# Some Chemistry with a Chiral Phosphine generated from Fenchone–Pinacolone Mixed Azine: Crystal Structure of *Z,E*-$Ph_2PCH_2C(Bu^t)$=N–N=$C_{10}H_{16}$ †

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Treatment of fenchone hydrazone with *tert*-butyl methyl ketone gave the mixed azine $MeC(Bu^t)$=N–N=$C_{10}H_{16}$ which on treatment with $LiBu^n$ followed by $PClPh_2$ gave the mixed azine monophosphine *Z,E*-$Ph_2PCH_2C(Bu^t)$=N–N=$C_{10}H_{16}$. This was converted into the corresponding phosphine oxide or phosphine sulfide. The azine monophosphine with [Mo(CO)$_4$(nbd)] (nbd =norbornadiene) gave the chelate complex [Mo(CO)$_4${$PPh_2CH_2C(Bu^t)$=N–N=$C_{10}H_{16}$}] which with L undergoes ring-opening to give [Mo(CO)$_4$L{$PPh_2CH_2C(Bu^t)$=N–N=$C_{10}H_{16}$}] (L = CO, $CNBu^t$ or CNMe) with monodentate phosphine. Corresponding tungsten complexes [W(CO)$_4${$PPh_2CH_2C(Bu^t)$=N–N=$C_{10}H_{16}$}] and [W(CO)$_4$L-{$PPh_2CH_2C(Bu^t)$=N–N=$C_{10}H_{16}$}] (L = $CNBu^t$ or CNMe) were also prepared. Crystals of *Z,E*-$Ph_2PCH_2C(Bu^t)$=N–N=$C_{10}H_{16}$ are monoclinic, space group $P2_1$ with $a$ = 11.0737(8), $b$ = 11.0377(9), $c$ = 11.1072(7) Å, β = 110.60(5)° and $Z$ = 2 for 3492 observed reflections. Proton, $^{31}P$-{$^1H$}, $^{13}C$-{$^1H$} NMR, IR and mass spectral data are given.

We have reported[1] that the *N,N*-dimethylhydrazone of *tert*-butyl methyl ketone (pinacolone), *viz.* $MeC(Bu^t)$=$NNMe_2$ can be lithiated by treatment with $LiBu^n$ and that the resultant carbanion, when treated with $PClPh_2$, gives the crystalline phosphine *Z*-$Ph_2PCH_2C(Bu^t)$=$NNMe_2$. We have described some complexes of this functionalised phosphine[1,2] but, more importantly, we found that, in the presence of acetic acid as catalyst the dimethylhydrazone functionality was displaced by hydrazine to give the corresponding crystalline phosphino hydrazone *Z*-$Ph_2PCH_2C(Bu^t)$=$NNH_2$.[1] This is opening up a lot of new chemistry since hydrazones (=$NNH_2$) are extremely nucleophilic and reactive.

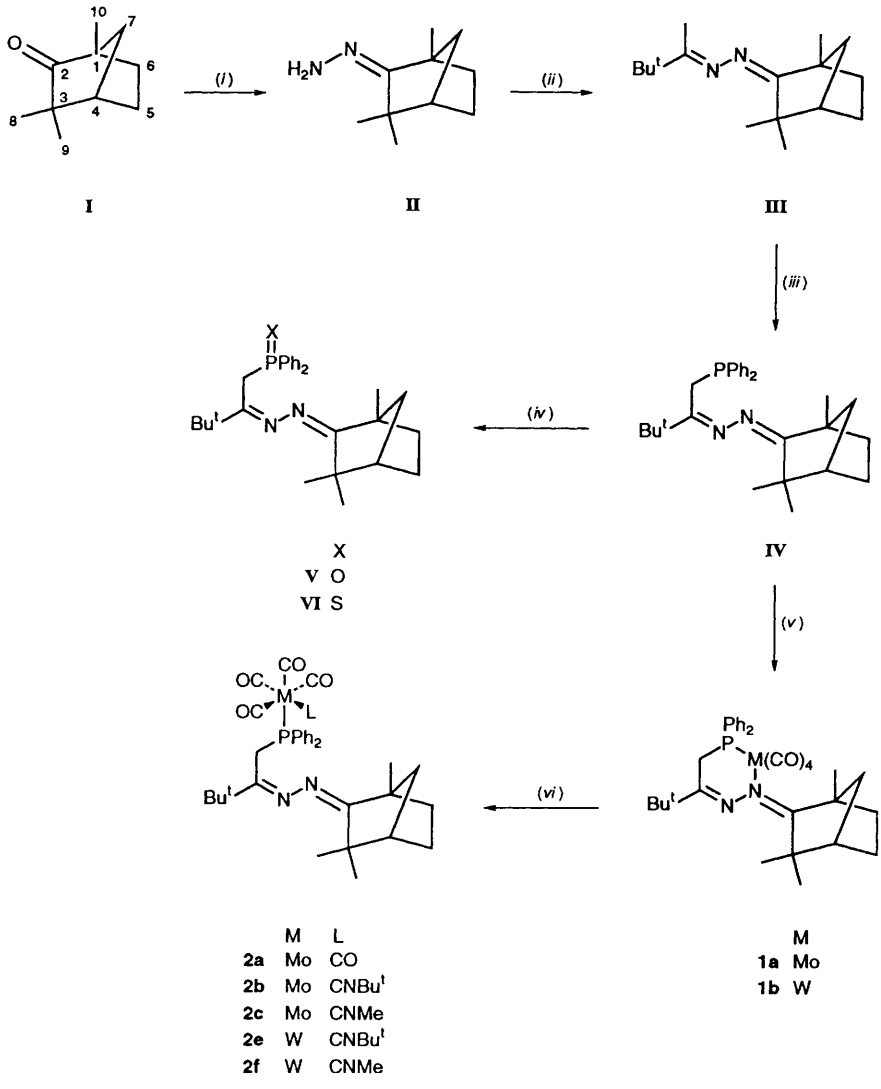
The hydrazone *Z*-$Ph_2PCH_2C(Bu^t)$=$NNH_2$ reacts with a whole range of aldehydes and ketones to give mixed azine monophosphines;[3] for example, it condenses rapidly with benzaldehyde and we have described some chemistry of the resultant mixed azine monophosphine *Z,E*-$Ph_2PCH_2C(Bu^t)$=N–N=CHPh.[1,2] Since chiral ligands based on camphor or related terpenes are used in enantioselective catalysis[4–6] we attempted to condense *Z*-$Ph_2PCH_2C(Bu^t)$=$NNH_2$ with (1*R*)-(+)-camphor [(1*R*)-(+)-1,7,7-trimethylnorban-2-one] or (1*R*)-(−)-fenchone but found that condensation did not occur, presumably for steric reasons. In the present paper we describe a different approach to making a monophosphine of fenchone–pinacolone mixed azine. It is in general difficult to stop the condensation of hydrazine with a ketone at the hydrazone stage[7,8] but if the ketone is very sterically hindered then the hydrazone can often be isolated.[9] Thus the very sterically hindered ketone (1*R*)-(−)-fenchone **I** readily gives the crystalline fenchone hydrazone of *E* configuration **II**.[9,10] We anticipated that this hydrazone would condense with *tert*-butyl methyl ketone (pinacolone) to give the mixed azine, probably with the *E,E* configuration **III**. A feature of fenchone is that it has no α-hydrogens and therefore three of the four α-carbons in the mixed azine **III** have no active hydrogens *i.e.* we hoped that on deprotonation by treatment with butyllithium only the methyl carbon ($CH_3C$=N) would be deprotonated and therefore on treatment with $PClPh_2$ the phosphine **IV** would be formed. As described below this has proved to be the case and constitutes a new method for the systematic synthesis of a mixed azine monophosphine. We have reported the conversion of the symmetrical azine of *tert*-butyl methyl ketone to the azine diphosphine *Z,Z*-$Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$.[11]

## Results and Discussion

For the convenience of the reader, the various reactions and compounds are shown in Scheme 1. The compounds described in this paper were characterised by elemental analysis and by mass spectrometry (data in the Experimental section), proton NMR spectroscopy (Table 1), $^{31}P$-{$^1H$} NMR and IR spectroscopy (Table 2), and by carbon-13 NMR spectroscopy (Table 3). Fenchone hydrazone **II** was made in *ca.* 90% yield by heating (1*R*)-(−)-fenchone with an excess of hydrazine and when fenchone hydrazone **II** was heated with *tert*-butyl methyl ketone (pinacolone) in ethanol for 24 h the mixed azine **III** was isolated in >90% yield as a single isomer and as an easily distillable liquid. Details of the preparation and elemental analytical data are in the Experimental section. The proton NMR spectrum (at 100 MHz) of **III** was very complex with many overlapping resonances but a singlet at δ 1.15 (15 H) was assigned to the *tert*-butyl group and the two methyls on $C^3$. We suggest that the mixed azine has the *E,E* configuration **III**. Successive treatment of this mixed azine **III** with *n*-butyllithium followed by $PClPh_2$ gave the hoped for phosphine **IV** as a crystalline solid in 82% yield. Because **IV** was a key compound we determined its crystal structure and this is shown in Fig. 1 and discussed later. To our knowledge this is the first chiral phosphine derived from (1*R*)-(−)-fenchone although chiral phosphines derived from camphor and other norbornane derivatives are known.[12–15] The proton (Table 1) and carbon-13 (Table 3) data for **IV** were assigned by $^1H$-$^{13}C$ correlation spectroscopy at 400 MHz and by comparison with published data for (1*R*)-(−)-fenchone.[16] Interestingly, in the carbon-13 NMR spectrum of **IV** a long range coupling [$^7J$(PC) = 1.7 Hz] was observed between phosphorus and $C^8$ or $C^9$. Recently, we reported the observation of a seven-bond coupling, $^7J$(PP) of 4.8 Hz between two phosphorus atoms of the azine

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

Fenchone = 1,3,3-trimethylnorban-2-one, pinacolone = *tert*-butyl methyl ketone.




**Scheme 1** (*i*) $NH_2NH_2{\cdot}H_2O$; (*ii*) $MeCOBu^t$; (*iii*) LiBu then $PClPh_2$; (*iv*) $H_2O_2$ or S; (*v*) $[Mo(CO)_4(nbd)]$ or $[W(CO)_3(NCEt)_3]$ + CO; (*vi*) L, 20 °C

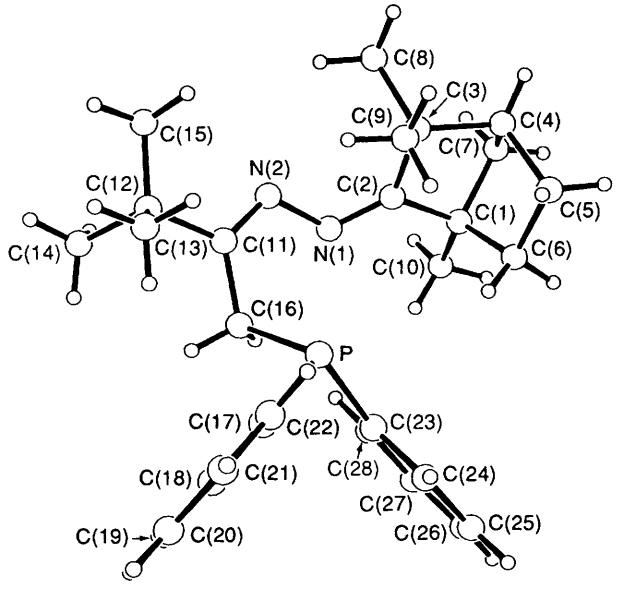



**Fig. 1** ORTEP representation of the molecular structure of compound **IV**. Ellipsoids are shown at the 30% probability level

diphosphine $Z,Z$-$Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$,[17] *i.e.* through an azine backbone similar to that in **IV**. The azine phosphine **IV** was converted into the corresponding phosphine oxide **V** by treatment with hydrogen peroxide and into the phosphine sulfide **VI** by treatment with monoclinic sulfur; see Experimental section and Tables 1 and 2 for preparative details and characterising data.

We anticipated that this azine phosphine **IV** would act as a chelate ligand through phosphorus and the azine nitrogen bonded to the fenchone residue, giving a six-membered chelate ring as with $Ph_2PCH_2C(Bu^t)$=N–N=CHPh[1,2] and with hydrazone phosphines.[1,2] We treated $[Mo(CO)_4(nbd)]$[18] (nbd = norbornadiene) with **IV** and obtained the hoped for chelate **1a**. The carbon-13 NMR spectrum of **1a** showed four separated doublet resonances for the four C≡O ligands. The value of δ 25.8 for the chemical shift of the methylene carbon is as expected for a methylene in a six-membered chelate ring whereas in a five-membered ring a higher value of δ *ca.* 40 is found.[2,19]

Since the azine nitrogen which is co-ordinated is very hindered sterically, one might expect it to be only weakly co-ordinated to the molybdenum and when we exposed a solution of **1a** to carbon monoxide ring-opening occurred and the pentacarbonyl complex **2a** with a monodentate phosphine was formed. This pentacarbonyl complex **2a**, which was fully

**Table 1** Proton NMR data[a]

| Compound | $\delta_H$ Bu$^t$ | Fenchone methyls | Others |
|---|---|---|---|
| **III** | 1.15 | 1.15 (6 H), 1.26 (3 H) | 1.77 (3 H, Me) |
| **IV**[b] | 1.05 | 1.08 (3 H, $H^{10}$), 1.24 (3 H), 1.25 (3 H) ($H^8$ or $H^9$) | 3.31 [1 H, dd, $^2J$(HH) 12.7, $^2J$(PH) 4.4, $CH_2P$]<br>3.43 [1 H, dd, $^2J$(HH) 12.7, $^2J$(PH) 4.4, $CH_2P$] |
| **V** | 1.16 | 1.02, 1.19, 1.21 | 3.81 [1 H, dd, $^2J$(HH) 13.5, $^2J$(PH) 15.8, $CH_2P$]<br>4.08 [1 H, dd, $^2J$(HH) 13.5, $^2J$(PH) 17.1, $CH_2P$] |
| **VI** | 1.09 | 0.85 (3 H), 1.28 (6 H) | 3.94 [1 H, dd, $^2J$(HH) 12.8, $^2J$(PH) 14.7, $CH_2P$]<br>4.43 [1 H, dd, $^2J$(HH) 12.8, $^2J$(PH) 16.9, $CH_2P$] |
| **1a** | 0.83 | 1.06, 1.43, 1.45 | 2.68 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 9.5, $CH_2P$]<br>3.15 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 10.8, $CH_2P$] |
| **1b** | 0.84 | 1.08, 1.43, 1.46 | 2.75 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 10.3, $CH_2P$]<br>3.24 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 10.7, $CH_2P$] |
| **2a** | 0.89 | 0.76, 1.17, 1.21 | 3.86 [1 H, dd, $^2J$(HH) 12.6, $^2J$(PH) 7.3, $CH_2P$]<br>4.04 [1 H, dd, $^2J$(HH) 12.6, $^2J$(PH) 6.6, $CH_2P$] |
| **2b** | 0.88<br>1.32 | 0.65, 1.15, 1.20 | 3.84 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 6.5, $CH_2P$]<br>4.03 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 5.9, $CH_2P$] |
| **2c** | 0.88 | 0.71, 1.16, 1.21 | 3.83 [1 H, dd, $^2J$(HH) 12.6, $^2J$(PH) 6.1, $CH_2P$]<br>4.01 [1 H, dd, $^2J$(HH) 12.6, $^2J$(PH) 5.8, $CH_2P$]<br>3.00 [3 H, d, $^5J$(PH) 1.2, CNMe] |
| **2e** | 0.87<br>1.31 | 0.63, 1.15, 1.20 | 3.93 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 7.3, $CH_2P$]<br>4.14 [1 H, dd, $^2J$(HH) 12.5, $^2J$(PH) 6.9, $CH_2P$] |
| **2f** | 0.87 | 0.68, 1.16, 1.21 | 3.93 [1 H, dd, $^2J$(HH) 12.6, $^2J$(PH) 7.3, $CH_2P$]<br>4.13 [1 H, dd, $^2J$(HH) 12.6, $^2J$(PH) 6.7, $CH_2P$]<br>3.03 [3 H, d, $^5J$(PH) 1.5, CNMe] |

[a] Recorded at 100 MHz, chemical shifts are in ppm relative to $SiMe_4$, solvent $CDCl_3$, coupling constants $J$ are in Hz, d = doublet, dd = doublet of doublets. [b] Recorded at 400 MHz, δ 1.28 [1 H, dd, $^2J$(HH) 9.9, $^3J$(HH) 1.4 Hz, $H^7$], 1.37 (2 H, m, $H^6$), 1.49 (1 H, m, $H^5$), 1.69 (1 H, m, $H^7$), 1.75 (1 H, m, $H^5$) and 1.77 (1 H, m, $H^4$).

**Table 2** $^{31}P$-{$^1H$} NMR data[a] and IR data[b]

| Compound | $\delta_P$ | $^1J$(WP) | ν(C=N)[c] | ν(C≡O)[d] | ν(C≡N)[d] |
|---|---|---|---|---|---|
| **IV** | −12.4 | | 1645 | | |
| **V** | 27.5 | | 1650 | | |
| **VI** | 38.4 | | 1650 | | |
| **1a** | 53.1 | | 1610 | 2020s, 1905s, 1850s | |
| **1b** | 48.7 | 260 | 1615 | 2020s, 1895s, 1845s | |
| **2a** | 28.2 | | 1640 | 2075m, 1945s | |
| **2b** | 29.5 | | 1640 | 2020m, 1910s, 1890 (sh) | 2145m |
| **2c** | 30.8 | | 1635 | 2025m, 1915s, 1995 (sh) | 2170m |
| **2e** | 10.3 | 238 | 1635 | 2020m, 1910s, 1890 (sh) | 2145m |
| **2f** | 11.8 | 238 | 1635 | 2020m, 1910s, 1890 (sh) | 2170m |

[a] Recorded at 36.2 MHz, chemical shifts (δ) are in ppm relative to 85% $H_3PO_4$, solvent $CDCl_3$, $^1J$(WP) in Hz. [b] In $cm^{-1}$, s = strong, m = medium and sh = shoulder. [c] KBr disc. [d] In $CH_2Cl_2$.

characterised, was also prepared by heating molybdenum hexacarbonyl with **IV** at 180 °C for 10 min. The carbon-13 NMR spectrum of **2a** showed that four of the carbonyls were equivalent *i.e. cis* to phosphorus whilst the carbon of the fifth carbonyl (*trans* to phosphorus) was strongly coupled to the phosphorus [$^2J$(PC) = 23.6 Hz]. Ring opening of the chelate ring in **1a** was also brought about by treating **1a** with either *tert*-butyl isocyanide or methyl isocyanide, giving respectively, the tetracarbonyl isocyanide complexes **2b** or **2c** containing monodentate **IV**. In the carbon-13 NMR spectrum of the *tert*-butyl isocyanide complex **2c** all four carbonyl carbons were non-equivalent, in agreement with the *cis* structure **2b**; the proton NMR spectrum of **2c** showed a $^5J$(PH) value of 1.2 Hz for $CNCH_3$.

Treatment of [W(CO)$_4$(nbd)] with **IV** in benzene solution at 75 °C gave a mixture of products including **1b**, which was not prepared in a pure state. However, treatment of [W(CO)$_3$(NCEt)$_3$][20] with **IV** under mild conditions (20 °C) followed by carbon monoxide gave the hoped for tetracarbonyl chelate complex **1b**, in satisfactory yield (53%), which was fully characterised. The $^{31}P$-{$^1H$} NMR spectrum of **1b** consisted of a singlet at δ 48.7 with satellites due to coupling to tungsten-183 [$^1J$(WP) = 260 Hz] and the $^{13}C$-{$^1H$} NMR spectrum showed a $CH_2$ resonance at δ 25.4 in agreement with a six-membered chelate ring. Tungsten is less labile than molybdenum and we found that **1b** did not undergo ring opening with carbon monoxide to give [W(CO)$_5${$PPh_2CH_2C(Bu^t)$=N–N=$C_{10}H_{16}$}] **2d**; ring opening with *tert*-butyl isocyanide to give **2e** or with methyl isocyanide to give **2f** occurred and these complexes were fully characterised.

*Crystal Structure of Z,E*-$Ph_2PCH_2C(Bu^t)$=N–N=$C_{10}H_{16}$.—The molecular structure of the phosphino-azine **IV** is shown in Fig. 1 with selected bond lengths and angles in Table 4 and atom co-ordinates in Table 5. The most important features are the configurations around the C=N bonds; around $PPh_2CH_2C(Bu^t)$=N– it is *Z* and around –N=$C_{10}H_{16}$ it is *E*, *i.e.* as shown for **IV**. The geometry around the $PPh_2CH_2C(Bu^t)$=N– moiety is virtually identical with that found for the symmetrical diphosphine *Z,Z*-$Ph_2PCH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$[11] and there appears to be nothing abnormal about the geometry of the fenchone residue.

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

| Compound | $\delta_C$ |
|---|---|
| **IV** | 17.1 (1C, s, $C^{10}$), 22.8 [1C, d, $^7J$(PC) 1.7, $C^8$ or $C^9$], 23.1 (1C, s, $C^8$ or $C^9$), 25.3 (1C, s, $C^5$), 27.8 [1C, d, $^1J$(PC) 22.8, $CH_2P$], 28.5 [3C, d, $^4J$(PC) 1.4, $CMe_3$], 33.6 (1C, s, $C^6$), 38.6 (1C, s, $CMe_3$), 42.9 (1C, s, $C^7$), 44.6 (1C, s, $C^3$), 48.6 (1C, s, $C^4$), 51.0 (1C, s, $C^1$), 169.0 [1C, d, $^2J$(PC) 4.9, C=N], 178.4 [1C, d, $^5J$(PC) 1.8, $C^2$] |
| **1a**[b] | 21.3 (1C, s, $C^{10}$), 22.3 (1C, s, $C^8$ or $C^9$), 24.7 (1C, s, $C^8$ or $C^9$), 25.4 (1C, s, $C^5$), 25.8 [1C, d, $^1J$(PC) 5.4, $CH_2P$], 27.3 (3C, s, $CMe_3$), 33.9 (1C, s, $C^6$), 39.1 [1C, d, $^3J$(PC) 1.9, $CMe_3$], 45.9 (1C, s, $C^7$), 49.3 (1C, s, $C^4$), 50.1 (1C, s, $C^3$), 52.5 (1C, s, $C^1$), 168.5 (1C, s, C=N), 191.4 [1C, d, $^3J$(PC) 3.2, $C^2$], 209.3 [1C, d, $^2J$(PC) 9.6, C≡O], 210.1 [1C, d, $^2J$(PC) 7.1, C≡O], 216.3 [1C, d, $^2J$(PC) 37.1, C≡O (*trans* to P)], 221.6 [1C, d, $^2J$(PC) 6.6, C≡O] |
| **1b**[c] | 22.1 (1C, s, $C^{10}$), 22.5 (1C, s, $C^8$ or $C^9$), 24.7 (1C, s, $C^8$ or $C^9$), 25.4 [1C, d, $^1J$(PC) 10.1, $CH_2P$], 25.6 (1C, s, $C^5$), 27.3 (3C, s, $CMe_3$), 34.2 (1C, s, $C^6$), 39.3 [1C, d, $^3J$(PC) 2.1, $CMe_3$], 45.8 (1C, s, $C^7$), 46.5 (1C, s, $C^3$), 49.7 (1C, s, $C^4$), 50.7 (1C, s, $C^1$), 169.5 (1C, s, C=N), 191.9 [1C, d, $^3J$(PC) 3.1, $C^2$], 205.0 [1C, d, $^2J$(PC) 9.0, C≡O], 206.3 [1C, d, $^2J$(PC) 3.9, C≡O], 210.0 [1C, d, $^2J$(PC) 3.5, C≡O], 210.3 [1C, d, $^2J$(PC) 36.8, C≡O (*trans* to P)] |
| **2a**[b] | 17.4 (1C, s, $C^{10}$), 23.8 (1C, s, $C^8$ or $C^9$), 23.82 (1C, s, $C^8$ or $C^9$), 25.6 (1C, s, $C^5$), 29.0 (3C, s, $CMe_3$), 31.8 [1C, d, $^1J$(PC) 9.0, $CH_2P$], 34.3 (1C, s, $C^6$), 38.7 (1C, s, $CMe_3$), 43.3 (1C, s, $C^7$), 45.3 (1C, s, $C^3$), 48.9 (1C, s, $C^4$), 51.5 (1C, s, $C^1$), 169.0 [1C, d, $^2J$(PC) 8.6, C=N], 183.7 [1C, d, $^5J$(PC) 1.8, $C^2$], 206.1 [4C, d, $^2J$(PC) 8.7, 4 × C≡O], 210.7 [1C, d, $^2J$(PC) 23.6, C≡O (*trans* to P)] |
| **2b**[b] | 17.3 (1C, s, $C^{10}$), 23.6 (1C, s, $C^8$ or $C^9$), 23.7 (1C, s, $C^8$ or $C^9$), 25.6 (1C, s, $C^5$), 29.1 (3C, s, $CMe_3$), 30.0 (3C, s, $CMe_3$), 32.5 [1C, d, $^1J$(PC) 7.2, $CH_2P$], 34.4 (1C, s, $C^6$), 38.8 (1C, s, $CMe_3$), 43.3 (1C, s, $C^7$), 45.2 (1C, s, $C^3$), 48.9 (1C, s, $C^4$), 51.4 (1C, s, $C^1$), 56.5 (1C, s, C≡N*C*), 156.7 [1C, d, br, $^2J$(PC) 9.4, C≡N], 169.5 [1C, d, $^2J$(PC) 9.8, C=N], 182.2 [1C, d, $^5J$(PC) 1.3, $C^2$], 208.6 [1C, d, $^2J$(PC) 8.6, C≡O], 209.0 [1C, d, $^2J$(PC) 8.7, C≡O], 212.6 [1C, d, $^2J$(PC) 8.2, C≡O], 214.8 [1C, d, $^2J$(PC) 26.8, C≡O (*trans* to P)] |
| **2e** | 16.8 (1C, s, $C^{10}$), 23.3 (1C, s, $C^8$ or $C^9$), 23.4 (1C, s, $C^8$ or $C^9$), 25.2 (1C, s, $C^5$), 28.8 (3C, s, $CMe_3$), 30.5 (3C, s, $CMe_3$), 32.9 [1C, d, $^1J$(PC) 12.4, $CH_2P$], 33.9 (1C, s, $C^6$), 38.4 (1C, s, $CMe_3$), 43.0 (1C, s, $C^7$), 44.9 (1C, s, $C^3$), 48.5 (1C, s, $C^4$), 51.1 (1C, s, $C^1$), 56.7 (1C, s, C≡N*C*), 147.5 (1C, s, br, C≡N), 168.9 [1C, d, $^2J$(PC) 10.4, C=N], 182.0 (1C, s, $C^2$), 200.1 [1C, d, $^2J$(PC) 6.8, C≡O], 200.4 [1C, d, $^2J$(PC) 7.0, C≡O], 203.5 [1C, d, $^2J$(PC) 6.0, C≡O], 204.0 [1C, d, $^2J$(PC) 25.9, C≡O (*trans* to P)] |

[a] Recorded at 100.6 MHz, chemical shifts (δ) are in ppm relative to $SiMe_4$, *J* values are in Hz, solvent $CDCl_3$ unless otherwise stated. [b] In $C_6D_6$. [c] In $CD_2Cl_2$.

## Experimental

All the reactions were carried out in an atmosphere of dry nitrogen or argon. Tetrahydrofuran (thf) and benzene were distilled from Na under nitrogen immediately before use. Infrared spectra were recorded using a Perkin Elmer model 257 grating spectrometer, NMR spectra using a JEOL FX-90Q spectrometer (operating frequencies for $^1H$ and $^{31}P$ of 89.5 and 36.2 MHz), a JEOL FX-100 spectrometer (operating frequencies for $^1H$ and $^{31}P$ of 99.5 and 40.25 MHz) or a Bruker AM-400 spectrometer (operating frequencies for $^1H$, $^{13}C$ and $^{31}P$ of 400.13, 100.6 and 161.9 MHz) respectively. The $^1H$ and $^{13}C$ chemical shifts are relative to $SiMe_4$ and $^{31}P$ chemical shifts relative to 85% phosphoric acid. All the coupling constants are in Hz. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a VG Autospec instrument with 8 kV acceleration. For the metal complexes *m/z* values are quoted for $^{98}Mo$ and $^{184}W$.

**Table 4** Selected bond lengths (Å) and angles (°) for **IV** with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| C(1)–C(10) | 1.504(3) | C(1)–C(2) | 1.520(3) |
| C(1)–C(6) | 1.547(3) | C(1)–C(7) | 1.550(3) |
| C(2)–N(1) | 1.274(2) | C(2)–C(3) | 1.534(3) |
| C(3)–C(9) | 1.526(3) | C(3)–C(8) | 1.548(3) |
| C(3)–C(4) | 1.548(3) | C(4)–C(5) | 1.530(3) |
| C(4)–C(7) | 1.531(3) | C(5)–C(6) | 1.553(4) |
| N(1)–N(2) | 1.414(2) | N(2)–C(11) | 1.276(3) |
| C(11)–C(16) | 1.509(3) | C(11)–C(12) | 1.527(3) |
| C(12)–C(14) | 1.528(4) | C(12)–C(15) | 1.528(3) |
| C(12)–C(13) | 1.529(3) | C(16)–P | 1.864(2) |
| P–C(23) | 1.840(2) | P–C(17) | 1.847(2) |
| C(10)–C(1)–C(2) | 116.0(2) | C(10)–C(1)–C(6) | 115.5(2) |
| C(2)–C(1)–C(6) | 104.8(2) | C(10)–C(1)–C(7) | 117.8(2) |
| C(2)–C(1)–C(7) | 99.3(2) | C(6)–C(1)–C(7) | 101.0(2) |
| N(1)–C(2)–C(1) | 121.1(2) | N(1)–C(2)–C(3) | 131.0(2) |
| C(1)–C(2)–C(3) | 107.9(2) | C(9)–C(3)–C(2) | 113.4(2) |
| C(9)–C(3)–C(8) | 108.3(2) | C(2)–C(3)–C(8) | 110.8(2) |
| C(9)–C(3)–C(4) | 114.2(2) | C(2)–C(3)–C(4) | 100.2(2) |
| C(8)–C(3)–C(4) | 109.9(2) | C(5)–C(4)–C(7) | 100.5(2) |
| C(5)–C(4)–C(3) | 109.9(2) | C(7)–C(4)–C(3) | 102.5(2) |
| C(4)–C(5)–C(6) | 103.3(2) | C(1)–C(6)–C(5) | 103.8(2) |
| C(4)–C(7)–C(1) | 95.3(2) | C(2)–N(1)–N(2) | 114.9(2) |
| C(11)–N(2)–N(1) | 115.2(2) | N(2)–C(11)–C(16) | 123.2(2) |
| N(2)–C(11)–C(12) | 117.5(2) | C(16)–C(11)–C(12) | 119.3(2) |
| C(11)–C(16)–P | 113.43(13) | C(23)–P–C(17) | 99.02(8) |
| C(23)–P–C(16) | 103.13(9) | C(17)–P–C(16) | 100.66(10) |

*Syntheses.*—(1R)-(−)-*Fenchone hydrazone* **II**. A solution containing (1*R*)-(−)-fenchone **I** (30 g, 0.2 mol), hydrazine monohydrate (45 g, 0.8 mol) and acetic acid (12 $cm^3$) in ethanol (80 $cm^3$) was heated under reflux for 20 h. The ethanol was then removed on a rotary evaporator and diethyl ether (50 $cm^3$) added. The ether solution was washed with 10% aqueous NaOH solution (30 $cm^3$) and then with saturated NaCl solution (30 $cm^3$). The ether solution was dried over anhydrous $MgSO_4$ and the solvent removed on a rotary evaporator to give the required hydrazone **II** as a viscous oil (33 g, 100%) which on standing crystallised as colourless needles (28.7 g, 87%); m.p. 54–56 °C (lit.,[10] 56–57 °C).

*Pinacolone* (1R)-(−)-*fenchone mixed azine*, $MeC(Bu^t)$=N–N=$C_{10}H_{16}$ **III**. A solution containing pinacolone (19 g, 23.5 $cm^3$, 0.19 mol) and (1*R*)-(−)-fenchone hydrazone **II** (28.7 g, 0.17 mol) in ethanol (60 $cm^3$) was heated under reflux for 24 h. The ethanol was then removed and the residue distilled to give the mixed azine **III** as a colourless liquid (39.1 g, 92%); b.p. 84–86 °C/0.1 mbar (10 Pa) (Found: C, 77.0; H, 11.4; N, 11.6. $C_{16}H_{28}N_2$ requires C, 77.35; H, 11.35; N, 11.3%); $\nu_{max}$(C=N) (neat liquid) 1655 $cm^{-1}$. Mass spectrum (EI): *m/z* 248 ($M^+$), 233 ($M$ − Me) and 191 ($M$ − $Bu^t$).

*Z,E-*tert-*Butyl diphenylphosphinomethyl ketone* (1R)-(−)-*fenchone mixed azine*, $Ph_2PCH_2C(Bu^t)$=N–N=$C_{10}H_{16}$ **IV**. A solution of $LiBu^n$ in hexane (37.5 $cm^3$, 1.6 mol $dm^{-3}$, 60 mmol) was added to a stirred solution of the mixed azine **III** (15 g, 60 mmol) in dry thf (150 $cm^3$) at −15 °C. After 1 h, the solution was cooled to −70 °C and a solution of chloro(diphenyl)-phosphine (13.5 g, 60 mmol) in thf (50 $cm^3$) added dropwise, after which the mixture was allowed to warm to room temperature. The solution was then concentrated to a low volume (*ca.* 20 $cm^3$) under reduced pressure and methanol (20 $cm^3$) added, and the resultant solution was cooled to −30 °C. The required mixed azine phosphine **IV** was obtained as a white crystalline solid (21.4 g, 82%) (Found: C, 77.75; H, 8.75; N, 6.35. $C_{28}H_{37}N_2P$ requires C, 77.75; H, 8.6; N, 6.45%). Mass spectrum (EI): *m/z* 433 ($M$ + 1), 432 ($M^+$) and 375 ($M$ − $Bu^t$).

$Ph_2P(=O)CH_2C(Bu^t)$=N–N=$C_{10}H_{16}$ **V**. An excess of $H_2O_2$ (0.15 $cm^3$, 30% w/v) was added to a solution of the azine phosphine **IV** (0.23 g, 0.53 mmol) in acetone (8 $cm^3$). After 15 min the solution was evaporated to dryness and the residue

**Table 5** Fractional non-hydrogen atomic coordinates ($\times 10^4$) for compound **IV** with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| C(1) | −2815(2) | −1194(2) | −3694(2) |
| C(2) | −3461(2) | −1013(2) | −5137(2) |
| C(3) | −4459(2) | −2026(2) | −5651(2) |
| C(4) | −4265(2) | −2732(2) | −4392(2) |
| C(5) | −2965(3) | −3388(2) | −3957(3) |
| C(6) | −1970(2) | −2338(2) | −3557(2) |
| C(7) | −3973(3) | −1719(2) | −3388(2) |
| C(8) | −5843(2) | −1499(3) | −6186(3) |
| C(9) | −4241(2) | −2781(2) | −6706(2) |
| C(10) | −2137(3) | −105(2) | −2942(2) |
| N(1) | −3146(2) | −135.0(15) | −5709.8(15) |
| N(2) | −3892(2) | −26.7(15) | −7032.1(15) |
| C(11) | −3249(2) | 167(2) | −7768(2) |
| C(12) | −4010(2) | 386(2) | −9192(2) |
| C(13) | −5461(2) | 303(3) | −9471(2) |
| C(14) | −3709(3) | 1657(3) | −9554(3) |
| C(15) | −3637(3) | −576(3) | −9988(2) |
| C(16) | −1795(2) | 206(2) | −7291(2) |
| P | −1030.9(5) | −1321.0(4) | −6946.3(5) |
| C(17) | −173(2) | −1359(2) | −8102(2) |
| C(18) | 607(2) | −425(2) | −8217(2) |
| C(19) | 1222(2) | −464(3) | −9109(2) |
| C(20) | 1065(3) | −1467(3) | −9886(2) |
| C(21) | 333(3) | −2407(3) | −9774(3) |
| C(22) | −304(3) | −2363(2) | −8886(2) |
| C(23) | 358(2) | −1076(2) | −5457(2) |
| C(24) | 1325(2) | −1955(2) | −5126(2) |
| C(25) | 2363(2) | −1898(2) | −3989(2) |
| C(26) | 2467(2) | −958(2) | −3141(2) |
| C(27) | 1534(3) | −81(2) | −3441(2) |
| C(28) | 479(2) | −137(2) | −4586(2) |

triturated with ethanol to give the required phosphine oxide **V** as a white solid (0.21 g, 88%) (Found: C, 74.75: H, 8.25; N, 6.3. $C_{28}H_{37}N_2OP$ requires C, 75.0; H, 8.3; N, 6.25%).

$Ph_2P(=S)CH_2C(Bu^t)=N-N=C_{10}H_{16}$ **VI**. A mixture of monoclinic sulfur (20 mg, 0.6 mmol) and the azine phosphine **IV** (0.2 g, 0.46 mmol) in benzene (8 $cm^3$) was refluxed for 1 h. The solution was evaporated to dryness and the residue crystallised from benzene–ethanol to give the required phosphine sulfide **VI** as white needles (0.18 g, 82%) (Found: C, 72.25; H, 8.05; N, 6.05. $C_{28}H_{37}N_2PS$ requires C, 72.35; H, 8.0; N, 6.0%).

$[Mo(CO)_4\{PPh_2CH_2C(Bu^t)=N-N=C_{10}H_{16}\}]$ **1a**. A solution containing the azine phosphine **IV** (0.76 g, 17.6 mmol) and $[Mo(CO)_4(nbd)]$[18] (0.53 g, 17.6 mmol) in benzene (12 $cm^3$) was put aside at 20 °C for 5 h. The solution was then filtered, evaporated to dryness under reduced pressure and the residue recrystallised from $CH_2Cl_2$–MeOH to give the required complex **1a** as yellow microcrystals (0.60 g, 53%) (Found: C, 60.1; H, 5.9; N, 4.4. $C_{32}H_{37}MoN_2O_4P$ requires C, 60.0; H, 5.8; N, 4.35%). Mass spectrum (FAB): *m*/*z* 642 ($M^+$), 614 (*M* − CO), 586 (*M* − 2CO) and 530 (*M* − 4CO).

$[W(CO)_4\{PPh_2CH_2C(Bu^t)=N-N=C_{10}H_{16}\}]$ **1b**. The azine phosphine **IV** (60 mg, 0.13 mmol) was added to a solution of $[W(CO)_3(NCEt)_3]$[20] (50 mg, 0.115 mmol) in thf (2 $cm^3$). After 15 min carbon monoxide was bubbled through the reaction mixture for 30 min, after which the solution was filtered and concentrated to a low volume (*ca.* 0.2 $cm^3$) under reduced pressure. Addition of methanol to the residue gave the complex **1b** as yellow microcrystals (45 mg, 53%) (Found: C, 53.0; H, 5.15; N, 4.05. $C_{32}H_{37}N_2O_4PW$ requires C, 52.75; H, 5.1; N, 3.85%). Mass spectrum (EI): *m*/*z* 728 ($M^+$), 700 (*M* − CO), 672 (*M* − 2CO) and 616 (*M* − 4CO).

$[Mo(CO)_5\{PPh_2CH_2C(Bu^t)=N-N=C_{10}H_{16}\}]$ **2a**. (*i*) *From complex* **1a**. A solution of the tetracarbonyl complex **1a** (0.13 g, 0.21 mmol) in benzene (4 $cm^3$) was stirred at 20 °C in an atmosphere of carbon monoxide for 20 h. The solution was then filtered and evaporated to a low volume (*ca.* 0.2 $cm^3$) under reduced pressure. Addition of methanol to the residue gave the required pentacarbonyl complex **2a** as white microcrystals (0.10 g, 70%).

(*ii*) *From* $[Mo(CO)_6]$. A suspension of $[Mo(CO)_6]$ (0.80 g, 3.0 mmol) and the azine phosphine **IV** (1.34 g, 3.1 mmol) in *n*-decane (8 $cm^3$) was heated under reflux for 10 min, the resultant solution was then allowed to cool to room temperature. The solvent was then removed under reduced pressure and the residue recrystallised from $CH_2Cl_2$–MeOH to give the pentacarbonyl complex **2a** as white microcrystals (1.26 g, 63%) (Found: C, 59.05; H, 5.5; N, 4.4. $C_{33}H_{37}MoN_2O_5P$ requires C, 59.3; H, 5.6; N, 4.2%). Mass spectrum (FAB): *m*/*z* 670 ($M^+$), 614 (*M* − 2CO), 586 (*M* − 3CO) and 530 (*M* − 5CO).

*cis*-$[Mo(CO)_4(CNBu^t)\{PPh_2CH_2C(Bu^t)=N-N=C_{10}H_{16}\}]$ **2b**. *tert*-Butyl isocyanide (26 μl, 20.8 mg, 0.25 mmol) was added to a solution of **1a** (0.16 g, 0.25 mmol) in $CH_2Cl_2$ (3 $cm^3$). After 30 min, the solution was concentrated to a low volume (*ca.* 0.5 $cm^3$) under reduced pressure. Addition of methanol (*ca.* 1 $cm^3$) to the residue gave the required product **2b** as pale yellow microcrystals (0.12 g, 68%) (Found: C, 60.1; H, 6.1; N, 5.5. $C_{37}H_{46}MoN_3O_4P\cdot 0.25CH_2Cl_2$ requires C, 60.2; H, 6.3; N, 5.65%). Mass spectrum (FAB): *m*/*z* 725 ($M^+$), 699 (*M* − 2CO), 641 (*M* − 3CO) and 530 (*M* − 4CO − $CNBu^t$).

*cis*-$[Mo(CO)_4(CNMe)\{PPh_2CH_2C(Bu^t)=N-N=C_{10}H_{16}\}]$ **2c**. The monomethyl isocyanide complex **2c** was prepared from **1a** and isolated in a similar manner to the complex **2b** as white microcrystals in 85% yield (Found: C, 59.65; H, 5.8; N, 5.9. $C_{34}H_{40}MoN_3O_4P$ requires C, 59.9; H, 5.9; N, 6.15%). Mass spectrum (FAB): *m*/*z* 683 ($M^+$), 627 (*M* − 2CO), 599 (*M* − 3CO) and 530 (*M* − 4CO − CNMe).

*cis*-$[W(CO)_4(CNBu^t)\{PPh_2CH_2C(Bu^t)=N-N=C_{10}H_{16}\}]$ **2e**. This tungsten complex **2e** was prepared from **1b** and isolated in a similar manner to the molybdenum complex **2b** as white microcrystals in 89% yield, after a reaction time of 24 h (Found: C, 54.8; H, 5.7; N, 5.15. $C_{37}H_{46}N_3O_4PW$ requires C, 54.75; H, 5.7; N, 5.2%). Mass spectrum (FAB): *m*/*z* 811 ($M^+$), 783 (*M* − CO), 755 (*M* − 2CO), 727 (*M* − 3CO), 699 (*M* − 4CO) and 616 (*M* − 4CO − $CNBu^t$).

*cis*-$[W(CO)_4(CNMe)\{PPh_2CH_2C(Bu^t)=N-N=C_{10}H_{16}\}]$ **2f**. The monomethyl isocyanide complex **2f** was prepared from **1b** and isolated in a similar manner to the molybdenum complex **2b** as white microcrystals in 74% yield, after a reaction time of 24 h (Found: C, 52.9; H, 5.15; N, 5.75. $C_{34}H_{40}N_3O_4PW$ requires C, 53.05; H, 5.25; N, 5.45%). Mass spectrum (FAB): *m*/*z* 769 ($M^+$), 741 (*M* − CO), 713 (*M* − 2CO), 685 (*M* − 3CO), 657 (*M* − 4CO) and 616 (*M* − 4CO − CNMe).

*Single-crystal X-Ray Diffraction Analysis of* **IV**.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated copper-Kα X-radiation (λ = 1.541 84 Å). A unique set of data and its Friedel opposites were collected and corrected for absorption semiempirically using azimuthal ψ scans (maximum and minimum transmission factors 0.1682 and 0.2867 respectively).

The structure was determined by direct methods using SHELXS 86[21] and was refined by full-matrix least squares (based on $F^2$) using SHELXL 93.[22] All data were used for refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. Restraints were applied to the phenyl rings such that they were flat with overall $C_{2v}$ symmetry. All hydrogen atoms were included in calculated positions (C–H 0.95, 1.00, 0.99 and 0.98 Å for phenyl, methine, methylene and methyl hydrogen atoms respectively) and were assigned fixed isotropic thermal parameters of $n(U_{eq})$ of the parent carbon atom, where *n* was 1.5 for methyl hydrogens and 1.2 for all others. The absolute configuration was initially based on the known *R*-(−) configuration of the fenchone starting material and was confirmed by the refinement of a 'Flack'[23] parameter to 0.00(1). The weighting scheme $w = [\sigma^2(F_o^2) +$

$(0.0372P)^2 + 0.2691P]^{-1}$ [where $P = (F_o^2 + 2F_c^2)/3$] was used. The final Fourier difference synthesis was flat and showed no features of chemical significance (maximum and minimum electron densities 0.114 and $-0.145$ e Å$^{-3}$ respectively). Final atomic coordinates are given in Table 5. An ORTEP[24] diagram of **4** is given in Fig. 1.

*Crystal data.* $C_{28}H_{37}N_2P$, 0.60 × 0.45 × 0.45 mm, $M = 432.57$, monoclinic, space group $P2_1$, $a = 11.0737(8)$, $b = 11.0377(9)$, $c = 11.1072(7)$ Å, $\beta = 110.60(5)°$, $U = 1270.8(2)$ Å$^3$, $Z = 2$, $D_c = 1.130$ Mg m$^{-3}$, $\mu = 1.065$ mm$^{-1}$, $F(000) = 468$.

*Data collection.* $4.0 < 2\theta < 130.0°$, scan widths = 1.05 + α-doublet splitting, scan speed 1.0–8.0° min$^{-1}$. Number of data collected = 5406; number of unique data, $n = 3733$; number with $F_o > 4.0\sigma(F_o) = 3492$; $R_{int}\{=\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]\} = 0.0120$; $R_{sig}\{=\Sigma[\sigma F_o^2]/\Sigma[F_o^2]\} = 0.0171$; $T = 200$ K.

*Structure refinement.* Number of parameters, $p = 286$; $R\{=\Sigma||F_o| - |F_c||/\Sigma|F_o|\} = 0.0294$; $wR2$ $\{=(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{\frac{1}{2}}\} = 0.0771$; goodness of fit $S$ $(=\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{\frac{1}{2}}\} = 1.086$; maximum $\Delta/\sigma = 0.001$ [in $U_{22}$ of C(14)], mean $\Delta/\sigma = 0.000$.

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