New Bidentate Ligands $PPh_2CH_2C(Bu^t)=NNR_2$ (R = H or Me) and $PPh_2CH_2C(Bu^t)=NN=CHPh$ and their Complexes with Group 6 Metal Carbonyls†

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Treatment of *tert*-butylmethyl ketone dimethylhydrazone with LiBu, followed by PPh_2Cl, gave the crystalline phosphino dimethylhydrazone $PPh_2CH_2C(Bu^t)=NNMe_2$ **2a** having the $C=NNMe_2$ group in the *Z* configuration. This phosphine with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) gave $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNMe_2\}]$ **3a**, with a six-membered chelate ring; the corresponding tungsten **3b** and chromium **3c** complexes were made similarly. When phosphine **2a** was heated with $[Mo(CO)_6]$ some **3a** was formed together with the isomeric complex $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=N\text{-}NMe_2\}]$ **4**, with a five-membered chelate ring and an *E* arrangement around $C=NNMe_2$. When **3a** was heated in diglyme $[MeO(CH_2)_2O(CH_2)_2OMe]$ to *ca.* 150 °C the phosphino imine complex $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NH\}]$ **5** was formed. Compound **2a** with hydrazine gave the corresponding phosphino hydrazone **2c**, containing a $C=NNH_2$ moiety, in over 90% yield. The phosphines **2a** or **2c**, with sulfur, gave the corresponding phosphine sulfides. The phosphine **2c** with $[M(CO)_4(nbd)]$ gave $[M(CO)_4\{PPh_2CH_2C(Bu^t)=NNH_2\}]$ (M = Mo **3d**, W **3e** or Cr **3f**). When **3d** was heated in diglyme to *ca.* 150 °C it also gave complex **5**. The oxidation of molybdenum(0) complex **3d** with bromine gave the seven-co-ordinate molybdenum(II) complex $[MoBr_2(CO)_3\{PPh_2CH_2C(Bu^t)=NNH_2\}]$ **6**. Compound **2c** was condensed with benzaldehyde to give the phosphino mixed-azine $PPh_2CH_2C(Bu^t)=NN=CHPh$ **7a**, which with H_2O_2 formed the phosphine oxide **7b**. The phosphine **7a** reacted with $[M(CO)_4(nbd)]$ to give $[M(CO)_4\{PPh_2CH_2C(Bu^t)=NN=CHPh\}]$ (M = Mo **8a**, W **8b** or Cr **8c**). Complex **8a** with bromine gave the seven-co-ordinate molybdenum(II) complex $[MoBr_2(CO)_3\{PPh_2CH_2C(Bu^t)=NN=CHPh\}]$ **9**. Crystals of complex **3a** are monoclinic, space group $P2_1/n$ with $a = 892.3(1)$, $b = 1920.1(3)$, $c = 1493.6(3)$ pm, $\beta = 105.67(1)°$ and $Z = 4$, $R = 0.0250$ for 3530 observed reflections. The structure shows that the $C=NNMe_2$ group has the *Z* configuration and that the NMe_2 group is co-ordinated to molybdenum, giving a six-membered ring.

In previous papers we have described the preparation of *exo*-3-diphenylphosphino-(1*R*)-(+)-camphor (-bornan-2-one) dimethylhydrazone[1] and its complexes with Group 6 metal carbonyls,[1,2] and also with Pd^{II} and Pt^{II}.[3] We have also reported[4] the synthesis of a new azine diphosphine, (*Z,Z*)-*tert*-butyl diphenylphosphinomethyl ketone azine **1**, and its ability to co-ordinate to Group 6 metal carbonyls, either as a bi- or as a tri-dentate ligand. We have now extended this type of chemistry to phosphino hydrazones, also derived from *tert*-butylmethyl ketone. Since hydrazones have a very extensive chemistry and can be used as intermediates for the synthesis of many types of molecules and frameworks, we anticipate that these types of molecules will open up new areas of co-ordination chemistry.

Results and Discussion

tert-Butyldiphenylphosphinomethyl ketone dimethylhydrazone **2a** was prepared in *ca.* 80% yield by deprotonating *tert*-butylmethyl ketone dimethylhydrazone[5] with butyllithium and then treating the resulting carbanion with chlorodiphenyl phosphine. The preparative, microanalytical and mass spectral data for this new functionalised phosphine and other new compounds are in the Experimental section. Infrared and $^{31}P\text{-}\{^1H\}$ NMR data are in Table 1, and proton NMR data are in Table 2. The stereochemistry around the C=N bond of *exo*-3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone was shown to be *Z*[1] by X-ray crystallography and the crystal structure of the azine diphosphine **1** showed it to have the *Z,Z* configuration around the C=N bonds.[4] Therefore we suggest that the phosphino dimethylhydrazone **2a** also has the *Z* configuration. It was converted into the corresponding phosphine sulfide **2b** by the treatment with monoclinic sulfur.

First we have investigated this phosphino dimethylhydrazone **2a** as a ligand for Group 6 metal carbonyls. Treatment of **2a** with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) gave the expected product $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNMe_2\}]$ **3a**, containing a six-membered chelate ring. The structure of **3a** was determined by X-ray crystallography and is shown in Fig. 1; the compound was also fully characterised by elemental analysis and spectroscopy. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at δ(P) 48.0 and the proton NMR spectrum showed both NMe_2 methyls to be equivalent. The corresponding tungsten **3b** or chromium **3c** complexes were obtained as yellow crystalline solids by displacing norbornadiene from $[M(CO)_4(nbd)]$ (M = W or Cr) with the phosphino dimethylhydrazone **2a**.

In our previous work the molybdenum tetracarbonyl complex of (*Z*)-*exo*-3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone was isomerised to the corresponding *E* complex, with a five-membered chelate ring, by heating it in boiling diglyme (2,5,8-trioxanonane) or decane.[1] Also when (*Z*)-*exo*-3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone was heated with molybdenum hexacarbonyl in

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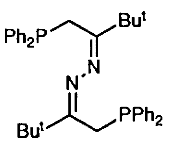
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

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

Compound	IR bands (cm^{-1})			
	ν(C=N)[b]	ν(N–H)[b]	ν(C≡O)[c]	$^{31}P-\{^1H\}$ NMR,[a] δ_P
2a	1610m			−9.7
2b	1620m			37.6
2c	1640w	3350m, 3330m (br)		−22.6
2d	1620 (br)w	3320m, 3200w		34.7
3a	1620w		2025, 1910, 1850	48.0
3b	1625m		2010, 1890, 1840	43.8 (266)
3c	1630m		2010, 1890, 1840	65.7
3d	1630w	3355m, 3225w	2020, 1910, 1850	49.6
3e	1625w	3330m, 3220w	2020, 1900, 1850	42.0 (264)
3f	1635w	3340m, 3220w	2010, 1895, 1845	66.9
4	1585w		2025, 1910, 1850	38.2
5	1600w	3300m	2020, 1905, 1850	47.8
6	1625m		2060, 1985, 1925	61.8[d]
7a	1615m			−10.0
7b	1615m			24.6
8a	1595w		2010, 1900, 1850	49.6
8b	1600w		2015, 1890, 1850	42.9 (263)
8c	1600w		2010, 1900, 1850	67.1
9	1595w		2060, 1990, 1920	55.4

[a] Recorded at 36.2 MHz, chemical shifts (±0.1 ppm) relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise stated, $^1J(WP)$/Hz in parentheses. [b] As KBr disc. [c] In CH_2Cl_2, all carbonyl bands are strong. [d] In CD_2Cl_2.



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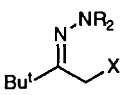
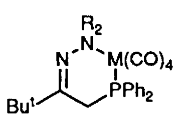
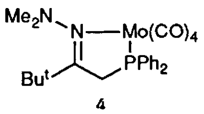


	R	X
2a	Me	PPh$_2$
2b	Me	P(S)Ph$_2$
2c	H	PPh$_2$
2d	H	P(S)Ph$_2$



	R	M
3a	Me	Mo
3b	Me	W
3c	Me	Cr
3d	H	Mo
3e	H	W
3f	H	Cr



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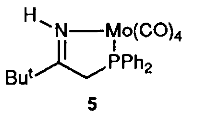

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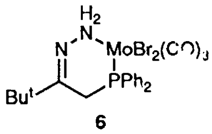

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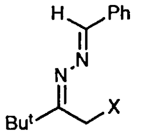
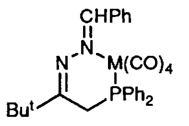
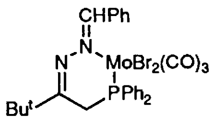


	X
7a	PPh$_2$
7b	P(O)Ph$_2$



	M
8a	Mo
8b	W
8c	Cr



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decane the same *E* complex was formed.[1] In an attempt to prepare an analogous five-membered chelate ring complex, the dimethylhydrazone **2a** was heated with [Mo(CO)$_6$] in boiling decane for *ca.* 15 min. Some decomposition occurred and we were able to demonstrate the formation of the hoped-for complex **4**, but it was contaminated with some of the six-membered ring isomer **3a** as shown by elemental analysis and by the IR, mass and proton NMR data (the ratio of **3a**:**4** present in the mixture was 1.7:1). Attempts to prepare pure samples of **4** were unsuccessful; an attempt to prepare it by heating a solution of the six-membered chelate ring chelate, **3a**, in diglyme to *ca.* 150 °C for 3 h caused a lot of decomposition and the only product isolated was the imine complex **5** [δ(P) 47.8] as shown by microanalytical, IR, mass and proton NMR data. Separate experiments (followed by $^{31}P-\{^1H\}$ NMR spectroscopy) suggested that complex **4** was present in the reaction mixture formed by heating **3a** in diglyme at 150 °C but we could not isolate it. The $^{31}P-\{^1H\}$ NMR studies also showed that, when **3a** was heated in diglyme in the presence of traces of acetic acid, conversion into **5** was somewhat faster, although the yield was no better.

It is known that dimethylhydrazones of aldehydes or ketones can be converted into hydrazones by heating them with hydrazine.[6] We therefore attempted to convert the phosphino dimethylhydrazone (=NNMe$_2$) **2a** into the corresponding phosphino hydrazone (=NNH$_2$) by such a hydrazine-exchange reaction. On heating **2a** with hydrazine in ethanol the exchange was slow but in the presence of acetic acid as catalyst, it was complete in 2 h and the crystalline phosphino hydrazone **2c** was isolated in over 90% yield. This new functionalised phosphino hydrazone was fully characterised. The $^{31}P-\{^1H\}$ NMR spectrum showed a singlet at δ(P) −22.6 and in the infrared spectrum ν(N–H) occurred at 3350 and 3330 cm^{-1}. Prolonged (16 h) treatment of azine **1**[4] with hydrazine hydrate in the presence of acetic acid also gave the phosphino hydrazone **2c** but the yield was less good. Treatment of **2c** with sulfur gave the corresponding phosphine sulfide hydrazone **2d**, which was fully characterised.

Treatment of phosphino hydrazone **2c** with Group 6 metal carbonyl norbornadiene derivatives [M(CO)$_4$(nbd)] (M = Cr, Mo or W) gave the chelate complexes **3d**–**3f**. We formulate these as six-membered ring chelates by analogy with the chelates described above but also because in the ^1H NMR spectra coupling of 7–8 Hz was found for *J*(PH). This value is much more in keeping with a three- than a four-bond coupling, as it would be if the chelate ring were five-membered and the configuration around the C=N were *E*.

We found that the phosphino hydrazone complex of molybdenum, **3d**, when heated in diglyme at 150 °C for 2–3 h, gave the imino complex **5** together with a lot of decomposition, *i.e.* the behaviour is similar to that of the corresponding phosphino dimethylhydrazone complex, **3a**, which also decomposed to **5** at 150 °C, as described above. The oxidation of the tetracarbonylmolybdenum(0) complex **3d** with 1 equivalent of bromine gave the tricarbonylmolybdenum(II) complex

Table 2 Proton NMR data[a]

Compd.	δ($\mathrm{Bu^t}$)	δ(CH_2)	Others
2a	1.12 (s)	3.05 [2 H, d, ^2J(PH) 2.9]	2.10 (6 H, s, NMe_2)
2b	1.17 (s)	3.50 [2 H, d, ^2J(PH) 13.6]	1.90 (6 H, s, NMe_2)
2c	0.98 (s)	3.10 [2 H, d, ^2J(PH) 2.2]	4.75 (2 H, s, br, NH_2)
2d	0.82 (s)	3.80 [2 H, d, ^2J(PH) 15.0]	5.60 (2 H, s, br, NH_2)
3a	0.77 (s)	3.18 [2 H, d, ^2J(PH) 9.3]	3.02 (6 H, s, NMe_2)
3b	0.78 (s)	3.24 [2 H, d, ^2J(PH) 9.7]	3.20 (6 H, s, NMe_2)
3c	0.77 (s)	3.10 [2 H, d, ^2J(PH) 9.5]	2.90 (6 H, s, NMe_2)
3d	0.76 (s)	3.10 [2 H, d, ^2J(PH) 8.8]	5.40 [2 H, d, br, ^3J(PH) 6.8, NH_2]
3e	0.77 (s)	3.10 [2 H, d, ^2J(PH) 9.8]	5.70 [2 H, d, br, ^3J(PH) 8.0, NH_2]
3f	0.76 (s)	3.01 [2 H, d, ^2J(PH) 9.3]	4.90 [2 H, d, br, ^3J(PH) 8.3, NH_2]
4	1.42 (s)	3.55 [2 H, d, ^2J(PH) 7.8]	2.41 (6 H, s, NMe_2)
5	1.23 (s)	3.34 [2 H, d, ^2J(PH) 21.9]	9.46 [1 H, d, br, ^4J(PH) 5.6, NH]
6[b]	0.64 (s)	3.60 [2 H, d, ^2J(PH) 14.0]	6.60 (2 H, s, br, NH_2)
7a	1.22 (s)	3.52 [2 H, d, ^2J(PH) 3.2]	8.04 (1 H, s, N=CH)
7b	1.25 (s)	3.90 [2 H, d, ^2J(PH) 15.6]	8.00 (1 H, s, N=CH)
8a	0.91 (s)	2.90 [2 H, d, ^2J(PH) 10.0]	8.10 [1 H, d, ^4J(PH) 1.5, N=CH]
8b	0.92 (s)	3.00 [2 H, d, ^2J(PH) 10.2]	8.27 [1 H, d, ^4J(PH) 1.7, N=CH]
8c	0.91 (s)	2.84 [2 H, d, ^2J(PH) 10.0]	8.09 [1 H, d, ^4J(PH) 2.0, N=CH]
9	0.79 (s)	3.20 [2 H, d, ^2J(PH) 13.0]	9.00 [1 H, d, ^4J(PH) 1.0, N=CH]

[a] Recorded at 100 MHz, chemical shifts (±0.01 ppm) relative to $SiMe_4$, solvent $CDCl_3$ unless otherwise stated, coupling constants *J* in Hz; s = singlet, d = doublet and br = broad. [b] In CD_2Cl_2.

Table 3 Bond lengths (pm) and angles (°) for compound **3a** with estimated standard deviations (e.s.d.s) in parentheses

N(2)–Mo(1)	237.0(4)	P(6)–Mo(1)	250.7(4)
C(7)–Mo(1)	204.7(5)	C(8)–Mo(1)	195.0(5)
C(9)–Mo(1)	199.8(5)	C(10)–Mo(1)	204.5(5)
C(21)–N(2)	149.8(4)	C(22)–N(2)	149.5(4)
N(3)–N(2)	146.3(4)	C(4)–N(3)	128.3(4)
C(41)–C(4)	153.4(5)	C(5)–C(4)	151.3(5)
C(42)–C(41)	153.2(6)	C(43)–C(41)	153.9(5)
C(44)–C(41)	152.5(6)	P(6)–C(5)	185.7(4)
C(611)–P(6)	184.8(3)	C(621)–P(6)	184.3(3)
O(7)–C(7)	113.9(4)	O(8)–C(8)	116.4(4)
O(9)–C(9)	114.6(4)	O(10)–C(10)	114.7(4)
P(6)–Mo(1)–N(2)	82.9(1)	C(7)–Mo(1)–N(2)	92.5(2)
C(7)–Mo(1)–P(6)	95.2(2)	C(8)–Mo(1)–N(2)	174.4(1)
C(8)–Mo(1)–P(6)	91.7(2)	C(8)–Mo(1)–C(7)	89.6(2)
C(9)–Mo(1)–N(2)	99.0(2)	C(9)–Mo(1)–P(6)	177.3(1)
C(9)–Mo(1)–C(7)	86.6(2)	C(9)–Mo(1)–C(8)	86.2(2)
C(10)–Mo(1)–N(2)	86.1(2)	C(10)–Mo(1)–P(6)	91.1(2)
C(10)–Mo(1)–C(7)	173.4(1)	C(10)–Mo(1)–C(8)	92.4(2)
C(10)–Mo(1)–C(9)	87.2(2)	C(21)–N(2)–Mo(1)	115.2(2)
C(22)–N(2)–Mo(1)	108.8(2)	C(22)–N(2)–C(21)	106.2(3)
N(3)–N(2)–Mo(1)	111.0(2)	N(3)–N(2)–C(21)	112.2(3)
N(3)–N(2)–C(22)	102.5(3)	C(4)–N(3)–N(2)	121.3(3)
C(41)–C(4)–N(3)	115.4(3)	C(5)–C(4)–N(3)	127.6(3)
C(5)–C(4)–C(41)	117.1(3)	C(42)–C(41)–C(4)	109.8(3)
C(43)–C(41)–C(4)	108.6(3)	C(43)–C(41)–C(42)	109.7(3)
C(44)–C(41)–C(4)	112.1(3)	C(44)–C(41)–C(42)	108.2(3)
P(6)–C(5)–C(4)	113.2(3)	C(5)–P(6)–Mo(1)	110.7(2)
C(611)–P(6)–Mo(1)	117.7(2)	C(611)–P(6)–C(5)	102.7(2)
C(621)–P(6)–Mo(1)	119.9(2)	C(621)–P(6)–C(5)	102.0(2)
C(621)–P(6)–C(611)	101.4(2)	O(7)–C(7)–Mo(1)	174.4(2)
O(8)–C(8)–Mo(1)	178.7(2)	O(9)–C(9)–Mo(1)	174.3(2)
O(10)–C(10)–Mo(1)	176.9(2)		

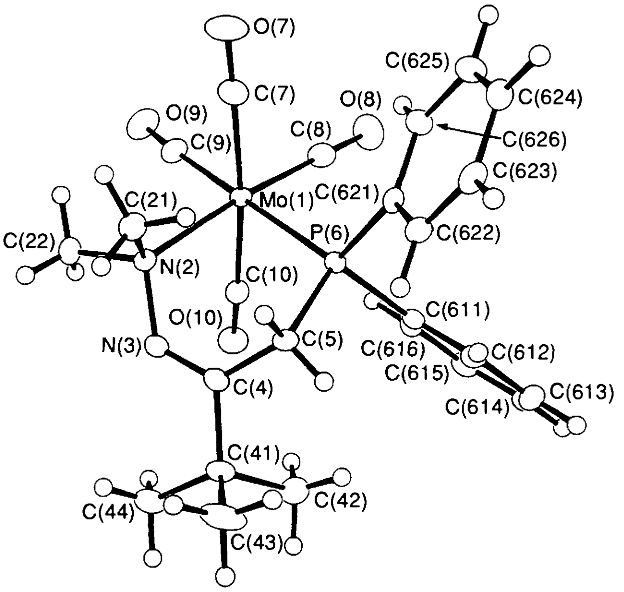

Fig. 1 An ORTEP[8] representation of the crystal and molecular structure of $\mathrm{Mo(CO)_4\{PPh_2CH_2C(Bu^t){=}NNMe_2\}}$] **3a**

$\mathrm{[MoBr_2(CO)_3\{PPh_2CH_2C(Bu^t){=}NNH_2\}]}$ **6**; characterising data are in the Experimental section or in Tables 1 and 2. The strong carbonyl absorptions, ν(C≡O), at 2060, 1985 and 1925 cm^{-1} is in the expected range for a tricarbonyl derivative of molybdenum(II).[2,7]

Attempts were also made to deprotonate the NH_2 group in complex **3d** by treatment with lithium bis(trimethylsilyl)amide in dry tetrahydrofuran (thf). The resultant solution was examined by $^{31}P-\{^1H\}$ NMR spectroscopy, which showed a singlet at δ(P) 65.4, *i.e.* 14.6 ppm downfield from the starting material. It is possible that the hoped-for deprotonated product was formed but attempts to methylate this product, by treatment with methyl iodide, or to introduce a trimethylsilyl group, by treatment with trimethylsilyl chloride, were not successful and the only solid product isolated from these mixtures was the starting material **3d**.

Since the NH_2 group of a hydrazone is often very nucleophilic and will condense readily with aldehydes or ketones, we have treated phosphino hydrazone **2c** with benzaldehyde. Condensation was rapid and the expected phosphino mixed azine **7a** was readily isolated as a pale yellow crystalline solid in 59% yield; it is likely that the orientation around the $\mathrm{PPh_2CH_2C(Bu^t){=}N{-}N}$ moiety is *Z* and around N–N=CHPh is *E*. This novel ligand was fully characterised and also converted into the corresponding phosphine oxide **7b** by treatment with hydrogen peroxide.

We have studied the mixed azine **7a** as a ligand for the Group 6 metal carbonyls. Treatment of $\mathrm{[Mo(CO)_4(nbd)]}$ or $\mathrm{[Mo(CO)_6]}$ with **7a** gave the chelate complex $\mathrm{[Mo(CO)_4\{PPh_2CH_2C(Bu^t){=}NN{=}CHPh\}]}$ **8a**. The corresponding tungsten **8b** and chromium **8c** complexes were made similarly. The characterising data for complex **8a**–**8c** are in the Experimental section or in Tables 1 and 2. The observed weak coupling [*J*(PH) = 1.5–2.0 Hz] between the olefinic proton (N=CH) and the phosphorus is most likely a four- than a five-bond coupling. Therefore we formulate these complexes as six-membered chelates. We also oxidised the molybdenum complex **8c** with 1 equivalent of bromine to give the seven-co-ordinate complex $\mathrm{[MoBr_2(CO)_3\{PPh_2CH_2C(Bu^t){=}NN{=}CHPh\}]}$ **9**, which was fully characterised. Although the configuration around the N–N=CHPh double bond in **7a** or **7b** is probably *E*, as stated above, the corresponding configuration in the complexes of type **8** or **9** is not known.

Hydrazones show many kinds of reactions and we anticipate that the phosphino hydrazones such as **2c** could be used as

Table 4 Atom coordinates (× 10⁴) for compound **3a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo(1)	1401.3(2)	1890.1(1)	7723.1(1)
N(2)	3746(2)	1459(1)	8727(1)
C(21)	4962(3)	1999(1)	9111(2)
C(22)	3388(3)	1121(1)	9546(2)
N(3)	4358(2)	879(1)	8297(1)
C(4)	4895(3)	973(1)	7591(2)
C(41)	5485(3)	315(1)	7213(2)
C(42)	4531(3)	187(2)	6208(2)
C(43)	7208(3)	422(2)	7243(2)
C(44)	5358(3)	−329(1)	7785(2)
C(5)	4999(3)	1651(1)	7095(2)
P(6)	3090.4(7)	2091.5(3)	6652.0(4)
C(611)	2400(2)	1755(1)	5452(1)
C(612)	3255(2)	1874(1)	4811(1)
C(613)	2734(2)	1608(1)	3911(1)
C(614)	1357(2)	1224(1)	3652(1)
C(615)	502(2)	1105(1)	4293(1)
C(616)	1023(2)	1371(1)	5193(1)
C(621)	3679(2)	2984(1)	6445(1)
C(622)	5133(2)	3138(1)	6314(1)
C(623)	5484(2)	3818(1)	6112(1)
C(624)	4381(2)	4345(1)	6040(1)
C(625)	2927(2)	4191(1)	6171(1)
C(626)	2576(2)	3511(1)	6373(1)
C(7)	1738(3)	2860(1)	8312(2)
O(7)	1817(2)	3391(1)	8661(2)
C(8)	−433(3)	2236(1)	6799(2)
O(8)	−1513(2)	2441(1)	6234(1)
C(9)	−24(3)	1712(1)	8525(2)
O(9)	−940(2)	1626(1)	8924(1)
C(10)	986(3)	886(1)	7266(2)
O(10)	716(2)	319(1)	7039(1)

intermediates for the synthesis of whole new types of ligands, including multidentate ligands, macrocycles, *etc*., this we are investigating.

Crystal Structure of $[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNMe_2\}]$ **3a**.—The crystal structure of compound **3a** is shown in Fig. 1, selected bond lengths and angles in Table 3, and atom coordinates in Table 4. The structure shows that the C=NNMe$_2$ group is in the *Z* configuration and that the NMe$_2$ nitrogen is co-ordinated to molybdenum, giving a six-membered ring. There is nothing abnormal about the bond lengths and angles.

Experimental

The apparatus used and general techniques were the same as in other recent papers from this laboratory.[4] *tert*-Butyl methyl ketone dimethylhydrazone was prepared according to a literature procedure.[5]

Preparations.—tert-*Butyl diphenylphosphinomethyl ketone dimethylhydrazone* **2a**. A solution of LiBu^n in hexane (1.6 mol dm^{-3}, 27.0 cm^3, 0.042 mol) was added to a solution of *tert*-butylmethyl ketone dimethylhydrazone (6.0 g, 7.4 cm^3, 0.042 mol) in dry tetrahydrofuran (90 cm^3) at −15 °C. After 1 h a solution of chlorodiphenylphosphine (7.5 cm^3, 0.042 mol) in dry tetrahydrofuran (40 cm^3) was added with stirring, and the reaction mixture then allowed to warm to room temperature, after which it was evaporated to a low volume under reduced pressure. Addition of methanol to the residue gave the required phosphine **2a** as white needles, m.p. 85–87 °C. Yield 10.1 g, 81% (Found: C, 73.6; H, 8.5; N, 8.5. $C_{20}H_{27}N_2P$ requires C, 73.6; H, 8.35; N, 8.6%). Mass spectrum (electron impact, EI); *m/z* 326 (M^+) and 269 (M − Bu^t).

Conversion of compound **2a** *into the corresponding phosphine sulfide* **2b**. A mixture of the phosphino dimethylhydrazone **2a** (0.20 g, 0.61 mmol) and monoclinic sulfur (20 mg, 0.62 mmol) was refluxed in benzene (5 cm^3) for 2 h. The sulfide **2b** separated and was isolated as white prisms. Yield 0.20 g, 92% (Found: C, 67.45; H, 7.85; N, 7.90. $C_{20}H_{27}N_2PS$ requires C, 67.4; H, 7.65; N, 7.85%).

tert-*Butyl diphenylphosphinomethyl ketone hydrazone* **2c**. (*i*) *From compound* **2a**. A mixture of compound **2a** (2.0 g, 61.4 mmol), an excess of hydrated hydrazine (0.7 cm^3) and glacial acetic acid (0.5 cm^3) was refluxed in ethanol (7 cm^3) for 2 h. The solution was evaporated to low volume under reduced pressure and the concentrate was cooled to −30 °C, which gave compound **2c** as white needles, m.p. 88–90 °C. Yield 1.78 g, 94% (Found: C, 73.25; H, 7.95; N, 9.65. $C_{18}H_{23}N_2P$ requires C, 72.45; H, 7.75; N, 9.4%). Mass spectrum (EI): *m/z* 298 (M^+), 282 (M − NH$_2$) and 241 (M − Bu^t).

(*ii*) *From compound* **1**. A mixture of the azine diphosphine **1** (0.65 g, 1.15 mmol), an excess of hydrated hydrazine (1.0 cm^3) and acetic acid (1.0 cm^3) was refluxed in propan-2-ol for 16 h. The reaction mixture was then concentrated to a small volume under reduced pressure, and ethanol (*ca*. 5 cm^3) added. It was then cooled to −30 °C, after which the required compound **2c** separated and was isolated as white needles. Yield 0.35 g, 51%.

Conversion of compound **2c** *into the corresponding sulfude* **2d**. The phosphino hydrazone **2c** (0.20 g, 0.67 mmol) and monoclinic sulfur (22 mg, 0.69 mmol) were refluxed together in benzene (5 cm^3) for 1 h. The solution was then evaporated to a low volume under reduced pressure and methanol added to the residue. This gave the required sulfide **2d** as white prisms. Yield 112 mg, 51% (Found: C, 65.5; H, 7.15; N, 8.5. $C_{18}H_{23}N_2PS$ requires C, 65.5; H, 7.0; N, 8.5%).

$[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNMe_2\}]$ **3a**. A solution containing the phosphino dimethylhydrazone **2a** (0.49 g, 1.50 mmol) and $[Mo(CO)_4(nbd)]$ (0.48 g, 1.60 mmol) in benzene (5 cm^3) was put aside for 15 h. It was then filtered and the filtrate evaporated to a low volume under reduced pressure. Addition of ethanol to the residue gave complex **3a** as yellow microcrystals. Yield 0.62 g, 77% (Found: C, 53.85; H, 5.1; N, 5.25. $C_{24}H_{27}MoN_2O_4P$ requires C, 53.95; H, 5.1; N, 5.25%). Mass spectrum (EI): *m/z* 536 (M^+), 508 (M − CO), 480 (M − 2CO) and 424 (M − 4CO).

$[W(CO)_4\{PPh_2CH_2C(Bu^t)=NNMe_2\}]$ **3b**. A solution containing phosphino dimethylhydrazone **2a** (0.10 g, 0.31 mmol) and $[W(CO)_4(nbd)]$ (0.12 g, 0.30 mmol) was refluxed in benzene (5 cm^3) for 20 h. The reaction mixture was then filtered and the filtrate evaporated to low volume under reduced pressure. Addition of methanol to the residue gave the required product **3b** as yellow microcrystals. Yield 0.125 g, 66% (Found: C, 46.5; H, 4.5; N, 4.55. $C_{24}H_{27}N_2O_4PW$ requires C, 46.3; H, 4.4; N, 4.5%). Mass spectrum (EI): *m/z* 622 (M^+), 566 (M − 2CO) and 510 (M − 4CO).

$[Cr(CO)_4\{PPh_2CH_2C(Bu^t)=NNMe_2\}]$ **3c**. A solution containing phosphino dimethylhydrazone **2a** (0.10 g, 0.31 mmol) and $[Cr(CO)_4(nbd)]$ (78 mg, 0.30 mmol) in benzene (4 cm^3) was refluxed for 24 h. The solution was then evaporated to low volume under reduced pressure. Addition of methanol to the residue gave the required product **3c** as yellow microcrystals. Yield 120 mg, 80% (Found: C, 58.7; H, 5.65; N, 5.85. $C_{24}H_{27}CrN_2O_4P$ requires C, 58.8; H, 5.55; N, 5.7%). Mass spectrum (EI): *m/z* 490 (M^+) and 406 (M − 3CO).

$[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=NNH_2\}]$ **3d**. A solution of the phosphino hydrazone **2c** (0.15 g, 0.5 mmol) and $[Mo(CO)_4(nbd)]$ (0.15 g, 0.4 mmol) in benzene (5 cm^3) was put aside at *ca*. 20 °C for 1 h. The required complex **3d** deposited as yellow prisms, which were filtered off and washed with benzene. Yield 0.175 g, 86% (Found: C, 57.0; H, 4.95; N, 4.8. $C_{22}H_{23}MoN_2O_4P\cdot 0.9C_6H_6$ requires C, 57.0; H, 4.95; N, 4.85%). Mass spectrum (EI): *m/z* 508 (M^+), 480 (M − CO), 452 (M − 2CO) and 396 (M − 4CO).

$[W(CO)_4\{PPh_2CH_2C(Bu^t)=NNH_2\}]$ **3e**. A solution of the phosphino hydrazone **2c** (65 mg, 0.22 mmol) and [W(CO)$_4$(nbd)] (80 mg, 0.21 mmol) in benzene (2 cm^3) was refluxed for 24 h. Complex **3e** was deposited as yellow microcrystals, which were filtered off and washed with cyclohexane. Yield 74 mg, 61% (Found: C, 49.7; H, 4.2; N, 4.15. $C_{22}H_{23}N_2O_4PW{\cdot}0.9C_6H_6$ requires C, 49.5; H, 4.3; N, 4.2%). Mass spectrum (EI): *m/z* 594 (M^+), 538 (M − 2CO) and 482 (M − 4CO).

[Cr(CO)$_4${PPh$_2$CH$_2$C(Bu^t)=NNH$_2$}] **3f**. The phosphino hydrazone **2c** (95 mg, 0.32 mmol) and [Cr(CO)$_4$(nbd)] (80 mg, 0.31 mmol) were refluxed in benzene (2 cm^3) for 18 h. The required product **3f** was deposited as yellow microcrystals, which were filtered off and washed with cold methanol. Yield 112 mg, 77% (Found: C, 59.95; H, 5.35; N, 5.35. $C_{22}H_{23}CrN_2O_4P{\cdot}0.5C_6H_6$ requires C, 59.95; H, 5.25; N, 5.6%). Mass spectrum (EI): *m/z* 462 (M^+), 447 (M − NH), 406 (M − 2CO), 378 (M − 3CO) and 350 (M − 4CO).

Reaction of compound **2a** *with* [Mo(CO)$_6$]. A mixture of [Mo(CO)$_6$] (0.52 g, 2.0 mmol) and the phosphine **2a** (0.65 g, 2.0 mmol) was gently refluxed in decane (8 cm^3) for 15 min. Some decomposition occurred; the resulting dark solution was allowed to cool to *ca.* 20 °C. The supernatant liquid was decanted from the precipitate, which was then crystallised from dichloromethane–ethanol to give a mixture (≈1.7:1) of complexes **3a** and **4**. Yield 0.55 g, 51% (Found: C, 54.05; H, 5.1; N, 5.25. $C_{24}H_{27}MoN_2O_4P$ requires C, 53.95; H, 5.1; N, 5.25%). Mass spectrum (EI): *m/z* 536 (M^+), 508 (M − CO), 480 (M − 2CO) and 424 (M − 4CO).

[Mo(CO)$_4${PPh$_2$CH$_2$C(Bu^t)=NH}] **5**. A solution containing the dimethylhydrazone complex **3a** (0.48 g, 0.89 mmol) and a trace of acetic acid in diglyme (6 cm^3) was heated to *ca.* 150 °C for 30 min and allowed to cool. The solvent was removed under reduced pressure, and the residue extracted into dichloromethane (5 cm^3) which was filtered through Celite. The filtrate was concentrated to a low volume (*ca.* 0.5 cm^3) and methanol (*ca.* 1.5 cm^3) added to give the imine complex **5** as yellow prisms. Yield 0.085 g, 19% (Found: C, 53.85; H, 4.55; N, 2.85. $C_{22}H_{22}MoNO_4P$ requires C, 53.75; H, 4.5; N, 2.85%). Mass spectrum (EI): *m/z* 493 (M^+), 465 (M − CO), 437 (M − 2CO), 409 (M − 3CO) and 381 (M − 4CO).

[MoBr$_2$(CO)$_3${PPh$_2$CH$_2$C(Bu^t)=NNH$_2$}] **6**. A solution of bromine in carbon tetrachloride 0.533 mol dm^{-3}, 0.38 cm^3, 0.2 mmol) was added to a solution containing the tetracarbonylmolybdenum(0) complex **3d** (80 mg, 0.15 mmol) in dichloromethane (1.5 cm^3). A vigorous effervescence occurred. The reaction mixture was evaporated to a low volume under reduced pressure, and methanol added to the residue to give the dibromide **6** as yellow microcrystals. Yield 62 mg, 61% (Found: C, 38.7; H, 3.45; N, 4.35. $C_{21}H_{23}Br_2MoN_2O_3P{\cdot}0.25CH_2Cl_2$ requires C, 38.55; H, 3.5; N, 4.25%).

PPh$_2$CH$_2$C(Bu^t)=NN=CHPh **7a**. Benzaldehyde (0.35 cm^3, 3.44 mmol) was added to a solution containing the phosphino hydrazone **2c** (1.0 g, 3.35 mmol) in dry benzene (*ca.* 5 cm^3). After 30 min the solvent was removed under reduced pressure and the residue was triturated with degassed methanol to give the required product **7a** as a pale yellow solid. Yield 0.77 g, 59% (Found: C, 77.8; H, 7.2; N, 7.3. $C_{25}H_{27}N_2P$ requires C, 77.7; H, 7.05; N, 7.25%).

Conversion of the phosphine **7a** *into the corresponding phosphine oxide* **7b**. An excess of hydrogen peroxide (0.5 cm^3, 30% w/v) was added to a solution of the phosphine **7a** (0.15 g, 0.39 mmol) in ethanol (50 cm^3). After 30 min the reaction mixture was poured into water (*ca.* 5 cm^3), and the resultant white precipitate was filtered off, washed with water and then dried over P$_2$O$_5$. This gave the required phosphine oxide **7b**. Yield 0.12 g, 76% (Found: C, 74.85; H, 6.85; N, 7.15. $C_{25}H_{27}N_2OP$ requires C, 74.6; H, 6.75; N, 6.95%).

[Mo(CO)$_4${PPh$_2$CH$_2$C(Bu^t)=NN=CHPh}] **8a**. (*i*) *From* [Mo(CO)$_4$(nbd)]. A solution containing phosphino mixed-azine **7a** (0.16 g, 0.14 mmol) and [Mo(CO)$_4$(nbd)] (0.15 g, 0.40 mmol) in benzene (5 cm^3) was put aside at *ca.* 20 °C for 3 h. The solution was filtered and the filtrate evaporated to a low volume under reduced pressure. The residue was then triturated with methanol to give the required product **8a** as yellow microcrystals. Yield 67 mg, 27%.

(*ii*) *From* [Mo(CO)$_6$]. The phosphino mixed-azine **7a** (0.67 g, 1.75 mmol) and [Mo(CO)$_6$] (0.40 g, 1.52 mmol) were refluxed together in decane (5 cm^3) for 10 min. The resultant red solution gave a precipitate when it was cooled to *ca.* 20 °C. This was filtered off and recrystallised from dichloromethane–methanol to give the required product **8a** as bright orange crystals. Yield 0.39 g, 43% (Found: C, 58.4; H, 4.4; N, 4.85. $C_{29}H_{27}MoN_2O_4P$ requires C, 58.6; H, 4.6; N, 4.7%). Mass spectrum (fast atom bombardment, FAB): *m/z* 596 (M^+), 568 (M − CO), 540 (M − 2CO), 512 (M − 3CO) and 484 (M − 4CO).

[W(CO)$_4${PPh$_2$CH$_2$C(Bu^t)=NN=CHPh}] **8b**. A solution containing the phosphino mixed-azine **7a** (0.15 g, 0.38 mmol) and [W(CO)$_4$(nbd)] (0.15 g, 0.38 mmol) in benzene (*ca.* 5 cm^3) was heated under reflux for 20 h. The solvent was then removed under reduced pressure and the residue triturated with methanol to give the required product **8b** as orange-red microcrystals. Yield 0.165 g, 62% (Found: C, 51.1; H, 4.0; N, 4.1. $C_{29}H_{27}N_2O_4PW$ requires C, 51.05; H, 4.0; N, 4.1%). Mass spectrum (FAB): *m/z* 682 (M^+), 654 (M − CO), 626 (M − 2CO) and 570 (M − 4CO).

[Cr(CO)$_4${PPh$_2$CH$_2$C(Bu^t)=NN=CHPh}] **8c**. This complex was prepared and isolated in an analogous manner to that of complex **8b**, as dark red microcrystals in 62% yield (Found: C, 62.4; H, 5.05; N, 4.8. $C_{29}H_{27}CrN_2O_4P$ requires C, 63.25; H, 4.95; N, 5.1%). Mass spectrum (FAB): *m/z* 550 (M^+), 466 (M − 3CO) and 438 (M − 4CO).

[MoBr$_2$(CO)$_3${PPh$_2$CH$_2$C(Bu^t)=NN=CHPh}] **9**. The molybdenum(II) complex **9** was prepared and isolated in an analogous manner to that of the molybdenum(II) complex **6**, as yellow microcrystals in 62% yield (Found: C, 46.05; H, 3.75; N, 3.85. $C_{29}H_{27}Br_2MoN_2O_3P$ requires C, 46.3; H, 3.75; N, 3.85%). Mass spectrum (FAB): *m/z* 728 (M^+).

Single-crystal X-Ray Diffraction Analysis of Complex **3a**.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using an on-line profile-fitting method[9] and graphite-monochromated Mo-Kα X-radiation (λ = 71.069 pm). The data set was corrected for absorption semiempirically using azimuthal ψ scans.

The structure was determined *via* standard heavy-atom (for the Mo atom) and Fourier difference techniques and was refined by full-matrix least squares using the SHELX program system.[10] All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). All hydrogen atoms were included in calculated positions (C–H 96 pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + 0.0002(F_o)^2]^{-1}$ was used. Final non-hydrogen atomic coordinates are given in Table 4.

Crystal data. $C_{24}H_{27}MoN_2O_4P$, $M = 534.40$, monoclinic, space group $P2_1/n$, $a = 892.3(1)$, $b = 1920.1(3)$, $c = 1493.6(3)$ pm, $\beta = 105.67(1)°$, $U = 2.4639(7)$ nm^3, $Z = 4$, $D_c = 1.44$ Mg m^{-3}, $\mu = 5.83$ cm^{-1}, $F(000) = 1095.82$.

Data collection. $4.0 < 2\theta < 50.0°$, 4638 data collected, 3530 with $I > 2.0\sigma(I)$ considered observed, $T = 120$ K.

Structure refinement. Number of parameters = 281, $R = 0.0250$, $R' = 0.0274$.

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