DALTON

Reactivity of $[M(CO)_4(nbd)]$ (M = Cr or Mo; nbd = norbornadiene) toward $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ and $C_6H_4\{C[N(SiMe_3)_2](NPPh_2)\}_2$-1,4

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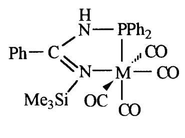
The interaction of $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ with 1 equivalent of $[M(CO)_4(nbd)]$ (M = Cr or Mo, nbd = norbornadiene) in diethyl ether gave *cis*-$[M(CO)_4\{(Me_3SiN)C(Ph)(NHPPh_2)\}]$ (M = Cr **1** or Mo **2**) in good yield. The interaction of $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 with 2 equivalents of $[M(CO)_4(nbd)]$ (M = Cr or Mo) in tetrahydrofuran gave the symmetric dimer *cis*-$[\{M(CO)_4\}\{(Ph_2PNH)(Me_3SiN)CC_6H_4C(NSiMe_3)(NHPPh_2)\}]$ (M = Cr **3** or Mo **4**) in moderate yield. However, in diethyl ether, this reaction (M = Mo) gave the unsymmetric *cis*-$[(OC)_4Mo\{(Ph_2PNH)(Me_3SiN)CC_6H_4C[N(SiMe_3)_2](NPPh_2)\}Mo(CO)_5]$ **5** in moderate yield. Compounds **1**–**5** have been fully characterized by analytical and spectroscopic methods and the structures of **3** and **5** have been established by X-ray crystallography. A 1,3-silyl shift mechanism has been proposed for the formation of the products. The NH proton of the bidentate iminophosphine ligand undergoes facile deuterium exchange with D_2O at ambient temperature.

Phosphorus–nitrogen compounds are π-electron-rich with unusual properties.[1] This has led to a considerable interest in their syntheses[2] and their co-ordination chemistry toward transition metals.[3] The co-ordination chemistry of $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$[3,4] and $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$-1,4[5] have been briefly examined recently. Herein we report the results of the interaction of $[M(CO)_4(nbd)]$ (M = Cr or Mo; nbd = 2-norbornadiene = bicyclo[2.2.1]hepta-2,5-diene) with $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ and $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$-1,4.

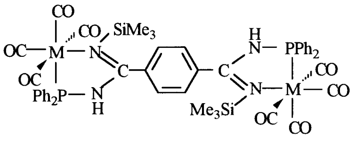
Results and Discussion

Preparation of *cis*-$[M(CO)_4\{(Me_3SiN)C(Ph)(NHPPh_2)\}]$

M = Cr 1. When $[Cr(CO)_4(nbd)]$ was allowed to react with 1 equivalent of $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ in diethyl ether for 2 d at room temperature, subsequent work-up gave yellow crystals of stoichiometry $Cr(CO_4)(C_{22}H_{25}N_2SiP)$ **1** in good yield (75%) after recrystallization from a diethyl ether–hexane mixture. In the carbonyl region, compound **1** exhibits four absorptions at 2002s, 1900vs, 1880vs and 1822s cm^{-1} in the IR spectrum (KBr), and three doublets at δ 220.0 (J_{P-CO} = 14.7), 227.7 (2.5) and 228.8 (13.4 Hz) in the $^{13}C-\{^1H\}$ NMR spectrum for the four terminal carbonyls. The IR and $^{13}C-\{^1H\}$ NMR absorption patterns are indicative of a *cis*-$Cr(CO)_4L(L')$ complex. The IR spectrum also contains an absorption at 3352s cm^{-1} indicating the presence of a NH group. The $^{31}P-\{^1H\}$ NMR spectrum in C_6D_6 exhibited a singlet at δ 112.0 for the PPh_2 group. The positive increase in its chemical shift relative to the free ligand (from δ 37.4 to 112.0) is characteristic of chelate-ring formation.[6] In addition to the phenyl resonances, the ^1H NMR spectrum also contains a doublet and a singlet of relative intensity 1:9 at δ 5.90 (J_{P-NH} = 6.3 Hz) and 0.17 for the NH and $SiMe_3$ protons, respectively, and the $^{13}C-\{^1H\}$ NMR spectrum exhibits a doublet and a singlet at δ 169.7 and 1.4 for the C=N carbon and the $SiMe_3$ carbons, respectively. Based on the above spectroscopic data, structure **A** can be assigned to **1** and was confirmed by an X-ray diffraction study.[7]



A



B

M = Mo 2. When $[Mo(CO)_4(nbd)]$ was allowed to react with 1 equivalent of $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ in diethyl ether for 2 d at room temperature, subsequent work-up gave yellow crystals of stoichiometry $Mo(CO)_4(C_{22}H_{25}N_2SiP)\cdot H_2O$, **2**·$H_2O$, in good yield (70%) after recrystallization from a diethyl ether–hexane mixture. Compound **2** exhibited similar IR and $^{13}C-\{^1H\}$ NMR absorption patterns to those of **1**. In the carbonyl region there are four absorptions at 2012s, 1908vs, 1876vs and 1834s cm^{-1} in the IR spectrum (KBr); and three doublets at δ 208.7 (J_{P-CO} = 9.8), 217.0 (36.6) and 220.7 (8.5 Hz) in the $^{13}C-\{^1H\}$ NMR spectrum for the four terminal carbonyls. The IR spectrum also contains an absorption at 3356s cm^{-1} indicating the presence of a NH group. The $^{31}P-\{^1H\}$ NMR spectrum in C_6D_6 exhibited a singlet at δ 89.6 for the PPh_2 group. Other than the phenyl resonances, the ^1H NMR spectrum shows a doublet and a singlet of relative intensity 1:9 at δ 5.79 (J_{P-NH} = 4.6 Hz) and 0.15 for the NH and $SiMe_3$ protons, respectively, and the $^{13}C-\{^1H\}$ NMR spectrum a doublet and a singlet at δ 169.9 (J_{P-NC} = 18.2 Hz) and 1.6 for the C=N carbon and the $SiMe_3$ carbons, respectively. The low-resolution mass spectrum (electron-impact mode) exhibited the parent peak (*M* for ^{98}Mo) at *m*/*z* 586. The spectroscopic data for **2** are very similar to those of **1** and thus structure **A** can also be assigned to **2**.

Preparation of *cis*-$[\{M(CO)_4\}\{(Ph_2PNH)(Me_3SiN)CC_6H_4C(NSiMe_3)(NHPPh_2)\}]$

M = Cr 3. When $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 was allowed to react with 2 equivalents of $[Cr(CO)_4(nbd)]$ in tetrahydrofuran for 16 h at room temperature, subsequent work-up gave yellow crystals of stoichiometry $[Cr(CO)_4]_2(C_{38}H_{44}N_4Si_2P_2)\cdot 2CH_2Cl_2$, **3**·$2CH_2Cl_2$, in good yield (50%) after recrystal-

Table 1 Selected bond lengths (Å) and angles (°) for compound **3**

Cr(1)–P(1)	2.291(2)	Cr(1)–N(1)	2.214(5)
Cr(1)–C(1)	1.821(7)	Cr(1)–C(2)	1.889(8)
Cr(1)–C(3)	1.874(8)	Cr(1)–C(4)	1.844(8)
C(1)–O(1)	1.163(9)	C(2)–O(2)	1.143(10)
C(3)–O(3)	1.154(10)	C(4)–O(4)	1.155(9)
P(1)–N(2)	1.720(5)	N(1)–C(20)	1.281(8)
N(2)–C(20)	1.373(7)	P(1)–C(5)	1.817(7)
P(1)–C(11)	1.809(6)		
C(1)–Cr(1)–C(2)	93.9(3)	C(1)–Cr(1)–C(3)	88.4(3)
C(1)–Cr(1)–C(4)	88.1(3)	C(1)–Cr(1)–N(1)	169.7(3)
C(1)–Cr(1)–P(1)	90.0(2)	C(2)–Cr(1)–C(3)	175.8(3)
C(2)–Cr(1)–C(4)	87.1(3)	C(2)–Cr(1)–N(1)	86.7(3)
C(2)–Cr(1)–P(1)	93.2(2)	C(3)–Cr(1)–C(4)	89.5(3)
C(3)–Cr(1)–N(1)	91.7(3)	C(3)–Cr(1)–P(1)	90.3(2)
C(4)–Cr(1)–N(1)	102.2(3)	C(4)–Cr(1)–P(1)	178.1(2)
N(1)–Cr(1)–P(1)	79.7(1)	C(20)–N(1)–Si(1)	126.9(4)
N(1)–C(20)–N(2)	122.0(5)	P(1)–N(2)–C(20)	117.7(4)

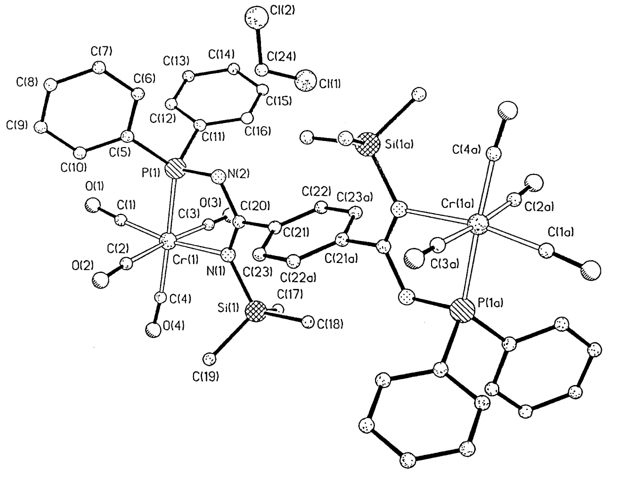


Fig. 1 Perspective view of the molecular structure of compound **3**

lization from a dichloromethane–diethyl ether mixture. In the carbonyl region compound **3** exhibits four absorptions at 2012s, 1898vs, 1884vs (sh) and 1840vs cm^{-1} in the IR spectrum (KBr), and a doublet, a broad singlet and a doublet at δ 219.9 ($J_{\mathrm{P-CO}} = 14.6$), 227.3 and 228.5 ($J_{\mathrm{P-CO}} = 13.4$ Hz), respectively, in the ^{13}C-{^{1}H} NMR spectrum for the terminal carbonyl groups of the two $Cr(CO)_4$ moieties. The IR and the ^{13}C-{^{1}H} NMR absorption patterns of **3** are similar to those of **1**. This suggests that the two $Cr(CO)_4$ moieties adopt a *cis*-$Cr(CO)_4L(L')$ configuration. The IR spectrum also exhibited an absorption at 3348w cm^{-1} indicating the presence of a NH group. The ^{31}P-{^{1}H} NMR spectrum in C_6D_6 contains only a broad singlet at δ 112.3 for the PPh_2 groups indicating the formation of two equivalent chelating rings. In addition to the phenyl resonances, the ^{1}H NMR spectrum has two broad singlets of relative intensity 2 : 18 at δ 6.02 and 0.24 for the NH and $SiMe_3$ protons, respectively, and the ^{13}C-{^{1}H} NMR spectrum a doublet and a broad singlet at δ 167.9 ($J_{\mathrm{P-NC}} = 26.7$ Hz) and 4.3 for the C=N carbons and the $SiMe_3$ carbons, respectively. The low-resolution mass spectrum (FAB, positive-ion mode) exhibited the $M + 1$ peak at m/z 1003. Based on the above spectroscopic data, a symmetric dimer with structure **B** can be assigned to **3**.

The structure of compound **3** was confirmed by an X-ray diffraction study. Suitable crystals were grown from a dichloromethane–diethyl ether mixture as a dichloromethane solvate, **3**·$2CH_2Cl_2$. A perspective drawing of **3** is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The structure is consistent with the spectroscopic data. The dimeric species is centrosymmetric and the ligand acts in a bridging bidentate mode with the imino group N(1) and the phosphino group P(1) co-ordinated to each of the two $Cr(CO)_4$ moieties forming two five-membered rings. The geometry of the chromium centres is approximately octahedral with the Cr–C distances of the two $Cr(CO)_4$ moieties showing the expected pattern for a *cis*-$Cr(CO)_4L_2$ complex where L is a poorer π acid than CO. The Cr–C distances of the two mutually *trans*-carbonyls are 1.889(8) and 1.874(8) Å for Cr(1)–C(2) and Cr(1)–C(3), respectively, slightly longer than the 1.821(7) and 1.844(8) Å for the carbonyls *trans* to the imino N(1) and phosphino P(1) groups, respectively.

Within the tetradentate bridging iminophosphine ligand the P(1)–N(2) bond length of 1.720(5) Å is in the normal range for a phosphorus–nitrogen single bond. The C(20)–N(1) and C(20)–N(2) distances of 1.281(8) and 1.373(7) Å, respectively, are intermediate between those expected for single (1.46 Å) and double (1.26 Å) bonds indicating some delocalization about the N–C–N framework. The delocalization is also reflected in the P(1)–N(2)–C(20) bond angle of 117.7(4)° which deviates significantly from that expected for a tetrahedral sp^3 nitrogen atom and is closer than for a sp^2 nitrogen atom. Similar observations have been made for related palladium,[5] chromium[7] and rhodium complexes.[3] The $SiMe_3$ groups of the imino groups and the CH_2Cl_2 solvent molecules are disordered.

M = Mo 4. When $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}$-1,4 was allowed to react with 2 equivalents of $[Mo(CO)_4(nbd)]$ in tetrahydrofuran for 16 h at room temperature, subsequent work-up gave yellow crystals of stoichiometry $[Mo(CO)_4]_2(C_{38}H_{44}N_4Si_2P_2)$ **4** in good yield (55%) after recrystallization from a dichloromethane–diethyl ether mixture. Compound **4** exhibited similar absorption patterns to those of **3**. In the carbonyl region there are five absorptions at 2023s, 1920vs, 1877vs, 1843s and 1827vs cm^{-1} in the IR spectrum (KBr) and three doublets at δ 207.6 ($J_{\mathrm{P-CO}} = 9.8$), 216.2 (36.6) and 220.5 (8.6 Hz) in the ^{13}C-{^{1}H} NMR spectrum for the terminal carbonyl groups of the two $Mo(CO)_4$ moieties. The IR spectrum also contains an absorption at 3361m cm^{-1} indicating the presence of a NH group. The ^{31}P-{^{1}H} NMR spectrum in $CDCl_3$ exhibited only a singlet at δ 89.5 indicating the presence of two equivalent PPh_2 groups. In addition to the phenyl resonances, the ^{1}H NMR spectrum in $CDCl_3$ reveals two broad singlets of relative intensity 2 : 18 at δ 6.15 and 0.13 for the NH and $SiMe_3$ protons, respectively, and the ^{13}C-{^{1}H} NMR spectrum a doublet and a broad singlet at δ 167.5 ($J_{\mathrm{P-NC}} = 18.3$ Hz) and 4.1 for the C=N carbons and the $SiMe_3$ carbons, respectively. The low-resolution mass spectrum (FAB, positive ion mode) exhibited the parent peak ($M + 1$) at m/z 1095. Thus, based on the above spectroscopic data, structure **B** can also be assigned to **4**.

Preparation of *cis*-$[(OC)_4Mo\{(Ph_2PNH)(Me_3SiN)CC_6H_4C[N(SiMe_3)_2](NPPh_2)\}Mo(CO)_5]$ 5

When $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 and $[Mo(CO)_4(nbd)]$ were allowed to react in a 1 : 2 molar ratio in diethyl ether for 16 h at room temperature, subsequent work-up gave yellow crystals of stoichiometry $Mo_2(CO)_9(C_{41}H_{52}N_4Si_3P_2)\cdot H_2O$, **5**·$H_2O$, in good yield (60%) after recrystallization from a diethyl ether–hexane mixture. Crystals of 5·$0.5C_6H_{14}$ suitable for X-ray diffraction study were grown from a solution of hexane and the structure was established. A perspective drawing of **5** is shown in Fig. 2. Selected bond lengths and angles given in Table 2. The structure shows that one of the two $=NPPh_2$ groups of the symmetric ligand $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$-1,4 has been transformed into a $HNPPh_2$ group; and the resultant unsymmetric ligand, $(Ph_2PNH)(Me_3SiN)CC_6H_4C[N(SiMe_3)_2](NPPh_2)$, acts as a tridentate bridge having N(2) and P(1) of the $NHPPh_2$ group co-ordinated to the $Mo(CO)_4$ moiety forming a five-membered ring, and P(2) of the $=NPPh_2$ group co-ordinated to the $Mo(CO)_5$ moiety. The geometry of the two molybdenum centres is approximately octahedral with

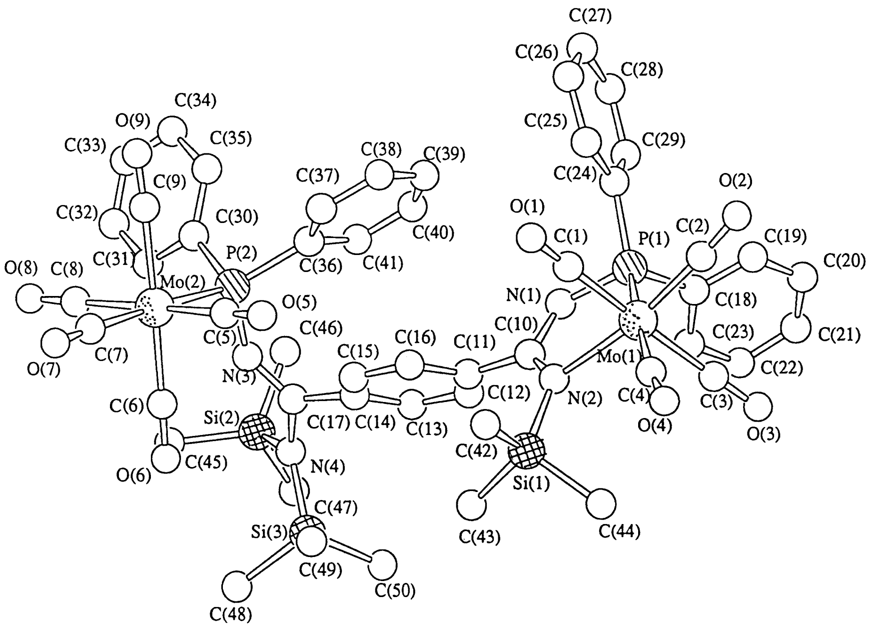


Fig. 2 Perspective view of the molecular structure of compound **5**

Table 2 Selected bond lengths (Å) and angles (°) for compound **5**

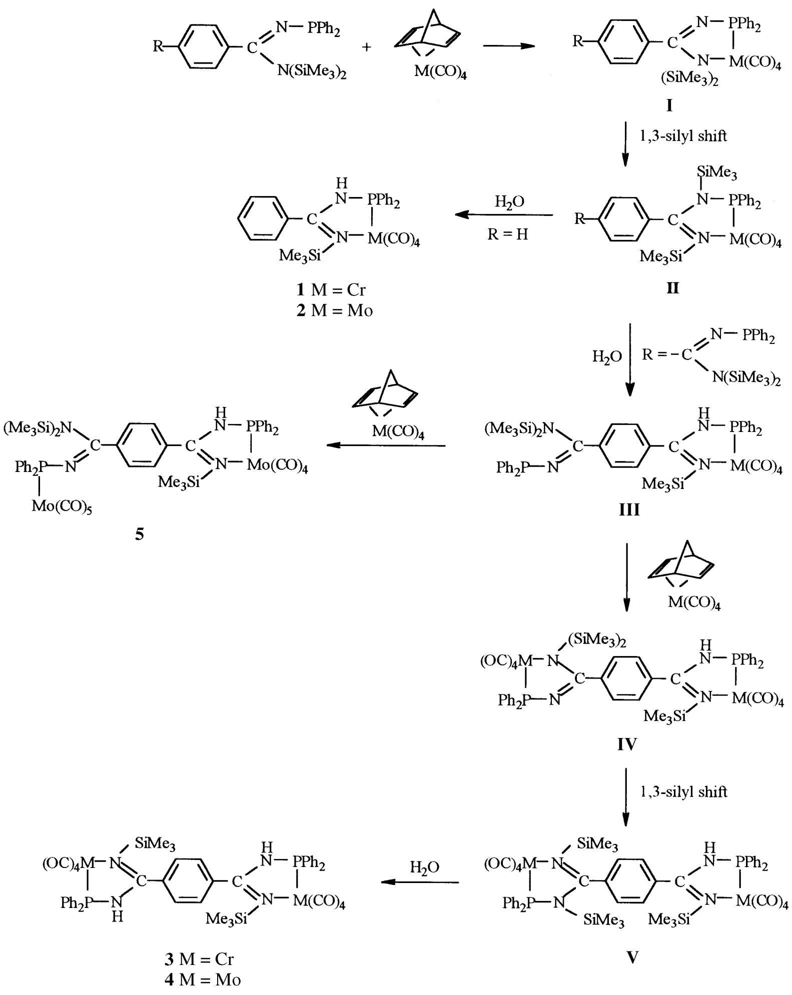
Mo(1)–P(1)	2.469(3)	Mo(1)–N(2)	2.345(8)
Mo(1)–C(1)	2.03(1)	Mo(1)–C(2)	1.94(1)
Mo(1)–C(3)	2.02(1)	Mo(1)–C(4)	1.95(1)
Mo(2)–P(2)	2.555(4)	Mo(2)–C(5)	2.04(1)
Mo(2)–C(6)	2.01(2)	Mo(2)–C(7)	2.00(1)
Mo(2)–C(8)	2.03(2)	Mo(2)–C(9)	2.07(2)
C(1)–O(1)	1.13(1)	C(2)–O(2)	1.16(1)
C(3)–O(3)	1.15(1)	C(4)–O(4)	1.17(1)
C(5)–O(5)	1.14(1)	C(6)–O(6)	1.15(2)
C(7)–O(7)	1.13(1)	C(8)–O(8)	1.12(2)
C(9)–O(9)	1.11(2)	P(1)–N(1)	1.727(8)
P(2)–N(3)	1.677(10)	N(1)–C(10)	1.38(1)
N(2)–C(10)	1.32(1)	N(3)–C(17)	1.27(1)
N(4)–C(17)	1.40(1)	P(1)–C(18)	1.84(1)
P(1)–C(24)	1.81(1)	P(2)–C(30)	1.85(1)
P(2)–C(36)	1.84(1)		
C(1)–Mo(1)–C(2)	87.7(6)	C(1)–Mo(1)–C(3)	172.3(5)
C(1)–Mo(1)–C(4)	89.8(5)	C(1)–Mo(1)–N(2)	87.4(4)
C(1)–Mo(1)–P(1)	97.7(4)	C(2)–Mo(1)–C(3)	89.1(5)
C(2)–Mo(1)–C(4)	89.5(5)	C(2)–Mo(1)–N(2)	167.8(4)
C(2)–Mo(1)–P(1)	93.2(4)	C(3)–Mo(1)–C(4)	83.2(5)
C(3)–Mo(1)–N(2)	97.1(4)	C(3)–Mo(1)–P(1)	89.4(4)
C(4)–Mo(1)–N(2)	101.6(4)	C(4)–Mo(1)–P(1)	172.1(4)
N(2)–Mo(1)–P(1)	76.4(2)	C(5)–Mo(2)–C(6)	92.3(7)
C(5)–Mo(2)–C(7)	87.2(6)	C(5)–Mo(2)–C(8)	172.3(6)
C(5)–Mo(2)–C(9)	89.8(6)	C(5)–Mo(2)–P(2)	95.5(4)
C(6)–Mo(2)–C(7)	89.3(6)	C(6)–Mo(2)–C(8)	89.4(7)
C(6)–Mo(2)–C(9)	177.9(7)	C(6)–Mo(2)–P(2)	87.5(4)
C(7)–Mo(2)–C(8)	85.3(6)	C(7)–Mo(2)–C(9)	90.7(7)
C(7)–Mo(2)–P(2)	175.9(5)	C(8)–Mo(2)–C(9)	88.6(7)
C(8)–Mo(2)–P(2)	92.1(4)	C(9)–Mo(2)–P(2)	92.4(5)
P(1)–N(1)–C(10)	119.8(7)	Mo(1)–N(2)–C(10)	117.4(7)
Mo(1)–N(2)–Si(1)	116.4(4)	N(1)–C(10)–N(2)	122.8(10)
C(10)–N(2)–Si(1)	126.2(8)	P(2)–N(3)–C(17)	135.4(9)
N(3)–C(17)–N(4)	120(1)	Si(2)–N(4)–C(17)	114.8(8)
Si(3)–N(4)–C(17)	121.9(8)	Si(2)–N(4)–Si(3)	122.4(6)

the Mo–C distances of the $Mo(CO)_4$ and $Mo(CO)_5$ moieties showing the expected pattern of a *cis*-$Mo(CO)_4L_2$ and a $Mo(CO)_5L$ complex, respectively, with L being a poorer π acid than CO. For the $Mo(CO)_4$ moiety the Mo–C distances of the two mutually *trans*-carbonyls are 2.03(1) and 2.02(1) Å for Mo(1)–C(1) and Mo(1)–C(3), respectively, slightly longer than the 1.94(1) and 1.95(1) Å for the carbonyls *trans* to the imino N(2) and phosphino P(1) groups, respectively. For the $Mo(CO)_5$ moiety the Mo(2)–C(7) distance of 2.00(1) Å for the carbonyl *trans* to the phosphino P(2) group is slightly shorter than the Mo–C distances of the four mutually *trans*-carbonyls which range from 2.01(2) to 2.07(2) Å.

Delocalization about the N–C–N framework of the $HNPPh_2$ group is observed and reflected by the C(10)–N(1) and C(10)–N(2) distances of 1.38(1) and 1.32(1) Å, respectively, and the P(1)–N(1)–C(10) bond angles of 119.8(7)° which is typical of a sp^2 nitrogen atom. For the unidentate $=NPPh_2$ group the geometry of N(4) of the $N(SiMe_3)_2$ group is approximately trigonal planar with bond angles ranging from 114.8(8), 121.9(8) and 122.4(6)° for Si(2)–N(4)–C(17), Si(3)–N(4)–C(17) and Si(2)–N(4)–Si(3), respectively. This suggests that the lone pair on N(4) has primarily p character and the right symmetry to interact with the neighbouring empty π* orbital. This p–π* interaction is reflected in the C(17)–N(4) distance of 1.40(1) Å.

The spectroscopic data for compound **5** are consistent with its solid-state structure. The IR spectrum (KBr) in the carbonyl region exhibited absorptions at 2068m, 2016m, 1940s (br), 1908vs, 1878s and 1830s cm^{-1}. The IR spectrum also showed ν_{N-H} and $\nu_{C=N}$ at 3368m and 1578s cm^{-1}, respectively. The assignment of the NMR data is based on the chemical shifts of **2**, *cis*-$[Mo(CO)_4\{(Me_3SiN)C(Ph)(NHPPh_2)\}]$. The ^{31}P-$\{^1H\}$ NMR spectrum in C_6D_6 exhibited two singlets at δ 72.5 and 90.4 for the $=NPPh_2$ and the $NHPPh_2$ group, respectively. In the carbonyl region the ^{13}C-$\{^1H\}$ NMR spectrum revealed five doublets at δ 2106.5 ($J_{P-CO} = 8.5$), 208.7 (9.8), 210.8 (23.1), 216.9 (36.5) and 220.6 (8.5 Hz) for the terminal carbonyls. The resonances at δ 206.5 and 210.8 can be assigned to the four carbonyls *cis* to and the carbonyl *trans* to the PPh_2 group of the $Mo(CO)_5$ moiety, respectively. Those at δ 208.7, 216.9 and 220.6 can be assigned to the two mutually *trans* carbonyls, the carbonyl *trans* to the PPh_2 group, and that *trans* to the $N(SiMe_3)$ group of the $Mo(CO)_4$ moiety, respectively. In addition to the phenyl resonances, the ^{13}C-$\{^1H\}$ NMR spectrum also exhibited two doublets at δ 167.7 ($J_{P-NC} = 6.1$) and 168.7 (18.3 Hz) for the carbons of the N–C–N frameworks of the $=NPPh_2$ and the $NHPPh_2$ group, respectively, and two singlets at δ 1.4 and 4.2 for methyl carbons of the imino $N(SiMe_3)$ group and the amino $N(SiMe_3)_2$ group, respectively. In addition to the phenyl proton resonances the ^1H NMR spectrum contains a doublet ($J_{P-NH} = 4.9$ Hz) and two singlets of relative intensity 1 : 18 : 9 at δ 5.69, 0.22 and 0.15 for the NH, $N(SiMe_3)_2$ and $N(SiMe_3)$ protons, respectively.

A possible mechanism for the formation of compounds **1**–**5** is shown in Scheme 1. The compound $[M(CO)_4(nbd)]$ reacts



Scheme 1 Possible mechanism for the formation of compounds **1**–**5**

with the amidine to produce the intermediate **I**, which undergoes a rapid 1,3-silyl shift to give intermediate **II**. The latter is then hydrolysed to give **1** or **2** when R = H, or to produce **III** when R = $C(NPPh_2)[N(SiMe_3)_2]$ which reacts with $[M(CO)_4(nbd)]$ to give either the unsymmetric **5** or intermediate **IV**. The latter then undergoes a rapid 1,3-silyl shift to give **V** which is hydrolysed to give the symmetric dimer **3** or **4**. A similar mechanism has been proposed for related complexes.[5,7]

The iminophosphine ligand has two possible resonance structures, **C** and **D**, as shown. Structural data for compounds **1**,[7] **3** and **5** indicate significant delocalization about the N–C–N framework. The contribution of the ionic resonance form **D** is further supported by the fact that the imino proton of **1**–**5** undergoes facile deuterium exchange in D_2O at ambient temperature. The above data suggest that both resonance forms are important contributors to the iminophosphine ligand.

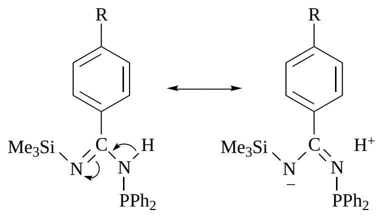
Experimental

Procedures

All operations were carried out in an atmosphere of dry nitrogen or *in vacuo*. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. The compounds $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$,[3] $C_6H_4\{C(NPPh_2)[N(SiMe_3)_2]\}_2$-1,4[3] and $[M(CO)_4(nbd)]_4$[8] (M = Cr or Mo) were prepared according to literature methods. Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. Infrared spectra (KBr pellets) were recorded either on a Hitachi 270-30 or on a Nicolet Nagna-IR 550 spectrometer, NMR spectra on a JEOL EX270 spectrometer. Chemical shifts of ^1H and ^{13}C-$\{^1H\}$ spectra were referenced to internal deuteriated solvents and then recalculated to $SiMe_4$ (δ 0.00), those of ^{31}P-$\{^1H\}$ spectra to external 85% H_3PO_4. Low-resolution mass spectra were obtained on a Finnigan MAT SSQ-710 spectrometer in electron-impact or FAB (positive-ion) mode.

Preparations

***cis*-$[Cr(CO)_4\{(Me_3SiN)C(Ph)(NHPPh_2)\}]$ 1**. To a cooled (0 °C) solution of $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ (0.42 g, 0.93 mmol) in diethyl ether (20 cm^3) was added a solution of $[Cr(CO)_4(nbd)]$ (0.24 g, 0.93 mmol) in hexane (20 cm^3) dropwise over 10 min. The resultant yellow solution was allowed to warm to room temperature slowly and stirred for 2 d. The solvents were removed *in vacuo* to give a yellow residue which was washed with hexane (3 × 10 cm^3), redissolved in diethyl ether and filtered. The filtrate was concentrated to *ca.* 5 cm^3 and hexane was added to the diethyl ether solution slowly until it just turned cloudy. The solution was then cooled to −20 °C to give yellow crystals which was filtered off and dried *in vacuo*. (yield: 0.38 g, 75%), m.p. 173–175 °C (decomp.) (Found: C, 57.9; H, 4.7; N, 5.1. Calc. for $C_{26}H_{25}CrN_2O_4PSi$: C, 57.8; H, 4.7; N, 5.2%). IR (cm^{-1}, in KBr): 3352s, 3056w, 2956w, 2002s, 1900vs, 1880vs, 1822s, 1606w, 1584s, 1484w, 1436m, 1408s, 1328w, 1252m, 1184w, 1156w, 1098m, 1024w, 998w, 932m, 824s, 760m, 696s, 682s, 644s, 560m and 492w. NMR (C_6D_6): ^{31}P-$\{^1H\}$, δ 112,0 (s); ^{13}C-$\{^1H\}$, carbonyl carbons, δ 220.0 (d, J_{P-CO} = 14.7), 227.7 (d, 2.5) and 228.8 (d, 13.4); C=N carbons, 169.7 (d, J_{P-NC} = 19.6); phenyl carbons of CPh, 126.9, 128.9, 130.0 and 130.6; phenyl carbons of PPh_2, 128.8 (d,



C **D**

$J_{P\text{–}C}$ = 2.4), 130.8 (d, 13.4), 137.6 (d, 4.8) and 137.7 (d, 39.1); methyl carbons of imino N(SiMe$_3$) group, 1.4 (s); ^{1}H, phenyl protons, δ 7.46 (4 H, m), 7.02 (7 H, m), 6.86 (2 H, t, J = 7.5) and 6.59 (2 H, d, J = 7.5); NH proton, δ 5.90 (1 H, d, $J_{P\text{–}NH}$ = 6.3 Hz); protons of imino N(SiMe$_3$) group, δ 0.17 (9 H, s).

***cis*-[Mo(CO)$_4${(Me$_3$SiN)C(Ph)(NHPPh$_2$)}] 2.** This compound was prepared as described for **1**: [Mo(CO)$_4$(nbd)] (0.32 g, 1.06 mmol) and (Ph$_2$PN)C(Ph)[N(SiMe$_3$)$_2$] (0.48 g, 1.06 mmol) were used. Yield: 0.45 g, 70%. Yellow crystals, m.p. 132–134 °C (decomp.) (Found: C, 51.7; H, 4.4; N, 4.3. Calc. for $C_{26}H_{25}MoN_2O_4PSi\cdot H_2O$: C, 51.8; H, 4.5; N, 4.7%). IR (cm^{-1}, in KBr): 3356s, 3056w, 2956w, 2012s, 1908vs, 1876vs, 1834s, 1604w, 1582s, 1482w, 1414s, 1250m, 1182w, 1156w, 1128w, 1094m, 1024w, 998w, 930m, 842s, 828s, 740m, 694s, 622m, 584s, 560m and 506w. NMR (C$_6$D$_6$): ^{31}P-{^{1}H}, δ 89.6 (s); ^{13}C-{^{1}H}, carbonyl carbons, δ 208.7 (d, $J_{P\text{–}CO}$ = 9.8), 217.0 (d, 36.6) and 220.7 (d, 8.5); C=N carbons, 169.9 (d, $J_{P\text{–}NC}$ = 18.2); phenyl carbons of CPh, 127.0, 129.6, 130.2 and 130.9; phenyl carbons of PPh$_2$, 129.1 (d, $J_{P\text{–}C}$ = 8.5), 131.2 (d, 15.9), 138.0 (d, J 39.0) and 138.1 (d, 4.9); methyl carbons of imino N(SiMe$_3$) group, 1.6 (s); ^{1}H, phenyl protons, δ 7.41 (4 H, m), 7.00 (2 H, m), 6.83 (2 H, t, J = 7.3) and 6.60 (2 H, d, J = 7.3); NH proton, 5.79 (1 H, d, $J_{P\text{–}NH}$ = 4.6 Hz); protons of imino N(SiMe$_3$) group, 0.15 (9 H, s); and H$_2$O protons, 0.29 (2 H, s). Electron impact mass spectrum: *m/z*: 586 (*M* for ^{98}Mo), 558 (*M* − CO), 530 (*M* − 2CO), 502 (*M* − 3CO) and 474 (*M* − 4CO).

***cis*-[{Cr(CO)$_4$}$_2${(Ph$_2$PNH)(Me$_3$SiN)CC$_6$H$_4$C(NSiMe$_3$)-(NHPPh$_2$)}], 3.** To a cooled (−78 °C) solution of C$_6$H$_4$-{C(NPPh$_2$)[N(SiMe$_3$)$_2$]}$_2$-1,4 (0.50 g, 0.61 mmol) in tetrahydrofuran (30 cm^3) was added to a solution of [Cr(CO)$_4$(nbd)] (0.31 g, 122 mmol) in tetrahydrofuran (10 cm^3) dropwise over 10 min. The resultant orange solution was allowed to warm to room temperature slowly and stirred for 2 d. It was concentrated to *ca.* 10 cm^3 and hexane (30 cm^3) added to afford a yellow solid. The solid was filtered off, washed with diethyl ether (3 × 2 cm^3), dissolved in CH$_2$Cl$_2$ (5 cm^3) and filtered. Hexane was added to the CH$_2$Cl$_2$ solution slowly until it just turned cloudy. It was then cooled to −20 °C to give yellow crystals which were filtered off and dried *in vacuo*. (yield: 0.33 g, 50%), m.p. 126–128 °C (decomp.) (Found: C, 49.6; H, 4.3; H, 4.9. Calc. for $C_{46}H_{44}Cr_2N_4O_8P_2Si_2\cdot 2CH_2Cl_2$: C, 49.2; H, 4.1; N, 4.8%). IR (cm^{-1}, in KBr): 3348w, 3200w, 3060w, 2959w, 2012s, 1898vs, 1884vs (sh), 1840vs, 1578m, 1414m, 1252m, 1105m, 937m, 843m, 698m, 649s, 527w and 501w. NMR (C$_6$D$_6$): ^{31}P-{^{1}H}, PPh$_2$: δ 112.3 (br, s); ^{13}C-{^{1}H}, carbonyl carbons, δ 219.9 (d, $J_{P\text{–}CO}$ = 14.6), 227.3 (br, s) and 228.5 (d, J 13.4); C=N carbons, 167.9 (d, $J_{P\text{–}NC}$ = 26.7); phenylene carbons, 127.6 and 130.9; phenyl carbons of PPh$_2$, 129.90 (d, $J_{P\text{–}C}$ = 9.8), 130.7 (d, 13.4), 137.5 (d, 39.0) and 139.4 (d, J 6.1 Hz); methyl carbons of imino N(SiMe$_3$) group, 4.3 (br, s); ^{1}H, phenyl protons, δ 7.51 (8 H, m) and 7.01 (12 H, m); phenylene protons, 6.55 (2 H, s) and 4.25 (2 H, s); NH proton, 6.02 (2 H, br, s); protons of imino N(SiMe$_3$) group, 0.24 (18 H, br, s). Positive-ion FAB mass spectrum: *m/z*: 1003 (*M* + 1), 918 (*M* − 3CO), 890 (*M* − 4CO), 862 (*M* − 5CO), 834 (*M* − 6CO), 806 (*M* − 7CO) and 778 (*M* − 8CO).

***cis*-[{Mo(CO)$_4$}$_2${(Ph$_2$PNH)(Me$_3$SiN$_3$)CC$_6$H$_4$C(NSiMe$_3$)-(NHPPh$_2$)}] 4.** This compound was prepared as described for **3** C$_6$H$_4${C(NPPh$_2$)[N(SiMe$_3$)$_2$]}-1,4 (0.50 g, 0.61 mmol) and [Mo(CO)$_4$(nbd)] (0.37 g, 1.23 mmol) were used. Yield: 0.37 g, 55%. Yellow crystals, m.p. 168–170 °C (decomp.) (Found: C, 50.8; H, 3.8; N, 4.9. Calc. for $C_{46}H_{44}Mo_2N_4O_8P_2Si_2$: C, 50.6; H, 4.0; N, 5.1%). IR (cm^{-1}, in KBr): 3361m, 3060w, 2956w, 2023s, 1920vs, 1877vs, 1843s, 1827vs, 1582m, 1505w, 1436m, 1410s, 1248m, 1107m, 927m, 835s, 748m, 695m, 632m, 585m, 518m and 433w. NMR (CDCl$_3$): ^{31}P-{^{1}H}, PPh$_2$, δ 89.5 (s); ^{13}C-{^{1}H}, carbonyl carbons, δ 207.6 (d, $J_{P\text{–}CO}$ = 9.8), 216.2 (d, 36.6) and 220.5 (d, 8.6); C=N carbons, 167.5 (d, $J_{P\text{–}NC}$ = 18.3); phenylene carbons, 127.6 and 130.9; phenyl carbons of PPh$_2$, 129.9 (d, $J_{P\text{–}C}$ = 9.8), 130.7 (d, 14.6), 137.0 (d, 37.9) and 139.8 (d, $J_{P\text{–}C}$ = 4.9 Hz); methyl carbons of imino N(SiMe$_3$) group, 4.1 (br, s); ^{1}H, phenyl and phenylene protons, δ 7.42–7.53 (24 H, m); NH proton, 6.15 (2 H, br, s); protons of imino N(SiMe$_3$) group, 0.13 (18 H, br, s). Positive-ion FAB mass spectrum: *m/z* 1095 (*M* + 1 for ^{98}Mo), 1066 (*M* − CO), 1038 (*M* − 2CO), 1010 (*M* − 3CO), 982 (*M* − 4CO), 954 (*M* − 5CO), 926 (*M* − 6CO), 898 (*M* − 7CO) and 870 (*M* − 8CO).

***cis*-[(OC)$_4$Mo{Ph$_2$PNH)(Me$_3$SiN$_3$)CC$_6$H$_4$C[N(SiMe$_3$)$_2$]-(NPPh$_2$)}Mo(CO)$_5$] 5.** This compound was prepared as described for **1**: [Mo(CO)$_4$(nbd)] (0.49 g, 1.60 mmol) and C$_6$H$_4${C(NPPh$_2$)[N(SiMe$_3$)$_2$]}$_2$-1,4 (0.67 g, 0.80 mmol) were used. Yield: 0.58 g, 60%. Yellow crystals, m.p. 144–146 °C (decomp.) (Found: C, 49.7; H, 4.5; N, 4.3. Calc. for $C_{50}H_{52}Mo_2N_4O_9P_2Si_3\cdot H_2O$: C, 49.7; H, 4.5; N, 4.6%). IR (cm^{-1}, in KBr): 3368m, 3060w, 2956w, 2068m, 2016m, 1940s (br), 1908vs, 1878s, 1830s, 1578s, 1432w, 1406m, 1252s, 1180w, 1136m, 1092m, 964w, 926w, 828s, 686m, 580m and 520m. NMR (C$_6$D$_6$): ^{31}P-{^{1}H}, =NPPh$_2$, δ 72.5 (s); HNPPh$_2$, 90.4 (s); ^{13}C-{^{1}H}, carbonyl carbons, 206.5 (d, $J_{P\text{–}CO}$ = 8.5), 208.7 (d, 9.8), 210.8 (d, 23.1), 216.9 (d, 36.5) and 220.6 (d, 8.5); C=N carbons, 167.7 (d, $J_{P\text{–}NC}$ = 6.1) and 168.7 (d, 18.3); phenyl and phenylene carbons, 126.4 (s), 128.8–132.1 (m), 137.3 (s), 137.9 (s), 138.6 (d, $J_{P\text{–}C}$ = 4.9) and 141.5 (d, 3.7); methyl carbons of imino N(SiMe$_3$) group, 1.4 (s); methyl carbons of the amino N(SiMe$_3$)$_2$ group, δ 4.2 (s); ^{1}H, phenyl and phenylene protons, δ 7.70, (4 H, m), 7.38 (7 H, m), 7.10 (8 H, m), 6.79 (4 H, m), 6.59 (2 H, m) and 6.45 (2 H, d, J = 8.4); NH proton, 5.69 (1 H, d, $J_{P\text{–}NH}$ = 4.9 Hz); protons of amino N(SiMe$_3$)$_2$ group, 0.22 (18 H, s); protons of imino N(SiMe$_3$) group, 0.15 (9 H, s); H$_2$O protons, 0.29 (2 H, s).

X-Ray crystallography

Crystals of compound **3** suitable for X-ray diffraction study were grown by slow diffusion of diethyl ether into a saturated solution of the compound **3** in CH$_2$Cl$_2$ as a solvate of stoichiometry **3**·2CH$_2$Cl$_2$. A yellow block of dimensions 0.20 × 0.38 × 0.45 mm was mounted on a glass fibre with epoxy resin. Intensity data were collected on a Siemens P4 diffractometer at 294 K with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using ω–2θ scans. Crystal stability was monitored by recording three check reflections at intervals of 97 data measurements, and no significant variation was detected. An empirical absorption correction based on ψ scans was applied, resulting in relative transmission factors ranging from 0.8751 to 0.9485. A total of 5110 unique reflections ($3 \leqslant 2\theta \leqslant 50°$) were measured; 2637 of these had $I > 2.0\sigma(I)$ and were considered observed. Crystal data, data collection parameters, and results of the analysis are given in Table 3. The structure was solved by the direct method using the program package SHELXTL PLUS[9] and refined against F^2 using SHELXL 93.[10] Non-hydrogen atoms were refined anisotropically by full-matrix least squares. The SiMe$_3$ group and the CH$_2$Cl$_2$ solvent molecules were positionally disordered. The atomic positional and thermal parameters of the carbon atoms of the SiMe$_3$ group and the

Table 3 Data collection and processing parameters for compounds **3** and **5***

	3	**5**
Empirical formula	$C_{48}H_{48}Cl_4Cr_2N_4O_8$-$P_2Si_2$	$C_{53}H_{59}Mo_2N_4O_9$-P_2Si_3
M	1172.8	1234.1
D_c/g cm^{-3}	1.348	1.290
Crystal size/mm	0.20 × 0.38 × 0.45	0.32 × 0.33 × 0.36
Space group	$I2/a$ (no. 15, non-standard)	$P2_1/n$ (no. 14, non-standard)
a/Å	17.337(3)	16.080(3)
b/Å	15.055(3)	17.933(3)
c/Å	22.652(4)	23.105(3)
β/°	102.22(1)	107.67(1)
U/Å^3	5778(2)	6348(1)
μ/cm^{-1}	7.08	5.51
F(000)	2400	2528
Scan rate/° min^{-1} in ω	Variable, 6.00–60.00	16.0 (up to 4 scans)
Scan range (ω)	(0.60 + 0.35 tan θ)°	(1.68 + 0.35 tan θ)°
Reflections collected	5230	8981
Independent reflections (R_{int})	5110 (0.0335)	8622 (0.041)
Observed reflections	2637 [$I_o > 2.0\ \sigma(I_o)$]	5230 [$I_o > 1.5\ \sigma(I_o)$]
Quantity minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o - F_c)^2$
Weighting scheme, w^{-1}	$\sigma^2(F_o) + 0.0005F_o^2$	$\sigma^2(F_o)$
R, R' (observed data)	0.063, 0.065	0.065, 0.068
Goodness of fit	1.32	3.33
Largest Δ/σ	0.009	0.09
Number of parameters, p	376	631
Residual extrema/e Å^{-3}	0.36 to −0.43	0.84 to −0.48

* Details in common: yellow block; monoclinic; $Z = 4$.

non-hydrogen atoms of the CH_2Cl_2 solvent molecules were refined with occupancy 0.5. Hydrogen atoms were generated in their idealized positions (C−H 0.95 and N−H 0.85 Å) and allowed to ride on their respective parent carbon and nitrogen atoms. These hydrogen atoms were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations but not in the refinement. The relatively high R values are due to poor crystal quality, thermal disorder of the $SiMe_3$ groups, and severe positional disorder of the CH_2Cl_2 molecules.

Crystals of compound **5** suitable for X-ray diffraction study were grown by slow diffusion of hexane into a saturated solution of it in CH_2Cl_2 as a solvate of stoichiometry **5**·$0.5C_6H_{14}$. A yellow block of dimensions 0.32 × 0.33 × 0.36 mm was mounted on a glass fibre with epoxy resin. Intensity data were collected on a Rigaku AFC7R diffractometer at 298 K with graphite-monochromated. Mo-Kα radiation using ω–2θ scans. Crystal stability was monitored by recording three check reflections at intervals of 150 data measurements, and no significant variation was detected. A total of 8622 unique reflections ($6 \leqslant 2\theta \leqslant 45°$) were measured; 5230 of these had $I > 1.5\sigma(I)$ and were considered observed. The data were corrected for Lorentz-polarization factors and absorption using the ψ-scan method. The structure was solved by direct methods and refined by full-matrix least-squares analysis, with all non-hydrogen atoms assigned anisotropic displacement parameters. Half-occupancy was assigned to the carbons of the disordered hexane solvent molecule which were restrained during refinement. Hydrogen atoms were treated as in **3**. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[11] The relatively high R values are due to poor crystal quality and severe positional disorder of the hexane molecule.

Atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/338.

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