Preparation of α-Diazines and α-2-Pyridylazines containing (1*R*)-(+)-Camphor or (1*R*)-(−)-Fenchone Residues and their Complexes with Group 6 Metal Carbonyls†

Bernard L. Shaw,* Mark Thornton-Pett and Jonathan D. Vessey
School of Chemistry, Leeds University, Leeds LS2 9JT, UK

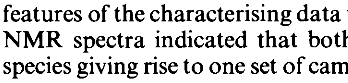
New 2,3,6,7-tetraaza-1,3,5,7-octatetraene (α-diazine) derivatives camph=N–N=CH–CH=N–N=camph **I**, where camph is a (1*R*)-(+)-camphor residue, $C_{10}H_{16}$, and fench=N–N=CH–CH=N–N=fench **II**, where fench is a 1*R*-(−)-fenchone residue, $C_{10}H_{16}$, have been obtained together with the 2′-pyridyl derivatives camph=N–N=CHC_5H_4N **III** and fench=N–N=CHC_5H_4N **IV**. The configurations around the four C=N bonds of **I** or **II** are *E,E,E,E* whilst those around the two azine C=N bonds in **III** and **IV** are *E,E*. Complexes of the types $[M(CO)_4L]$ (M = Cr, Mo or W; L = **I**–**IV**), $[Mo(CO)_3LL']$ (L = **I**, L′ = NCMe, PPh_3 or $AsPh_3$; L = **II**–**IV**, L′ = PPh_3), $[Mo(CO)_2L(PPh_3)_2]$ (L = **III** or **IV**) and $[Mo(CO)_2Br(\eta^3\text{-}CH_2CH{=}CH_2)L]$ (L = **I**, **III** or **IV**) containing these azines as ligands have also been obtained. Complexes of **II** are the most unstable and these together with tetracarbonyl complexes of **IV** appear to show restricted rotation around the N–N bond(s) caused by the steric requirements of the methyl groups on the fenchone residue(s). All the complexes have been characterised by multinuclear NMR (^1H, ^{13}C and ^{31}P), IR and UV/VIS spectroscopies and mass spectrometry. The crystal structures of camph=N–N=CH–CH=N–N=camph **I** and fench=N–N=CHC_5H_4N **IV** have been determined.

The co-ordination chemistry of α-diimines and related ligands, many of which are of the type RN=CH–CH=NR where R is a sterically demanding group such as *tert*-butyl or isopropyl, has been extensively studied. These ligands have several different co-ordination modes and their transition-metal complexes have been used in catalysis, including chiral catalysis.[1] Related ligands of type $RN{=}CHC_5H_4N$, generated from pyridine-2-carbaldehyde, have also been studied. Several reviews have appeared detailing the preparation of the ligands and the uses of their complexes.[1,2] Our work reports new ligands related to these in that they possess the –N=CH–CH=N– moiety but this is contained within a diazine (C=N–N=CH–CH=N–N=C); our α-diazines and α-2-pyridylazines also contain bulky chiral auxiliaries in the form of either (1*R*)-(+)-camphor or (1*R*)-(−)-fenchone $C_{10}H_{16}$ residues. We wished to see to what extent the replacement of imine by azine functions and the use of new, bulky groups would affect the chemistry. The ligating properties of α-diimines of type RN=CH–CH=NR towards the Group 6 metal carbonyls have been particularly well studied and we chose to study the behaviour of our new types of ligands towards these metal carbonyls first.

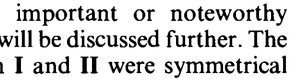
Results and Discussion

The condensation of (1*R*)-(+)-camphor hydrazone[3] with glyoxal gave the hoped-for α-diazine camph=N–N=CH–CH=N–N=camph **I** as a bright yellow crystalline solid; camph is a (1*R*)-(+)-camphor residue, $C_{10}H_{16}$. Similarly, 1*R*-(−)-fenchone hydrazone[4] gave fench=N–N=CH–CH=N–N=fench **II**. These α-diazines were fully characterised by elemental analysis, mass spectrometry and IR spectroscopy (see Table 1) and by ^1H and ^{13}C NMR spectroscopies (see Tables 2 and 3). The ^{13}C NMR spectra were assigned with the aid of spectra acquired with an attached proton test pulse sequence and by comparison with values reported for camphor and fenchone.[5] Other new compounds reported in this paper were similarly characterised and only specially important or noteworthy features of the characterising data will be discussed further. The NMR spectra indicated that both **I** and **II** were symmetrical species giving rise to one set of camphor or fenchone resonances each whilst the central protons appeared in both cases as a singlet [at δ 8.48 (**I**) and 8.31 (**II**)]. The camphor derivative **I** was also characterised by a single-crystal X-ray diffraction study which revealed that it adopted the *E,E,E,E* stereochemistry, see Fig. 1. Atomic coordinates are given in Table 4, whilst bond lengths and angles are in Table 5.

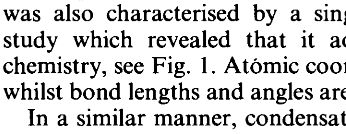
In a similar manner, condensation of (1*R*)-(+)-camphor or (1*R*)-(−)-fenchone hydrazone with pyridine-2-carbaldehyde gave the α-2-pyridylazines **III** and **IV** again as yellow crystalline materials which were also fully characterised. Thus **III** and **IV** are related to pyridine-2-carbaldehyde azine which has itself been shown to form complexes with iron(II) and nickel(II)[6] and more recently with iridium(I).[7] In the ^1H NMR spectra of both **III** and **IV** the resonances for the protons in the 4-pyridyl positions (shown as H^{14} in **III** and **IV**) showed a coupling $^5J(HH)$ to the azine protons of *ca.* 0.7 Hz which was taken as evidence that the compounds adopted *s-trans* conformations about the 2-pyridyl-CH=N moiety in which the coupled



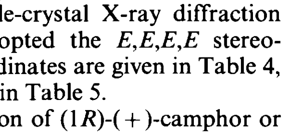
I



III



II



IV

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Camphor = 1,7,7-trimethylnorbornan-2-one, fenchone = 1,3,3-trimethylnorbornan-2-one.

Table 1 Elemental analysis[a] (C, H and N), IR,[b] mass spectral[c] and UV/VIS[d] data

	Analysis			IR		Mass spectrum		UV/VIS	
Compound	C	H	N	ν(C≡O)	ν(C≡N)	*m*/*z* (intensity)	Assignment	λ_{max}	$10^{-3}\ \varepsilon_{max}$
I	74.8(74.55)	9.85(9.65)	15.85(15.8)	—	1645	354(31) 339(14) 204(100)	M $M - \mathrm{CH_3}$ $M - \mathrm{C_{10}H_{16}N}$	—	—
II	74.55(74.55)	9.75(9.65)	15.75(15.8)	—	1640	204(100)	$M - \mathrm{C_{10}H_{16}N}$	—	—
III	75.55(75.25)	8.3(8.3)	16.7(16.45)	—	1670	255(31) 240(28) 119(40) 106(68)	M $M - \mathrm{CH_3}$ $M - \mathrm{C_{10}H_{16}}$ $(M + 1) - \mathrm{C_{10}H_{16}N}$	—	—
IV	75.15(75.25)	8.45(8.3)	16.5(16.45)	—	1650	255(40) 119(51) 106(100)	M $M - \mathrm{C_{10}H_{16}}$ $(M + 1) - \mathrm{C_{10}H_{16}N}$	—	—
1a	60.0(60.2)	6.9(6.6)	11.05(10.8)	2010, 1915, 1865	1650	518(14) 406(77)	M $M - \mathrm{(CO)_4}$	544	9.41
1b	55.25(55.5)	6.35(6.1)	9.9(9.95)	2020, 1920, 1860	1645	564(30) 508(19) 452(14)	M $M - \mathrm{(CO)_2}$ $M - \mathrm{(CO)_4}$	521	11.6
1c	47.75(48.0)	5.2(5.25)	8.6(8.6)	2015, 1910, 1860	1645	650(14) 538(11)	M $M - \mathrm{(CO)_4}$	519	16.6
2a	—	—	—	2010, 1930, 1880	—	—	—	—	—
2b	—	—	—	2020, 1920, 1860	—	564(19) 536(6) 508(5)	M $M - \mathrm{CO}$ $M - \mathrm{(CO)_2}$	—	—
2c	—	—	—	2020, 1925, 1875	—	—	—	—	—
3a	57.15(57.3)	5.1(5.05)	10.15(10.0)	2010, 1900(br), 1840	1650w	419(7) 355(16) 307(35)	M $M - \mathrm{(CO)_3}$ $M - \mathrm{(CO)_4}$	544	4.99
3b	51.65(51.85)	4.35(4.55)	9.0(9.05)	2015, 1900(br), 1840	1650w	465(7) 407(20) 379(8) 351(19)	M $M - \mathrm{(CO)_2}$ $M - \mathrm{(CO)_3}$ $M - \mathrm{(CO)_4}$	510	6.71
3c	43.05(43.6)	3.75(3.85)	7.6(7.6)	2005, 1895(br), 1840	1650w	551(9) 493(20) 439(47)	M $M - \mathrm{(CO)_2}$ $M - \mathrm{(CO)_4}$	521	9.12
4a	56.3(57.3)	4.95(5.05)	9.9(10.05)	2005, 1890(br), 1840	1650w	419(9) 335(14) 307(36)	M $M - \mathrm{(CO)_3}$ $M - \mathrm{(CO)_4}$	544	5.14
4b	51.85(51.85)	4.55(4.55)	9.15(9.05)	2015, 1910, 1890(sh), 1840	1650w	465(16) 437(13) 409(28) 379(10) 351(86)	M $M - \mathrm{CO}$ $M - \mathrm{(CO)_2}$ $M - \mathrm{(CO)_3}$ $M - \mathrm{(CO)_4}$	508	6.68
4c	43.3(43.6)	3.65(3.85)	7.5(7.6)	2005, 1895(br), 1840	1650w	551(12) 493(10) 439(43)	M $M - \mathrm{(CO)_2}$ $M - \mathrm{(CO)_4}$	522	8.57
5 0.2$\mathrm{C_6H_6}$	57.35(57.3)	6.4(6.5)	11.2(11.85)	1925, 1828(br)[e]	1650w[e]	425(6) 397(6)	$M - \mathrm{C_{10}H_{16}N}$ 425 − CO	612[e]	—
6	64.95(64.8)	6.2(6.2)	6.95(7.05)	1940, 1830(br)	1650w	798(10) 742(10) 660(60) 360(63)	M $M - \mathrm{(CO)_2}$ $M - \mathrm{C_{10}H_{16}}$ $\mathrm{MoPPh_3}$	557	11.6
7	61.25(61.45)	5.8(5.85)	6.65(6.65)	1930, 1830(br)	1650w	842(17) 786(11) 704(14)	M $M - \mathrm{(CO)_2}$ $786 - \mathrm{C_6H_{12}}$	559	10.1
8	64.5(64.8)	5.9(6.2)	5.7(7.05)	1930, 1830	1640w	660(6)	$M - \mathrm{C_{10}H_{16}}$	564	8.32
9	64.45(63.7)	5.25(5.2)	5.4(6.0)	1920, 1825(sh), 1808	1655w	699(8) 671(8) 649(3) 615(40) 465(6)	M $M - \mathrm{CO}$ $M - \mathrm{(CO)_2}$ $M - \mathrm{(CO)_3}$ $615 - \mathrm{C_{10}H_{16}N}$	570	3.11
10	63.4(63.7)	5.15(5.2)	5.75(6.0)	1920, 1820(sh), 1805	1645w	615(26) 360(58)	$M - \mathrm{(CO)_3}$ $\mathrm{MoPPh_3}$	570	2.95
11	63.5(69.6)	5.15(5.5)	4.35(4.5)	1828, 1750	1650w	934(33) 679(34)	M $M - \mathrm{C_{16}H_{21}N_3}$	690[e]	—
12	68.55(69.6)	5.5(5.5)	4.45(4.5)	1832, 1755	1620w	673(40)	$M - \mathrm{PPh_3}$	698[e]	1.64
13[f]	51.45(51.7)	6.25(6.25)	8.75(8.9)	1955, 1875	1645w	628(7) 572(22) 531(44)	M $M - \mathrm{(CO)_2}$ $572 - \mathrm{C_3H_5}$	596	4.66
14[g]	47.55(47.75)	4.95(4.95)	7.85(7.95)	1948, 1860	1650w	529(59) 501(27) 473(16) 431(27)	M $M - \mathrm{CO}$ $M - \mathrm{(CO)_2}$ $473 - \mathrm{C_3H_6}$	557	2.55
15[h]	47.5(47.75)	4.85(4.95)	7.9(7.95)	1942, 1855	1635w	473(26) 431(34)	$M - \mathrm{(CO)_2}$ $473 - \mathrm{C_3H_6}$	564	2.95

[a] In %; calculated values in parentheses. [b] In $\mathrm{cm^{-1}}$. Spectra recorded in $\mathrm{CH_2Cl_2}$ solution; all bands are strong unless stated otherwise. sh = Shoulder, br = broad, w = weak. [c] Intensity given is relative to the largest peak in the spectrum. [d] In $\mathrm{CH_2Cl_2}$ solution unless stated otherwise. λ_{max} in nm, ε_{max} in $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$. [e] In $\mathrm{C_6H_6}$ solution. [f] Br: 12.65 (12.75)%. [g] Br: 15.4 (15.1)%. [h] Br: 15.5 (15.1)%.

Table 2 Proton NMR data[a]

Compound	H–C=N	2-Pyridyl protons H^{13}	H^{14}	H^{15}	H^{16}	Methyl groups
I[b]	8.48	—	—	—	—	1.11, 0.68, 0.63
II[b]	8.31	—	—	—	—	1.36, 1.21, 1.20
III[b]	8.81	8.09	7.07	6.61	8.41	1.14, 0.70, 0.69
IV	8.66	7.99	7.15	6.71	8.43	1.36, 1.30, 1.29
1a	6.77	—	—	—	—	1.11, 0.73, 0.67
1b	6.79	—	—	—	—	1.07, 0.73, 0.67
1c	7.07[c]	—	—	—	—	1.09, 0.72, 0.67
3a	7.06	6.43	6.69	6.18	8.77	1.11, 0.82, 0.71
3b	7.22	6.56	6.79	6.29	8.60	1.11, 0.82, 0.71
3c[d]	8.25[e]	7.74	7.91	7.35	9.14	1.13, 0.99, 0.93
4a[f]	6.98	6.40	6.62	6.07	8.75	1.41, 1.12, 0.99
4b[f]	7.04	6.39	6.65	6.11	8.58	1.40, 1.14, 1.04
4c[d,f]	8.30[e]	7.70	7.90	7.33	9.15	1.30, 1.25, 1.22
5[g]	7.69[h]	—	—	—	—	1.07, 0.98, 0.91
	7.68[h]					1.06, 0.98, 0.89
6	6.76[h,i]	—	—	—	—	1.28, 1.17, 0.76
	6.66[h,i]					1.14, 0.73, 0.66
7	6.82[h]	—	—	—	—	1.25, 1.15, 0.73
	6.69[h]					1.11, 0.70, 0.66
8[j]	6.98[h,i]	—	—	—	—	1.34, 1.33, 1.28
	6.96[h,i]	—	—	—	—	1.28, 1.27, 1.25
	6.79[h,i]	—	—	—	—	1.24, 1.21, 1.20
	6.69[h,i]	—	—	—	—	1.18, 1.17, 1.10
9′	7.04[i]	6.21	6.61	5.99	8.46	1.31, 1.29, 0.77
9″	7.03[i]	6.23	6.63	5.98	8.51	1.11, 0.71, 0.65
10	6.98[i]	6.30	6.63	5.95	8.44	1.52, 1.15, 1.14
11[d]	*k*	7.57	7.49	6.09	7.04	0.97, 0.87, 0.65
12[l]	*k*	6.36	6.56	5.67	7.86	1.70, 1.14, 0.22
13	7.37	—	—	—	—	1.09, 1.08, 1.00
	7.37					1.00, 0.95, 0.89
14[m]	*k*	6.55	6.85	6.48	8.70	1.12, 1.09, 0.74
14′[m]	*k*	6.55	6.89	6.44	8.70	0.91, 0.69, 0.45
15[b]	7.74	7.64	7.97	7.57	9.91	1.58, 1.19, 1.17
15′[m]	7.68	*k*	*k*	*k*	*k*	1.42, 1.38, 1.22

[a] In C_6D_6 solution at 400.13 MHz and 301 K unless stated otherwise. Resonances were singlets except for those arising from the 2-pyridyl groups, for which the protons are numbered as in **III** or **IV**. The couplings between these protons were as follows: $^3J(H^{13}, H^{14})$ 7.9, $^4J(H^{13}, H^{15})$ 1.2, $^5J(H^{13}, H^{16})$ 1.0, $^3J(H^{14}, H^{15})$ 7.4, $^4J(H^{14}, H^{16})$ 1.7 and $^3J(H^{15}, H^{16})$ 4.8 Hz. These values varied by less than 0.3 Hz in all cases and are not listed individually here for brevity. Long range couplings of *ca.* 0.7 Hz were also detected between the azine proton and either H^{14} (in **III** and **IV**) or H^{16} (in **3a–3c** and **4a–c**). [b] Recorded at 99.56 MHz. [c] ^3J(WH) = 4.5 Hz. [d] In CD_2Cl_2 solution. [e] ^3J(WH) = 4.2 Hz. [f] Resonances listed for major form only. [g] Recorded in CD_3CN solution. [h] Resonance exhibits a coupling ^3J(HH) *ca.* 1.5 ± 0.2 Hz. [i] Resonance exhibits a coupling ^4J(PH) *ca.* 2.7 ± 0.2 Hz. [j] Resonances listed for two major forms only. Assignment of methyl groups to particular forms is arbitrary. [k] Resonance obscured. [l] In C_6D_6 solution. [m] In $C_6D_5CD_3$ solution at 363 K.

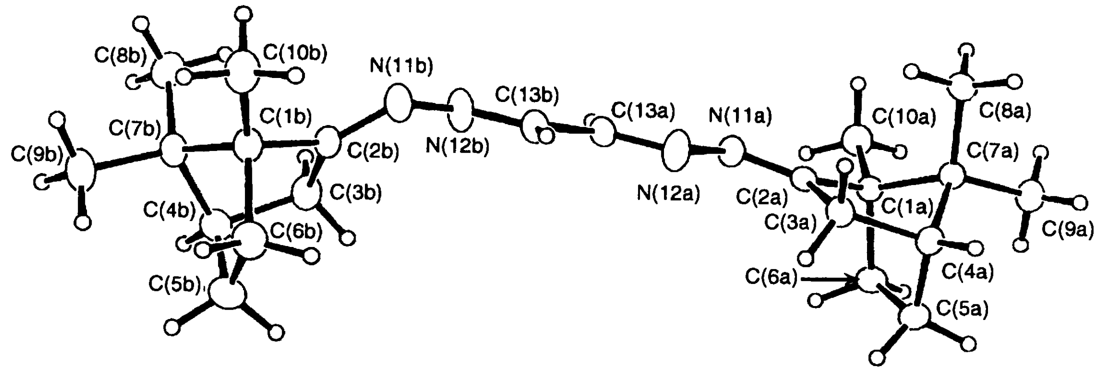


Fig. 1 Crystal structure of **I**

hydrogens are placed in a W-type arrangement. A single-crystal X-ray diffraction study of **IV** confirmed this and demonstrated that **IV** adopted the *E,E* configuration, see Fig. 2. Atomic coordinates are given in Table 6 and bond lengths and angles are in Table 7. Comparing the crystal structures of **I** and **IV**, we find the bond lengths for the N=C–C=N groups are very similar to those of comparable compounds.[8] The C=N bonds attached to the $C_{10}H_{16}$ fragments are slightly longer than those in the less substituted positions. In **I**, the atoms in the N(11a)–N(11b) chain are contained within a plane as are those in **IV** from the pyridyl ring to N(11). The camphor residues in **I** have similar bond lengths and angles to other crystal structures containing camphor residues. Examples include the crystal structures of 3-diphenylphosphino-(1*R*)-camphor dimethylhydrazone[9] and (1*R*)-camphor oxime.[10] Very few crystal structures containing a fenchone moiety have been determined. We have reported the

Table 3 Carbon-13 NMR data[a]

	Camphor or fenchone carbons											2-Pyridyl carbons					
Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}	C^{16}	Carbonyl
I[b,c]	52.5	181.1	35.3	43.5	26.9	32.2	47.6	18.5	19.3	10.9	154.9	—	—	—	—	—	—
II[b]	51.3	184.4	45.4	48.7	25.3	34.1	42.9	23.8	23.6	17.4	156.2	—	—	—	—	—	—
III[b]	52.9	181.4	36.0	44.2	27.6	32.9	47.8	18.8	19.7	11.5	158.4	154.9	121.0	135.8	124.1	149.8	—
IV	51.4	184.3	45.5	48.9	25.6	34.3	43.2	24.7	24.2	17.6	158.2	154.8	120.7	135.9	124.1	149.9	—
1a[d]	53.7	177.5	33.9	44.0	27.3	32.5	48.1	18.6	19.6	11.4	145.5	—	—	—	—	—	232.4, 216.5
1b	53.9	178.3	34.3	44.1	27.3	32.5	48.2	18.6	19.6	11.3	146.5	—	—	—	—	—	224.2, 204.4
1c	54.0	179.3	33.8	44.1	27.3	32.6	48.3	18.6	19.6	11.3	147.5	—	—	—	—	—	209.1(br)
3a	53.9	177.3	34.1	44.1	27.4	32.6	48.1	18.7	19.6	11.4	149.2	153.9	125.0	135.0	123.7	153.1	230.9, 229.4 214.1, 213.7
3b	54.0	178.5	34.4	44.2	27.4	32.7	48.2	18.7	19.7	11.4	151.2	152.8	126.0	136.3	124.8	152.8	223.9, 222.6 204.5, 204.4
3c[e]	54.2	180.3	34.2	44.3	27.4	32.8	48.6	18.9	19.7	11.3	153.1	154.7	127.0	137.3	126.2	153.1	216.8, 214.5 199.5, 199.4
4a[e,f]	53.3	176.2	47.2	46.4	25.6	33.0	46.4	26.9	24.6	21.5	149.0	154.0	125.7	136.6	124.4	153.7	230.6, 229.2 214.0, 213.2
4b[e,f]	53.4	176.8	47.2	46.4	25.6	32.6	46.4	26.9	24.6	21.5	150.0	153.4	126.4	137.5	125.3	153.3	224.1, 222.8 205.0, 203.6
4c[e,f]	53.4	178.3	47.3	46.5	25.6	32.7	46.4	26.9	24.6	21.3	151.6	154.5	126.6	137.2	125.9	153.3	217.1, 214.9 200.6, 199.3
5[g]	54.3	179.1	35.9	45.1	27.9	33.4	49.1	19.2	20.0	11.8	149.7	—	—	—	—	—	231.3, 231.0
	54.1	178.7	35.6	45.0	27.8	33.4	49.0	19.1	19.9	11.7	149.4						216.6
6	53.7	177.0	34.3	44.3	27.5	33.1	48.1	18.9	19.9	11.7	143.2[h]	—	—	—	—	—	231.7,[i] 230.9[i]
	53.5	176.8	33.7	44.3	27.4	32.5	47.8	18.7	19.6	11.6	142.6[h]						215.2[j]
7	53.8	177.6	34.4	44.3	27.5	33.1	48.1	18.9	19.9	11.7	144.2	—	—	—	—	—	231.1, 230.3
	53.6	177.1	33.9	44.3	27.4	32.5	47.9	18.7	19.6	11.6	143.5						215.0
8[k]	53.4	176.0	46.5	46.3	29.0	34.8	47.0	25.9	25.1	20.4	143.2[h]	—	—	—	—	—	231.8,[l] 231.3[l]
	53.3	175.6	46.4	45.8	27.4	34.5	46.9	25.6	25.0	18.3	142.8[h]						217.7[m]
	53.0	175.5	43.2	50.6	27.2	33.0	46.9	24.7	24.1	17.8	142.6[h]	—	—	—	—	—	231.6,[l], 231.1[l]
	52.8	175.1	42.7	49.2	27.2	32.8	46.7	24.2	23.7	17.3	141.9[h]						215.4[m]
9′	54.1	178.2	34.9	44.3	27.4	32.6	48.2	18.9	19.6	11.7	148.7[n]	152.4	125.0	133.1	123.4	151.9	230.1,[l] 229.2[l]
9″	53.8	177.7	34.4	44.3	27.4	33.2	48.0	18.9	20.1	11.8	148.0[n]	152.4	125.0	133.1	123.4	152.1	223.3,[l] 222.5[l] 204.1[o]
10	53.1	175.4	47.1	46.1	25.8	32.7	46.4	27.1	25.3	20.9	146.8[n]	152.1	124.4	133.1	123.3	152.1	230.1,[l] 229.5,[l] 213.9[o]
11[e]	53.9	176.4	34.1	44.5	26.9	32.5	48.2	18.9	19.7	11.9	147.0	152.3	124.8	130.8	122.2	150.7	240.0,[p] 238.8[q]
12	51.1	174.8	47.5	45.6	25.6	36.8	45.8	28.1	25.1	17.5	142.9	150.9	124.0	133.3	121.2	150.5	241.2,[r] 240.3[r]
13[s]	54.3	178.9	36.1	44.1	27.4	33.1	48.0	18.7	19.8	11.2	143.4	—	—	—	—	—	221.4
	54.2	178.1		44.0	26.8	32.6	47.8	18.7	19.6	11.1							

[a] Spectra recorded in C_6D_6 solution at an operating frequency of 100.6 MHz unless stated otherwise. Carbon atoms are numbered as in **III** and **IV**. [b] Recorded at an operating frequency of 22.5 MHz. [c] Recorded in $CDCl_3$ solution. [d] Recorded at an operating frequency of 75 MHz. [e] Recorded in CD_2Cl_2 solution. [f] Resonances listed for major form only. [g] Recorded in CD_3CN solution. [h] $^3J(PC)$ 1.7 ± 0.1 Hz. [i] $^2J(PC)$ 11.0 ± 0.2 Hz. [j] $^2J(PC)$ 26.0 Hz. [k] Recorded in CD_2Cl_2 solution. Assignment of carbon atoms to particular groups is arbitrary. [l] $^2J(PC)$ 9.5 ± 0.1 Hz. [m] $^2J(PC)$ 27.6 ± 0.1 Hz. [n] $^3J(PC)$ 3.4 ± 0.2 Hz. [o] $^2J(PC)$ 33.9 ± 0.3 Hz. [p] $^2J(PC)$ 9.9 Hz. [q] $^2J(PC)$ 8.8 Hz. [r] $^2J(PC)$ 11.9 Hz. [s] Spectrum recorded at 323 K and 25 MHz. Where only one chemical shift appears the resonance was a broad singlet.

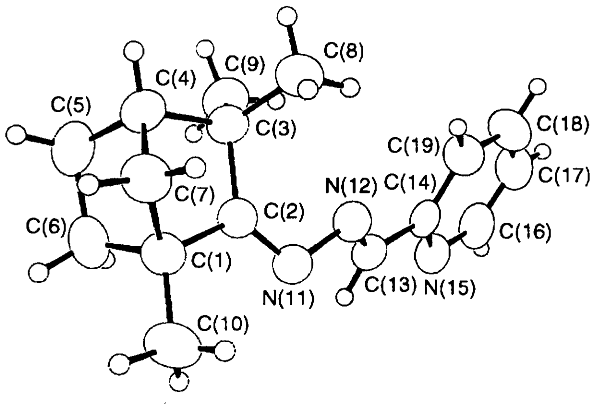


Fig. 2 Crystal structure of **IV**

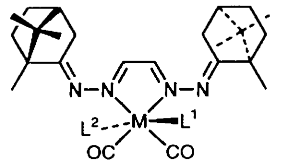
crystal structure of a fenchone–pinacolone mixed azine phosphine *Z,E*-$Ph_2PCH_2C(Bu^t){=}N{-}N{=}C_{10}H_{16}$, derived from (1*R*)-fenchone[4a] and the crystal structure of (1*S*)-fenchone oxime has also been determined.[11] The dimensions of the fenchone moiety in the crystal structure of **IV** are similar to the dimensions in these two structures.

Treatment of **I** with $[M(CO)_6]$ (M = Cr, Mo or W) gave purple solutions but we were unable to isolate pure products from them. However, treatment of $[M(nbd)(CO)_4]$ {M = Cr, Mo or W; nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)} under N_2 in pentane or hot cyclohexane readily gave the substitution products **1a**–**1c** which were isolated either as intensely coloured prisms that were dark green to reflected light and purple to transmitted light or as purple powders. The complexes were fully characterised spectroscopically and by elemental analysis. In the ^1H and ^{13}C NMR spectra the camphor residues gave rise to a single set of resonances indicating that the diazine had bonded to the metal as a symmetrical ligand. Again the central N=CH–CH=N protons gave rise to a singlet in all cases although the resonance in compound **1c** exhibited coupling to ^{183}W. In the ^{13}C-{^1H} NMR spectra, two carbonyl resonances were observed for each of the chromium and molybdenum complexes **1a** or **1b** but for the tungsten complex **1c** at ambient temperature a single broad carbonyl resonance was observed and so it seems that the carbonyl ligands in this compound scramble on the NMR time-

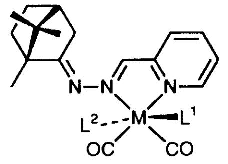
Table 4 Fractional atomic coordinates (× 10^4) for **I** with estimated standard deviations (e.s.d.s) in parentheses.

Atom	*x*	*y*	*z*
C(1a)	403(2)	9 194.1(12)	−630.5(14)
C(2a)	1 457(3)	8 592.8(13)	424.6(14)
C(3a)	285(3)	8 719.1(15)	1 269.9(14)
C(4a)	−1 395(3)	9 439.1(14)	614(2)
C(5a)	−486(3)	10 521(2)	572(2)
C(6a)	795(3)	10 355.5(14)	−255(2)
C(7a)	−1 791(2)	9 048.9(14)	−621.4(14)
C(8a)	−2 497(3)	7 921.6(14)	−810(2)
C(9a)	−3 246(3)	9 733(2)	−1 487(2)
C(10a)	942(3)	8 904(2)	−1 702(2)
N(11a)	3 085(2)	8 120.0(12)	520.1(13)
N(12a)	3 829(2)	7 658.7(15)	1 603.7(14)
C(13a)	5 538(3)	7 290.0(14)	1 762(2)
C(1b)	11 693(3)	5 717.8(15)	5 744.8(15)
C(2b)	10 682(2)	6 161.4(14)	4 592.6(14)
C(3b)	12 062(3)	6 939(2)	4 291(2)
C(4b)	13 804(3)	6 904(2)	5 367(2)
C(5b)	13 087(4)	7 441(2)	6 295(2)
C(6b)	11 638(3)	6 636(2)	6 551(2)
C(7b)	13 882(3)	5 734(2)	5 711(2)
C(8b)	14 280(3)	4 988(2)	4 837(2)
C(9b)	15 376(3)	5 508(2)	6 853(2)
C(10b)	10 867(3)	4 692(2)	6 025(2)
N(11b)	8 927(2)	5 910.7(14)	4 046.1(13)
N(12b)	8 233(2)	6 432(2)	3 001.2(14)
C(13b)	6 508(3)	6 777.1(14)	2 814(2)

scale. Such a process has been observed in other, analogous complexes although it appears that the process has a considerably lower energy for the tungsten complex than for the chromium or molybdenum complexes.[12] The nature of the bonding in complexes **1a**–**1c** was assigned as shown: both the coupling of the tungsten to the HC=N protons and, more obviously, the intense purple coloration suggest that the N=CH–CH=N group co-ordinates to the metal forming a five-membered ring. A similarly intense colour is found where this arrangement is adopted in complexes of α-diimines with these metal carbonyls.[2]



1a M = Cr; L^1 = L^2 = CO
1b M = Mo; L^1 = L^2 = CO
1c M = W; L^1 = L^2 = CO
5 M = Mo; L^1 = CO; L^2 = NCMe
6 M = Mo; L^1 = CO; L^2 = PPh$_3$
7 M = Mo; L^1 = CO; L^2 = AsPh$_3$
13 M = Mo; L^1 = Br; L^2 = η^3-CH$_2$CHCH$_2$



3a M = Cr; L^1 = L^2 = CO
3b M = Mo; L^1 = L^2 = CO
3c M = W; L^1 = L^2 = CO
9′ M = Mo; L^1 = CO; L^2 = PPh$_3$
9″ M = Mo; L^1 = PPh$_3$; L^2 = CO
11 M = Mo; L^1 = L^2 = PPh$_3$
14 M = Mo; L^1 = Br; L^2 = η^3-CH$_2$CHCH$_2$
14′ M = Mo; L^1 = η^3-CH$_2$CHCH$_2$; L^2 = Br

Treatment of **II** with [M(nbd)(CO)$_4$] (M = Cr, Mo or W) under N$_2$ at ambient temperature or in refluxing methylcyclohexane, cyclohexane or *n*-hexane rapidly produced an intensely purple solution. The progress of the reaction was monitored by IR spectroscopy using the ν(C≡O) bands and in each case a set of bands, very similar in position to those in **1a**–**1c**, appeared and were assumed to be due to complexes **2a**–**2c**. However, before all the [M(nbd)(CO)$_4$] had reacted, the peaks in the IR spectrum due to the substitution product began to decline being replaced in part by a peak due to [M(CO)$_6$] indicating the decomposition of the product. When the reaction between [Mo(nbd)(CO)$_4$] and **II** was carried out in the presence of a large excess of the diazine, we were able to obtain a sample of **2b** contaminated only by [Mo(CO)$_6$] and by free **II**. Mass spectrometry of this sample showed a peak corresponding to a substitution product similar to **1b** but the ^{1}H NMR spectrum contained many peaks in the region of the central N=CH–CH=N protons. Whilst this may be taken to indicate species with several different types of bonding, the 'cleanness' of the IR spectrum, which showed only one set of bands due to a tetracarbonyl species and the intense colour (indicating a five-membered ring) led us to believe that **2b** is analogous to **1b** and that in fact the complex pattern of resonances in the ^{1}H NMR spectrum is due to conformational isomers related by restricted rotation about the N–N bonds. This view was reinforced by studies of the complexes of **IV** (see below).

Treatment of **III** or **IV** with [M(nbd)(CO)$_4$] (M = Cr, Mo or W) under N$_2$ in refluxing cyclohexane readily gave complexes **3a**–**3c** or **4a**–**4c** respectively. The complexes, which were all fully characterised, were again very intensely coloured and isolated as red-brown or purple solids. Complexation caused some changes in the ^{1}H NMR spectra, in particular the chemical shifts of the pyridyl protons but little change in the couplings between them (see Table 2). The change in conformation about the pyridyl-CH=N moiety caused the disappearance of the long-range coupling between the CH=N and pyridyl H^{14} protons this being replaced by a coupling between the CH=N and pyridyl H^{16} protons. In compounds **3c** and **4c**, as with **1c**, the CH=N proton showed a coupling to ^{183}W. The ^{13}C-{^{1}H} NMR spectra of each of the three species **3a**, **3b** or **3c** all showed four metal carbonyl resonances indicating that these complexes were rigid at the metal centre. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of **4a**, however, showed the presence of three closely related species in the approximate ratio of 5 : 2 : 1; similarly **4b** or **4c** showed the presence of three closely related species, again in the approximate ratios of 5 : 2 : 1. The presence of these three species was most apparent in the ^{1}H NMR spectrum as three sets of resonances most easily distinguished in the pyridine/CH=N region but even there the difference in chemical shifts between the corresponding protons was less than 0.05 ppm in all cases. In the ^{13}C-{^{1}H} NMR spectrum the separation between corresponding resonances was generally 0.2 ppm or less. Only the chemical shifts of the predominant species, *i.e.* the one present with approximate relative intensity 5, are given in Table 3 for **4a**, **4b** and **4c**. The extremely similar chemical shifts of the three species for **4a**–**4c** and the IR spectra (in which separate peaks for the three forms could not be resolved) led us to believe that the species were conformational isomers related by restricted rotation around the N–N bond, the only bond in these complexes which could give rise to rotamers. The restriction of rotation is probably caused by the geminal dimethyl groups attached to the C^3 of the fenchone residue which, if the ligand retains its *E* configuration in the complexes that it has in the free state, come into close contact with the M(CO)$_4$ moiety. These non-bonding

Table 5 Bond lengths (Å) and angles (°) for **I** with e.s.d.s in parentheses

C(1a)–C(2a)	1.513(2)	C(1b)–C(2b)	1.508(2)
C(1a)–C(10a)	1.516(2)	C(1b)–C(10b)	1.512(3)
C(1a)–C(6a)	1.555(2)	C(1b)–C(6b)	1.543(3)
C(1a)–C(7a)	1.565(2)	C(1b)–C(7b)	1.559(3)
C(2a)–N(11a)	1.275(2)	C(2b)–N(11b)	1.275(2)
C(2a)–C(3a)	1.508(2)	C(2b)–C(3b)	1.508(3)
C(3a)–C(4a)	1.540(3)	C(3b)–C(4b)	1.536(3)
C(4a)–C(5a)	1.530(3)	C(4b)–C(5b)	1.533(3)
C(4a)–C(7a)	1.548(2)	C(4b)–C(7b)	1.549(3)
C(5a)–C(6a)	1.554(3)	C(5b)–C(6b)	1.544(4)
C(7a)–C(8a)	1.520(3)	C(7b)–C(8b)	1.520(3)
C(7a)–C(9a)	1.530(2)	C(7b)–C(9b)	1.531(3)
N(11a)–N(12a)	1.417(2)	N(11b)–N(12b)	1.408(2)
N(12a)–C(13a)	1.259(2)	N(12b)–C(13b)	1.255(2)
C(13a)–C(13b)	1.442(3)		
C(2a)–C(1a)–C(10a)	115.99(14)	C(2b)–C(1b)–C(10b)	115.3(2)
C(2a)–C(1a)–C(6a)	103.01(14)	C(2b)–C(1b)–C(6b)	103.2(2)
C(10a)–C(1a)–C(6a)	115.1(2)	C(10b)–C(1b)–C(6b)	115.5(2)
C(2a)–C(1a)–C(7a)	100.67(13)	C(2b)–C(1b)–C(7b)	100.53(14)
C(10a)–C(1a)–C(7a)	117.8(2)	C(10b)–C(1b)–C(7b)	117.8(2)
C(6a)–C(1a)–C(7a)	101.86(14)	C(6b)–C(1b)–C(7b)	102.1(2)
N(11a)–C(2a)–C(3a)	129.9(2)	N(11b)–C(2b)–C(1b)	122.4(2)
N(11a)–C(2a)–C(1a)	122.3(2)	N(11b)–C(2b)–C(3b)	129.5(2)
C(3a)–C(2a)–C(1a)	107.67(14)	C(1b)–C(2b)–C(3b)	108.0(2)
C(2a)–C(3a)–C(4a)	101.19(14)	C(2b)–C(3b)–C(4b)	100.7(2)
C(5a)–C(4a)–C(3a)	106.7(2)	C(5b)–C(4b)–C(3b)	106.1(2)
C(5a)–C(4a)–C(7a)	102.74(14)	C(5b)–C(4b)–C(7b)	102.8(2)
C(3a)–C(4a)–C(7a)	102.92(14)	C(3b)–C(4b)–C(7b)	102.8(2)
C(4a)–C(5a)–C(6a)	103.05(14)	C(4b)–C(5b)–C(6b)	103.3(2)
C(5a)–C(6a)–C(1a)	103.7(2)	C(5b)–C(6b)–C(1b)	103.8(2)
C(8a)–C(7a)–C(9a)	107.9(2)	C(8b)–C(7b)–C(9b)	108.3(2)
C(8a)–C(7a)–C(4a)	114.6(2)	C(8b)–C(7b)–C(4b)	114.3(2)
C(9a)–C(7a)–C(4a)	113.6(2)	C(9b)–C(7b)–C(4b)	113.3(2)
C(8a)–C(7a)–C(1a)	113.25(14)	C(8b)–C(7b)–C(1b)	113.0(2)
C(9a)–C(7a)–C(1a)	113.7(2)	C(9b)–C(7b)–C(1b)	114.1(2)
C(4a)–C(7a)–C(1a)	93.50(13)	C(4b)–C(7b)–C(1b)	93.5(2)
C(2a)–N(11a)–N(12a)	111.8(2)	C(2b)–N(11b)–N(12b)	113.7(2)
C(13a)–N(12a)–N(11a)	112.9(2)	C(13b)–N(12b)–N(11b)	114.0(2)
N(12a)–C(13a)–C(13b)	120.2(2)	N(12b)–C(13b)–C(13a)	121.2(2)

Table 6 Atomic coordinates (× 10^4) for **IV** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
C(1)	−3517(4)	821(2)	350.3(14)
C(2)	−3902(3)	−19.5(14)	−199.0(13)
C(3)	−5442(4)	−701.0(14)	214.0(14)
C(4)	−5775(4)	−157(2)	1007.7(14)
C(5)	−3785(5)	−204(2)	1517(2)
C(6)	−2210(5)	415(2)	1049.2(14)
C(7)	−5703(4)	897(2)	739(2)
C(8)	−7544(4)	−771(2)	−236.7(15)
C(9)	−4550(5)	−1716(2)	312(2)
C(10)	−2591(5)	1704(2)	−35(2)
N(11)	−3000(3)	−75.6(13)	−878.6(11)
N(12)	−3611(3)	−889.9(14)	−1326.0(11)
C(13)	−2113(4)	−1296(2)	−1691.2(13)
C(14)	−2491(4)	−2147(2)	−2187.2(12)
N(15)	−765(3)	−2516(2)	−2525.6(11)
C(16)	−1048(5)	−3303(2)	−2977.3(15)
C(17)	−2947(5)	−3733(2)	−3101.9(15)
C(18)	−4697(5)	−3340(2)	−2755(2)
C(19)	−4482(5)	−2533(2)	−2291.1(15)

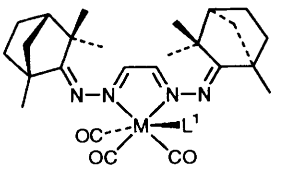
interactions also explain the instability of the complexes **2a**–**2c** where two such fenchone residues come close to the metal. In the camphor derivatives **1a**–**1c** and **3a**–**3c** no conformational isomerism similar to that in fenchone derivatives **4a**–**4c** was observed.

We attempted to carry out reactions of the co-ordinated α-diazine including protonation. When a solution of **1b** in CD_2Cl_2 at −80 °C was treated with one mole equivalent of $HBF_4·Et_2O$ and the progress of the reaction followed by ^1H NMR spectroscopy, a new peak appeared at δ 8.67 for the azine protons (N=CH–CH=N) which was approximately 25% of the height of the resonance for the remaining **1b** (at δ 8.22). Addition of more $HBF_4·Et_2O$ caused an increase in this new peak at the expense of that for the starting material and when no **1b** remained the solution appeared pale brown with a pale coloured precipitate. Addition of an excess of NaO_2CMe to this solution caused the purple colour due to **1b** to return but not as strongly as at first. Addition of NaO_2CMe to an isolated sample of the precipitate (which in the IR spectrum exhibited no stretches due to metal carbonyls) produced free **I**. We had hoped to be able to protonate the ligand exclusively but the results appear to indicate that in fact under the reaction conditions, the ligand became decomplexed and protonated whilst the metal remained in solution possibly as an unstable solvent complex.

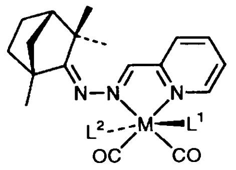
Attempts to effect substitution of the metal carbonyl ligands by phosphine were unsatisfactory and reaction of **1b** or **4b** with one mole equivalent of $PPh_2CH_2CH_2PPh_2$ produced $[Mo(CO)_4(PPh_2CH_2CH_2PPh_2)]$; however, substituted molybdenum carbonyl complexes were prepared by starting from *fac*-$[Mo(CO)_3(NCMe)_3]$. Treatment of this triacetonitrile complex with **I** gave a solution with an intense royal blue colour from which *fac*-$[Mo(CO)_3(NCMe)$(camph=N–N=CH–CH=N–N=camph)] **5** was isolated as a purple thermally sensitive solid. The ^1H NMR spectra of **5** in CD_3CN showed that the two camphor moieties in the complex were no longer equivalent and the central azine protons (–N=CH–CH=N–) appeared as a strongly coupled AB pair with ^3J(HH) 1.5 Hz. The $^{13}C-\{^1H\}$

Table 7 Bond lengths (Å) and angles (°) for **IV** with e.s.d.s in parentheses

C(1)–C(10)	1.509(3)	C(1)–C(2)	1.512(3)
C(1)–C(7)	1.535(3)	C(1)–C(6)	1.545(4)
C(2)–N(11)	1.280(3)	C(2)–C(3)	1.528(3)
C(3)–C(9)	1.533(3)	C(3)–C(8)	1.535(4)
C(3)–C(4)	1.550(3)	C(4)–C(5)	1.525(4)
C(4)–C(7)	1.537(3)	C(5)–C(6)	1.536(4)
N(11)–N(12)	1.416(3)	N(12)–C(13)	1.264(3)
C(13)–C(14)	1.470(3)	C(14)–N(15)	1.335(3)
C(14)–C(19)	1.382(4)	N(15)–C(16)	1.347(3)
C(16)–C(17)	1.360(4)	C(17)–C(18)	1.367(4)
C(18)–C(19)	1.376(4)		
C(10)–C(1)–C(2)	115.6(2)	C(10)–C(1)–C(7)	118.5(2)
C(2)–C(1)–C(7)	99.7(2)	C(10)–C(1)–C(6)	114.7(2)
C(2)–C(1)–C(6)	105.5(2)	C(7)–C(1)–C(6)	100.6(2)
N(11)–C(2)–C(1)	121.4(2)	N(11)–C(2)–C(3)	130.7(2)
C(1)–C(2)–C(3)	107.9(2)	C(2)–C(3)–C(9)	112.8(2)
C(2)–C(3)–C(8)	111.6(2)	C(9)–C(3)–C(8)	108.3(2)
C(2)–C(3)–C(4)	100.0(2)	C(9)–C(3)–C(4)	114.2(2)
C(8)–C(3)–C(4)	109.8(2)	C(5)–C(4)–C(7)	100.5(2)
C(5)–C(4)–C(3)	110.5(2)	C(7)–C(4)–C(3)	102.2(2)
C(4)–C(5)–C(6)	103.0(2)	C(5)–C(6)–C(1)	104.4(2)
C(1)–C(7)–C(4)	95.0(2)	C(2)–N(11)–N(12)	113.7(2)
C(13)–N(12)–N(11)	114.4(2)	N(12)–C(13)–C(14)	121.0(2)
N(15)–C(14)–C(19)	122.8(2)	N(15)–C(14)–C(13)	114.8(2)
C(19)–C(14)–C(13)	122.3(2)	C(14)–N(15)–C(16)	116.5(2)
N(15)–C(16)–C(17)	124.3(3)	C(16)–C(17)–C(18)	118.3(3)
C(17)–C(18)–C(19)	119.4(3)	C(18)–C(19)–C(14)	118.7(3)



2a M = Cr; L^1 = CO
2b M = Mo; L^1 = CO
2c M = W; L^1 = CO
8 M = Mo; L^1 = PPh_3



4a M = Cr; L^1 = L^2 = CO
4b M = Mo; L^1 = L^2 = CO
4c M = W; L^1 = L^2 = CO
10 M = Mo; L^1 = CO; L^2 = PPh_3
12 M = Mo; L^1 = L^2 = PPh_3
15 M = Mo; L^1 = Br; L^2 = η^3-CH_2CHCH_2
15′ M = Mo; L^1 = η^3-CH_2CHCH_2; L^2 = Br

NMR spectrum, also in CD_3CN, confirmed the inequivalence of the camphor residues and also that the complex was indeed a tricarbonyl complex (see Tables 1–3). Treatment of **5** with one mole equivalent of PPh_3 displaced the acetonitrile and gave the tricarbonyl-monophosphine complex **6** as a violet solid. This complex gave a singlet resonance in the ^{31}P-$\{^1H\}$ NMR spectrum and, as with **5**, the ^1H and ^{13}C-$\{^1H\}$ NMR spectra confirmed the inequivalence of the camphor residues and the *fac*-stereochemistry. The particularly noticeable features of the ^1H NMR spectrum of **6** were (*i*) the shift to low field of one of the methyl resonances in one of the camphor residues by 0.5 ppm and (*ii*) the shift to low field by 0.5–1 ppm of the *exo*-H^3 proton from one camphor residue and the *endo*-H^3 proton from the other, *e.g.* for **1b** the *exo*-H^3 resonance appeared at δ 2.16 and the *endo*-H^3 proton at δ 2.27 whereas for **6** the corresponding resonances were at δ 3.09 and 2.18 (*exo*) and δ 2.94 and 2.04 (*endo*). This deshielding is presumably due to the close approach of these protons to a phosphine phenyl group and would imply that the methyl protons affected are attached to the C^8 in the camphor residue. In an analogous reaction, treatment of the acetonitrile complex **5** with $AsPh_3$ gave the arsine complex **7** corresponding to **6**. The NMR spectra of **7** were very similar to those of **6**, apart from the effect of substituting PPh_3 by $AsPh_3$.

Compound [Mo(CO)$_3$(fench=N–N=CH–CH=N–N=fench)-(PPh$_3$)] **8** was prepared in a similar fashion to that used to prepare **6**. This complex showed three singlets in the ^{31}P-$\{^1H\}$ NMR spectrum in an approximate 2:2:1 ratio. In the ^1H, ^1H-$\{^{31}P\}$ and ^{13}C-$\{^1H\}$ NMR spectra most of the resonances due to the fench=N–N=CH–CH=N–N=fench moieties for the two more abundant of the three forms detected in the ^{31}P-$\{^1H\}$ NMR spectrum were resolved. We suggest that **8** exists in solution as three conformational isomers probably related by rotation around an N–N bond. This is discussed further after consideration of the complex of **IV**, see below.

Treatment of [Mo(CO)$_3$(MeCN)$_3$] with **III** and **IV** produced intense dark blue solutions which are ascribed as being due to tricarbonyl complexes containing the α-2-pyridylazine ligand **III** or **IV** and one remaining acetonitrile ligand. Attempts to isolate these complexes were unsuccessful: after concentration of the solution and addition of pentane dark oils were produced that could not be induced to crystallise and additionally, when C_6D_6 solutions of each complex were monitored over a period of a few hours, some of the tetracarbonyl complexes were formed by decomposition.

Addition of [Mo(CO)$_3$(MeCN)$_3$] to **III** or **IV**, followed by one mole equivalent of PPh_3 gave dark blue solution containing the hoped-for complexes [Mo(CO)$_3$(PPh$_3$)(camph=N–N=CHC$_5$H$_4$N)] **9** and [Mo(CO)$_3$(PPh$_3$)(fench=N–N=CHC$_5$H$_4$N)] **10** which were isolated and fully characterised. The ^{31}P-$\{^1H\}$, ^1H, ^1H-$\{^{31}P\}$ and ^{13}C-$\{^1H\}$ NMR spectroscopic studies showed that **9** was formed as both possible isomers (**9′** and **9″**) in a ratio of *ca.* 55:45 and, although many of the resonances in the NMR spectra could be assigned to either the major or minor form, we were unable to assign either isomer to the structures **9′** or **9″**. The ^1H NMR spectrum suggested that the camphor residues in **9′** and **9″** are arranged differently with respect to the PPh_3 ligand and akin to the arrangement of the two camphor residues in **6**; in particular one *exo*-H^3 and one *endo*-H^3 proton are at 1 ppm to low field of the corresponding resonances from the other camphor residue.

In contrast to the camphor derivatives **9′** and **9″**, the corresponding fenchone ligand **IV** gave only one isomer [Mo(CO)$_3$(PPh$_3$)(fench=N–N=CHC$_5$H$_4$N)] **10**, *i.e.* there is one preferred orientation of the fenchone ligand with respect to the PPh_3 ligand.

The compounds **I**–**IV** were also treated with *cis*-[Mo(CO)$_2$-(NCMe)$_2$(PPh$_3$)$_2$].[13] The diazines **I** and **II** did not give stable complexes displacing some PPh_3 and giving mixtures containing some tricarbonyl complexes. Treatment of *cis*-[Mo-(CO)$_2$(NCMe)$_2$(PPh$_3$)$_2$] with **III** or **IV** gave a dark green complex in either case which could not be obtained in a completely pure state but the spectroscopic data indicated that these were the hoped-for bis(phosphine) complexes [Mo-(CO)$_2$L(PPh$_3$)$_2$] **11** (L = **III**) and **12** (L = **IV**). The ^{31}P-$\{^1H\}$ NMR spectra of **11** and **12** each showed a strongly coupled AB pattern with $^2J(PP)$ *ca.* 80 Hz, thus indicating that the phosphine ligands are mutually *trans*; this was confirmed in the ^1H, ^1H-$\{^{31}P\}$ and ^{13}C-$\{^1H\}$ NMR spectra in which the H or C nuclei coupled to ^{31}P all gave triplets. The IR spectra showed two bands of similar intensities at *ca.* 1830 and 1750 cm^{-1} due to $\nu(C{\equiv}O)$ indicating, as expected, that the carbonyl ligands are mutually *cis*. The instability of complexes of the type $[M(CO)_2L(PPh_3)_2]$ (L = *N,N*-chelating ligand, *e.g.* diimine) has been reported by others.[14]

The reactions of **I**–**IV** with the η^3-allyl complex $[Mo(CO)_2(NCMe)_2(\eta^3\text{-}CH_2CHCH_2)Br]$[15] were also studied. From the reaction with **I** the molybdenum(II) complex $[Mo(CO)_2(\text{camph=N–N=CH–CH=N–N=camph})(\eta^3\text{-}CH_2CHCH_2)Br]$ **13**, was isolated as a purple solid which was fully characterised. In contrast, **II** did not react with $[Mo(CO)_2(NCMe)_2(\eta^3\text{-}CH_2CHCH_2)Br]$ in refluxing MeCN and the uncomplexed ligand was recovered unchanged. The pyridylazines **III** and **IV** both reacted with the η^3-allyl molybdenum(II) complex to form stable complexes of type $[Mo(CO)_2L(\eta^3\text{-}CH_2CHCH_2)Br]$ **14** (L = **III**) and **15** (L = **IV**) isolated as a maroon solid (**14**) or black crystals (**15**); these complexes were also fully characterised. The IR spectra suggested that only one isomer for **13**, **14** or **15** was formed and that the carbonyl groups are approximately *cis*. However, the NMR spectra of **13**, **14** and **15** indicated that the complexes were fluxional on the NMR time-scale. We were unable to fully explain the fluxionality of these complexes but from the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **13** recorded close to the high-temperature limit for the fluxional process it appeared that it did *not* involve the scrambling of the two camphor residues, which remained magnetically inequivalent. Furthermore, both **14** and **15** appeared to exist in solution as two isomers (designated **14** and **14′** and **15** and **15′**) which were themselves fluxional but did not interconvert up to 363 K.

Characterisation of the various complexes **1a**–**1c** and **3**–**15** was also carried out by UV/VIS spectroscopy and the results are given in Table 1. The complexes generally gave rise to a very intense band at *ca.* 300 nm together with one further band above 500 nm arising from the metal-to-ligand charge transfer. For the charge-transfer band, the values obtained for λ_{max} decrease in the order Cr > Mo $\geqslant$ W. For the molybdenum complexes λ_{max} increases with increasing substitution of the carbonyls or increases on going from Mo^0 to Mo^{II}. The values of ε_{max} for a given ligand increase in the order Cr < Mo < W and the values were also greater for complexes of **I** and **II** than for **III** and **IV**. In addition carbonyl substitution or increase in oxidation state decrease the ε_{max} values. These results are in line with other similar complexes and are as expected from arguments that have been put forward concerning the complexes of α-2-pyridylimines and α-diimines.[2] It should be noted however that the α-2-pyridylazine complexes of chromium, **3a** and **4a**, and the substituted carbonyl complexes **6**–**10** were unstable under the conditions used for measuring the electronic spectra, decomposing completely within 3 h, and even though the solutions were prepared immediately prior to recording of the spectrum the ε_{max} values may nevertheless be underestimates. Complexes **5**, **11** and **12** were too unstable to use CH_2Cl_2 as solvent, benzene being used instead, but even so decomposition was so rapid that accurate values for the absorption coefficient were not obtained.

Experimental

General methods were the same as reported in previous papers from this laboratory.[16] The UV/VIS spectra were recorded using a Perkin-Elmer SP200 spectrophotometer.

Preparations.—camph=N–N=CH–CH=N–N=camph **I**. The method was adapted from the preparation of diimines reported by tom Dieck and Dietrich.[17] A mixture of glyoxal (40% solution in water, 4.1 cm^3, 35 mmol) and CH_2Cl_2 (75 cm^3) was stirred with anhydrous Na_2SO_4 (20 g) for 5 min after which HCO_2H (98%, 0.3 cm^3) and (1*R*)-(+)-camphor hydrazone (12.2 g, 73 mmol) were added. The mixture, which became yellow within 5 min, was stirred for 2.5 h. It was then filtered to remove the Na_2SO_4 and the solvent removed under reduced pressure to leave a yellow-orange solid which was dissolved in *n*-pentane (80 cm^3). The solution was washed with water, dried over $MgSO_4$ and the solvent removed under reduced pressure to give the required product as yellow crystals. Yield = 8.18 g, 66%.

Compounds **II**, **III** *and* **IV**. These compounds were prepared from either (1*R*)-(+)-camphor hydrazone or (1*R*)-(−)-fenchone hydrazone and glyoxal or pyridine-2-carbaldehyde, respectively, using the same method as for **I**. Each was obtained as a pale yellow crystalline solid in the following yields: **II** 69%, **III** 90% and **IV** 70%.

$[Cr(CO)_4(\text{camph=N–N=CH–CH=N–N=camph})]$ **1a**. A mixture of $[Cr(nbd)(CO)_4]$ (323 mg, 1.26 mmol) and **I** (451 mg, 1.27 mmol) was stirred in *n*-pentane (15 cm^3) under N_2 for 4 d. The purple solid produced was collected, washed with *n*-pentane and dried. Yield = 251 mg, 38%.

$[Mo(CO)_4(\text{camph=N–N=CH–CH=N–N=camph})]$ **1b**. The compound $[Mo(nbd)(CO)_4]$ (234 mg, 0.78 mmol) and **I** (300 mg, 0.85 mmol) were dissolved in cyclohexane (20 cm^3) under N_2. The resultant solution was heated to reflux and the reaction was followed by IR spectroscopy monitoring $\nu(C{\equiv}O)$. After 105 min all the $[Mo(nbd)(CO)_4]$ had reacted. The solution was then allowed to cool whereupon **1b** was deposited as a purple powder and green-black prisms which were filtered off and washed with cyclohexane. Yield = 364 mg, 83%.

Compounds **1c**, **3a**–**3c** *and* **4a**–**c**. These complexes were all prepared from the appropriate $[M(nbd)(CO)_4]$ complex with either **I**, **III** or **IV** using the method described for **1b**. All the complexes were obtained as red-brown to purple powders and with the reaction times and in the yields as follows: **1c** reaction time = 2 d, yield 50%; **3a** 5.3 h, 81%; **3b** 5 min, 89%; **3c** 18 h, 80%; **4a** 5 h, 84%, **4b** 10 min, 86%; and **4c** 18 h, 74%.

$[Mo(CO)_3(NCMe)(\text{camph=N–N=CH–CH=N–N=camph})]$ **5**. Compound $[Mo(CO)_3(NCMe)_3]$ (185 mg, 0.610 mmol) was added to a solution of **I** (225 mg, 0.635 mmol) in oxygen-free benzene (10 cm^3) under N_2 and the resultant dark blue solution was stirred for 2.5 h after which the solution was concentrated to *ca.* 2 cm^3 and *n*-pentane (12 cm^3) added. The solution was then cooled to −20 °C whereupon the required complex **5** was deposited as a purple solid. This was collected, washed with a little *n*-pentane and dried briefly *in vacuo* before being stored under argon at −20 °C. Yield = 248 mg, 69%.

$[Mo(CO)_3(\text{camph=N–N=CH–CH=N–N=camph})(PPh_3)]$ **6**. Triphenylphosphine (163 mg, 0.621 mmol) was added to a benzene solution of **5** which had been prepared *in situ* from **I** (217 mg, 0.613 mmol) and $[Mo(CO)_3(NCMe)_3]$ (185 mg, 0.610 mmol). The solution immediately became violet and after 15 min was concentrated to *ca.* 2 cm^3, *n*-pentane added and cooled to −20 °C. Compound **6** was formed as a purple solid which was filtered off, washed with diethyl ether–*n*-hexane (1 : 1) and then methanol before being dried *in vacuo*. Yield = 353 mg, 73%.

$[Mo(CO)_3(\text{camph=N–N=CH–CH=N–N=camph})(AsPh_3)]$ **7**. The acetonitrile complex **5** (109 mg, 0.184 mmol) was added to a solution of $AsPh_3$ (65.5 mg, 0.214 mmol) in oxygen-free acetonitrile (15 cm^3) under N_2. The solution, which immediately became violet, was stirred for 10 min before being concentrated to *ca.* 2 cm^3. Methanol (10 cm^3) was added whereupon **7** was precipitated as a violet solid which was filtered off, washed with methanol and dried *in vacuo*. Yield = 122 mg, 79%.

Compounds **8**, **9** *and* **10**. These complexes were prepared as purple or maroon solids by treating the acetonitrile complex **5** with **II**, **III** or **IV** in a manner analogous to that used for the preparation of **6**. The yields were as follows: **8**, 67%; **9**, 89%; **10**, 84%.

$[Mo(CO)_2(\text{camph=N–N=CHC}_5H_4N)(PPh_3)_2]$ **11**. The compound *cis*-$[Mo(CO)_2(NCMe)_2(PPh_3)_2]$ (252 mg, 0.332 mmol) was added to a solution of **III** (91.7 mg, 0.359 mmol) in oxygen-free benzene under N_2. The solution became dark green within a few seconds and the reaction mixture was stirred for 5 h. After this time the solvent was removed and the residue was triturated with methanol–benzene (1 : 1). Compound **11** was isolated as a

Table 8 Crystallographic data for compounds **I** and **IV**

	I	**IV**
Formula	$C_{22}H_{34}N_4$	$C_{16}H_{21}N_3$
M	354.53	255.36
Crystal dimensions/mm	0.5 × 0.4 × 0.3	0.45 × 0.35 × 0.3
Crystal system	Monoclinic	Orthorhombic
a/Å	7.0647(5)	6.3310(4)
b/Å	12.7711(9)	13.9409(9)
c/Å	12.2981(7)	16.8246(14)
β/°	106.215(5)	
U/Å^3	1065.44(12)	1484.9(2)
Space group	$P2_1$	$P2_12_12_1$
Z	2	4
D_c/g cm^{-3}	1.105	1.142
F(000)	388	552
μ/mm^{-1}	0.505	0.531
T/K	200	250
Scan width (° + α-doublet splitting)	[a]	1.05
Scan speed/° min^{-1}	1.5–8.0	1.5–8.0
$2\theta_{\text{min,max}}$/°	4.0, 120.0	4.0, 130.0
No. of data collected	3277	2623
No. of unique data, n	3095	2173
No. of observed data[b]	3036	1751
R_{int}[c]	0.0194	0.0193
R_{sig}[d]	0.0132	0.0300
ρ_{max}, ρ_{min}/e Å^{-3}	0.15, −0.14	0.10, −0.09
$\Delta/\sigma_{\text{max}}$	0.001	0.001
wR_2[e]	0.0975	0.1031
R_1[f]	0.0370	0.0388
Weighting parameters x, y[g]	0.0678, 0.1521	0.058, 0.1529
Extinction parameter, x[h]	0.0231(15)	0.0037(5)
No. of parameters, p	260	185
Goodness of fit[i]	1.042	1.092
'Flack' parameter[j]	0.1(4)	−0.7(7)

[a] Scan divided into 30 steps, scan width and step sizes calculated from a learnt profile. [b] Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$, used only in calculation of R_1. [c] $R_{\text{int}} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)$. [d] $R_{\text{sig}} = \Sigma[\sigma(F_o^2)]/\Sigma(F_o^2)$. [e] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. [f] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [g] Weighting scheme used $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. [h] Least-squares extinction expression used $F_c' = kF_c(1 + 0.001xF_c^2\lambda^3)^{-\frac{1}{4}}$. [i] Goodnes of fit $= \Sigma[w(F_o^2 - F_c^2)^2]/(n - p)^{\frac{1}{2}}$. [j] See ref. 4.

dark green solid which was washed with a little methanol and dried *in vacuo*. Yield = 149 mg, 48%.

The corresponding fenchone derivative **12** was prepared as a dark green solid in 90% yield by the same method using **IV** and *cis*-[Mo(CO)$_2$(NCMe)$_2$(PPh$_3$)$_2$].

[Mo(CO)$_2$(camph=N–N=CH–CH=N–N=camph)(η^3-CH$_2$CHCH$_2$)Br] **13**. Compound **I** (631 mg, 1.78 mmol) was added to a solution of [Mo(CO)$_2$(NCMe)$_2$(η^3-CH$_2$CHCH$_2$)Br][12] (622 mg, 1.75 mmol) in oxygen-free acetonitrile (15 cm^3) under N$_2$. The solution which became purple immediately, was heated to reflux for 10 min, allowed to cool and then stored at 2 °C. This gave the required product **13** as a purple solid which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield = 880 mg, 80%.

Complexes **14** and **15** were prepared in an analogous fashion in 59 and 64% yields respectively.

Single-crystal X-Ray Diffraction Analysis of **I** *and* **IV**.—All crystallographic measurements for both structures were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated Cu-Kα X-radiation (λ = 1.541 84 Å) and, for compound **I**, an on-line profile fitting method.[18] Crystal data are listed in Table 8 together with details of data collection and structure refinement. The data-sets were corrected for Lorentz and polarisation factors but not for absorption.

Both structures were determined by direct methods using SHELXS 86[19] and were refined by full-matrix least squares (based on F^2) using SHELXL 93.[20] In both cases all hydrogen atoms were included in calculated positions (C–H 0.93, 1.00, 0.97 and 0.96 Å for aromatic, methine, methylene and methyl hydrogen atoms respectively) with a fixed isotropic thermal parameter of $n(U_{\text{eq}})$ of the parent carbon atom, where n was 1.5 for methyl hydrogens and 1.2 for all others.

In both cases refinement of a 'Flack' parameter[21] proved inconclusive so their absolute configurations were based on the known absolute configurations of the starting materials [(1*R*)-(+)-camphor for **I** and (1*R*)-(−)-fenchone for **IV**].

Figs. 1 and 2 were drawn using ORTEP II.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

References

1 G. Zassinovich, G. Mestroni and S. Gladiali, *Chem. Rev.*, 1992, **92**, 1051.

2 G. Van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 151; D. J. Stufkens, *Coord. Chem. Rev.*, 1990, **104**, 39.

3 W. Reusch, M. W. DiCarlo and L. Trayner, *J. Org. Chem.*, 1961, **26**, 1711.

4 (*a*) S. D. Perera, B. L. Shaw and M. Thonton-Pett, *J. Chem. Soc., Dalton Trans.*, 1994, 713; (*b*) W. Huckel, *Annalen*, 1941, **539**, 186.

5 A. L. Waterhouse, *Magn. Reson. Chem.*, 1989, **27**, 37; E. Kolehmainen, K. Laihia, J. Korvola, R. Kauppinen, M. Pikänen, B. Mannila and E. Mannila, *Magn. Reson. Chem.*, 1990, **28**, 812.

6 W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, 1958, **80**, 1286.

7 M. Ghedini, M. Longeri and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1986, 2669; M. Ghedini, M. Longeri, F. Neve, A. M. Manotti Lanfredi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1989, 1217.

8 J. Keijsper, H. Van der Poel, L. H. Polm, G. Van Koten, K. Vrieze, P. F. A. B. Seignette, R. Varenhorst and C. Stam, *Polyhedron*, 1983, **2**, 1111.

9 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 1183.

10 F. Baert and R. Fouret, *Acta Crystallogr. Sect. B*, 1978, **34**, 2546.

11 K. Rissanen, K. Laihia, J. Korvola and E. Kolehmainen, *Acta Chem. Scand.*, 1991, **45**, 751.
12 W. Majunke, D. Leibfritz, T. Mack and H. tom Dieck, *Chem. Ber.*, 1975, **108**, 3025.
13 H. tom Dieck and H. Friedel, *Chem. Commun.*, 1969, 411; H. Friedel, I. W. Renk and H. tom Dieck, *J. Organomet. Chem.*, 1971, **26**, 247.
14 H. tom Dieck and I. W. Reng, *Angew. Chem. Int. Ed. Engl.*, 1970, **9**, 793.
15 H. tom Dieck and H. Friedel, *J. Organomet. Chem.*, 1968, **14**, 375.
16 B. L. Shaw and J. D. Vessey, *J. Chem. Soc., Dalton Trans.*, 1991, 3303.
17 H. tom Dieck and J. Dietrich, *Chem. Ber.*, 1984, **117**, 694.
18 W. Clegg, *Acta Crystallogr., Sect. A*, 1987, **37**, 22.
19 G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467.
20 G. M. Sheldrick, *J. Appl. Crystallogr.*, in the press.
21 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 2387.
22 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.

Received 8*th July* 1994; *Paper* 4/04165H