DALTON
FULL PAPER

Complexes of the (1*R*)-(+)-camphor azine diphosphines *Z*,*Z*-3,3′-$Ph_2P^nC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$ and *Z*,*Z*-3,3′-$Ph_2P^xC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$ (x = *exo*, n = *endo*) with Group 6 metal carbonyls: crystal structures of the ligands and *fac*-[$W(CO)_3$(*E*,*Z*-$Ph_2P^xC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$)]

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Treatment of (1*R*)-(+)-camphor azine with 2 mole equivalents of butyllithium, followed by chlorodiphenylphosphine, gave the azine diphosphines *Z*,*Z*-3,3′-$Ph_2P^nC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$ **I** and *Z*,*Z*-3,3′-$Ph_2P^xC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$ **II** (x = *exo*, n = *endo*); the structures of these were determined by X-ray diffraction. On boiling an ethanol solution of the *exo*,*exo*-diphosphine **II** with sodium ethoxide or a propan-2-ol solution containing hydrazine hydrate and acetic acid the diphosphine isomerised to the corresponding *exo*,*endo*-diphosphine **I**. The corresponding diphosphine dioxides **III** and **IV** were prepared by treating **I** or **II** with H_2O_2, respectively. Treatment of **I** with [$Mo(CO)_4$(nbd)] (nbd = norbornadiene) or with [$Mo(CO)_3$(cht)] (cht = cyclohepta-1,3,5-triene) gave *fac*-[$Mo(CO)_3$($Ph_2P^nC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$)] **1a**. Treatment of **I** with [$W(CO)_4$(nbd)] gave the tricarbonyltungsten(0) complex *fac*-[$W(CO)_3$($Ph_2P^nC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$)] **1b** and the analogous *mer* complex *mer*-[$W(CO)_3$($Ph_2P^nC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$)] **2**. Treatment of **II** with [$W(CO)_6$] gave the *mer*,*exo*,*endo* tricarbonyl complex **2**, and the *fac*,*endo*,*endo* complex *fac*-[$W(CO)_3$($Ph_2P^nC_{10}H_{15}$=N−N=$C_{10}H_{15}P^nPh_2$)] **3**. Treatment of **II** with [$M(CO)_4$(nbd)] (M = Mo, W or Cr) gave mainly a complex of type *fac*-[$M(CO)_3$($Ph_2P^xC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$)] (M = Mo **4a**, W **4b** or Cr **4c**). The crystal structure of the tricarbonyltungsten(0) complex **4b** was determined by X-ray diffraction and the chirality around tungsten shown to be *C*, *i.e.* clockwise. Treatment of **4b** with 1 mole equivalent of bromine gave the tricarbonyltungsten(II) bromide salt [$WBr(CO)_3$($Ph_2P^xC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$)]Br **5**. Infrared, proton, phosphorus-31 and some carbon-13 NMR data are given.

We have described the *tert*-butyl diphenylphosphinomethyl ketone azine, $Ph_2PCH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$, prepared by lithiation of *tert*-butyl methyl ketone azine followed by treatment with PPh_2Cl.[1] This diphosphine is in a *Z*,*Z* configuration but even so it can form a nine-membered chelate ring with gold(I).[2] More commonly this *Z*,*Z*-azine diphosphine bridges metals and, for example, we have made binuclear palladium(II) complexes with 18-atom rings or a polynuclear complex with platinum(II), probably hexanuclear, with a 54-atom ring.[3] The energy barrier to rotation around a C=N bond is low and the azine diphosphine $Ph_2PCH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$ frequently reacts in the *E*,*Z* configuration with metals. Again a nine-membered chelate ring can form, *e.g.* with Cr, Mo, W[1] or Pt.[3,4] More commonly $Ph_2PCH_2C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$ acts as a terdentate *P*,*N*,*P*-bonded ligand with five, six-membered fused rings, as with Cr, Mo or W,[1] Pd^{II}, Pt^{II} or Pt^{IV} [3,4] or Ir^I.[5,6] We have also shown that in some metal complexes containing the terdentate *E*,*Z*-diphosphine ligand Ph_2PCH_2-$C(Bu^t)$=N−N=$C(Bu^t)CH_2PPh_2$ reversible deprotonation of a CH_2 group adjacent to co-ordinated PPh_2 can occur giving an ene hydrazone diphosphine ligand Ph_2PCH=$C(Bu^t)$−N−N=$C(Bu^t)CH_2PPh_2$. This has been developed into a new method of generating co-ordinative unsaturation.[5,6] Transannular reactions of nine-membered chelate rings derived from the *E*,*Z*-diphosphine ligand have also been observed.[3]

We have now started a study of some new types of azine diphosphines generated from (1*R*)-(+)-camphor azine (camphor = 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one). This introduces chirality into the chelates and also the possibility of many more isomers or types of complexes. We report results in this paper. We and others have previously studied several other tertiary phosphine ligands containing camphor residues including ones derived from camphor itself[7–10] and also from camphor *N*,*N*-dimethylhydrazone.[11–13]

Results and Discussion

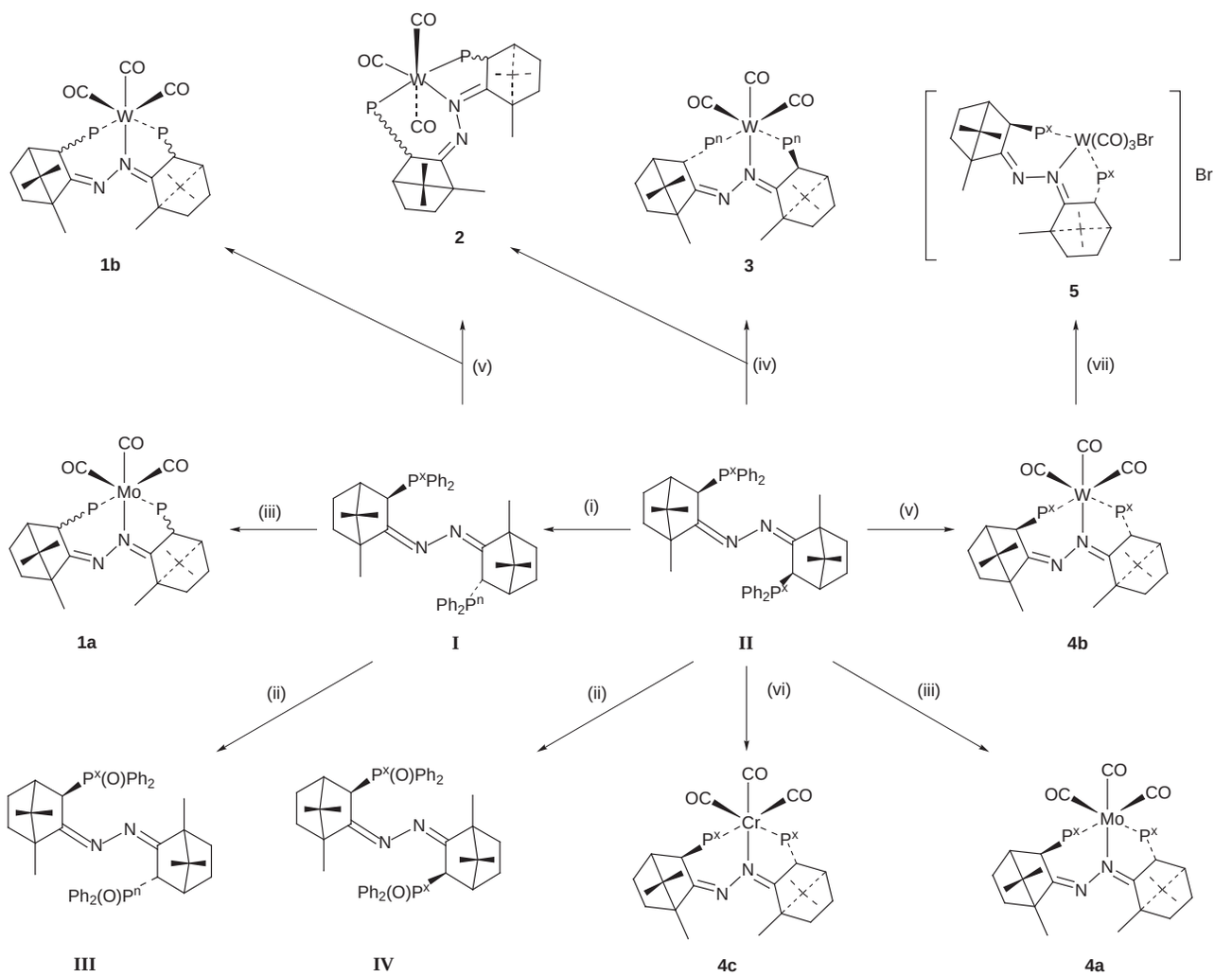
In this paper we describe the syntheses of two new types of diphosphines *Z*,*Z*-3,3′-$Ph_2P^nC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$ **I** and *Z*,*Z*-3,3′-$Ph_2P^xC_{10}H_{15}$=N−N=$C_{10}H_{15}P^xPh_2$ **II** (x = *exo*, n = *endo*), prepared from (1*R*)-(+)-camphor azine,[14] and the co-ordination chemistry of their *E*,*Z* isomers with chromium, molybdenum or tungsten carbonyls. For the convenience of the reader the various reactions are summarised in Scheme 1. The structures of **I** and **II** were established by X-ray diffraction, as was one of the tungsten tricarbonyl complexes. The structures of the other compounds were established by mass spectrometry, IR, NMR, in particular ^1H, ^1H-{^{31}P} and ^{13}C-{^1H} spectroscopy, together with two-dimensional COSY experiments. Spectroscopic data for the various compounds are given in Tables 1 (^{31}P-{^1H}NMR), 1 (IR), 2 (^1H and ^1H-{^{31}P} NMR) and 3 (^{13}C-{^1H} NMR). The numbering of the carbon atoms, and of some of the hydrogens, in the camphor residues is shown in Scheme 2.

Treatment of (1*R*)-(+)-camphor azine[14] with 2 mole equivalents of butyllithium at −20 °C, followed by addition of 2 mole equivalents of chlorodiphenylphosphine, gave two azine diphosphines, which were easily separated by fractional crystallisation. The less soluble *endo*,*exo*-azine diphosphine *Z*,*Z*-(3-*endo*-Ph_2P)$C_{10}H_{15}$=N−N=$C_{10}H_{15}$(3-*exo*-PPh_2), (P^nN–NP^x) **I**, was isolated in 22% yield and the isomeric *exo*,*exo*-diphosphine *Z*,*Z*-(3-*exo*-Ph_2P)$C_{10}H_{15}$=N−N=$C_{10}H_{15}$(3-*exo*-PPh_2), (P^xN–NP^x) **II**, was isolated in 42% yield. Isomerisation of **II** to **I** was achieved by boiling **II** in acidic or basic ethanol solutions. These

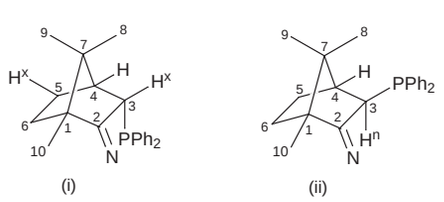
Table 1 ^{31}P-{^{1}H} NMR [a] and IR data

Compound	$\delta(P_A)$	$\delta(P_B)$	$^{2}J(PP)$	$^{1}J(WP_A)$	$^{1}J(WP_B)$	$\nu(C{=}N)$ [b]/cm^{-1}	$\nu(C{\equiv}O)$ [c]/cm^{-1}
I	0.2	−7.3	—	—	—	1640s	—
II	−0.4	—	—	—	—	1640s	—
III [d]	30.1	29.4	—	—	—	1645s	—
IV [d]	29.2	—	—	—	—	1655s	—
1a	40.2	39.5	19	—	—	1630w	1925, 1825 (sh), 1810
1b	33.1	27.5	13	206	229	1630w	1915, 1815, 1800 (sh)
2	64.8	55.5	114	382	386	1640w	2005, 1880, 1840
3	54.7	34.0	24	288	279	1635w	1920, 1810, 1800
4a [e]	54.5	52.8	24	—	—	1630w	1930, 1830, 1810
4b	48.3	42.7	26	223	250	1630w	1925, 1830, 1810
4c	72.9	66.0	33	—	—	1635w	1920, 1825, 1805
5	51.7	39.6	158	479	446	1625w	2015, 1965, 1930

[a] Recorded at 36.2 MHz, chemical shifts (δ) are in ppm relative to 85% H_3PO_4, solvent $CDCl_3$ unless otherwise indicated; J values are in Hz. [b] As compressed KBr disc; s = strong, w = weak. [c] In CH_2Cl_2; all carbonyl bands are strong, sh = shoulder. [d] In $(CD_3)_2CO$ (NMR); ν(P=O) 1195 cm^{-1}. [e] In C_6D_6.



Scheme 1 (i) $NH_2NH_2{\cdot}H_2O$–H^+; (ii) H_2O_2; (iii) $[Mo(CO)_4(nbd)]$ or $[Mo(CO)_3(cht)]$; (iv) $[W(CO)_6]$; (v) $[W(CO)_4(nbd)]$; (vi) $[Cr(CO)_4(nbd)]$, (vii) Br_2–CCl_4



Scheme 2 Numbering scheme for the carbons and some of the hydrogens in (i) an *endo*-phosphine moiety and (ii) an *exo*-phosphine moiety

azine diphosphines were characterised by elemental microanalysis, mass spectrometry, NMR spectroscopy and also by X-ray crystallography (see Figs. 1 and 2 and Tables 4 and 5).

The two P^xPh_2 groups in **II** were chemically equivalent and gave rise to a single resonance at δ −0.4 in the phosphorus-31 NMR spectrum. The phosphino groups in **I** were inequivalent, and this diphosphine gave two singlets, at δ 0.2 (probably *exo*) and −7.3 (probably *endo*).

The H^{3n} proton of **I** gave a doublet at δ 3.25 with $^{2}J(P^xH)$ = 2.6 Hz whereas the H^{3x} proton, on the same carbon atom as the P^nPh_2 group, gave a multiplet at δ 3.90 with $^{2}J(P^nH) \approx 0$ Hz. The H^4 proton of **I**, at δ 1.57 was coupled to phosphorus, $^{3}J(P^xH) \approx 4$ Hz whilst the H^4 proton absorbing at δ 1.62 did not show coupling to phosphorus. For the ligand **II**, the two H^{3n} protons were chemically equivalent and gave a doublet at δ 3.46

Table 2 Proton NMR data[a]

Compound	δ(Me)	δ(H^3)	δ(H^4)
I	0.11 (s), 0.16 (s), 0.51 (s)	3.25 [d, ^2J(PH) 2.6, H^{3n}]	1.57 (m)
	0.67 (s), 0.84 (s), 0.88 (s)	3.90 [m, ^2J(PH) ≈ 0, H^{3x}]	1.62 (m)
II	0.35 (s), 0.44 (s), 1.02 (s)	3.46 [d, ^2J(PH) 1.5, H^{3n}]	1.65 (m)
III[b]	0.07 (s), 0.25 (s), 0.42 (s), 0.49 (s), 0.87 (s), 0.13 (s)	4.20 [d, ^2J(PH) 15.6, H^{3n}]	1.7–2.0[c]
		4.35 (m, H^{3x})	
IV[b]	0.01 (s), 0.59 (s), 0.95 (s)	3.7 [d, ^2J(PH) 16.8, H^{3n}]	2.00 (m)
1a	0.23 (s), 0.35 (s), 0.59 (s), 0.82 (s), 1.02 (s), 1.19 (s)	2.57 [d, ^2J(PH) 12.8, H^{3n}]	2.24 (m)
		3.40 [m, ^2J(PH) 10.2, H^{3x}]	1.97 (m)
1b	0.17 (s), 0.72 (s), 0.91 (s), 0.98 (s), 1.08 (s), 1.22 (s)	2.52 [d, ^2J(PH) 14.2, H^{3n}]	2.41 (m)
		3.29 [m, ^2J(PH), 11.0, H^{3x}]	2.11 (m)
2	0.20 (s), 0.46 (s), 0.49 (s), 0.54 (s), 1.11 (s), 1.24 (s)	2.76 [d, ^2J(PH) ≈ 5.7, H^{3n}]	2.77 (m)[d]
		4.15 [m, ^3J(HH) 4.0, H^{3x}]	2.10 (m)
3	0.43 (s), 0.69 (s), 0.71 (s), 0.94 (s), 1.09 (s), 1.26 (s)	3.29 [m, H^{3x}]	2.44 (m)
		4.39 (m, H^{3x})	2.11 (m)
4a[e]	−0.34 (s), 0.01 (s), 0.62 (s), 0.76 (s), 1.08 (s), 1.20 (s)	2.62 [d, ^2J(PH) 9.9, H^{3n}]	2.98 (m)
		3.61 [dd, ^2J(PH) 10.1, ^4J(PH) 1.5, H^{3n}]	2.31 (m)
4b	−0.45 (s), −0.10 (s), 0.51 (s), 0.65 (s), 0.95 (s), 1.09 (s)	2.48 [d, ^2J(PH) 10.8, H^{3n}]	2.88 (m)
		3.47 [dd, ^2J(PH) 11.0, ^4J(PH) 2.0, H^{3n}]	2.2 (m)
4c	−0.05 (s), −0.09 (s), 0.43 (s), 0.67 (s), 0.97 (s), 1.07 (s)	3.61 [d, ^2J(PH) 9.3, H^{3n}]	2.92 (m)
		2.38 [dd, ^2J(PH) 9.9, ^4J(PH) 2.0, H^{3n}]	2.05 (m)
5	0.03 (s), 0.88 (s), 1.06 (s), 1.10 (s), 1.20 (s), 1.36 (s)	3.01 [d, ^2J(PH) 14.3, H^{3n}]	3.06 (m)
		5.94 [d, ^2J(PH) 11.2, H^{3n}]	2.53 (m)

[a] Recorded at 400.1 MHz, chemical shifts (δ) are in ppm relative to $SiMe_4$, solvent $CDCl_3$ unless otherwise indicated; *J* in Hz. [b] In $(CD_3)_2CO$. [c] Unresolved. [d] Overlap with H^{3n}. [e] In C_6D_6.

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

Compound	C^1	C^2	C^3	C^4	C≡O
I	54.4 (d, 3.7)	177.9 (d, 7.7)	41.7 (d, 23.6)	48.6 (d, 3.6)	—
	55.1 (d, 2.9)	180.2 (d, 8.5)	44.7 (d, 31.7)	49.2 (s)	
II	54.6 (d, 4.2)	180.5 (d, 8.5)	45.3 (d, 33.5)	49.0 (d, 3.5)	—
III[b]	54.5 (d, 2.0)	172.4 (d, 6.5)	42.9 (d, 75.4)	49.1 (s)	—
	55.3 (d, 2.4)	177.0 (d, 9.0)	46.6 (d, 64.0)	49.8 (s)	
IV[b]	48.7 (s)	174.5 (d, 8.8)	47.6 (d, 69.4)	47.3 (s)	—
1a	57.2 (d, 3.5)	178.9 (d, 2.4)	40.6 (d, 11.0)	49.1 (d, 4.8)	219.3 (dd, 34.7, 20.7, *trans* to P)
	57.7 (d, 3.3)	180.9 (dd, 5.5, 9.0)	56.8 (d, 3.4)	50.0 (d, 5.1)	224.5 (dd, 33.0, 10.6, *trans* to P)
					230.9 (t, 8.7, *cis* to P)
1b	55.9 (d, 3.5)	178.5 (s, br)	39.4 (d, 15.9)	46.5 (d, 5.7)	212.2 (dd, 34.4, 8.9, *trans* to P)
	57.2 (d, 3.6)	182.5 (dd, 5.5, 8.0)	58.5 (d, 7.7)	48.1 (d, 4.8)	217.1 (dd, 32.7, 8.5, *trans* to P)
					221.1 (t, 3.5, *cis* to P)
2	55.3 (d, 2.4)	180.2 (dd, 1.6, 2.8)	50.5 (d, 5.6)	48.4 (d, 4.3)	205.0 (t, 5.6, *cis* to P)
	57.8 (d, 3.6)	182.8 (dd, 3,5, 8.4)	63.4 (d, 14.9)	55.3 (d, 4.2)	213.7 (t, 7.8, *cis* to P)
					220.6 (t, 3.0, *cis* to P)
4a[c]	54.9 (d, 2.5)	176.2 (t, 2.2)	45.9 (d, 4.8)	41.9 (d, 1.1)	218.3 (dd, 34.9, 6.8, *trans* to P)
	57.0 (d, 3.5)	181.4 (dd, 4.4, 6.2)	58.6 (d, 10.9)	46.9 (d, 4.4)	222.6 (dd, 34.3, 11.6, *trans* to P)
					227.6 (dd, 8.8, 6.0, *cis* to P)
4b	54.8 (d, 2.3)	177.3 (d, 1.6)	46.1 (d, 4.8)	42.0 (d, 1.9)	212.3 (dd, 31.7, 2.5, *trans* to P)
	57.3 (d, 3.2)	183.8 (t, 5.1)	61.5 (d, 15.5)	47.4 (d, 3.0)	215.5 (dd, 34.3, 8.8, *trans* to P)
					220.0 (dd, 5.6, 3.6, *cis* to P)
4c	55.0 (d, 2.4)	177.1 (s)	46.2 (d, 5.6)	42.2 (d, 4.6)	228.5 (dd, 11.5, 4.3)
	57.4 (d, 3.4)	181.8 (dd, 5.1, 7.3)	58.6 (d, 10.6)	47.4 (d, 5.2)	232.6 (dd, 18.2, 5.9)
					235.6 (dd, 16.2, 9.3)

[a] Recorded at 100.6 MHz, chemical shift (δ) in ppm relative to tetramethylsilane, *J* values (Hz) in parentheses. Solvent is $CDCl_3$ unless otherwise indicated. [b] In $(CD_3)_2CO$. [c] In C_6D_6.

[$^2J(P^xH)$ = 1.5 Hz]. Both **I** and **II** were oxidised by hydrogen peroxide to the corresponding diphosphine dioxides **III** and **IV**, respectively; see Experimental section for details and Tables 1–3 for characterising data.

Before describing the co-ordination chemistry derived from the Group 6 metal carbonyls and **I** or **II** it is appropriate to outline the reasoning used in assigning the structures from consideration of the NMR data. In Scheme 2 the position of a nucleus on the camphor framework is indicated by a numbered superscript, *i.e.* H^4 denotes the hydrogen atom attached to carbon-4 (C^4). The positions of hydrogens attached to carbon atoms 3 and 5 are either assigned as H^x for *exo*, or H^n for *endo*. Thus, H^{3x} refers to the *exo*-proton at C^3 on the same side of the six-membered ring as the *gem*-dimethyl groups, whereas H^{3n} refers to the *endo*-proton on the opposite side. Resonances due to H^3 protons are to high frequency of all the other proton resonances of the camphor residues and are easily identified. Coupling patterns of H^{3x} and H^{3n} protons are very different and have been studied extensively.[15] There are many examples from the work of others[15–18] and from work in this laboratory,[11–13] which show that $^3J(H^{3n}H^4)$ is *ca.* zero. An *endo*-hydrogen on carbon-3 (H^{3n}) shows only coupling to phosphorus and not significantly to other hydrogens, *i.e.* it gives a singlet in the ^1H-{^{31}P} NMR spectrum and a doublet in the ^1H NMR spectrum. On the other hand, an H^{3x} resonance appears as a multiplet with couplings to phosphorus, to H^4 (*ca.* 4 Hz) and to H^{5x}, through a four-bond 'W' coupling.[11–13] We have found this previously with 3-diphenylphosphinocamphor and its complexes and with 3-diphenylphosphinocamphor *N*,*N*-dimethylhydrazone and its complexes. In the present paper we report the chemical shifts of H^4 protons in Table 2 but have not studied the resonances or analysed them in detail. The chemical shifts of

the H^4 hydrogens are similar to what we and others have reported previously for camphor residues.

The ^{13}C NMR spectra of norbornane (bicyclo[2.2.1]heptane) and camphor systems have been well studied [16–18] including our own work.[7,8,11–13] The ^{13}C resonances in the present paper have been assigned with the aid of Attached Proton Tests as well as by using two-dimensional ^{13}C–^1H COSY experiments. For the sake of simplicity, only data for the resonances of C^1, C^2, C^3, C^4 and auxiliary ligands, such as carbonyls, are listed in Table 3; C^3 and C^4 are methine (CH) carbons.

In our previous work on the complexes of the azine diphosphine $Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$ [1,19] with carbonyls of chromium, molybdenum and tungsten we found that the azine diphosphine displaced norbornadiene (nbd) from a complex of type $[M(CO)_4(nbd)]$ to give derivatives such as $[M(CO)_4\{Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2\}]$ containing a nine-membered chelate ring. Under slightly more vigorous conditions, a terdentate complex $[M(CO)_3\{Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2\}]$ of *fac* geometry formed.[1] We anticipated that the new azine diphosphines based on camphor would react more slowly with $[M(CO)_4(nbd)]$ than does $Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$ for steric reasons and it was difficult to predict the products; clearly, because of the additional possibility of *endo*- or *exo*-phosphines, many different geometries and stereochemistries were possible for the resultant chelates. In this paper we describe our results.

When we treated $[Mo(CO)_4(nbd)]$ with the *endo*,*exo*-diphosphine **I** in hot benzene for 20 min we obtained, after chromatography on silica gel, the *fac*-tricarbonyl derivative *fac*-$[Mo(CO)_3(Ph_2P^nC_{10}H_{15}$=N–N=$C_{10}H_{15}P^xPh_2)]$, *i.e.* *fac*-$[Mo(CO)_3(P^nN$–$NP^x)]$ **1a** in 36% yield. Complex **1a** was also formed by treating $[Mo(CO)_3(cht)]$ (cht = cycloheptа-1,3,5-triene) with **I**. The elemental analytical and mass spectral data established that this product was a tricarbonyl (see Experimental section). In the mass spectrum one, two and finally three COs were lost, and the NMR and IR data (Tables 1–3) established the *fac* geometry with mutually *cis*-co-ordinated *exo*- and *endo*-PPh_2 groups [^2J(PP) = 19 Hz]. The ^1H NMR data established that one of the H^3 protons was *exo* and the other *endo* but we cannot say which of these is in the five-membered ring and which is in the six-membered ring, hence in Scheme 1 we have not defined which is *endo* and which is *exo*. Treatment of $[W(CO)_4(nbd)]$ with **I** gave the corresponding tungsten complex, *fac*-$[W(CO)_3(Ph_2P^nC_{10}H_{15}$=N–N=$C_{10}H_{15}P^xPh_2)]$ **1b** [^2J(PP) = 13 Hz] and *mer*-$[W(CO)_3(Ph_2P^nC_{10}H_{15}$=N–N=$C_{10}H_{15}P^xPh_2)]$ **2**, readily separated by thin-layer chromatography. The ^{31}P-{^1H} NMR data (Table 1) with ^2J(PP) = 114 Hz established mutually *trans*-phosphines, one of which was *exo* and the other *endo*; again we cannot say which is which and have not defined the stereochemistry in Scheme 1.

Treatment of $[W(CO)_6]$ with **II** at *ca.* 110 °C gave a mixture of complex **2** and the *endo*,*endo* *fac* isomer *fac*-$[W(CO)_3(P^nN$–$NP^n)]$ **3** [^2J(PP) = 24 Hz]; this has both H^3 resonances in the ^1H-{^{31}P} spectrum as multiplets (Table 2), showing that both H^3 are *exo* and therefore both P are *endo*.

As reported above, treatment of $[Mo(CO)_4(nbd)]$ with the *endo*,*exo*-diphosphine **I** gave the *fac*-tricarbonyl complex **1a** with co-ordinated *endo*- and *exo*-diphosphine. Similar treatment of $[Mo(CO)_4(nbd)]$ with the *exo*,*exo*-diphosphine **II** gave the *fac*-tricarbonyl complex **4a** in which the terdentate ligand retained its *exo*,*exo*-diphosphine geometry, *i.e.* both H^3 are *endo* and give singlet resonances in the ^1H-{^{31}P} NMR spectrum, see Table 2. Interestingly, one of these H^{3n} protons (δ 3.61) was coupled to both phosphorus nuclei. In the ^{13}C-{^1H} NMR spectrum of **4a** two carbonyls are *trans* to P and give large values of ^2J(PC) > 30 Hz (Table 3). Similar treatment of $[M(CO)_4(nbd)]$ (M = W or Cr) with **II** gave the *fac*-tricarbonyl complexes *fac*-$[M(CO)_3(P^xN$–$NP^x)]$ in which the *exo*,*exo* configuration of the diphosphine was again retained, giving **4b** (M = W) or **4c** (M = Cr). The crystal structure of the tungsten complex *fac*-$[W(CO)_3(P^xN$–$NP^x)]$ **4b** was determined and is shown in Fig. 3.

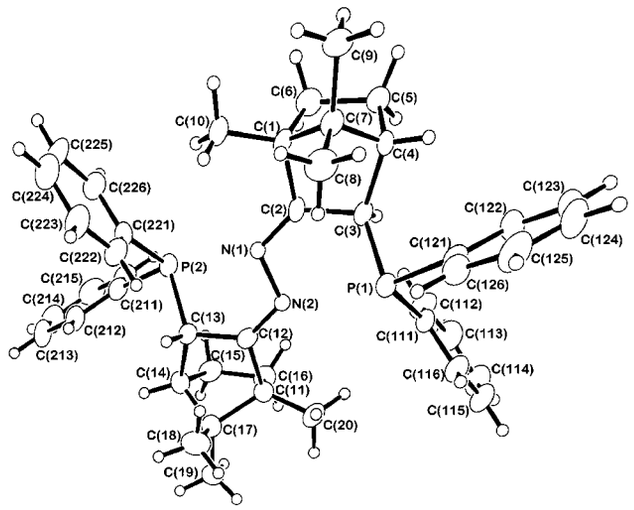


Fig. 1 Crystal structure of the *exo*,*endo*-diphosphine **I**

A feature of tertiary phosphine-substituted tungsten tricarbonyl complexes is their oxidation to seven-co-ordinated tungsten(II) complexes by Cl_2, Br_2 or I_2.[1,20,21] We treated the *exo*,*exo* tungsten complex **4b** with 1 mole equivalent of Br_2 and obtained the seven-co-ordinate cation, isolated as its bromide salt $[WBr(CO)_3(Ph_2P^xC_{10}H_{15}$=N–N=$C_{10}H_{15}P^xPh_2)]Br$ **5** in which the *exo*,*exo* configuration was retained; see Experimental section and Tables 1 and 2 for the characterising data. The FAB mass spectrum showed species corresponding to successive loss of one and then two bromines (see Experimental section). As expected, the values of ν(C≡O) are much higher for this tungsten(II) complex than for the tungsten(0) complexes (Table 1). The proton NMR data (Table 2) show that both C^3 protons are *endo*, *i.e.* both C^3 phosphoruses are *exo*.

Crystal structures of compounds I, II and 4b

We have previously determined the crystal structures of some compounds containing 3-diphenylphosphino-substituted camphor residues. These included 3-*exo*-diphenylphosphino-(1*R*)-camphor dimethylhydrazone and its complex with $Mo(CO)_4$ [12] and with $PdCl_2$ [11] and also 3-*endo*-diphenylphosphino-(1*R*)-camphor [8] and its complex with $PdCl_2$.[8] Cole-Hamilton and co-workers [10] have described the crystal structure of *cis*,*mer*-trichlorobis[(1*R*)-*endo*-3-diphenylphosphinocamphor]-rhodium(III). We have also determined the crystal structure of the α-diazine formed from glyoxal and (1*R*)-camphor, *viz.* $C_{10}H_{16}$=N–N=CH–CH=N–N=$C_{10}H_{16}$ [22] and of the $PdCl_2$ complex with the mixed azine from camphor and pyridine-2-carbaldehyde.[23]

The crystal structure of the diphosphine **I** is shown in Fig. 1 with selected bond length and angle data given in Table 4. The structure shows that the configuration around both C=N bonds is *Z* and that one PPh_2 group is *exo* and the other *endo*. There is nothing unusual about the bond lengths and angles. The crystal structure of the diphosphine **II** is shown in Fig. 2 with selected data in Table 5. The structure again shows that the configurations around the C=N are *Z* and that both PPh_2 groups are *exo*. The crystal structure of the tungsten complex **4b** is shown in Fig. 3 with bond lengths and angles in Table 6. The structure shows a *fac* arrangement around the tungsten and that the PPh_2 group in the five-membered ring and the PPh_2 group in the six-membered ring are both *exo*. The configuration around the tungsten is *C* (clockwise).[24] The bond lengths and angles of the camphor moieties in the crystal structures of **I**, **II** and **4b** are very similar to those found by others [10,15] and by our-

Table 4 Structural data for the camphor azine diphosphine **I**. Interatomic distances (Å) and angles between interatomic vectors (°), with estimated standard deviations (e.s.d.s) in parentheses

P(1)–C(111)	1.845(5)	P(1)–C(121)	1.843(5)
P(1)–C(3)	1.875(5)	P(2)–C(221)	1.847(6)
P(2)–C(211)	1.859(6)	P(2)–C(13)	1.886(5)
C(2)–N(1)	1.281(7)	C(2)–C(3)	1.521(7)
N(1)–N(2)	1.425(5)	N(2)–C(12)	1.284(8)
C(12)–C(13)	1.532(7)		
N(1)–C(2)–C(3)	129.7(5)	C(221)–P(2)–C(13)	103.0(3)
C(111)–P(1)–C(121)	97.5(2)	C(111)–P(1)–C(3)	102.7(2)
C(121)–P(1)–C(3)	104.7(2)	C(221)–P(2)–C(211)	97.2(2)
C(211)–P(2)–C(13)	101.4(2)	C(2)–C(3)–P(1)	113.7(4)
C(2)–N(1)–N(2)	110.8(4)	C(12)–N(2)–N(1)	112.3(4)
N(2)–C(12)–C(13)	130.8(5)	C(12)–C(13)–P(2)	114.9(3)

Table 5 Structural data for the camphor azine diphosphine **II**. Interatomic distances (Å) and angles between interatomic vectors (°), with e.s.d.s in parentheses

P(1)–C(121)	1.846(2)	P(1)–C(111)	1.859(2)
P(1)–C(3)	1.897(3)	N(1)–C(2)	1.277(3)
N(1)–N(2)	1.420(2)	C(2)–C(3)	1.536(3)
P(2)–C(211)	1.833(3)	P(2)–C(221)	1.853(2)
P(2)–C(13)	1.880(2)	N(2)–C(12)	1.265(3)
C(12)–C(13)	1.537(3)		
C(121)–P(1)–C(111)	96.27(11)	C(121)–P(1)–C(3)	102.01(12)
C(111)–P(1)–C(3)	106.75(12)	C(2)–N(1)–N(2)	112.1(2)
N(1)–C(2)–C(3)	129.4(2)	C(2)–C(3)–P(1)	112.7(2)
C(211)–P(2)–C(221)	96.41(10)	C(211)–P(2)–C(13)	105.87(11)
C(221)–P(2)–C(13)	99.90(10)	C(12)–N(2)–N(1)	114.6(2)
N(2)–C(12)–C(13)	132.1(2)	C(12)–C(13)–P(2)	115.6(2)

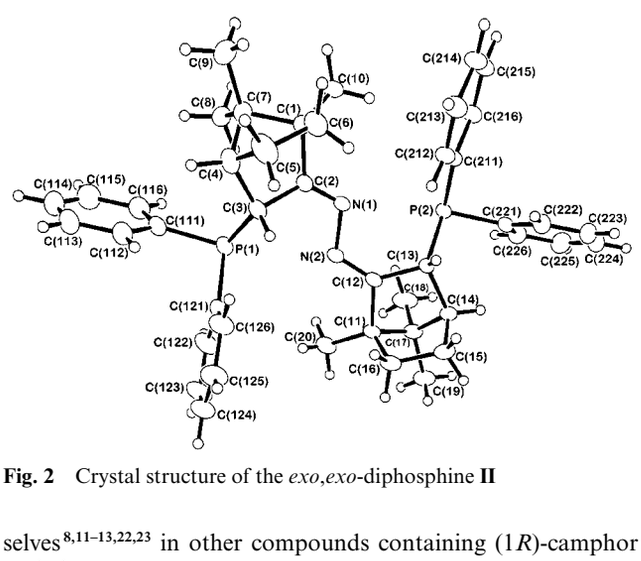


Fig. 2 Crystal structure of the *exo*,*exo*-diphosphine **II**

selves[8,11–13,22,23] in other compounds containing (1*R*)-camphor moieties.

Experimental

All the reactions were carried out in a dry atmosphere of nitrogen or argon. Toluene, tetrahydrofuran (thf) and benzene were distilled from sodium under argon and used immediately. Infrared spectra were recorded using a Perkin-Elmer model 257 grating spectrometer, NMR spectra using a JEOL FX-90Q (operating frequencies for ^{1}H and ^{31}P were 89.5 and 36.2 MHz respectively), a JEOL FX-100 (operating frequencies for ^{1}H and ^{31}P of 99.5 and 40.25 MHz respectively) or a Bruker AM-400 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 to 85% phosphoric acid. Mass spectra were recorded using a VG Autospec instrument with 8 kV acceleration.

Table 6 Structural data for the camphor azine diphosphine–tungsten complex **4b**. Interatomic distances (Å) and angles between interatomic vectors (°), with e.s.d.s in parentheses

W–C(22)	1.947(4)	W–C(21)	1.957(4)
W–C(23)	1.980(4)	W–N(2)	2.255(3)
W–P(1)	2.4991(10)	W–P(2)	2.5501(1)
P(1)–C(3)	1.880(4)	N(1)–C(2)	1.273(5)
N(1)–N(2)	1.432(4)	C(2)–C(3)	1.528(5)
P(2)–C(13)	1.858(4)	N(2)–C(12)	1.287(5)
C(12)–C(13)	1.520(5)	C(23)–O(23)	1.162(5)
C(21)–O(21)	1.173(5)	C(22)–O(22)	1.180(5)
C(22)–W–C(21)	93.1(2)	C(22)–W–C(23)	82.2(2)
C(21)–W–C(23)	87.2(2)	C(22)–W–N(2)	91.24(14)
C(21)–W–N(2)	174.4(2)	C(23)–W–N(2)	96.9(2)
C(22)–W–P(1)	87.10(12)	C(21)–W–P(1)	91.88(13)
N(2)–W–P(1)	84.73(8)	N(2)–W–P(2)	76.91(8)
P(1)–W–P(2)	108.55(4)	C(3)–P(1)–W	107.69(12)
C(2)–N(1)–N(2)	117.0(3)	N(1)–C(2)–C(3)	130.6(3)
C(2)–C(3)–P(1)	117.6(3)	C(12)–N(2)–N(1)	114.9(3)
N(1)–N(2)–W	121.7(2)	N(2)–C(12)–C(13)	118.2(3)
C(12)–C(13)–P(2)	112.1(3)		

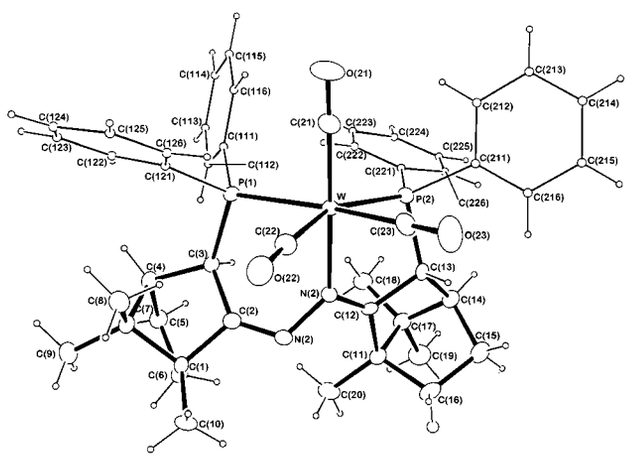


Fig. 3 Crystal structure of the tungsten complex *fac*-[W(CO)$_3$(P^{x}N–NP^x)] **4b**

(1*R*)-(+)-Camphor azine was prepared by a modification of a literature method.[14] A solution of (1*R*)-(+)-camphor (40.0 g, 0.26 mol), hydrazine hydrate $NH_2NH_2{\cdot}H_2O$ (7.5 g, 0.15 mmol) and glacial acetic acid (6 cm^3) in *n*-propanol (85 cm^3) was boiled for 16.5 h. The solvent was then evaporated under reduced pressure and the residue recrystallised from hot ethanol, to give the required (1*R*)-(+)-camphor azine in 70% yield.

Preparations

***Z*,*Z*-(*endo*-Ph$_2$P)C$_{10}$H$_{15}$=N–N=C$_{10}$H$_{15}$(3-*exo*-PPh$_2$), (P^{n}N–NP^x) I and *Z*,*Z*-(*exo*-Ph$_2$P)C$_{10}$H$_{15}$=N–N=C$_{10}$H$_{15}$(3-*exo*-PPh$_2$), (P^{x}N–NP^x) II.** Butyllithium (1.6 M in *n*-hexane, 39 cm^3, 0.060 mol) was added to a stirred solution of (1*R*)-(+)-camphor azine (9.0 g, 0.030 mol) in thf (160 cm^3) at −20 °C. Stirring was continued at −20 °C for 1 h, after which a solution of PPh_2Cl (13.2 g, 0.06 mol) in thf (60 cm^3) was added slowly over 1 h. The reaction mixture was then allowed to warm to room temperature. A ^{31}P-{^{1}H} NMR spectrum showed the presence of the two required products in the approximate ratio of 1:3. The solvent was evaporated under reduced pressure, and the residue dissolved in diethyl ether (20 cm^3). Methanol (50 cm^3) was added to the ether solution which was then put aside at 0 °C. The *endo*,*exo*-diphosphine **I** crystallised out as colourless prisms (4.4 g, 22%) (Found: C, 78.8; H, 7.2; N, 4.2. $C_{44}H_{50}N_2P_2$ requires C, 79.0; H, 7.55; N, 4.2%). *m*/*z* (EI) 668 (M^+). The mother-liquor was concentrated under reduced pressure and the residue cooled to −30 °C. This gave the required

Table 7 Crystal data for compounds **I**, **II** and **4b**

	II	**I**	**4b**
Empirical formula	$C_{44}H_{50}N_2P_2\cdot 3CHCl_3$	$C_{44}H_{50}N_2P_2$	$C_{47}H_{50}N_2O_3P_2W\cdot C_2H_5OH$
M	1026.90[a]	660.80	982.75[a]
T/K	200	200	160
λ/Å	1.541 84	1.541 84	0.710 73
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	C_2	$P2_1$	$P2_12_12_1$
a/Å	26.172(2)	23.9559(12)	11.308(2)
b/Å	10.8054(8)	6.6755(4)	11.867(3)
c/Å	17.568(2)	24.0682(12)	32.999(6)
β/°	93.796(8)	103.882(5)	
U/Å^3	4957.2(8)	3736.5(3)	4428(2)
Z	4	2	4
D_c/Mg m^{-3}	1.376	1.189	1.474
μ/mm^{-1}	5.529	1.295	2.727
F(000)	2128	1432	2000
Absorption correction	DIFABS[b]	None	ψ Scans
Maximum, minimum transmission factors	1.000, 0.781	—	0.8283, 0.6725
Crystal size/mm	0.48 × 0.35 × 0.26	0.55 × 0.35 × 0.13	0.65 × 0.42 × 0.34
θ_{min}, θ_{max}/°	2.52, 64.52	1.89, 64.23	1.82, 25.00
hkl Ranges	−30, 30; 0, 12; 0, 20	−28, 28; −7, 7; −26, 28	−13, 13; −14, 14; −39, 39
Reflections collected	4258	4091	8772
Independent reflections, p	4258	3832	7804
R_{int}[c]	0.000	0.0237	0.0199
Reflections with $F_o^2 > 2\sigma F_o^2$	3489	3559	7213
Weighting scheme parameters a,b[d]	0.1017, 2.1829	0.0423, 1.4127	0.0272, 3.2199
Extinction coefficient, x[e]	0.000 11(6)	0.000 68(6)	—
Data, restraints, parameters (n)	4248, 205, 557	3832, 203, 440	7801, 202, 531
Absolute structure parameter	0.02(2)	0.00(2)	−0.011(5)
Goodness of fit on F^2, S[f]	1.138	1.057	1.015
$R1$[g]	0.0508	0.0287	0.0266
$wR2$[h]	0.1517	0.0775	0.0561
Largest difference map peak and hole/e Å^{-3}	0.524, −0.539	0.212, −0.166	0.415, −0.461

[a] Includes solvate molecule(s). [b] Ref. 25. [c] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$. [d] $w = [\sigma^2(F_o^2) + aP^2 + bP)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [e] F_c has been multiplied by $k(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)$ where k is the overall scale factor. [f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{\frac{1}{2}}$. [g] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [h] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{\frac{1}{2}}$.

exo,*exo*-diphosphine **II** (8.32 g, 42%) (Found: C, 78.95; H, 7.45; N, 4.15%). *m*/*z* (EI) 668 (M^+).

Conversion of the *exo*,*exo*-diphosphine II into the *endo*,*exo*-diphosphine I. A solution of **II** (0.33 g, 0.5 mmol) in propan-2-ol (8 cm^3) containing hydrazine hydrate (0.25 g, 5.0 mmol) and acetic acid (80 mg) was heated under reflux for 16 h. The reaction mixture was then allowed to cool to ambient temperature, after which the pure *endo*,*exo*-diphosphine **I** separated out as colourless prisms (0.22 g, 63%). Alternatively, the *exo*,*exo*-diphosphine **II** was heated under reflux in ethanol solution containing sodium ethoxide (5×10^{-4} M) for 22 h. The solution was cooled, giving the pure *endo*,*exo*-diphosphine **I** in 57% yield.

Conversion of the *endo*,*exo*-diphosphine I into the corresponding diphosphine dioxide III. A solution of the *endo*,*exo*-diphosphine **I** (0.13 g, 0.2 mmol) in acetone (5 cm^3) was warmed with an excess of hydrogen peroxide (0.25 cm^3, 30% w/v) at 20 °C. After 15 min the solution was concentrated to low volume under reduced pressure, and water (5 cm^3) was added. This gave the required product **III** as white microcrystals (0.11 g, 81%) (Found: C, 75.5; H, 7.15; N, 3.85. $C_{44}H_{50}N_2O_2P_2$ requires C, 75.4; H, 7.2; N, 4.0%). The *exo*,*exo*-diphosphine dioxide **IV** was similarly prepared and isolated in 74% yield (Found: C, 74.95; H, 7.4; N, 3.8. $C_{44}H_{50}N_2O_2P_2$ requires C, 75.4; H, 7.2; N, 4.0%).

***fac*-[Mo(CO)$_3$(P^{n}N–NP^x)] 1a.** (*i*) *From* [Mo(CO)$_4$(nbd)]. A solution of the *endo*,*exo*-diphosphine **I** (0.13 g, 0.20 mmol) and [Mo(CO)$_4$(nbd)] (60 mg, 0.20 mmol) in benzene (3 cm^3) was refluxed for 20 min; the solvent was then removed under reduced pressure. The required molybdenum complex **1a** was isolated as a yellow solid by preparative TLC on silica gel using benzene as eluent. Yield 95 mg (36%) (Found: C, 65.85; H, 5.9; N, 3.25. $C_{47}H_{50}MoN_2O_3P_2\cdot 0.1C_6H_6$ requires C, 65.90; H, 5.9; N, 3.3%). *m*/*z* (EI, for ^{96}Mo) 848 (M^+), 820 (M − CO), 792 (M − 2CO) and 764 (M − 3CO).

(*ii*) *From* [Mo(CO)$_3$(cht)]. The required complex **1a** was isolated in 40% yield starting with equimolar amounts of the *endo*,*endo*-diphosphine **I** and [Mo(CO)$_3$(η-cht)] and using the procedure described in (*i*).

***fac*-[W(CO)$_3$(P^{x}N–NP^n)] 1b and *mer*-[W(CO$_3$)(P^{x}N–NP^n)] 2.** A solution of the *endo*,*exo*-diphosphine **I** (0.20 g, 0.30 mmol) and [W(CO)$_4$(nbd)] (0.12 g, 0.30 mmol) in toluene (8 cm^3) was refluxed for 35 min. The ^{31}P-{^{1}H} NMR spectrum showed a mixture of two products, in the ratio of *ca.* 1:1.5. The complexes were isolated by preparative TLC on a silica gel plate using benzene as the eluent. The more polar **1b** was isolated as a yellow solid (76 mg, 27%) (Found: C, 60.1; H, 5.65; N, 2.85. $C_{47}H_{50}N_2O_3P_2W$ requires C, 60.25; H, 5.4; N, 3.0%). *m*/*z* (FAB, for ^{184}W) 936 (M^+), 908 (M − CO), 880 (M − 2CO) and 852 (M − 3CO). The less polar **2** was isolated as yellow-orange microcrystals (55 mg, 17%) (Found: C, 59.45; H, 5.25; N, 2.90. $C_{47}H_{50}N_2O_3P_2W\cdot 0.1C_6H_6$ requires C, 59.75; H, 5.35; N, 2.95%). *m*/*z* (FAB for ^{184}W) 936 (M^+), 908 (M − CO), 880 (M − 2CO) and 852 (M − 3CO).

***mer*-[W(CO)$_3$(P^{x}N–NP^n)] 2 and *fac*-[W(CO)$_3$(P^{n}N–NP^n)] 3.** A solution containing the diphosphine **II** (134 mg, 0.20 mmol) and [W(CO)$_6$] (71 mg, 0.02 mmol) in toluene (1 cm^3) was heated under reflux for 20 h. The solution was evaporated to low volume and the residue chromatographed on a silica gel TLC plate using benzene as eluent. This gave the *mer* complex **2** (50 mg, 27%) and the *fac* complex **3** (90 mg, 48%).

***fac*-[Mo(CO)$_3$(P^{x}N–NP^x)] 4a.** A solution of the diphosphine **II** (134 mg, 0.2 mmol) and [Mo(CO)$_4$(nbd)] (60 mg, 0.20 mmol) in benzene (3 cm^3) was boiled for 3 h. The solution was evapor-

ated to low volume and the residue chromatographed on a silica gel TLC plate using benzene as eluent. This gave the required product **4a** (85 mg, 50%) (Found: C, 66.25; H, 5.9; N, 3.15. $C_{47}H_{50}MoN_2O_3P_2$ requires C, 66.50; H, 5.95; N, 3.30%).

***fac*-[W(CO$_3$)(P^{x}N–NP^x)] 4b.** A solution of the *exo*,*exo*-diphosphine **II** (0.27 g, 0.4 mmol) and [W(CO)$_4$(nbd)] (0.155 g, 0.4 mmol) was refluxed in toluene (8 cm^3) for 5 h. The solvent was evaporated to a low volume (*ca.* 2 cm^3). Addition of methanol to the residue gave the required tungsten complex **4b** as yellow microcrystals (0.19 g, 50%) (Found: C, 60.1; H, 5.8; N, 2.85. $C_{47}H_{50}N_2O_3P_2W$ requires C, 60.25; H, 5.4; N, 3.0%). *m*/*z* (EI for ^{184}W) 936 (M^+), 908 (M − CO), 880 (M − 2CO) and 852 (M − 3CO).

***fac*-[Cr(CO)$_3$(P^{x}N–NP^x)] 4c.** A solution of *exo*,*exo*-azine diphosphine **II** (0.27 g, 0.4 mmol) and [Cr(CO)$_4$(nbd)] (0.1 g, 0.4 mmol) in toluene (6 cm^3) was boiled for 4 h; the reaction mixture was then concentrated by evaporation under reduced pressure. Addition of methanol to the residue gave the *exo*,*exo* complex **4c** which formed yellow microcrystals from acetone–methanol. Yield 0.15 g, 47% (Found: C, 70.25; H, 6.2; N, 3.4. $C_{47}H_{50}CrN_2O_3P_2$ requires C, 70.15; H, 6.25; N, 3.5%). *m*/*z* (EI for ^{52}Cr) 804 (M^+) and 720 (M − 3CO).

[WBr(CO)$_3$(P^{x}N–NP^x)]Br 5. A solution of bromine (0.46 M in carbon tetrachloride, 0.3 cm^3, 0.14 mmol) was added to a solution of the tungsten(0) complex **4b** (93.6 mg, 0.1 mmol) in dichloromethane (3 cm^3). The reaction mixture was put aside at *ca.* 20 °C for 10 min. The solvent was then removed under reduced pressure. Addition of *n*-hexane to the residue gave the required tungsten(II) complex as a yellow solid (90 mg, 82%) (Found: C, 51.35; H, 4.9; N, 2.3. $C_{47}H_{50}Br_2N_2P_2O_3W$ requires C, 51.5; H, 4.6; N, 2.55%). *m*/*z* (FAB for ^{184}W and ^{79}Br) 1015 (M − Br) and 936 (M − 2Br).

Crystallography

All crystallographic measurements were made on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite monochromated Cu-Kα radiation for **I** and **II**, and Mo-Kα radiation for **4b**. Crystal data for all three complexes are given in Table 7 together with refinement details. Cell dimensions were refined from the values of 40 selected reflections (together with their Freidel opposites) measured at ±2θ in order to minimise systematic errors.

All three structures were solved by direct methods using SHELXS 86[26] and developed by full-matrix least-squares refinement (on F^2) using SHELXL 93.[27] The asymmetric part of the unit cell of two of the complexes contains solvate molecules; **4b** has a molecule of ethanol whilst **II** has three molecules of chloroform (of which one is comprised of two half molecules disordered about the C_2 axis at $-x$, y, $-z$). Refinement was essentially the same for all three complexes. All non-hydrogen atoms were refined with anisotropic displacement parameters, including those of the solvate molecules in **II** and **4b**. Restraints were applied to the phenyl rings so that they remained flat with overall C_{2v} symmetry. All hydrogen atoms were constrained to idealised positions with a riding model including free rotation of methyl groups. In all three cases the absolute configuration was initially based on the known configuration of the camphor starting material and later confirmed by the refinement of a Flack enantiopole parameter.[28]

CCDC reference number 186/958.

See http://www.rsc.org/suppdata/dt/1998/1885/ for crystallographic files in .cif format.

Acknowledgements

We thank the SERC for general support and for fellowships (to S. D. Perera and J. D. Vessey) and to Shiraz University, Iran for granting leave of absence to Professor Nasser Iranpoor.

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Received 25*th February* 1998; *Paper* 8/01585F