3-Diphenylphosphino-(1*R*)-(+)-camphor Dimethylhydrazone and its Complexes with Group 6 Metal Carbonyls: Crystal Structures of the Hydrazone and $[Mo(CO)_4(PPh_2C_{10}H_{15}NNMe_2)]$†

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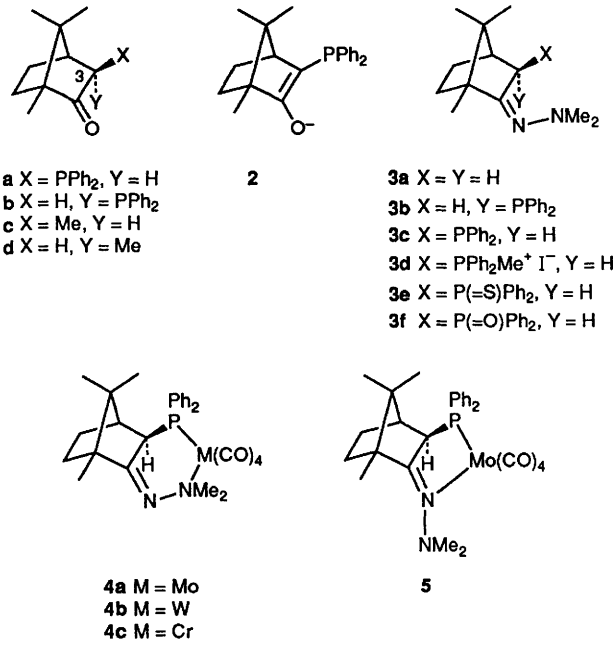
Prolonged treatment of (1*R*)-(+)-camphor with 1,1-dimethylhydrazine gives (1*R*)-(+)-camphor dimethylhydrazone **3a** which with LiBu, followed by PPh_2Cl, gives the corresponding compound **3c** which has the Ph_2P group in 3-*exo* position and the C=N–NMe_2 group in the *Z* configuration. This new phosphine was quaternized with MeI to give a phosphonium salt and converted into the corresponding sulphide and oxide. Treatment of $[M(CO)_4(nbd)]$ (M = Cr, Mo or W; nbd = norbornadiene) with **3c** gives $[M(CO)_4(PPh_2C_{10}H_{15}NNMe_2)]$ **4** in which the phosphine is chelated to the metal in a six-membered ring. However, when $[Mo(CO)_6]$ was heated with **3c** in decane, isomerization around the C=N bond occurred and the isomeric complex $[Mo(CO)_4(PPh_2C_{10}H_{15}NNMe_2)]$ **5** was formed. When **4a** was heated in diglyme it isomerized to **5**. Proton and ^{31}P-$\{^1H\}$ NMR and infrared data are given. Crystals of compound **3c** are orthorhombic, space group $P2_12_12_1$ with a = 1119.9(2), b = 1166.3(2), c = 1690.7(2) pm and Z = 4; final R factor 0.0443 for 3910 observed reflections. Crystals of complex **5** are orthorhombic, space group $P2_12_12_1$, with a = 974.8(2), b = 1658.9(4), c = 1982.0(4) pm and Z = 4; R 0.0425 for 2991 observed reflections. The structure shows that the co-ordinated PPh_2 group is in the 3-*exo* position whilst the C=NNMe_2 moiety is co-ordinated through the C=N nitrogen, giving a five-membered co-ordinated ring and an uncoordinated NMe_2 group. The arrangement around the C=N is *E*, *i.e.* the opposite to that in **3c**.

In a previous paper[1] we described the introduction of a diphenylphosphino group at the 3 positions of (1*R*)-(+)-camphor (bornan-2-one) by first deprotonating the camphor with lithium diisopropylamide to give a carbanion which was then treated with chlorodiphenylphosphine. This gave a mixture of the 3-*exo*- and 3-*endo*-phosphines **1a** and **1b**, respectively; one of these was the favoured kinetic product and we tentatively suggested that this was the *exo* isomer, but on storage the other isomer (the *endo*) became the more favoured. It has been well established that deprotonation of (1*R*)-(+)-camphor, followed by methylation, gives the *exo* isomer **1c** as the kinetic product but that subsequent isomerization shows that the *endo* isomer **1d** is more favoured, thermodynamically.[2,3] Most of the complexes made in our previous work were with the corresponding diphenylphosphino-substituted camphor enolate anion **2**.

Very recently (1*R*)-*endo*-(+)-3-diphenylphosphinocamphor has been synthesised by treating (1*R*)-*endo*-(+)-3-bromocamphor with butyllithium followed by chlorodiphenylphosphine. Several palladium and platinum complexes were made with this chiral β-ketophosphine ligand.[4]

Since there is increasing interest in complexes of functionalized or chiral tertiary phosphines in synthesis and catalysis we have now extended this work to the dimethylhydrazone derivative of camphor. The Me_2NN= group has been used to protect and develop the chemistry of ketones.[5,6] A particularly interesting property is that it promotes lithiation specifically at the α position which is *syn* to the NMe_2 and that in simple derivatives of cyclohexanone dimethylhydrazone (*e.g.* the 4-*tert*-butyl derivative) lithiation occurs specifically in the axial position and subsequent treatment with an electrophile (*e.g.* methyl iodide) introduces the substituent into the axial position.[7,8] Although camphor can be regarded as a derivative of cyclohexanone, it is very sterically hindered and its dimethylhydrazone might behave in a very different way from simple derivatives of cyclohexanone on lithiation, *etc.* In this paper we describe the synthesis of camphor dimethylhydrazone,



1a X = PPh_2, Y = H
1b X = H, Y = PPh_2
1c X = Me, Y = H
1d X = H, Y = Me

2

3a X = Y = H
3b X = H, Y = PPh_2
3c X = PPh_2, Y = H
3d X = PPh_2Me^+ I^-, Y = H
3e X = P(=S)Ph_2, Y = H
3f X = P(=O)Ph_2, Y = H

4a M = Mo
4b M = W
4c M = Cr

5

† Tetracarbonyl[3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone-κ²*N*¹*P*]molybdenum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Proton NMR data[a]

Compound	Camphor methyls	NMe_2	Others[b]
3a	0.77(s), 0.91(s), 0.99(s)	2.25(s)	
3c	0.73(s), 1.05(s), 1.07(s)	1.89(s)	3.14 [d, C^3H, J(PH) = 1.7]
3d	0.71(s), 0.93(s), 1.21(s)	2.05(s), 2.14(s)	2.36 [d, PMe, J(PH) = 12.7]
3e	0.61(s), 0.82(s), 1.14(s)	1.94(br)	3.73 (m, C^3H)
3f	0.61(s), 0.82(s), 1.14(s)	1.96(br)	3.76 (m, C^3H and C^4H)
4a	−0.03(s), 0.69(s), 0.93(s)	2.51(s), 3.30(s)	2.65 (m, C^4H), 2.72 [d, C^3H, J(PH) = 10.7]
4b	−0.04(s), 0.70(s), 0.92(s)	2.73(s), 3.53(s)	2.66 (m, C^3H and C^4H)
4c	−0.04(s), 0.69(s), 0.91(s)	2.36(s), 3.23(s)	2.54 [d, C^3H, J(PH) = 10.5], 2.64 (m, C^4H)
5	−0.21(s), 0.70(s), 1.28(s)	2.32(s), 2.50(s)	3.20 [d, C^3H, J(PH) = 11.3], 2.43 (m, C^4H)

[a] Measured in $CDCl_3$, chemical shifts are in ppm relative to $SiMe_4$, J values in Hz. s = Singlet, m = multiplet, br = broad. [b] Tentative assignment of C^3H and C^4H.

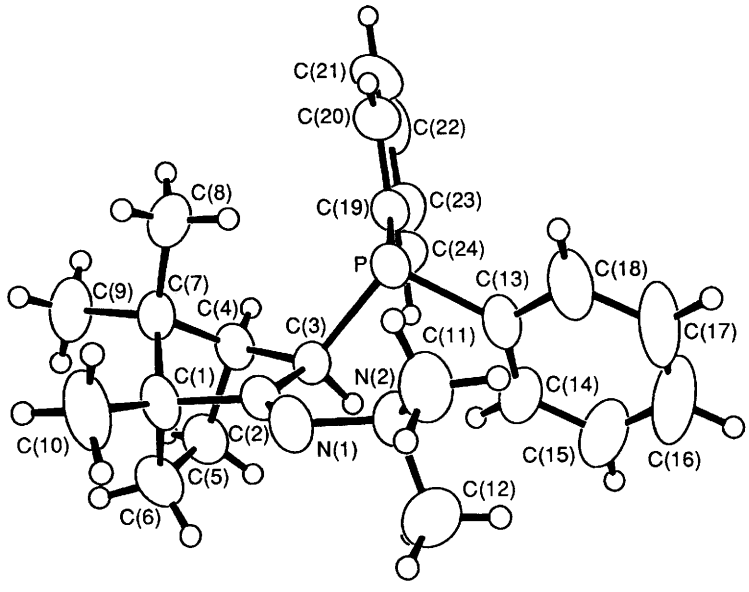


Fig. 1 ORTEP drawing of the molecular structure of 3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone **3c**

its 3-diphenylphosphino derivative, including the crystal structure, and various derivatives of the Group 6 metal carbonyls with this new chiral and functionalized phosphine, including one crystal structure.

Results and Discussion

(1*R*)-(+)-Camphor dimethylhydrazone was prepared in excellent yield by heating (1*R*)-(+)-camphor with 1,1-dimethylhydrazine in ethanol in the presence of acetic acid as catalyst. Preparative and elemental analytical data are in the Experimental section and proton NMR data in Table 1. One would expect that this hydrazone would have the *E* configuration **3a**, and the subsequent chemistry, in particular the conversion into the diphenylphosphino derivative **3c** (crystal structure), showed this to be the case.

In view of previous work with dimethylhydrazones (see above), one would expect that deprotonation of (1*R*)-(+)-camphor dimethylhydrazone would remove the 3-*endo* hydrogen, *i.e.* 'Y' in **3a**, and that on treating the resultant carbanion with PPh_2Cl the PPh_2 group would occupy the *endo* position, *i.e.* to give **3b**. However, one would expect that the more favoured position for the bulky PPh_2 group would be *exo*, as in **3c**, and there would be the possibility of an initially formed *endo* product **3b** isomerizing to the more favoured isomer **3c**.

When we treated (1*R*)-(+)-camphor dimethylhydrazone *with LiBu at* −15 °C and added PPh_2Cl to the resultant carbanion the 3-diphenylphosphino-substituted (1*R*)-(+)-camphor dimethylhydrazone was obtained as a white crystalline solid in *ca.* 80% yield. Preparative details are in the Experimental section as are microanalytical and ^{31}P NMR and IR data; ^1H NMR data are in Table 1. Since it was important to determine the stereochemistry of this phosphine, we determined its structure by X-ray diffraction. This was shown to be **3c** and is shown in more detail in Fig. 1 and discussed below. Two of the more important features are (*i*) the PPh_2 group is in the 3-*exo* position and (*ii*) the arrangement around the C=N bond is *Z*.

This new phosphine was converted into the phosphonium iodide **3d** by treatment with methyl iodide, into the corresponding phosphine sulphide **3e** by treatment with sulphur and into the phosphine oxide **3f** by treatment with hydrogen peroxide. Preparative, analytical, ^{31}P NMR and IR data are given in the Experimental section; ^1H NMR data are given in Table 1.

We have investigated this phosphine dimethylhydrazone **3c** as a ligand for Group 6 metal carbonyls. We anticipated that the phosphorus would co-ordinate to the Group 6 metal and, because of the chelate effect, so would the NMe_2 group, giving a six-membered ring. We therefore treated $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) with the phosphine **3c** and readily obtained a complex formulated as **4a** containing the expected chelated ligand. Elemental analytical data are in the Experimental section and ^1H NMR data in Table 1. The ^1H NMR data showed non-equivalent NMe_2 methyls.

One would not expect an NMe_2 group to be a particularly good donor towards the Group 6 metal carbonyls and we hoped to be able to co-ordinate the phosphine **3c** to molybdenum carbonyl in a monodentate fashion through phosphorus only. Thus we hoped to be able to displace cycloheptatriene (cht) from $[Mo(CO)_3(\eta^6\text{-cht})]$ with two molecules of the phosphine

Table 2 Bond lengths (pm) and angles (°) for compound **3c**

C(3)–P	187.7(4)	C(13)–P	184.7(3)
C(19)–P	184.6(3)	C(6)–C(1)	153.3(6)
C(2)–C(1)	151.5(5)	C(10)–C(1)	151.1(6)
C(7)–C(1)	154.9(6)	C(4)–C(3)	155.5(5)
C(3)–C(2)	151.1(5)	C(7)–C(4)	154.4(6)
C(5)–C(4)	153.5(6)	C(8)–C(7)	152.7(6)
C(6)–C(5)	153.9(6)	C(2)–N(1)	126.8(4)
C(9)–C(7)	154.3(5)	C(12)–N(2)	145.6(5)
N(2)–N(1)	145.5(4)		
C(11)–N(2)	144.9(5)		
C(13)–P–C(3)	104.1(2)	C(19)–P–C(3)	101.7(2)
C(19)–P–C(13)	99.3(2)	C(7)–C(1)–C(2)	100.3(3)
C(6)–C(1)–C(2)	103.7(3)	C(10)–C(1)–C(2)	115.1(3)
C(7)–C(1)–C(6)	102.2(3)	C(10)–C(1)–C(7)	117.7(3)
C(10)–C(1)–C(6)	115.5(4)	N(1)–C(2)–C(1)	121.9(3)
C(3)–C(2)–C(1)	108.0(3)	C(2)–C(3)–P	111.9(3)
N(1)–C(2)–C(3)	130.0(3)	C(4)–C(3)–C(2)	100.3(3)
C(4)–C(3)–P	120.1(3)	C(5)–C(4)–H(4)	115.2(3)
C(5)–C(4)–C(3)	105.8(3)	C(7)–C(4)–H(4)	116.7(2)
C(7)–C(4)–C(3)	104.1(3)	C(6)–C(5)–C(4)	103.2(3)
C(7)–C(4)–C(5)	101.1(3)	C(4)–C(7)–C(1)	94.0(3)
C(5)–C(6)–C(1)	104.0(3)	C(8)–C(7)–C(4)	114.0(3)
C(8)–C(7)–C(1)	114.1(3)	C(9)–C(7)–C(4)	113.1(3)
C(9)–C(7)–C(1)	114.0(3)	C(11)–N(2)–N(1)	107.3(3)
C(9)–C(7)–C(8)	107.4(4)	C(12)–N(2)–C(11)	110.4(3)
N(2)–N(1)–C(2)	111.5(3)		
C(12)–N(2)–N(1)	108.1(3)		

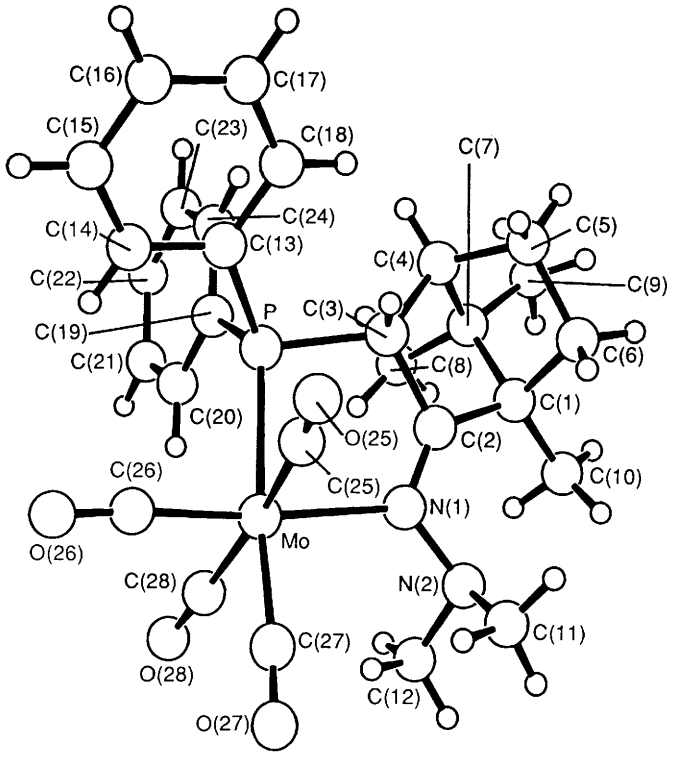


Fig. 2 ORTEP drawing of the molecular structure of $[Mo(CO)_4(PPh_2C_{10}H_{15}NNMe_2)]$ **5**

3c so that one would chelate and the second would bond only through phosphorus. However, the only product we could isolate was the tetracarbonyl **4a**, *i.e.* carbon monoxide scrambling must have occurred.

Treatment of the corresponding tungsten or chromium complexes of type $[M(CO)_4(nbd)]$, M = W or Cr, with the phosphine **3c** gave chelate complexes which we formulate as **4b** and **4c**, respectively. Details of the preparation and characterization data are in the Experimental section whilst the ^1H NMR data are in Table 1. Also, as was the case with the molybdenum complexes, when we treated $[M(CO)_3(\eta^6\text{-cht})]$ with the phosphine **3c**, carbon monoxide scrambling occurred and only the tetracarbonyl complexes **4b** and **4c** were obtained; similarly, with $[W(CO)_3(NCMe)_3]$.

As discussed above, the stereochemistry around the C=N bond of the phosphine **3c** is *Z* and hence when this phosphine chelates the NMe_2 nitrogen is complexed to the metal and a six-membered ring is formed. We thought that if we could induce rotation around the C=N bond, to give the *E* isomer of **3c**, then chelation could occur through the C=N nitrogen giving a five-membered chelate ring. We therefore heated $[Mo(CO)_6]$ with the phosphine **3c** in the high-boiling solvent decane (b.p. 174 °C) for 40 min. Some decomposition occurred but a yellow crystalline product was isolated in very good yield and shown by elemental analysis and by $^{31}P\text{-}\{^1H\}$ and ^1H NMR and infrared spectroscopy to be isomeric with **4a**. The crystal structure of this product was determined and shown to be the hoped-for complex **5**; see below for further details. The proton NMR spectrum of this complex (Table 1) showed the NMe_2 methyls to be non-equivalent and therefore one assumes that inversion through nitrogen is prevented for steric reasons. We also heated the six-membered chelate complex **4a** in diglyme (2,5,8-trioxanonane) (b.p. 160 °C) for 1.5 h and obtained the isomeric complex **5**, with the five-membered chelate ring, in 47% yield. In separate studies we could find no evidence for isomerization of **4a** to **5** in diglyme at or below 140 °C.

Crystal Structures of $PPh_2C_{10}H_{15}NNMe_2$ **3c** *and* $[Mo(CO)_4(PPh_2C_{10}H_{15}NNMe_2)]$ **5**.—The crystal structure of compound **3c** is shown in Fig. 1 and selected bond lengths and angles are shown in Table 2. The structure shows that the PPh_2 group is in the 3-*exo* position and that the $C{=}NNMe_2$ group in the 2 position is *Z*.

The crystal structure of complex **5** is shown in Fig. 2 and selected bond lengths and angles are shown in Table 3. The structure shows that the co-ordinated PPh_2 group is in the 3-*exo* position whilst the $C{=}NNMe_2$ moiety is co-ordinated through the C=N nitrogen, giving a five-membered co-ordinated ring and an unco-ordinated NMe_2 group. The arrangement around the C=N is thus the opposite to that in **3c**, *i.e. E*.

Experimental

The general methods and instruments used were the same as in another recent publication from this laboratory.[9]

Preparation of (1R)-(+)-*Camphor Dimethylhydrazone* **3a**.—A solution of (1*R*)-(+)-camphor (12.0 g, 80 mmol), 1,1-dimethylhydrazine (19.2 g, 320 mmol) and acetic acid (4.5 cm^3) in ethanol (40 cm^3) was heated under reflux for 43 h. The ethanol was then removed on a rotor-evaporator and diethyl ether (*ca.* 30 cm^3) added. The ether solution was washed with 10% aqueous sodium hydroxide (12 cm^3) and then with saturated sodium chloride solution (12 cm^3). The ether was removed on a rotor-evaporator and the residue distilled. This gave the required product as a colourless liquid, b.p. 58–60 °C (2 mbar, 200 Pa); yield 13.4 g, 87% (Found: C, 74.1; H, 11.7; N, 14.55. Calc. for $C_{12}H_{22}N_2$: C, 74.15; H, 11.4; N, 14.4%). Infrared (neat liquid): ν(C=N) 1665 cm^{-1}.

Preparation of 3-*Diphenylphosphino*-(1R)-(+)-*camphor Dimethylhydrazone* **3c**.—A solution of LiBu in hexane (40.5 cm^3, 1.55 mol dm^{-3}, 0.062 mol) was added to a stirred solution of (1*R*)-(+)-camphor dimethylhydrazone (12.0 g, 0.062 mol) in dry tetrahydrofuran (thf) (120 cm^3) at −15 °C. After 35 min a solution of chloro(diphenyl)phosphine (13.6 g, 0.062 mol) in dry thf (80 cm^3) was added at −15 °C, after which the mixture was allowed to warm to room temperature.

Table 3 Bond lengths (pm) and angles (°) for complex **5**

P–Mo	251.4(5)	N(1)–Mo	233.1(7)
C(25)–Mo	204.7(9)	C(26)–Mo	192.4(10)
C(27)–Mo	195.1(9)	C(28)–Mo	201.1(9)
C(2)–C(1)	152.7(10)	C(6)–C(1)	155.9(10)
C(7)–C(1)	157.0(11)	C(10)–C(1)	151.9(11)
C(3)–C(2)	151.8(10)	C(4)–C(3)	155.6(9)
C(5)–C(4)	153.6(11)	C(7)–C(4)	154.1(11)
C(6)–C(5)	155.2(11)	C(8)–C(7)	152.6(12)
C(9)–C(7)	155.3(11)	C(13)–P	182.0(5)
P–C(3)	184.9(7)	N(2)–N(1)	142.3(8)
P–C(19)	181.5(5)	C(12)–N(2)	143.7(10)
C(2)–N(1)	127.1(8)	O(26)–C(26)	117.2(10)
C(11)–N(2)	143.8(10)	O(28)–C(28)	116.3(10)
O(25)–C(25)	112.4(9)		
O(27)–C(27)	115.1(10)		
N(1)–Mo–P	77.4(2)	C(25)–Mo–P	83.2(3)
C(25)–Mo–N(1)	94.7(3)	C(26)–Mo–P	96.7(4)
C(26)–Mo–N(1)	174.0(3)	C(26)–Mo–C(25)	85.2(4)
C(27)–Mo–P	171.3(2)	C(27)–Mo–N(1)	99.9(4)
C(27)–Mo–C(25)	88.8(4)	C(27)–Mo–C(26)	86.1(4)
C(28)–Mo–P	102.2(3)	C(28)–Mo–N(1)	94.7(4)
C(28)–Mo–C(25)	170.0(3)	C(28)–Mo–C(26)	85.8(5)
C(28)–Mo–C(27)	86.2(4)	C(7)–C(1)–C(2)	98.1(6)
C(6)–C(1)–C(2)	104.6(6)	C(10)–C(1)–C(2)	120.6(6)
C(7)–C(1)–C(6)	102.6(6)	C(10)–C(1)–C(7)	115.5(7)
C(10)–C(1)–C(6)	113.0(7)	N(1)–C(2)–C(1)	133.9(6)
C(3)–C(2)–C(1)	106.1(5)	H(3)–C(3)–C(2)	121.5(4)
N(1)–C(2)–C(3)	120.0(6)	P–C(3)–C(2)	112.9(5)
C(4)–C(3)–C(2)	102.5(5)	C(5)–C(4)–C(3)	104.5(6)
P–C(3)–C(4)	127.9(5)	C(7)–C(4)–C(5)	102.6(6)
C(7)–C(4)–C(3)	102.4(6)	C(5)–C(6)–C(1)	104.3(6)
C(6)–C(5)–C(4)	103.1(6)	C(8)–C(7)–C(1)	113.0(7)
C(4)–C(7)–C(1)	94.8(6)	C(9)–C(7)–C(1)	112.4(7)
C(8)–C(7)–C(4)	116.4(7)	C(9)–C(7)–C(8)	107.8(7)
C(9)–C(7)–C(4)	112.1(7)	C(13)–P–Mo	115.8(3)
C(3)–P–Mo	97.0(3)	C(19)–P–Mo	127.8(3)
C(13)–P–C(3)	103.3(3)	C(19)–P–C(13)	100.7(3)
C(19)–P–C(3)	110.1(3)	N(2)–N(1)–Mo	126.0(4)
C(2)–N(1)–Mo	120.7(5)	C(11)–N(2)–N(1)	109.4(6)
N(2)–N(1)–C(2)	113.4(6)	C(12)–N(2)–C(11)	110.1(7)
C(12)–N(2)–N(1)	110.8(6)	O(26)–C(26)–Mo	174.7(8)
O(25)–C(25)–Mo	173.3(6)	O(28)–C(28)–Mo	173.7(8)
O(27)–C(27)–Mo	174.2(7)		

The solvent was then evaporated to low volume under reduced pressure and ethanol added to the residue. This gave the required product as white plates. Yield 18.5 g, 79% (Found: C, 76.15; H, 8.4; N, 7.4. Calc. for $C_{24}H_{31}N_2P$: C, 76.15; H, 8.25; N, 7.4%). NMR: ^{31}P-{^1H} (CH_2Cl_2), δ 1.5(s); ^{13}C-{^1H} ($CDCl_3$), δ 45.66 (s, NMe_2), 45.69 [d, C^3, $^1J(PC)$ = 27.7] and 184.13 [d, C^2, $^2J(PC)$ = 7.1 Hz]. Infrared (KBr disc): ν(C=N) 1655w cm^{-1}.

Reactions of Compound **3c**.—*Quaternization with methyl iodide.* An excess of methyl iodide (0.5 cm^3) was added to a solution of the phosphine **3c** (0.3 g, 0.8 mmol) in dichloromethane (8 cm^3). After 2.5 h the solution was filtered and evaporated to dryness. The residue was recrystallized from ethanol–diethyl ether to give the required product **3d** as white microcrystals. Yield 0.33 g, 79% (Found: C, 57.45; H, 6.6; N, 5.4. Calc. for $C_{25}H_{34}IN_2P$: C, 57.7; H, 6.6; N, 5.4%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ 10.0(s).

Conversion into the corresponding phosphine sulphide **3e**. A mixture of the phosphine **3c** (0.23 g, 0.61 mmol) and monoclinic sulphur (24 mg, 0.75 mmol) was heated under reflux in benzene (7 cm^3) for 3.5 h. The solvent was evaporated under reduced pressure and the residue recrystallized from benzene–ethanol to give the required product **3e** as white needles. Yield 0.21 g, 84% (Found: C, 70.35; H, 7.75; N, 6.85. Calc. for $C_{24}H_{31}N_2PS$: C, 70.2; H, 7.6; N, 6.8%). ^{31}P-{^1H} NMR (C_6D_6): δ 38.1. Infrared (KBr disc) ν(C=N) 1650m cm^{-1}.

Conversion into the corresponding phosphine oxide **3f**. An excess of hydrogen peroxide (1.6 cm^3, 30% w/v) was added to a solution of the phosphine **3c** (0.3 g, 0.8 mmol) in acetone (15 cm^3). After 1 h the solvent was evaporated under reduced pressure and the residue triturated with ethanol to give the required product **3f** as white microcrystals. Yield (0.2 g, 63%) (Found: C, 72.35; H, 7.95; N, 6.9. Calc. for $C_{24}H_{31}N_2OP\cdot 0.25C_2H_6O$: C, 72.45; H, 8.05; N, 6.9%). ^{31}P-{^1H} NMR (C_6D_6): δ 20.9(s). Infrared (KBr disc): ν(C=N) 1660m, ν(P=O) 1190s cm^{-1}.

Preparations of [$Mo(CO)_4(PPh_2C_{10}H_{15}NNMe_2)$] **4a**.—(*i*) *From* [$Mo(CO)_4$(nbd)]. A solution containing the phosphine **3c** (1.1 g, 2.9 mmol) and [$Mo(CO)_4$(nbd)] (0.8 g, 2.7 mmol) in benzene (15 cm^3) was put aside at *ca.* 20 °C for 20 h. The resulting solution was then filtered and evaporated to low volume under reduced pressure. Addition of methanol to the residue then gave the required product as yellow microcrystals. Yield 1.03 g, 66% (Found: C, 57.35; H, 5.35; N, 4.75. Calc. for $C_{28}H_{31}MoN_2O_4P$: C, 57.35; H, 5.35; N, 4.8%). ^{31}P-{^1H} NMR ($CDCl_3$): δ 54.3. Infrared: (CH_2Cl_2 solution) ν(C≡O) 2025, 1910 and 1850; (KBr disc) ν(C=N) 1645 cm^{-1}.

(*ii*) *From* [$Mo(CO)_3(\eta^6$-cht)]. A solution of the phosphine **3c** (0.22 g, 0.6 mmol) and [$Mo(CO)_3(\eta^6$-cht)] (0.12 g, 0.45 mmol) in benzene (2.5 cm^3) was heated at 60 °C for 8 h. The resultant solution was filtered through Celite and evaporated to dryness under reduced pressure. The residue was recrystallized from benzene–methanol to give the required product identical with that prepared by method (*i*). Yield 67 mg, 34% based on carbon monoxide.

Preparation of [$W(CO)_4(PPh_2C_{10}H_{15}NNMe_2)$] **4b**.—(*i*) *From* [$W(CO)_4$(nbd)]. A solution of this complex (0.15 g, 0.38 mmol) and the phosphine **3c** (0.17 g, 0.45 mmol) in benzene (2.5 cm^3) was heated at 60 °C for 16 h. The resulting yellow solution was filtered and evaporated to low volume under reduced pressure. Methanol was added to the residue giving the required product as yellow microcrystals. Yield 0.17 g, 65% (Found: C, 49.95; H, 4.6; N, 4.25. Calc. for $C_{28}H_{31}N_2O_4PW$: C, 49.85; H, 4.6; N, 4.15%). ^{31}P-{^1H} NMR (C_6H_6): δ 49.1 [$^1J(WP)$ = 261 Hz]. Infrared: (CH_2Cl_2) ν(C≡O) 2020, 1900 and 1845; (KBr disc) ν(C=N) 1650 cm^{-1}.

(*ii*) *From* [$W(CO)_3(NCMe)_3$]. A solution of [$W(CO)_3(NCMe)_3$] (70 mg, 0.18 mmol) and the phosphine **3c** (0.1 g, 0.26 mmol) in benzene (2 cm^3) was heated at 70 °C for 3 h. Work up as in method (*i*) then gave the tetracarbonyl **4b** (72 mg, 79% based on carbon monoxide).

(*iii*) *From* [$W(CO)_3(\eta^6$-cht)]. A solution of [$W(CO)_3(\eta^6$-cht)] (45 mg, 0.125 mmol) and the phosphine **3c** (65 mg, 0.17 mmol) in benzene (1.5 cm^3) was heated at 70 °C for 12 h. The product **4b** was isolated as above. Yield 48 mg, 76% (relative to carbon monoxide).

Preparation of [$Cr(CO)_4(PPh_2C_{10}H_{15}NNMe_2)$] **4c**.—(*i*) *From* [$Cr(CO)_4$(nbd)]. This preparation and isolation was very similar to that of the analogous tungsten complex with slightly less heating (11 h, 60 °C). Yellow microcrystals. Yield 41% (Found: C, 62.0; H, 5.75; N, 5.1. Calc. for $C_{28}H_{31}CrN_2O_4P$: C, 62.0; H, 5.75; N, 5.1%). ^{31}P-{^1H} NMR ($CDCl_3$): δ 69.8. Infrared: (CH_2Cl_2) ν(C≡O) 2010, 1900 and 1845; (KBr disc) ν(C≡N) 1650w cm^{-1}.

(*ii*) *From* [$Cr(CO)_3(\eta^6$-cht)]. A mixture of this cycloheptatriene complex (68 mg, 0.3 mmol) and the phosphine **3c** (112 mg, 0.3 mmol) was heated for 16 h at *ca.* 70 °C in a mixture of benzene (1 cm^3) and acetonitrile (0.5 cm^3). The solution was filtered and the filtrate evaporated to dryness. Light petroleum (b.p. 40–60 °C) was added to give the required product as yellow microcrystals. Yield 71 mg, 58% (relative to carbon monoxide).

Table 4 Data collection and structure solution and refinement parameters[a]

Compound	**3c**	**5**
Formula	$C_{24}H_{31}N_2P$	$C_{28}H_{31}MoN_2O_4P{\cdot}0.5CH_2Cl_2$
M	378.5	629.95[b]
Crystal dimensions/mm	0.75 × 0.4 × 0.2	0.4 × 0.3 × 0.3
a/pm	1119.9(2)	974.8(2)
b/pm	1166.3(2)	1658.9(4)
c/pm	1690.7(2)	1982.0(4)
U/nm^3	2.2083(5)	3.2054(12)
D_c/Mg m^{-3}	1.14	1.30[b]
$F(000)$	816.0	1307.99
μ(Mo-Kα)/cm^{-1}	0.99	5.07
No. of data collected	4615	3301
No. of data observed[c]	3910	2991
R[d]	0.0443	0.0425
R'[e]	0.0562	0.0594
Weighting parameter g[f]	0.0004	0.0008
No. of parameters	236	337

[a] Common to both structures; orthorhombic, space group $P2_12_12_1$, $Z = 4$, scan widths 2.0° + α-doublet splitting, scan speeds 2.0–29.3° min^{-1}. [b] Includes solvate molecule. [c] Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$. [d] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [e] $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$ [f] $w = [\sigma^2(|F_o|) + g(|F_o|)^2]^{-1}$.

Table 5 Non-hydrogen atom coordinates (× 10^4) for compound **3c**

Atom	x	y	z
P	−1 144.9(6)	−9 548.9(5)	−5 394.4(3)
C(1)	879(2)	−10 064(2)	−3 514(1)
C(10)	1 924(3)	−9 390(4)	−3 192(2)
C(2)	795(2)	−10 106(2)	−4 407(1)
C(3)	−450(2)	−10 497(2)	−4 625(1)
C(4)	−1 019(2)	−10 591(2)	−3 789(1)
C(5)	−479(3)	−11 672(2)	−3 413(2)
C(6)	829(3)	−11 328(3)	−3 268(2)
C(7)	−394(2)	−9 641(2)	−3 306(1)
C(8)	−668(3)	−8 428(2)	−3 593(2)
C(9)	−689(3)	−9 688(3)	−2 416(2)
N(1)	1 675(2)	−9 856(2)	−4 847(1)
N(2)	1 396(2)	−10 029(2)	−5 679(1)
C(11)	2 013(3)	−9 145(3)	−6 121(2)
C(12)	1 828(3)	−11 159(3)	−5 908(2)
C(13)	−1 067(2)	−10 405(1)	−6 312(1)
C(14)	−1 145(2)	−11 597(1)	−6 353(1)
C(15)	−1 031(2)	−12 152(1)	−7 080(1)
C(16)	−838(2)	−11 514(1)	−7 766(1)
C(17)	−760(2)	−10 322(1)	−7 725(1)
C(18)	−874(2)	−9 767(1)	−6 998(1)
C(19)	−2 750(1)	−9 711(1)	−5 172(1)
C(20)	−3 391(1)	−8 692(1)	−5 096(1)
C(21)	−4 612(1)	−8 724(1)	−4 934(1)
C(22)	−5 192(1)	−9 775(1)	−4 848(1)
C(23)	−4 550(1)	−10 794(1)	−4 924(1)
C(24)	−3 329(1)	−10 763(1)	−5 086(1)

Table 6 Non-hydrogen atom coordinates (× 10^4) for complex **5**

Atom	x	y	z
Mo	−674.1(5)	−8 606.9(3)	−8 666.6(2)
C(1)	2 348(6)	−6 462(4)	−8 256(3)
C(2)	1 477(6)	−7 202(4)	−8 418(3)
C(3)	2 462(5)	−7 911(3)	−8 441(3)
C(4)	3 824(6)	−7 531(4)	−8 184(3)
C(5)	4 381(7)	−7 058(4)	−8 792(4)
C(6)	3 320(7)	−6 368(4)	−8 876(3)
C(7)	3 309(7)	−6 857(4)	−7 713(3)
C(8)	2 541(10)	−7 126(4)	−7 082(4)
C(9)	4 484(9)	−6 284(5)	−7 489(5)
C(10)	1 676(8)	−5 674(4)	−8 048(4)
P	1 660(2)	−8 868(1)	−8 173(1)
N(1)	209(5)	−7 311(3)	−8 537(3)
N(2)	−547(5)	−6 580(3)	−8 588(3)
C(11)	−942(9)	−6 452(5)	−9 279(4)
C(12)	−1 742(8)	−6 603(5)	−8 164(5)
C(13)	2 685(4)	−9 629(2)	−8 601(2)
C(14)	2 151(4)	−10 409(2)	−8 598(2)
C(15)	2 870(4)	−11 035(2)	−8 908(2)
C(16)	4 125(4)	−10 880(2)	−9 222(2)
C(17)	4 659(4)	−10 099(2)	−9 225(2)
C(18)	3 939(4)	−9 474(2)	−8 914(2)
C(19)	2 088(4)	−9 079(3)	−7 299(2)
C(20)	1 057(4)	−9 028(3)	−6 813(2)
C(21)	1 367(4)	−9 162(3)	−6 135(2)
C(22)	2 708(4)	−9 346(3)	−5 943(2)
C(23)	3 738(4)	−9 397(3)	−6 430(2)
C(24)	3 428(4)	−9 264(3)	−7 108(2)
C(25)	313(6)	−8 821(4)	−9 560(4)
O(25)	792(6)	−9 008(4)	−10 052(3)
C(26)	−1 236(9)	−9 717(5)	−8 725(4)
O(26)	−1 656(8)	−10 373(4)	−8 796(4)
C(27)	−2 336(7)	−8 362(5)	−9 175(4)
O(27)	−3 310(5)	−8 282(5)	−9 497(3)
C(28)	−1 864(8)	−8 554(5)	−7 839(4)
O(28)	−2 634(8)	−8 571(5)	−7 391(3)

Preparation of [Mo(CO)$_4$(PPh$_2$C$_{10}$H$_{15}$NNMe$_2$)] **5**.—A mixture of molybdenum hexacarbonyl (2.4 g, 9.1 mmol), the phosphine **3c** (3.5 g, 9.3 mmol) and decane (30 cm^3) was heated under reflux for 40 min and then allowed to cool to *ca.* 20 °C. The supernatant liquid was decanted from the precipitate which was recrystallized from dichloromethane–methanol to give the required product **5** as yellow microcrystals. Yield 3.82 g, 72% (Found: C, 57.2; H, 5.35; N, 4.95. Calc. for $C_{28}H_{31}MoN_2O_4P$: C, 57.35; H, 5.35; N, 4.8%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ 57.5. Infrared: (CH_2Cl_2 solution) ν(C≡O) 2020, 1905 and 1850; (KBr disc) ν(C=N) 1610 cm^{-1}.

Isomerization of Complex **4a** *to* **5**.—A solution of complex **4a** (0.100 g, 0.26 mmol) in diglyme (2 cm^3) was heated at 160 °C for 1.5 h. The resultant solution was allowed to cool, filtered and the filtrate evaporated to dryness under reduced pressure. Trituration of the residue with methanol gave the isomeric tetracarbonyl **5** (47 mg, 47%) which was identified by NMR and IR spectroscopy.

Crystal Structure Determination.—All diffraction data were collected at 293 K on a Nicolet P3/F diffractometer using graphite monochromated Mo-Kα radiation (λ = 71.069 pm). The unit cell parameters and their estimated standard deviations for both compounds **3c** and **5** were derived from a least-squares fit of the setting angles of 25 centred reflections in the range $20.0 < 2\theta < 25.0°$. In both cases data were collected

in the range $4.0 < 2\theta < 50.0°$ using ω–2θ scans with no significant variation observed in two standard reflections. Lorentz and polarization corrections were applied to both data sets together with a post structure-solution empirical absorption correction.[10]

The structure of compound **3c** was determined by direct methods using SHELXS 86,[11] while that of **5** was determined by standard Patterson and Fourier difference techniques using SHELX 76.[12] Both structures were refined by full-matrix least squares using SHELX 76. In both cases all non-hydrogen atoms were refined with anisotropic thermal parameters except for the carbon and chlorine atoms of a disordered half-molecule of CH_2Cl_2 found in **5** which were refined with isotropic thermal parameters. Phenyl rings were treated as rigid bodies with idealized hexagonal symmetry (C–C 139.5 pm). All hydrogen atoms were included in calculated positions (C–H 96 pm) and were assigned an overall isotropic thermal parameter. Refinement of the inverted structures (*i.e.* the L-camphor based complexes) of both complexes led to significantly higher R factors. Details of data collection and structure solution and refinement are given in Table 4 whilst non-hydrogen atomic coordinates of **3c** and **5** are given in Tables 5 and 6 respectively.

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

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References

1 S. D. Perera and B. L. Shaw, *J. Organomet. Chem.*, 1991, **402**, 133.
2 J. H. Hutchinson and T. Money, *Can. J. Chem.*, 1984, **62**, 1899.
3 T. Money, *Natural Product Rep.*, 1985, p. 253 and refs. therein.
4 D. A. Knight, D. Cole-Hamilton and D. C. Cupertino, *J. Chem. Soc., Dalton Trans.*, 1990, 3051.
5 E. J. Corey and D. Enders, *Tetrahedron Lett.*, 1976, 1.
6 E. J. Corey and D. Enders, *Tetrahedron Lett.*, 1976, 11.
7 R. R. Fraser and K. L. Dhawan, *J. Chem. Soc., Chem. Commun.*, 1976, 674.
8 D. B. Collum, D. Kahne, S. A. Gut, R. T. De Pue, F. Moharnadi, R. A. Wanat, J. Clardy and G. Van Duyne, *J. Am. Chem. Soc.*, 1984, **106**, 4865.
9 X. L. R. Fontaine, E. H. Fowles, T. P. Layzell, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, in the press.
10 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
11 G. M. Sheldrick, SHELXS 86, Program System for X-Ray Structure Solution, University of Göttingen, 1986.
12 G. M. Sheldrick, SHELX 76, Program System for X-Ray Structure Determination, University of Cambridge, 1976.

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