

Syntheses and crystal structures of molybdenum(0) and palladium(II) complexes of 4-tert-butyl-2-diphenylphosphino-cyclohexanone *N,N*-dimethylhydrazone

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Abstract

Deprotonation of 4-tert-butyl-cyclohexanone *N,N*-dimethylhydrazone (**1**) with LiBu^n at -15°C , followed by addition of PPh_2Cl gave the corresponding phosphino dimethylhydrazone $Z\text{-PPh}_2\text{C}_{10}\text{H}_{17}=\text{NNMe}_2$ (**2**), in which the PPh_2 group is in the axial position. **2** reacts with $[\text{Mo}(\text{CO})_4(\text{nb})]$ (nb = norbornadiene) to give the tetracarbonyl complex $[\text{Mo}(\text{CO})_4(Z\text{-PPh}_2\text{C}_{10}\text{H}_{17}=\text{NNMe}_2)]$ (**3**), containing a six-membered chelate ring and an axial PPh_2 group. Treatment of **2** with Na_2PdCl_4 or $[\text{PdCl}_2(\text{NCPH})_2]$ gave the dichloropalladium(II) complex $[\text{PdCl}_2(E\text{-PPh}_2\text{C}_{10}\text{H}_{17}=\text{NNMe}_2)]$ (**4**), containing a five-membered chelate ring and an equatorial PPh_2 group due to isomerisations at C^2 and around $\text{C}=\text{N}$. Crystals of **3** are monoclinic, space group $P2_1/n$ with $a = 2083.4(4)$, $b = 1089.0(2)$, $c = 2521.9(5)$ pm, $\beta = 98.82(2)^\circ$ and $Z = 8$, $R = 0.0263$ for 6109 observed reflections with $I > 2.0\sigma(I)$. Crystals of **4** are monoclinic, space group $P2_1/n$ with $a = 11.271(2)$, $b = 13.205(3)$, $c = 17.849(3)$ Å, $\beta = 104.83(1)^\circ$ and $Z = 4$, $R_1 = 0.0304$ for 3994 observed reflections.

Keywords: Crystal structures; Molybdenum complexes; Phosphine hydrazone complexes

1. Introduction

As is well known, a C–H hydrogen α to an organic carbonyl group is activated towards deprotonation, giving a carbanion or enolate anion. However, the deprotonation is not selective; for example, with symmetrical ketones the α -hydrogens are effectively equally likely to be removed by a base. However, if the ketone is derivatised by condensation, as an oxime, *O*-methyl oxime or *N,N*-dimethylhydrazone, the α -hydrogens *syn* to the bent $=\text{N}-\text{R}$ group are activated preferentially [1–5]. Selectivity greater than that has been achieved with the *O*-methyl oxime of 4-tert-butyl-cyclohexanone. This when deprotonated by lithium diisopropylamide and the resultant enolate treated with MeI causes methylation exclusively in the *syn*-axial position α to the $=\text{NOMe}$ group; the very bulky tert-butyl group always stays equatorial [2]. Similarly, 4-tert-butyl-cyclohexanone *N,N*-dimethylhydrazone is exclusively methylated in the axial position [3,4], as are other ketone *N,N*-dimethylhydrazones [4,5].

In our previous work we have shown that the *N,N*-dimethylhydrazone of tert-butyl methyl ketone, when treated with LiBu^n followed by PPh_2Cl , is phosphinated to give *Z*-

$\text{PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2$ exclusively [6], and that (1*R*)-(+) -camphor *N,N*-dimethylhydrazone when treated with LiBu^n followed by PPh_2Cl gives the *exo*-3-diphenylphosphino-(1*R*)-(+) -camphor *N,N*-dimethylhydrazone as the *Z*-isomer [7]. We have reported on the chemistry of these dimethylhydrazone phosphines [6–10]. However, camphor and its *N,N*-dimethylhydrazone are very sterically hindered and it was of interest to study derivatives of a less sterically hindered cyclic ketone. We chose to study 4-tert-butyl-cyclohexanone *N,N*-dimethylhydrazone **1** since the tert-butyl group would have a strong preference to take up an equatorial position and therefore define the stereochemistry around the dimethylhydrazone group and yet exert relatively little steric hindrance at the two- and six-positions adjacent to the $\text{C}=\text{NNMe}_2$ group. We have therefore studied the stereochemistry of the diphenylphosphination of the anion produced by deprotonation of **1**, and the behaviour of the resultant phosphino dimethylhydrazone **2** as a ligand. We describe our results in this paper.

2. Results and discussion

Deprotonation of 4-tert-butyl-cyclohexanone *N,N*-dimethylhydrazone (**1**) with LiBu^n at -15°C , followed by

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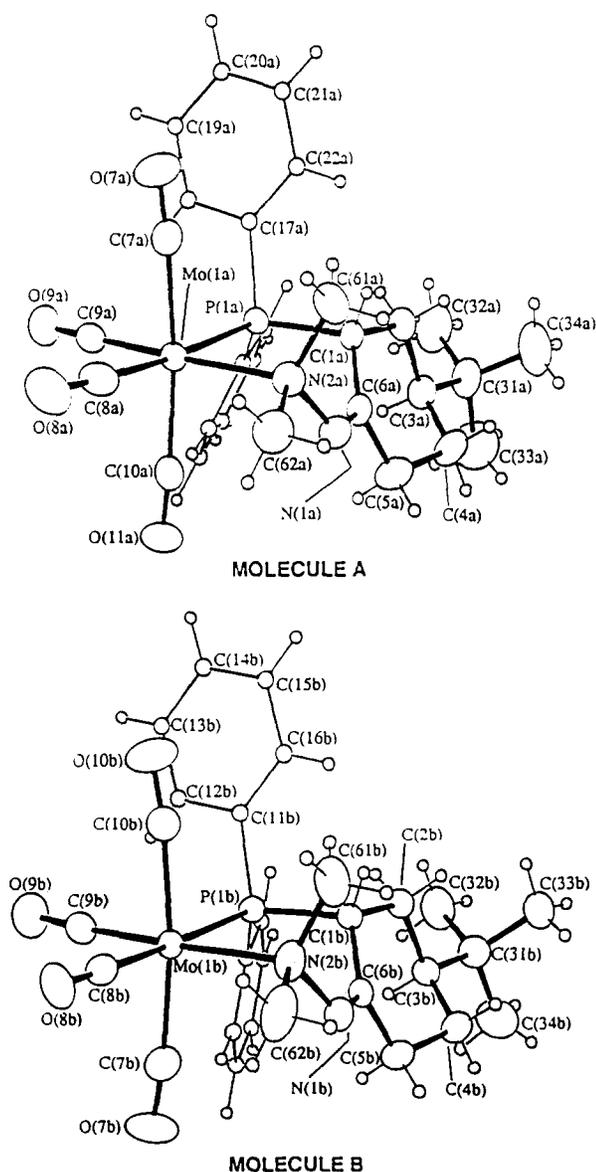


Fig. 1. Molecular structure of complex 3. Ellipses for non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are shown as circles with a small, arbitrary radius.

addition of PPh_2Cl gave the diphenylphosphino dimethylhydrazone (**2**) as white needles in 53% yield. Characterising elemental analytical data and $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR data are given in Section 3. The Bu^t and NMe_2 hydrogens are easily identified in the proton NMR spectrum but we did not attempt to analyse the complex patterns of the remaining hydrogens. We expected that the PPh_2 group would be axial as shown in **2**, by analogy with the methylation studies [2,4], and when **2** was treated with the labile molybdenum(0) complex $[\text{Mo}(\text{CO})_4(\text{nbd})]$ [11] ($\text{nbd} = \text{norbornadiene}$), the norbornadiene would be displaced by the potentially bidentate ligand **2** without any axial/equatorial isomerisation of the PPh_2 group. We therefore treated $[\text{Mo}(\text{CO})_4(\text{nbd})]$ with **2** at 20°C in benzene solution and followed the progress of the reaction by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Essentially only one

product was formed, with $\delta\text{P} = 70.8$ ppm, and it was isolated as yellow crystals and characterised by elemental analysis and by NMR and IR spectroscopy. The presence of two distinct NMe_2 methyls indicated that the NMe_2 nitrogen was coordinated and not the $\text{C}=\text{N}$ nitrogen.

Crystals of **3**, suitable for X-ray diffraction analysis, were grown from dichloromethane/methanol. There were two molecules in the asymmetric unit, and the structures of these are shown in Fig. 1, molecule A and molecule B. Crystal data for **3** are in Table 1, atom coordinates in Table 2, and selected bond lengths and angles in Table 3. We also compare some bond lengths (namely, 2.512, Mo–P; 2.377, Mo–N and 1.280 Å, C=N) for molecule A (very similar to those of molecule B) with the related molybdenum tetracarbonyl complexes containing phosphino dimethylhydrazone ligands e.g. $[\text{Mo}(\text{CO})_4\{\text{Z-PPh}_2\text{CH}_2\text{C}(\text{Bu}^t)=\text{NNMe}_2\}]$ (six-membered ring chelate) (2.507, Mo–P; 2.370, Mo–N and 1.283 Å, C=N) [6] and the camphor derivative $[\text{Mo}(\text{CO})_4\{E-$

Table 1
Crystallographic data for compounds **3** and **4**^a

	3	4
<i>Crystal data</i>		
Formula	$\text{C}_{28}\text{H}_{33}\text{MoN}_2\text{O}_4\text{P}$	$\text{C}_{24}\text{H}_{33}\text{Cl}_2\text{N}_2\text{PPd}$
<i>M</i>	588.50	557.84
Crystal dimensions (mm)	0.45 × 0.27 × 0.19	0.55 × 0.38 × 0.27
<i>a</i> (pm)	2083.4(4)	1127.1(2)
<i>b</i> (pm)	1089.0(2)	1320.5(3)
<i>c</i> (pm)	2521.9(5)	1784.9(3)
β (°)	98.82(2)	104.83(1)
<i>U</i> (nm ³)	5.654(2)	2.5678(8)
<i>Z</i>	8	4
<i>D_c</i> (g cm ⁻³)	1.38	1.44
<i>F</i> (000)	2432	1144
μ (mm ⁻¹)	0.487	0.911
<i>T</i> (K)	200	295
<i>Data collection</i>		
Diffractometer model	Stoe STADI4	Nicolet P3/F
Scan mode	ω - θ	ω - 2θ
Scan widths	1.05	2.0
(° + α -doublet splitting)		
Max., min. scan speed (° min ⁻¹)	1.5, 8.5	2.0, 29.3
No. data collected	10 514	5111
No. data observed ^b	6109	3994
Absorption correction	ψ -scans	DIFABS ^c
Max., min. transmission factors	0.889, 0.999	0.845, 1.071
<i>Refinement</i>		
$\rho_{\text{max.}}, \rho_{\text{min.}}$ (e Å ⁻³)	0.28, -0.29	0.52, -0.49
$\Delta/\sigma_{\text{max.}}$	0.70	0.24
<i>R</i> ^d	0.0263	0.0304
<i>R'</i> ^e	0.0283	0.0306
Weighting parameter <i>g</i> ^f	0.0001	0.0002
No. of parameters	634	263

^a Common to both compounds: crystal system monoclinic, space group $P2_1/n$, $4.0 > 2\theta > 50.0^\circ$.

^b Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$.

^c See Ref. [14].

^d $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

^e $R' = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

^f Weighting scheme used $w = [\sigma^2(|F_o|) + g(|F_o|)^2]^{-1}$.

$\text{PPh}_2\text{C}_{10}\text{H}_{15}=\text{NNMe}_2$] (five-membered ring chelate) (2.514, Mo–P; 2.331, Mo–N and 1.271 Å, C=N) [7].

The most important features about molecules A or B (Fig. 1) are (i) the PPh_2 is axial and *syn* to the NMe_2 group, (ii) the Bu^t group is equatorial, (iii) the ligand is coordinated to molybdenum via the phosphorus and the NMe_2 nitrogen, giving a six-membered chelate ring, and (iv) the Mo–N and C=N distances and the N–Mo–P bond angles (Table 3) are very similar for molecule A (or B) with the six-membered chelate ring complex [6] than for the five-membered chelate ring complex [7] referred to above. Other bond lengths and angles for molecules A (or B) on Table 3 are as might be expected for such molecules.

In our previous work with phosphino dimethylhydrazone ligands we have studied acid or base catalysed isomerisation, *exo*- $\text{PPh}_2 \rightarrow$ *endo*- PPh_2 [8] in the camphor complexes and also *Z* \rightarrow *E* isomerisation [6–8] around the C=N bond, i.e. six-membered chelate ring to five-membered chelate ring

Table 2
Fractional atom coordinates ($\times 10^4$) for compound 3 with e.s.d.s in parentheses

Atom	x	y	z
Molecule A			
Mo(1a)	3997.2(1)	4798.2(3)	890.4(1)
P(1a)	3808.2(4)	3918.9(7)	1774.4(3)
C(1a)	4439(2)	4501(3)	2331(1)
C(2a)	4361(2)	4154(3)	2920(1)
C(3a)	4028(2)	5112(3)	3226(1)
C(31a)	3945(2)	4729(4)	3807(1)
C(32a)	3557(2)	3533(4)	3796(2)
C(33a)	3560(3)	5727(5)	4046(2)
C(34a)	4591(2)	4553(5)	4168(2)
C(4a)	4395(2)	6319(3)	3197(1)
C(5a)	4325(2)	6751(3)	2617(1)
C(6a)	4548(2)	5846(3)	2233(1)
N(1a)	4765(1)	6374(2)	1843(1)
N(2a)	4940(1)	5691(2)	1393(1)
C(61a)	5498(2)	4844(4)	1551(1)
C(62a)	5186(2)	6683(3)	1064(2)
C(7a)	4464(2)	3203(3)	744(1)
O(7a)	4683(1)	2306(2)	629(1)
C(8a)	4159(2)	5355(3)	175(2)
O(8a)	4224(1)	5633(3)	–258(1)
C(9a)	3204(2)	4006(3)	535(1)
O(9a)	2739(1)	3518(3)	330(1)
C(10a)	3505(2)	6393(3)	956(1)
O(10a)	3208(1)	7278(2)	957(1)
C(11a)	3018(1)	4102(2)	2000(1)
C(12a)	2613(1)	5061(2)	1790(1)
C(13a)	2007(1)	5211(2)	1953(1)
C(14a)	1807(1)	4403(2)	2324(1)
C(15a)	2212(1)	3445(2)	2533(1)
C(16a)	2818(1)	3294(2)	2371(1)
C(17a)	3910(1)	2230(1)	1785(1)
C(18a)	3419(1)	1538(1)	1485(1)
C(19a)	3514(1)	289(1)	1401(1)
C(20a)	4100(1)	–267(1)	1616(1)
C(21a)	4590(1)	425(1)	1916(1)
C(22a)	4495(1)	1674(1)	2000(1)

(continued)

Table 2 (continued)

Atom	x	y	z
Molecule B			
Mo(1b)	3683.6(1)	–101.0(2)	6661.5(1)
P(1b)	3328.4(4)	1641.9(7)	6021.3(3)
C(1b)	2423(1)	1629(3)	5837(1)
C(2b)	2108(2)	2686(3)	5472(1)
C(3b)	1835(2)	3773(3)	5750(1)
C(31b)	1498(2)	4750(3)	5349(1)
C(32b)	1996(2)	5312(4)	5035(2)
C(33b)	1227(2)	5787(4)	5663(2)
C(34b)	936(2)	4211(3)	4954(2)
C(4b)	1400(2)	3265(3)	6136(1)
C(5b)	1801(2)	2493(3)	6562(1)
C(6b)	2140(1)	1426(3)	6349(1)
N(1b)	2185(1)	482(2)	6653(1)
N(2b)	2560(1)	–604(2)	6553(1)
C(61b)	2293(2)	–1235(3)	6042(2)
C(62b)	2436(2)	–1445(4)	6993(2)
C(7b)	3847(2)	–1107(3)	6017(1)
O(7b)	4001(1)	–1679(2)	5675(1)
C(8b)	3941(2)	–1533(3)	7127(1)
O(8b)	4100(1)	–2366(2)	7401(1)
C(9b)	4600(2)	346(3)	6713(1)
O(9b)	5144(1)	577(3)	6726(1)
C(10b)	3631(2)	818(3)	7358(2)
O(10b)	3648(2)	1256(3)	7770(1)
C(11b)	3640(1)	1428(2)	5389(1)
C(12b)	4295(1)	1696(2)	5387(1)
C(13b)	4589(1)	1379(2)	4946(1)
C(14b)	4230(1)	792(2)	4506(1)
C(15b)	3575(1)	524(2)	4507(1)
C(16b)	3281(1)	841(2)	4949(1)
C(17b)	3513(1)	3254(1)	6176(1)
C(18b)	3577(1)	4093(1)	5770(1)
C(19b)	3650(1)	5341(1)	5889(1)
C(20b)	3658(1)	5750(1)	6414(1)
C(21b)	3594(1)	4910(1)	6820(1)
C(22b)	3521(1)	3662(1)	6701(1)

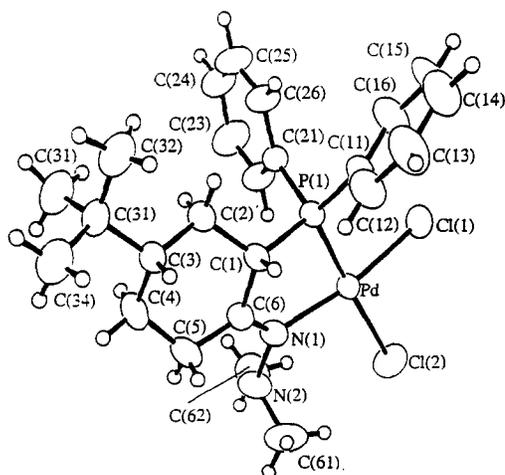


Fig. 2. Molecular structure of complex 4. Ellipsoids for non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are shown as circles with a small, arbitrary radius.

Table 3
Selected bond lengths (pm) angles (°) and torsion angles (°) for compound 3 with e.s.d.s in parentheses

	Molecule A	Molecule B
P(1)–Mo(1)	251.2(4)	252.8(4)
N(2)–Mo(1)	237.7(4)	237.9(5)
C(7)–Mo(1)	205.2(6)	203.9(6)
C(8)–Mo(1)	198.0(6)	195.6(5)
C(9)–Mo(1)	195.5(5)	197.6(5)
C(10)–Mo(1)	203.7(5)	203.1(5)
C(2)–C(1)	156.6(7)	155.5(6)
C(6)–C(1)	150.8(6)	151.6(6)
C(3)–C(2)	152.5(7)	152.9(7)
C(4)–C(3)	152.8(7)	153.2(7)
C(5)–C(4)	152.2(7)	151.2(6)
C(6)–C(5)	150.4(7)	150.1(7)
N(1)–C(6)	128.0(5)	127.7(5)
N(2)–N(1)	145.1(5)	146.0(5)
N(2)–Mo(1)–P(1)	85.0(2)	85.0(2)
C(7)–Mo(1)–P(1)	88.9(2)	87.9(2)
C(7)–Mo(1)–N(2)	93.8(2)	93.8(2)
C(8)–Mo(1)–P(1)	175.4(1)	176.5(1)
C(8)–Mo(1)–N(2)	96.8(2)	93.4(2)
C(8)–Mo(1)–C(7)	86.8(2)	85.5(2)
C(9)–Mo(1)–P(1)	90.1(2)	92.5(2)
C(9)–Mo(1)–N(2)	175.1(1)	177.1(1)
C(9)–Mo(1)–C(7)	86.2(2)	90.1(2)
C(9)–Mo(1)–C(8)	88.2(2)	89.1(2)
C(10)–Mo(1)–P(1)	96.0(2)	97.6(2)
C(10)–Mo(1)–N(2)	89.6(2)	91.7(2)
C(10)–Mo(1)–C(7)	174.3(1)	172.5(1)
C(10)–Mo(1)–C(8)	88.3(2)	89.2(2)
C(10)–Mo(1)–C(9)	90.7(2)	84.6(2)
C(1)–P(1)–Mo(1)	110.3(2)	109.8(2)
C(2)–C(1)–P(1)	117.7(3)	117.4(3)
C(6)–C(1)–P(1)	108.1(3)	107.4(3)
N(1)–C(6)–C(1)	129.9(4)	128.8(4)
N(1)–C(6)–C(5)	112.3(4)	113.8(4)
N(2)–N(1)–C(6)	122.2(4)	122.7(4)
N(1)–N(2)–Mo(1)	109.9(3)	109.7(3)
C(2)–C(3)–C(31)–C(34)	63.7(4)	58.5(4)
C(4)–C(3)–C(31)–C(34)	60.5(4)	54.7(4)
Mo(1)–P(1)–C(11)–C(12)	73.4(2)	76.7(2)
C(1)–P(1)–C(11)–C(12)	167.4(2)	164.8(2)
Mo(1)–P(1)–C(17)–C(18)	22.6(2)	35.7(2)
C(1)–P(1)–C(17)–C(18)	104.1(2)	89.5(2)

conversion. We therefore thought it a possibility that when we treated our phosphino dimethylhydrazone **2** with palladium(II) dichloride, which is much more labile and electron withdrawing than a molybdenum(0) tetracarbonyl moiety, similar isomerisation(s) might occur.

Treatment of **2** with Na₂PdCl₄ or with [PdCl₂(NCPH)₂] [12] gave the chelate complex **4**, in 64% yield and subsequently shown by X-ray crystallography (below) to have the molecular structure **4**. The complex was characterised by elemental analysis and by NMR spectroscopy, particularly in the proton NMR spectrum, both methyls of the NMe₂ group were equivalent suggesting that the NMe₂ nitrogen was not coordinated, instead a five-membered ring chelate had

formed involving C=N nitrogen coordination due to *Z*- to *E*-isomerisation. We have previously observed C=N isomerisation (*Z* to *E*) for some molybdenum(0) (thermally) [7] and palladium(II) (acid catalysed) [8] complexes of *exo*-3-diphenylphosphino-(1*R*)-(+)–camphor *N,N*-dimethylhydrazone.

The palladium(II) complex **4** was crystallised from dichloromethane/butanone as monoclinic yellow crystals in the space group *P*2₁/*n*. The molecular structure of **4** is shown in Fig. 2 with atom coordinates in Table 4, and selected bond lengths and angles in Table 5. The noteworthy features of the structure of **4** are (i) the chelate ring is five-membered, i.e. C=N nitrogen is bonded to palladium, (ii) the PPh₂ group is equatorial due to the isomerisation at C²; we have observed similar PPh₂ migration at C³ (i.e. **5** [8] → **6** [8]) when a CDCl₃ solution of **5** was left at room temperature (20 °C) for 24 h, (iii) the Bu^t is equatorial, (iv) Pd–Cl (*trans* to P) is considerably longer than Pd–Cl (*trans* to N) as expected [8,13], and (v) the geometry around palladium is very close to square planar.

We suggest that the structure and stereochemistry of the palladium(II) complex **4** is the thermodynamically preferred one out of all the isomers, i.e. with *Z*- or *E*-C=N, or with equatorial or axial Bu^t and PPh₂ groups.

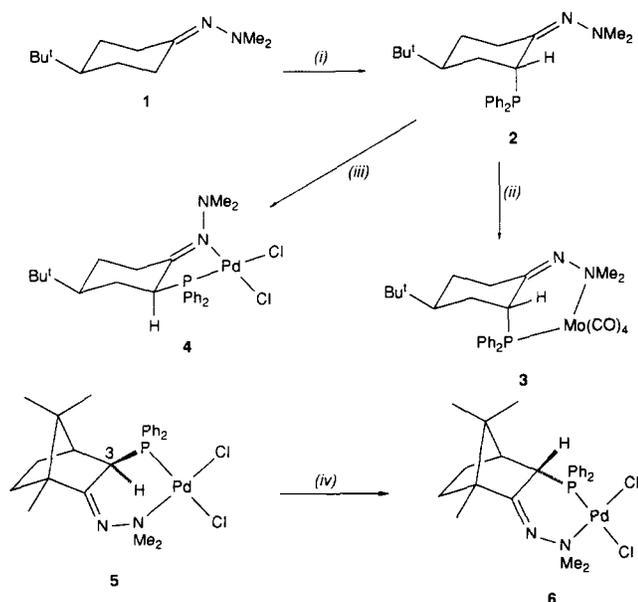
A summary of the reactions is given in Scheme 1.

Table 4
Fractional atom coordinates (× 10⁴) for compound **4** with e.s.d.s in parentheses

Atom	x	y	z
Pd	3349.1(2)	5627.8(2)	3507.8(1)
Cl(1)	2094(1)	4224(1)	3266(1)
Cl(2)	5042(1)	4592(1)	3449(1)
P(1)	1730(1)	6558(1)	3475(1)
C(11)	380(2)	6426(2)	2680(1)
C(12)	197(2)	7049(2)	2029(1)
C(13)	–860(2)	6942(2)	1424(1)
C(14)	–1733(2)	6211(2)	1470(1)
C(15)	–1549(2)	5589(2)	2121(1)
C(16)	–493(2)	5696(2)	2726(1)
C(21)	1233(2)	6460(2)	4352(1)
C(22)	2076(2)	6116(2)	5020(1)
C(23)	1741(2)	6060(2)	5719(1)
C(24)	564(2)	6348(2)	5751(1)
C(25)	–279(2)	6691(2)	5084(1)
C(26)	56(2)	6747(2)	4385(1)
C(1)	2309(3)	7855(2)	3419(2)
C(2)	1657(3)	8672(2)	3772(2)
C(3)	2222(3)	9712(2)	3739(2)
C(4)	3582(3)	9647(3)	4190(2)
C(5)	4288(3)	8866(2)	3868(2)
C(6)	3682(3)	7849(2)	3732(2)
C(31)	1526(3)	10598(2)	3995(2)
C(32)	155(4)	10532(3)	3600(3)
C(33)	1668(5)	10614(3)	4870(2)
C(34)	1983(5)	11592(3)	3735(3)
N(1)	4254(2)	6996(2)	3816(2)
N(2)	5552(2)	7087(2)	4126(2)
C(61)	5971(4)	6419(3)	4795(2)
C(62)	6197(4)	6998(4)	3517(3)

Table 5
Selected bond lengths (pm) and angles (°) for compound **4** with e.s.d.s in parentheses

Cl(1)–Pd	230.5(3)	Cl(2)–Pd	237.2(3)
P(1)–Pd	218.8(3)	N(1)–Pd	207.8(5)
C(1)–P(1)	184.5(5)	C(2)–C(1)	153.0(6)
C(6)–C(1)	150.4(6)	C(3)–C(2)	152.2(6)
C(4)–C(3)	154.0(7)	C(31)–C(3)	154.2(6)
C(5)–C(4)	150.5(7)	C(6)–C(5)	149.7(5)
N(1)–C(6)	128.9(5)	N(2)–N(1)	143.1(5)
C(61)–N(2)	146.2(6)	C(62)–N(2)	145.9(6)
Cl(2)–Pd–Cl(1)	89.4(1)	P(1)–Pd–Cl(1)	88.8(1)
P(1)–Pd–Cl(2)	175.9(1)	N(1)–Pd–Cl(1)	170.0(1)
N(1)–Pd–Cl(2)	99.6(2)	N(1)–Pd–P(1)	82.5(2)
C(1)–P(1)–Pd	102.6(2)	C(2)–C(1)–P(1)	114.7(3)
C(6)–C(1)–P(1)	108.7(3)	C(6)–C(1)–C(2)	114.0(3)
C(3)–C(2)–C(1)	111.7(4)	C(4)–C(3)–C(2)	107.5(4)
C(5)–C(4)–C(3)	113.0(4)	C(6)–C(5)–C(4)	114.4(4)
C(5)–C(6)–C(1)	116.1(4)	N(1)–C(6)–C(1)	118.9(4)
N(1)–C(6)–C(5)	124.8(4)	C(6)–N(1)–Pd	122.2(3)
N(2)–N(1)–Pd	124.0(3)	N(2)–N(1)–C(6)	113.8(4)
C(61)–N(2)–N(1)	110.4(4)	C(62)–N(2)–N(1)	111.1(4)
C(62)–N(2)–C(61)	116.2(4)		



Scheme 1. (i) LiBu^n , PPh_2Cl ; (ii) $[\text{Mo}(\text{CO})_4(\text{nbd})]$; (iii) Na_2PdCl_4 ; (iv) PdCl_2 , 20°C , 24 h.

3. Experimental

The general methods and instruments were the same as in other recent publications from this laboratory [12].

3.1. $Z\text{-PPh}_2\text{C}_{10}\text{H}_{17}=\text{NNMe}_2$ (**2**)

A solution of LiBu^n in hexane (10.0 cm^3 , 1.55M , 15.2 mmol) was added to a stirred solution of 4-tert-butyl-cyclohexanone N,N -dimethylhydrazone **1** (3.0 g , 15.2 mmol) in dry THF (30 cm^3) at -15°C . After 3 h, the solution was

cooled to -70°C and a solution of chloro-(diphenyl)phosphine (3.5 g , 15.2 mmol) in THF (15 cm^3) added dropwise, after which the mixture was allowed to warm to room temperature. The solution was then concentrated to a low volume under reduced pressure, ethanol (10 cm^3) was added and the resultant solution was cooled to -30°C . The required phosphine **2** was obtained as white needles (3.1 g , 53%). *Anal.* Calc. for $\text{C}_{24}\text{H}_{33}\text{N}_2\text{P}$: C, 75.75; H, 8.75; N, 7.35. Found: C, 75.6; H, 8.75; N, 7.15%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta\text{P} = -5.4\text{ ppm}$. ^1H NMR (CDCl_3): $\delta\text{H} = 0.77$ (9H, s, Bu^t), 2.23 (6H, s, NMe_2).

3.2. $[\text{Mo}(\text{CO})_4(Z\text{-PPh}_2\text{C}_{10}\text{H}_{17}=\text{NNMe}_2)]$ (**3**)

A solution containing the phosphine **2** (1.10 g , 2.89 mmol) and $[\text{Mo}(\text{CO})_4(\text{nbd})]^{11}$ (0.8 g , 2.66 mmol) in benzene (15 cm^3) was put aside at 20°C for 15 h. The solution was then filtered and concentrated to a low volume under reduced pressure. Addition of MeOH to the residue gave the tetracarbonyl-molybdenum(0) complex **3** as yellow microcrystals (0.83 g , 52%). *Anal.* Calc. for $\text{C}_{28}\text{H}_{33}\text{MoN}_2\text{O}_4\text{P}$: C, 57.15; H, 5.65; N, 4.75. Found: C, 57.35; H, 5.6; N, 4.75%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta\text{P} = 70.8\text{ ppm}$. ^1H NMR (CDCl_3): $\delta\text{H} = 0.68$ (9H, s, Bu^t), 2.90 (3H, s, NMe_2), 3.34 (3H, s, NMe_2). IR (CH_2Cl_2): $\nu(\text{C}=\text{O})$ 2020, 1910, 1860 cm^{-1} .

3.3. $[\text{PdCl}_2(E\text{-PPh}_2\text{C}_{10}\text{H}_{17}=\text{NNMe}_2)]$ (**4**)

A warm solution of **2** (0.30 g , 0.8 mmol) in ethanol (10 cm^3) was added to a solution of $\text{Na}_2\text{PdCl}_4 \cdot n\text{H}_2\text{O}$ (0.24 g , 0.75 mmol) in ethanol (15 cm^3), the resultant solution was then heated to $\sim 75^\circ\text{C}$ for 3 min. This gave a yellow precipitate **4** which was filtered off, washed with EtOH, water and again with EtOH, and dried. Yield 0.28 g , 64% . *Anal.* Calc. for $\text{C}_{24}\text{H}_{33}\text{Cl}_2\text{N}_2\text{PPd}$: C, 51.65; H, 5.95; Cl, 12.7; N, 5.0. Found: C, 51.7; H, 5.95; Cl, 13.0; N, 5.05%. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta\text{P} = 62.3\text{ ppm}$. ^1H NMR (CDCl_3): $\delta\text{H} = 0.75$ (9H, s, Bu^t), 3.01 (6H, s, NMe_2).

3.4. X-ray diffraction analysis

All diffraction measurements for **3** were made at 200 K on a Stoe STADI4 diffractometer operating in the ω - θ scan mode whilst those for **4** were made on a Nicolet P3/F diffractometer at ambient temperature operating in the ω - 2θ scan mode. In both cases graphite monochromated Mo $K\alpha$ X-radiation ($\lambda = 71.069\text{ pm}$) was used. Crystal data are listed in Table 1 together with details of data collection and structure refinement. Both data sets were corrected for absorption. **3** using azimuthal ψ -scans and **4** using an empirical post-structure solution method [14].

Both structures were solved by standard heavy-atom techniques and were refined by full-matrix least-squares using SHELX-76 [15]. The solution for **3** gave two independent molecules in the asymmetric unit which differed principally by a relative rotation about the P(1)–C(17) bond vector of

~ 15° of one of the phenyl groups (see Table 3 for comparative torsion angles). For both complexes all non-hydrogen atoms were refined with anisotropic thermal parameters. All phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C = 139.5 Å) and in both cases the hydrogen atoms were included in calculated positions (C–H = 96 Å) and were refined with an overall isotropic thermal parameter. ORTEP [16] diagrams of **3** and **4** are shown in Figs. 1 and 2, respectively.

4. Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises, further details of data collection and structure refinement, non-hydrogen atomic coordinates. H atom coordinates and isotropic and anisotropic thermal parameters.

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