2C(Bu^t){=}N{-}N{=}(Bu^t)CCH_2PPh_2$ **1** *and* $[Mo(CO)_3(E,Z\text{-}PPh_2CH_2C(Bu^t){=}N{-}N{=}(Bu^t)CCH_2PPh_2)]$ **3a**.—The crystal structure of the azine diphosphine **1** is shown in Fig. 1 with selected bond lengths and angles in Table 5 and atom coordinates in Table 6. The crystal structure of **1** shows that the arrangement around both C=N bonds is *Z*. The crystal structure of **3a**, Fig. 2, shows a *fac* arrangement of tricarbonyls with one essentially planar five-membered chelate ring and one puckered six-membered chelate ring. The geometry around the metal is distorted octahedral with *e.g.* the bond angle N(1)–Mo–P(1) 73.2(2)° in the five-membered ring much more acute than the bond angle N(1)–Mo–P(2) 81.3(2)° in the six-membered ring. There are no particularly noteworthy changes in bond lengths of the ligand upon co-ordination. Selected bond lengths for **3a** are in Table 7 and atom coordinates in Table 8.

Experimental

All the reactions were carried out in an atmosphere of dry nitrogen or dry argon. Tetrahydrofuran and benzene were distilled from sodium and benzophenone under argon immediately before use. Infra-red spectra were recorded using a Perkin-Elmer model 257 grating spectrometer. NMR spectra were recorded using a JEOL FX-90Q spectrometer (operating

Table 6 Non-hydrogen atomic coordinates ($\times 10^4$) for compound **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
N(1)	10 388(1)	−349(4)	5 313(1)
C(2)	10 242(2)	−1 577(5)	5 840(2)
C(3)	11 019(2)	−2 519(5)	6 525(2)
C(4)	10 973(2)	−1 730(7)	7 315(2)
C(5)	10 986(2)	−5 197(5)	6 479(2)
C(6)	11 862(2)	−1 705(6)	6 463(2)
C(7)	9 351(2)	−2 197(5)	5 796(2)
P(8)	8 699.9(4)	38.00(13)	5 857.6(4)
C(9)	7 588(1)	−653(3)	5 299(1)
C(10)	6 948(1)	941(3)	5 281(1)
C(11)	6 083(1)	423(3)	4 854(1)
C(12)	5 858(1)	−1 688(3)	4 445(1)
C(13)	6 498(1)	−3 281(3)	4 464(1)
C(14)	7 363(1)	−2 763(3)	4 891(1)
C(15)	8 706(1)	125(3)	6 878(1)
C(16)	9 073(1)	1 974(3)	7 393(1)
C(17)	9 080(1)	1 943(3)	8 165(1)
C(18)	8 720(1)	62(3)	8 423(1)
C(19)	8 353(1)	−1 787(3)	7 909(1)
C(20)	8 346(1)	−1 756(3)	7 136(1)

Table 7 Selected bond lengths (pm) and angles (°) for compound **3a** with e.s.d.s in parentheses

P(1)–Mo	248.3(3)	P(2)–Mo	250.2(4)
C(1)–Mo	194.7(6)	C(2)–Mo	198.0(6)
C(3)–Mo	197.6(6)	N(1)–Mo	230.2(5)
C(111)–P(1)	184.1(4)	C(121)–P(1)	182.7(4)
C(131)–P(1)	184.1(6)	C(211)–P(2)	183.8(4)
C(221)–P(2)	184.3(4)	C(231)–P(2)	186.6(5)
O(1)–C(1)	116.8(5)	O(2)–C(2)	114.9(6)
O(3)–C(3)	116.2(5)	C(132)–C(131)	150.9(7)
C(133)–C(132)	155.1(7)	N(1)–C(132)	129.4(5)
N(2)–N(1)	142.0(5)	C(232)–N(2)	128.3(5)
C(232)–C(231)	151.4(7)	C(233)–C(232)	153.1(7)
P(2)–Mo–P(1)	96.2(1)	C(1)–Mo–P(1)	103.1(2)
C(1)–Mo–P(2)	94.5(2)	C(2)–Mo–P(1)	88.4(2)
C(2)–Mo–P(2)	175.4(1)	C(2)–Mo–C(1)	84.7(3)
C(3)–Mo–P(1)	163.3(1)	C(3)–Mo–P(2)	90.3(2)
C(3)–Mo–C(1)	91.6(2)	C(3)–Mo–C(2)	85.2(3)
N(1)–Mo–P(1)	73.2(2)	N(1)–Mo–P(2)	81.3(2)
N(1)–Mo–C(1)	174.0(1)	N(1)–Mo–C(2)	99.8(2)
N(1)–Mo–C(3)	92.8(2)	C(131)–P(1)–Mo	98.2(2)
C(231)–P(2)–Mo	107.4(2)	O(1)–C(1)–Mo	178.3(3)
O(2)–C(2)–Mo	172.5(3)	O(3)–C(3)–Mo	176.3(3)
C(132)–C(131)–P(1)	111.8(3)	C(133)–C(132)–C(131)	120.1(4)
N(1)–C(132)–C(131)	114.0(4)	N(1)–C(132)–C(133)	125.8(4)
C(132)–N(1)–Mo	125.8(3)	N(2)–N(1)–Mo	114.9(3)
N(2)–N(1)–C(132)	118.7(4)	C(232)–N(2)–N(1)	116.9(4)
C(232)–C(231)–P(2)	113.0(3)	C(231)–C(232)–N(2)	124.0(4)
C(233)–C(232)–N(2)	116.7(4)	C(233)–C(232)–C(231)	119.2(4)

frequencies for ^{1}H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 spectrometer (operating frequencies for ^{1}H and ^{31}P of 99.5 and 40.25 MHz respectively) or a Bruker AM400 spectrometer (operating frequencies for ^{1}H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively); ^{1}H and ^{13}C shifts are relative to tetramethylsilane and ^{31}P shifts are relative to 85% phosphoric acid. Mass spectra were recorded using a VG Autospec with 8 kV acceleration.

Preparation of $PPh_2CH_2C(Bu^t)=N-N=(Bu^t)CCH_2PPh_2$ **1**.—A solution of $LiBu^n$ (65.0 cm^3, 0.10 mol) in hexane was added to a solution of $MeC(Bu^t)=NN=C(Bu^t)Me$ (10.0 g, 0.05 mol) in dry tetrahydrofuran (150 cm^3) at −15 °C. After 1 h, a solution of chlorodiphenylphosphine (22.0 g, 0.10 mol) in dry tetrahydrofuran (100 cm^3) was added with stirring and the resultant solution was allowed to warm to room temperature. The solution was then evaporated to a low volume (*ca.* 50 cm^3) under reduced pressure, after which, addition of methanol gave the required product **1** (15.5 g, 54%) as pale yellow needles. A sample for analysis was obtained by recrystallisation from dichloromethane–methanol; m.p. 130–131 °C (Found: C, 75.5; H, 7.45; N, 4.75. $C_{36}H_{42}N_2P_2\cdot0.125CH_2Cl_2$ requires C, 75.4; H, 7.4; N, 4.9%).

Conversion of the Azine Diphosphine **1** *into the Diphosphine Dioxide* **2a**.—An excess of hydrogen peroxide (0.20 cm^3, 30% w/v) was added to a solution containing the azine diphosphine **1** (0.15 g, 0.26 mmol) in acetone (5 cm^3). After 1 h at 20 °C the required product **2a** had crystallised out as white prisms. Yield (0.13 g, 84%) (Found: C, 72.5; H, 7.15; N, 4.55. $C_{36}H_{42}N_2O_2P_2$ requires C, 72.45; H, 7.1; N, 4.7%).

Conversion of the Azine Diphosphine **1** *into the Diphosphine Disulfide* **2b**.—The azine diphosphine **1** (0.10 g, 0.18 mmol) and monoclinic sulfur (15 mg, 0.47 mmol) were refluxed together in benzene (5 cm^3) for 3 h. The reaction mixture was then evaporated to low volume (*ca.* 2 cm^3), giving the required product **2b** as white needles. Yield (97 mg, 87%) (Found: C, 68.65; H, 6.65; N, 4.3. $C_{36}H_{42}N_2P_2S_2$ requires C, 68.75; H, 6.75; N, 4.45%).

Preparation of Complexes.—fac-$[Mo(CO)_3\{PPh_2CH_2C(Bu^t)=NN=(Bu^t)CCH_2PPh_2\}]$ **3a**. (*i*) *From* $[Mo(CO)_3(\eta^6\text{-cht})]$. A solution containing the azine diphosphine **1** (0.28 g, 0.50 mmol) and $[Mo(CO)_3(\eta^6\text{-cht})]$ (0.14 g, 0.50 mmol) in benzene (7 cm^3) was put aside at *ca.* 20 °C for 16 h; the solution was then evaporated to a low volume (*ca.* 2 cm^3) under reduced pressure and addition of methanol gave the required product **3a** (0.33 g, 88%) as yellow microcrystals (Found: C, 65.5; H, 5.85; N, 3.35. $C_{39}H_{42}MoN_2O_3P_2\cdot C_6H_6$ requires C, 65.7; H, 5.9; N, 3.4%). Mass spectrum (EI): *m*/*z* 746 (M^+), 718 (M − CO), 690 (M − 2CO) and 662 (M − 3CO).

(*ii*) *From* $[Mo(CO)_6]$. A mixture of molybdenum hexacarbonyl (0.52 g, 2.0 mmol) and the azine diphosphine **1** (1.13 g, 2.0 mmol) was refluxed in decane (8 cm^3) for 10 min and then allowed to cool to *ca.* 20 °C. The product **3a** was filtered off and washed with light petroleum (b.p. 40–60 °C). Yield (0.91 g, 61%).

fac-$[W(CO)_3\{PPh_2CH_2C(Bu^t)=NN=(Bu^t)CCH_2PPh_2\}]$ **3b**. (*i*) *From* $[W(CO)_3(\eta^6\text{-cht})]$. The complex **3b** was prepared and isolated in a similar manner to the analogous molybdenum complex. It formed as yellow microcrystals. Yield 73% (Found: 58.2; H, 5.1; N, 2.8. $C_{39}H_{42}N_2O_3P_2W\cdot0.7C_6H_6$ requires C, 58.45; H, 5.25; N, 3.15%). Mass spectrum (FAB): *m*/*z* 832 (M^+), 776 (M − 2CO) and 748 (M − 3CO).

(*ii*) *From* $[W(CO)_6]$. Complex **3b** was also prepared directly from the hexacarbonyl in a similar manner to the analogous molybdenum complex **3a** except that a reflux time of 1.5 h was used. The product was recrystallised from dichloromethane–methanol as yellow microcrystals. Yield 38%.

fac-$[Cr(CO)_3\{PPh_2CH_2C(Bu^t)=NN=(Bu^t)CCH_2PPh_2\}]$ **3c**. The preparation and isolation of the chromium complex **3c** from $[Cr(CO)_3(\eta^6\text{-cht})]$ was similar to that used for the analogous molybdenum complex **3a** except that a heating time of 24 h at *ca.* 75 °C was used. Complex **3c** was obtained in 85% yield as yellow microcrystals (Found: C, 69.25; H, 6.25; N, 3.5. $C_{39}H_{42}CrN_2O_3P_2\cdot C_6H_6$ requires C, 69.4; H, 6.2; N, 3.6%). Mass spectrum (EI): *m*/*z* 700 (M^+) and 616 (M − 3CO).

$[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NN=C(Bu^t)CH_2PPh_2\}]$ **4a**. A solution containing $[Mo(CO)_4(nbd)]$ (60 mg, 0.20 mmol) and the azine diphosphine **1** (110 mg, 0.19 mmol) in benzene (3 cm^3) was put aside at *ca.* 20 °C for 5 h. The solution was then evaporated to a low volume (*ca.* 0.5 cm^3) under reduced pressure and addition of methanol gave the required product **4a** (110 mg, 75%) as yellow microcrystals (Found: C, 62.85; H, 5.6;

Table 8 Non-hydrogen atomic coordinates (× 10^4) for compound **3a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	1596.4(3)	486.4(2)	2168.0(1)
P(1)	2466.1(9)	803.9(5)	1178.1(4)
P(2)	3587.5(8)	962.3(5)	2800.3(4)
C(1)	413(4)	1287(2)	2332(2)
O(1)	−323(3)	1756(2)	2429(2)
C(2)	−39(4)	82(2)	1728(2)
O(2)	−1070(3)	−111(2)	1516(2)
C(3)	989(4)	−50(2)	2869(2)
O(3)	594(4)	−389(2)	3259(1)
C(111)	4075(2)	1285(1)	1099(1)
C(112)	4045(2)	2030(1)	1083(1)
C(113)	5256(2)	2416(1)	1079(1)
C(114)	6497(2)	2056(1)	1092(1)
C(115)	6527(2)	1310(1)	1108(1)
C(116)	5316(2)	925(1)	1111(1)
C(121)	1414(2)	1149(1)	536(1)
C(122)	149(2)	1449(1)	630(1)
C(123)	−665(2)	1712(1)	143(1)
C(124)	−214(2)	1676(1)	−439(1)
C(125)	1050(2)	1376(1)	−534(1)
C(126)	1864(2)	1113(1)	−46(1)
C(131)	2847(4)	−106(2)	921(2)
C(132)	3502(3)	−556(2)	1424(2)
C(133)	4420(4)	−1197(2)	1275(2)
C(134)	4503(5)	−1277(3)	590(2)
C(135)	3823(4)	−1889(2)	1509(2)
C(136)	5886(4)	−1089(2)	1555(2)
N(1)	3168(3)	−373(1)	1956(1)
N(2)	3650(3)	−792(2)	2458(1)
C(211)	4508(2)	1785(1)	2632(1)
C(212)	3702(2)	2399(1)	2601(1)
C(213)	4307(2)	3071(1)	2570(1)
C(214)	5717(2)	3130(1)	2571(1)
C(215)	6524(2)	2517(1)	2602(1)
C(216)	5919(2)	1844(1)	2633(1)
C(221)	3364(2)	1161(1)	3601(1)
C(222)	2062(2)	1166(1)	3812(1)
C(223)	1879(2)	1351(1)	4410(1)
C(224)	2998(2)	1533(1)	4796(1)
C(225)	4300(2)	1529(1)	4585(1)
C(226)	4483(2)	1343(1)	3987(1)
C(231)	4960(3)	275(2)	2804(2)
C(232)	4432(3)	−481(2)	2862(2)
C(233)	4896(4)	−926(2)	3415(2)
C(234)	4678(5)	−497(2)	3988(2)
C(235)	6420(4)	−1083(3)	3382(2)
C(236)	4126(5)	−1621(2)	3428(2)

N, 3.55. $C_{40}H_{42}MoN_2O_4P_2{\cdot}0.2C_6H_6$ requires C, 62.75; H, 5.55; N, 3.55%).

$[W(CO)_4\{PPh_2CH_2C(Bu^t)\text{=}NN\text{=}(Bu^t)CCH_2PPh_2\}]$ **4b**. The tungsten tetracarbonyl complex **4b** was prepared and isolated in a similar manner to the analogous molybdenum complex **4a** with a heating time of 5 h at 60 °C. It formed pale yellow microcrystals. Yield 65% (Found: C, 56.25; H, 4.95; N, 3.15. $C_{40}H_{42}N_2O_4P_2W{\cdot}0.2C_6H_6$ requires C, 56.45; H, 4.95; N, 3.2%).

$[Cr(CO)_4\{PPh_2CH_2C(Bu^t)\text{=}NN\text{=}(Bu^t)CCH_2PPh_2\}]$ **4c**. The chromium complex **4c** was prepared and isolated in an analogous manner to the tungsten complex **4b**. Yellow microcrystals were obtained in 59% yield (Found: C, 69.0; H, 6.0; N, 3.4. $C_{40}H_{42}CrN_2O_4P_2{\cdot}1.25C_6H_6$ requires C, 69.0; H, 6.0; N, 3.4%).

$[MoBr_2(CO)_2\{PPh_2CH_2C(Bu^t)\text{=}NN\text{=}(Bu^t)CCH_2PPh_2\}]$ **5**. (*i*) *From the tricarbonyl complex* **3a**. A solution of bromine (0.16 mmol) in tetrachloromethane (0.30 cm^3) was added to a solution of complex **3a** (0.12 g, 0.16 mmol) in dichloromethane (3 cm^3) at 0 °C. The resulting brown solution was evaporated to a low volume under reduced pressure. Addition of methanol then gave the required complex **5** (0.11 g, 78%), as yellow microcrystals (Found: C, 50.7; H, 4.7; N, 3.0. $C_{38}H_{42}Br_2MoN_2O_2P_2{\cdot}0.4CH_2Cl_2$ requires C, 50.65; H, 4.75; N, 3.1%).

(*ii*) *From the tetracarbonyl complex* **4a**. The molybdenum(II) complex **5** was isolated in 84% yield after treating the tetracarbonyl complex **4a** with 1 mol equivalent of bromine. It was shown to be identical with a sample prepared by method (*i*) by IR and by proton and ^{31}P-$\{^1H\}$ NMR spectroscopy.

$[WBr(CO)_3\{PPh_2CH_2C(Bu^t)\text{=}NN\text{=}(Bu^t)CCH_2PPh_2\}]BPh_4$ **6**. (*i*) *From the tricarbonyl complex* **3b**. A solution of bromine (0.19 mmol) in tetrachloromethane (0.4 cm^3) was added to a solution of the tricarbonyl complex **3b** (0.16 g, 0.19 mmol) in dichloromethane (3 cm^3) at 0 °C. The solvent was then removed under reduced pressure and the residue redissolved in methanol (3 cm^3). Addition of a solution of $NaBPh_4$ (0.18 g) in methanol (0.5 cm^3) then gave the required product **6** (0.20 g, 84%) as pale yellow microcrystals (Found: C, 60.45; H, 4.95; N, 2.3. $C_{63}H_{62}BBrN_2O_3P_2W{\cdot}0.25CH_2Cl_2$ requires C, 60.65; H, 5.05; N, 2.25%).

(*ii*) *From the tetracarbonyl complex* **4b**. Complex **6** was isolated in 80% yield after treating complex **4b** with 1 mol equivalent of bromine in tetrachloromethane solution in a similar fashion to method (*i*).

X-Ray Diffraction Analysis.—All diffraction measurements for both compounds were made at 200 K on a Stoe STADI4 diffractometer using graphite-monochromated radiation. Crystal data are listed in Table 9 together with details of data collection and structure refinement. The unit cell parameters listed are those obtained from the refinement of 2θ values of reflections measured at ±ω (40 in the range $40.0 < 2\theta < 50.0°$ for **1**, 52 in the range $20.0 < 2\theta < 25.0°$ for **3a**). Data were collected using ω–θ scans and, in the case of compound **1**, an online profile fitting method.[13] In both cases no significant variation was observed in the intensities of three hourly measured standard reflections. The data sets were corrected for Lorentz and polarisation factors and also absorption (using azimuthal psi scans).

The structure of compound **1** was solved by direct methods using SHELXS 86,[14] whilst that of **3a** was solved using standard heavy-atom methods using SHELX 76.[15] Both were refined by full-matrix least squares using SHELX 76. In both cases all non-hydrogen atoms were refined with anisotropic thermal parameters, with the exception of a disordered benzene molecule in **3a** which was treated in terms of two idealised interlocking hexagons (C–C 139.5 pm), each with an occupancy factor of 0.5 and an overall isotropic thermal parameter. In both cases all hydrogen atoms were included in calculated positions (C–H 96 pm) and were refined with an overall isotropic thermal parameter.

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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Table 9 Crystallographic data for compounds **1** and **3a**

Crystal data	**1**	**3a**
Formula	$C_{36}H_{42}N_2P_2$	$C_{39}H_{42}N_2O_3MoP_2\cdot C_6H_6$
M	564.69	822.78[a]
Crystal dimensions/mm	0.7 × 0.4 × 0.2	0.45 × 0.2 × 0.15
Crystal system	Monoclinic	Monoclinic
a/pm	1667.2(2)	985.7(1)
b/pm	572.85(6)	1870.2(2)
c/pm	1811.0(2)	2220.8(2)
β/°	111.595(8)	93.71(1)
U/nm^{-3}	1.6085(3)	4.0854(3)
Space group	$P2_1/n$	$P2_1/n$
Z	2	4
D_c/g cm^{-3}	1.17	1.34
F(000)	604	1711.82
μ/cm^{-1}	14.01	4.29
Radiation	Cu-Kα	Mo-Kα
λ/pm	154.184	71.069
Data collection		
Scan mode	ω–θ	ω–θ
Scan width	1.05° + α-doublet splitting	*b*
Scan speeds/° min^{-1}	1.5–8.0	*b*
$2\theta_{min,max}$/°	4.0, 120.0	4.0, 50.0
No. of data collected	2730	7455
No. of data observed[c]	2049	5219
Refinement		
ρ_{max},ρ_{min}/e Å^{-3}	0.51, −0.35	0.54, −0.28
Δ/σ_{max}	0.01	0.17
R[d]	0.0519	0.0354
R′[e]	0.0602	0.0477
Weighting parameter *g*[f]	0.0001	0.0004
No. of parameters	167	409

[a] Includes benzene solvate. [b] Scan divided into 30 steps, scan width and step sizes calculated from a learnt profile, scan speeds 0.4–1.5 s per step. [c] Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$. [d] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [e] $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$. [f] $w = [\sigma^2(|F_o|) + g(|F_o|)^2]^{-1}$.

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