

# Reactions of quadruply chelated silyl- and germyl-molybdenum hydrido complexes with isocyanides: observation of the *trans*-influence on the silyl ligand

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The reactions of a series of silyl- and germyl-molybdenum hydrido complexes,  $[\text{MoH}_3\{\text{E}(\text{Ar})[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\text{-}o\}_2]$  (E = Si, Ge; Ar = Ph,  $\text{C}_6\text{F}_5$ , 4- $\text{Me}_2\text{NC}_6\text{H}_4$ ), with various isocyanides result in the liberation of hydrogen and formation of the molybdenum isocyanide complexes,  $[\text{MoH}(\text{CNR})\{\text{E}(\text{Ar})[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\text{-}o\}_2]$  (R = *t*-Bu, *cyclo*- $\text{C}_6\text{H}_{11}$ ,  $\text{PhCH}_2$ , Ph, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ ), in which the isocyanide ligand ligates at the site opposite to the E atom. The new complexes show in their solid-state IR spectra an intense band assignable to C=N stretching, which is found to be considerably lower than that of the corresponding free isocyanide (more than  $100\text{ cm}^{-1}$ ), demonstrating the existence of  $\pi$ -back-bonding from the electron-rich metal centre to the isocyanide ligand. Both X-ray crystallographic analyses and spectroscopic evidence confirm the strong *trans*-influence of the Si group.

## Introduction

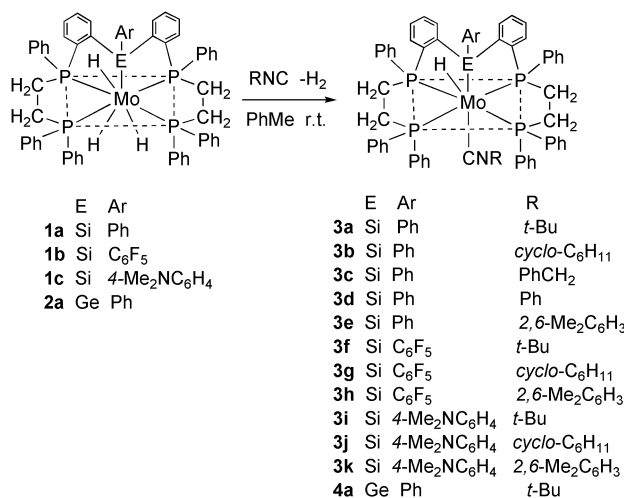
We have previously shown that the novel silyl- and germyl-molybdenum complexes  $[\text{MoH}_3\{\text{E}(\text{Ph})[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\text{-}o\}_2]$  (E = Si (**1a**) and Ge (**2a**)) are readily prepared by the thermal reaction of the molybdenum hydrido complex  $[\text{MoH}_4(\text{dppe})_2]$  (dppe =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) with  $\text{PhEH}_3$ .<sup>1,2</sup> These complexes possess an unusual quadruply chelated ligand comprised of a P–P–E–P–P framework and some interesting reactivity features of these species have been observed.<sup>3</sup> For example, **1a** reacted with carbon dioxide to give a formate complex at room temperature indicating that  $\text{CO}_2$  can insert into the Mo–H bond of the complex **1a**, although the parent complex,  $[\text{MoH}_4(\text{dppe})_2]$ , does not react with  $\text{CO}_2$  under the same conditions at all. Furthermore, **1a** has exhibited a unique characteristic for catalytic carbon dioxide fixation and has represented the first molybdenum compound which can catalyze hydrogenation of  $\text{CO}_2$  effectively.<sup>4</sup> We thought that the high reactivity of **1a** was due to the strong *trans*-effect of the Si fragment since it has been pointed out that the  $\text{R}_3\text{Si}$  group is a strong  $\sigma$ -donor and may labilize the ligand in the position *trans* to it.<sup>5</sup>

It is well known that spectral features of a coordinated isocyanide ligand reflect the property of the molecule under consideration and often afford reliable evidence for compound identity.<sup>6</sup> We have therefore studied isocyanide complexes derived from **1** or **2** in order to obtain more detailed information on the *trans*-influencing ability imparted by the Si and the Ge fragment. Isocyanides form complexes with transition metals and resultant isocyanide complexes are, in some respects, similar to metal carbonyls. However, isocyanide ligands are more basic and much weaker  $\pi$ -acceptors than carbon monoxide because of the competition for the carbon–nitrogen multiple bond antibonding orbitals between the nitrogen lone electron pair and the metal lone electron pairs.<sup>6,7</sup>

## Results and discussion

### Syntheses of the isocyanide complexes

Treatment of **1** or **2** with one equivalent of isocyanide such as *tert*-butyl isocyanide, cyclohexyl isocyanide, benzyl isocyanide, phenyl isocyanide, or 2,6-dimethylphenyl isocyanide in toluene at ambient temperature readily led to the formation of molybdenum isocyanide complexes (**3**, E = Si; **4**, E = Ge) in moderate



Scheme 1

to good yields (61–82%, Scheme 1 and Table 1). The resultant complexes were obtained as yellow or orange powders. They were found to be soluble in benzene, toluene, or THF, but not soluble in hexane and could be purified by recrystallization from toluene–hexane.

### Infrared spectra

In their solid-state IR spectra, the complexes show the intense band assignable to C=N stretching; these frequencies are listed in Table 2. The present values are found to be considerably lower than those of the corresponding free isocyanides (more than  $100\text{ cm}^{-1}$ ), demonstrating the existence of  $\pi$ -back-bonding from the electron-rich metal centre to the isocyanide ligand.<sup>8</sup> C=N Stretching frequencies can be regarded as an indicator of relative amounts of charge on a given metal centre and variations in  $\nu(\text{CN})$  are usually ascribed to differences in  $\pi$ -back-bonding.<sup>9</sup> In a series of the silylmolybdenum complexes studied in this work, the electron density on the molybdenum atom would be expected to increase in the order:  $\text{C}_6\text{F}_5$  compounds (**3f–h**) < Ph compounds (**3a,b,e**) < 4- $\text{Me}_2\text{NC}_6\text{H}_4$  compounds (**3i–k**). The observed spectroscopic trend for  $\nu(\text{CN})$  is partially in line with this order. The increased donor properties of 4- $\text{Me}_2\text{NC}_6\text{H}_4$  compared to phenyl result in a  $18\text{ cm}^{-1}$  shift to lower frequency for **3k** ( $1961\text{ cm}^{-1}$ ) compared with **3e** ( $1979$

**Table 1** Preparation of isocyanide complexes

Compound	Complex/mmol	Isocyanide (R/mmol)	Toluene (mL)	Yield (%)
<b>3a</b>	<b>1a</b> /0.088	<i>t</i> -Bu/0.088	10	72
<b>3b</b>	<b>1a</b> /0.14	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> /0.20	10	65
<b>3c</b>	<b>1a</b> /0.16	PhCH <sub>2</sub> /0.24	15	68
<b>3d</b>	<b>1a</b> /0.11	Ph/0.16	10	61
<b>3e</b>	<b>1a</b> /0.10	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> /0.30	10	82
<b>3f</b>	<b>1b</b> /0.092	<i>t</i> -Bu/0.74	10	67
<b>3g</b>	<b>1b</b> /0.092	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> /0.14	10	65
<b>3h</b>	<b>1b</b> /0.092	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> /0.28	10	69
<b>3i</b>	<b>1c</b> /0.096	<i>t</i> -Bu/0.77	10	74
<b>3j</b>	<b>1c</b> /0.096	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> /0.48	10	80
<b>3k</b>	<b>1c</b> /0.096	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> /0.29	10	75
<b>4a</b>	<b>2a</b> /0.11	<i>t</i> -Bu/0.11	10	72

**Table 2** Infrared spectra (CN stretching region, cm<sup>-1</sup>)

Compound	Ar	E	R	$\nu(\text{CN})^a$
<b>3a</b>	Ph	Si	<i>t</i> -Bu	2025
<b>3b</b>	Ph	Si	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub>	2038
<b>3c</b>	Ph	Si	PhCH <sub>2</sub>	2033
<b>3d</b>	Ph	Si	Ph	1969
<b>3e</b>	Ph	Si	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1979
<b>3f</b>	C <sub>6</sub> F <sub>5</sub>	Si	<i>t</i> -Bu	2039
<b>3g</b>	C <sub>6</sub> F <sub>5</sub>	Si	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub>	2053
<b>3h</b>	C <sub>6</sub> F <sub>5</sub>	Si	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1979
<b>3i</b>	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Si	<i>t</i> -Bu	2023
<b>3j</b>	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Si	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub>	2038
<b>3k</b>	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Si	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1961
<b>4a</b>	Ph	Ge	<i>t</i> -Bu	2031

<sup>a</sup> KBr disk.

cm<sup>-1</sup>). In addition, replacement of the phenyl group by the most electron-withdrawing C<sub>6</sub>F<sub>5</sub> leads to a 15 cm<sup>-1</sup> shift to higher frequency: 2053 cm<sup>-1</sup> for **3g** compared with 2038 cm<sup>-1</sup> for **3b** and similar higher shift is observed in the pair **3f** (2039 cm<sup>-1</sup>) and **3a** (2025 cm<sup>-1</sup>). However, it is quite unexpected that the  $\nu(\text{CN})$  frequencies in **3e** and **3h** are identical in spite of the large difference in the electronic effect of the substituents, as are the  $\nu(\text{CN})$  frequencies in **3b** and **3j**. Likewise, the  $\nu(\text{CN})$  frequencies in **3a** are nearly equal to those in **3i**. Consequently, in these complexes, the influence of the substituent in the aromatic ring on the  $\nu(\text{CN})$  frequencies can be completely ignored. An intriguing feature of the present results is as follows: the complexes containing a phenyl and a C<sub>6</sub>F<sub>5</sub> group on the silicon atom behave similarly with aryl isocyanide but behave differently with the aliphatic isocyanides, on the other hand the complexes containing a phenyl and 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> group behave similarly with aliphatic isocyanides but behave differently in the presence of an aryl isocyanide. Coordinated aryl isocyanides are generally capable of delocalizing excess charge density on a metal centre from M–L back-donation into the aromatic ring system, while such delocalization cannot be expected for coordinated aliphatic isocyanides, and aliphatic isocyanides impart somewhat more electron density on a metal centre than do aryl isocyanides.<sup>10</sup> The C<sub>6</sub>F<sub>5</sub> group in the aliphatic isocyanide complexes (**3f,g**) may be responsible for withdrawing the extra electron density through the Si–Mo–C linkage, although in **3h** its electron-withdrawing capability would not be enough to attract  $\pi$ -density from the coordinated aryl isocyanide. On the other hand, the *N,N*-dimethylamino substituent acts as a potent electron-donating group, rendering the silicon a good donor and a poor  $\pi$ -acceptor. This effect would play a significantly greater role in the aryl isocyanide complex (**3k**) since the  $\pi$ -acceptor strength of aliphatic isocyanides is much less than that of aryl ones.<sup>11</sup> The observed spectroscopic trend for  $\nu(\text{CN})$  is indicative of a temperate electronic communication between a functional group on the silicon atom and a coordinated isocyanide. These results show that the electronic

state of the metal centre can be tuned by the selection of substituents on the silicon atom. The value of  $\nu(\text{CN})$  for **3a** (2025 cm<sup>-1</sup>) is slightly lower than that of **4a** (2031 cm<sup>-1</sup>); this may be interpreted in terms of a difference in the  $\pi$ -interaction between the central molybdenum atom and the two elements (Si and Ge), increasing in the order Si < Ge.<sup>12</sup>

### NMR spectra

In the <sup>1</sup>H NMR spectra of **3**, which are collected in Table 3, a hydrido signal appears at around  $\delta$  –7 as a triplet of triplets (<sup>2</sup>*J*<sub>HP</sub> = *ca.* 28 and 4 Hz) corresponding to an A<sub>2</sub>K<sub>2</sub>X spin system. In the case of **3e**, the hydrido ligand is observed at  $\delta$  –6.90 as an apparent broad triplet (<sup>2</sup>*J*<sub>HP</sub> = 23.7 Hz). The hydride region of **4a** displays a triplet of triplets ( $\delta$  –6.80, <sup>2</sup>*J*<sub>HP</sub> = 6.2 and 42.1 Hz), which is at a lower field than that of **3a** by about 0.7 ppm. This would appear to suggest that the Si ligand imparts somewhat more electron density on the metal centre than does the Ge ligand. In the series of silylmolybdenum complexes studied in this work, the hydrido resonances for the C<sub>6</sub>F<sub>5</sub> compounds (**3f–h**) are shifted to higher field by about 0.2 ppm and those for the 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> compounds (**3i–k**) are shifted to lower field by about 0.1 ppm *versus* the corresponding resonances for the phenyl compounds (**3a,b,e**). Taking into account the electronic effect of the substituents, the present results are unexpected and somewhat puzzling at first glance. However, let us assume that the hydride and the Si ligand are positioned pseudo-*trans* to the isocyanide ligand, and the Mo ← H  $\sigma$ -donation is influenced by  $\sigma$ -donor effect of the coordinated isocyanide ligand.  $\sigma$ -Donor ability of the Si ligand increases in the order: C<sub>6</sub>F<sub>5</sub> compound < phenyl compound < 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> compound, suggesting that the relative  $\sigma$ -donor influence of the coordinated isocyanide toward the hydride decreases in this order.

All of the <sup>31</sup>P{<sup>1</sup>H} NMR spectra for **3** show a pair of doublets at around  $\delta$  105 and 80 with coupling constant <sup>2</sup>*J*<sub>PP</sub> = *ca.* 75 Hz in a 1 : 1 ratio due to the two inequivalent equatorial phosphines (see Table 3), indicating that the molecule **3** has an effective mirror plane which contains the Mo–Si bond.

### Crystal structures

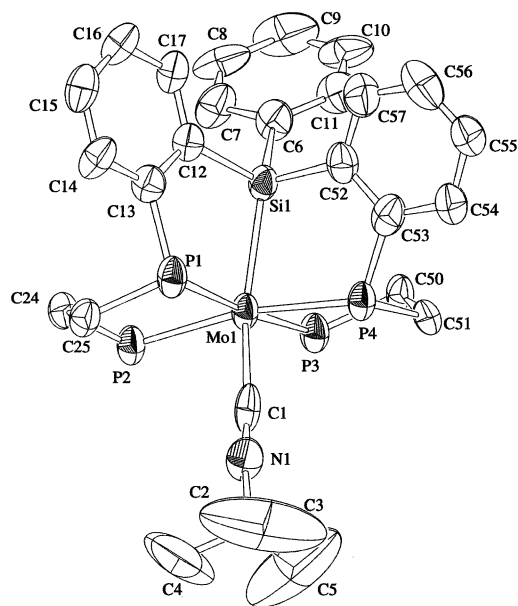
The solid-state structures of **3a**, **3b**, and **3e** were determined by X-ray crystallography (Figs. 1–3). Crystallographic data are listed in Table 4, and selected bond distances and angles are given in Table 5. Complex **3a** crystallizes as a C<sub>7</sub>H<sub>8</sub> solvate.

The molecular structures of all three complexes can be considered to consist of a seven-coordinate molybdenum centre. Although fairly weak the reflection intensity prevents us from defining the hydride ligand precisely, it is postulated as being at a similar site to the Si ligand (as described in the NMR section). In these structures, the quadruply chelated P–P–Si–P framework is found to be kept intact and the isocyanide ligand binds to the Mo centre in an end-on fashion. The Mo1–Si1 bond length is 2.519(3) Å in **3a**, 2.5188(9) Å in **3b**, and 2.5593(9) Å in

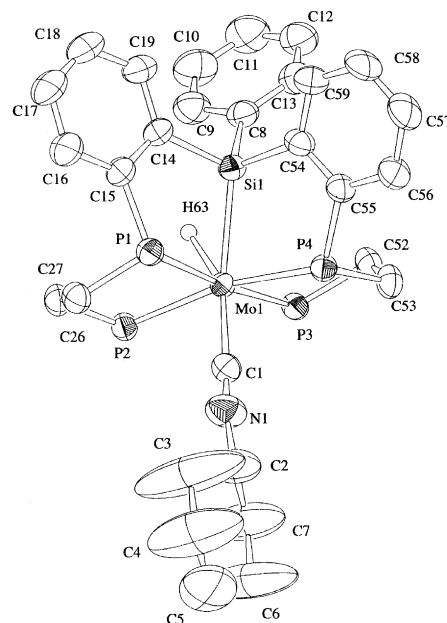
**Table 3**  $^1\text{H}$  and  $^{31}\text{P}$  NMR data ( $J$  in Hz)

Compound	$^1\text{H}$ NMR <sup>a</sup>		$^{31}\text{P}$ NMR <sup>b</sup>	
	$\delta$ (Mo-H)	$\delta$ (Others)	$\delta$	
<b>3a</b>	-7.50 (tt, $J_{\text{HP}} = 4.0, 30.0, 1\text{H}$ )	0.50 (s, 9H, $\text{CH}_3$ ), 1.8-3.6 (m, 8H, $\text{C}_2\text{H}_4$ ), 6.5-8.0 (m, 43 H, Ph protons)	80.8 (d, 2 P, $J_{\text{pp}} = 76.2$ ), 103.6 (d, 2 P, $J_{\text{pp}} = 76.2$ )	
<b>3b</b>	-7.50 (tt, $J_{\text{HP}} = 4.0, 287, 1\text{H}$ )	0.5-1.5 (m, 11 H, $\text{C}_6\text{H}_{11}$ ), 1.8-3.6 (m, 8 H, $\text{C}_2\text{H}_4$ ), 6.5-8.0 (m, 43 H, Ph protons)	81.1 (d, 2 P, $J_{\text{pp}} = 76.3$ ), 105.7 (d, 2 P, $J_{\text{pp}} = 73.2$ )	
<b>3c</b>	-6.90 (tt, $J_{\text{HP}} = 3.5, 27.7, 1\text{H}$ )	1.8-3.6 (m, 8 H, $\text{C}_2\text{H}_4$ ), 3.80 (s, 2 H, $\text{PhCH}_2$ ), 6.5-8.0 (m, 48 H, Ph protons)	81.0 (d, 2 P, $J_{\text{pp}} = 73.2$ ), 107.2 (d, 2 P, $J_{\text{pp}} = 73.3$ )	
<b>3d</b>	-6.40 (tt, $J_{\text{HP}} = 3.2, 26.8, 1\text{H}$ )	1.8-3.6 (m, 8 H, $\text{C}_2\text{H}_4$ ), 6.5-8.0 (m, 48 H, Ph protons)	77.3 (d, 2 P, $J_{\text{pp}} = 85.5$ ), 107.4 (d, 2 P, $J_{\text{pp}} = 86.9$ )	
<b>3e</b>	-6.90 (br t, $J_{\text{HP}} = 23.7, 1\text{H}$ )	1.5 (s, 6 H, $\text{CH}_3$ ), 1.8-3.6 (m, 8 H, $\text{C}_2\text{H}_4$ ), 6.5-8.0 (m, 46 H, Ph protons)	77.3 (d, 2 P, $J_{\text{pp}} = 76.3$ ), 101.8 (d, 2 P, $J_{\text{pp}} = 73.2$ )	
<b>3f</b>	-7.70 (tt, $J_{\text{HP}} = 3.6, 30.5, 1\text{H}$ )	0.50 (s, 9 H, $\text{CH}_3$ ), 1.8-2.8 (m, 8 H, $\text{C}_2\text{H}_4$ ), 6.3-8.0 (m, 38 H, Ph protons)	74.0 (d, 2 P, $J_{\text{pp}} = 73.2$ ), 103.6 (d, 2 P, $J_{\text{pp}} = 73.2$ )	
<b>3g</b>	-7.50 (tt, $J_{\text{HP}} = 4.1, 29.3, 1\text{H}$ )	0.5-1.5 (m, 11 H, $\text{C}_6\text{H}_{11}$ ), 1.7-2.8 (m, 8 H, $\text{C}_2\text{H}_4$ ), 6.3-8.0 (m, 38 H, Ph protons)	74.8 (d, 2 P, $J_{\text{pp}} = 67.1$ ), 105.3 (d, 2 P, $J_{\text{pp}} = 73.2$ )	
<b>3h</b>	-7.00 (tt, $J_{\text{HP}} = 3.9, 29.3, 1\text{H}$ )	0.55 (s, 9 H, $\text{CH}_3$ ), 2.1-2.7 (m, 8 H, $\text{C}_2\text{H}_4$ ), 2.73 (s, 6 H, $\text{NCH}_3$ ), 6.0-8.5 (m, 42 H, Ph protons)	72.8 (d, 2 P, $J_{\text{pp}} = 73.2$ ), 101.8 (d, 2 P, $J_{\text{pp}} = 70.2$ )	
<b>3i</b>	-7.44 (tt, $J_{\text{HP}} = 4.6, 31.1, 1\text{H}$ )	0.5-1.8 (m, 11 H, $\text{C}_6\text{H}_{11}$ ), 2.2-2.7 (m, 8 H, $\text{C}_2\text{H}_4$ ), 2.75 (s, 6 H, $\text{NCH}_3$ ), 6.0-8.3 (m, 42 H, Ph protons)	81.5 (d, 2 P, $J_{\text{pp}} = 76.3$ ), 103.5 (d, 2 P, $J_{\text{pp}} = 79.4$ )	
<b>3j</b>	-7.16 (tt, $J_{\text{HP}} = 3.4, 27.9, 1\text{H}$ )	1.48 (s, 6 H, $\text{CH}_3$ ), 2.2-2.6 (m, 8 H, $\text{C}_2\text{H}_4$ ), 2.73 (s, 6 H, $\text{NCH}_3$ ), 6.0-8.3 (m, 45 H, Ph protons)	81.7 (d, 2 P, $J_{\text{pp}} = 76.3$ ), 105.6 (d, 2 P, $J_{\text{pp}} = 76.3$ )	
<b>3k</b>	-6.83 (tt, $J_{\text{HP}} = 3.9, 29.3, 1\text{H}$ )	0.58 (s, 9 H, $\text{CH}_3$ ), 1.6-3.1 (m, 8 H, $\text{C}_2\text{H}_4$ ), 6.2-8.5 (m, 43 H, Ph protons)	78.1 (d, 2 P, $J_{\text{pp}} = 76.3$ ), 101.8 (d, 2 P, $J_{\text{pp}} = 76.3$ )	
<b>4a</b>	-6.80 (tt, $J_{\text{HP}} = 6.2, 42.1, 1\text{H}$ )		Not measured	

<sup>a</sup> 270 MHz,  $\text{C}_6\text{D}_6$ , 293 K. <sup>b</sup> 109.25 MHz,  $\text{C}_6\text{D}_6$ , 293 K.



**Fig. 1** Molecular structure and atom labeling for **3a**.



**Fig. 2** Molecular structure and atom labeling for **3b**.

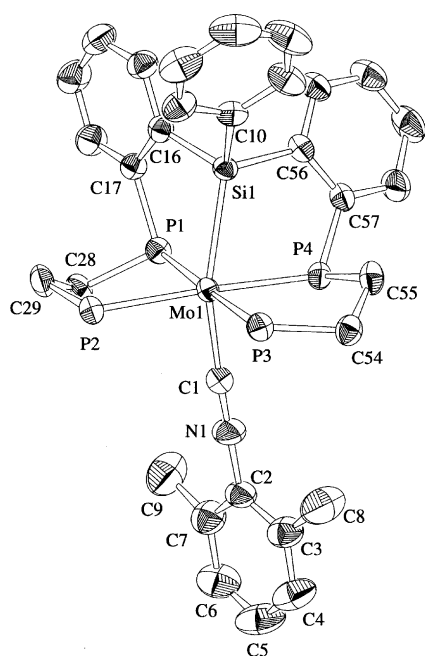
**3e** and the mean Mo-P distances (2.4465 Å for **3a**, 2.4391 Å for **3b**, and 2.4502 Å for **3e**) are nearly identical, indicating that geometries around the molybdenum and silicon atom in **3a**, **3b** and **3e** are similar. It is noteworthy that the Mo1-Si1 bond distances are closely correlated with the C1-N1 bond distances. Namely, the Mo1-Si1 bonds are elongated in the order **3b** < **3a** < **3e**, and accordingly the C1-N1 bond distances increase in the order **3b** (1.136(4) Å) < **3a** (1.15(2) Å) < **3e** (1.171(4) Å). The Si ligand is *trans* to the isocyanide and competes with the isocyanide ligand for  $\pi$ -density. The C1-N1 bond length reflects a degree of  $\pi$ -back-bonding from the metal into the isocyanide  $\pi^*$  frontier orbitals. Thus, we can anticipate that the extent of the  $\pi$ -interaction between the central molybdenum atom and the silicon atom decreases as the C1-N1 bond distance increases. The Mo1-C1 bonds are elongated in the order **3e** (2.072(3) Å) < **3b** (2.091(3) Å) < **3a** (2.10(1) Å) and hence **3e** has a significantly shortened Mo-C bond length. This indicates that 2,6-dimethylphenyl isocyanide is the strongest  $\pi$ -acceptor of the three ligand types, consistent with frontier molecular orbital studies which show that aryl isocyanides should be better  $\pi$ -acceptors

**Table 4** Crystallographic data for compounds **3a**, **3b** and **3e**

	<b>3a</b> ·C <sub>7</sub> H <sub>8</sub>	<b>3b</b>	<b>3e</b>
Formula	C <sub>70</sub> H <sub>69</sub> MoNP <sub>4</sub> Si	C <sub>65</sub> H <sub>63</sub> MoNP <sub>4</sub> Si	C <sub>67</sub> H <sub>61</sub> MoNP <sub>4</sub> Si
<i>M</i>	1172.24	1106.14	1128.15
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	14.42(2)	12.473(3)	14.298(6)
<i>b</i> /Å	17.611(5)	20.304(5)	17.097(9)
<i>c</i> /Å	13.275(4)	12.078(3)	12.788(4)
<i>a</i> <sup>o</sup>	90.50(2)	98.56(2)	104.04(4)
<i>β</i> <sup>o</sup>	109.72(5)	112.41(2)	113.30(3)
<i>γ</i> <sup>o</sup>	76.78(7)	78.80(2)	90.16(5)
<i>V</i> /Å <sup>3</sup>	3081(4)	2764(1)	2768(2)
<i>Z</i>	2	2	2
$\rho$ /g cm <sup>-3</sup>	1.263	1.317	1.353
$\mu$ /cm <sup>-1</sup>	0.377	0.412	0.417
<i>R</i> / <i>wR</i>	0.1316 (0.3214)	0.0562 (0.1563)	0.0398 (0.1273)
GOF	3.384	1.495	1.023
<i>T</i> /°C	23	-55	23

**Table 5** Selected bond distances (Å) and angles (°) for **3a**, **3b** and **3e**

	<b>3a</b>	<b>3b</b>	<b>3e</b>
Mo(1)–P(1)	2.414(3)	2.3964(8)	2.4207(9)
Mo(1)–P(2)	2.480(3)	2.4568(9)	2.4978(9)
Mo(1)–P(3)	2.454(3)	2.4715(8)	2.4612(9)
Mo(1)–P(4)	2.438(3)	2.4315(8)	2.4210(9)
Mo(1)–Si(1)	2.519(3)	2.5188(9)	2.5593(9)
Mo(1)–C(1)	2.10(1)	2.091(3)	2.072(3)
Si(1)–C	1.93(1)	1.911(4)	1.917(3)
	1.89(1)	1.904(3)	1.915(3)
	1.912(8)	1.918(3)	1.899(3)
C(1)–N(1)	1.15(2)	1.136(4)	1.171(4)
N(1)–C(2)	1.45(2)	1.429(5)	1.396(4)
P(1)–Mo(1)–P(2)	80.72(9)	80.48(3)	79.00(3)
P(2)–Mo(1)–P(3)	97.73(9)	99.78(3)	102.15(3)
P(3)–Mo(1)–P(4)	78.97(10)	78.97(3)	80.67(3)
P(1)–Mo(1)–P(4)	103.81(10)	102.33(3)	98.25(3)
C(1)–N(1)–C(2)	169.8(8)	172.3(5)	177.7(4)
Si(1)–Mo(1)–C(1)	149.9(3)	147.20(9)	154.76(9)

**Fig. 3** Molecular structure and atom labeling for **3e**.

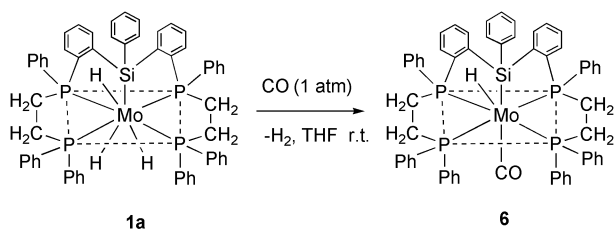
than aliphatic isocyanides, as noted above.<sup>11</sup> The Si1–Mo1–C1 linkages of **3a**, **3b**, and **3e** (149.9(3), 147.20(9) and 154.76(9)<sup>o</sup>, respectively) are bent, while the C1–N1–C2 angles [169.8(8), 172.3(5) and 177.7(4)<sup>o</sup>, respectively] are close to 180<sup>o</sup>. The iso-

cyanide ligand in **3a** and **3b** exhibits greater deviation from linearity than in **3e**. In general, bent C–N–C linkages are found in aliphatic isocyanides, bound to an electron-rich metal centre, while significant C–N–C bending is rare in aryl isocyanide ligands, due in large part to their ability to delocalize charge away from the nitrogen atom on the isocyanide into the aromatic ring.<sup>13</sup>

The structure of **3e** can be compared and contrasted with that of the related molybdenum isocyanide complex, *trans*-[Mo(PhNC)(CO)(dppe)<sub>2</sub>] (**5**), which was synthesized and characterized by Hidai's group.<sup>14</sup> The Mo–C1 bond distance (2.072(3) Å) is nearly identical to that found in **5** (2.072(4) Å) and is longer than that of the known Mo–C bond lengths in other related molybdenum isocyanide complexes, *trans*-[Mo(PhNC)(L)(dppe)<sub>2</sub>] (L = N<sub>2</sub>, PhNC, *p*-MeOC<sub>6</sub>H<sub>4</sub>CN), by about 0.04–0.1 Å.<sup>14</sup> The long bond in **3e** *trans* to the Si atom is thus entirely consistent with the purported strong *trans* influence of the silyl ligand. The C–N–C bond angle (177.7(4)<sup>o</sup>) agrees well with that found in **5** (177.6(3)<sup>o</sup>). Of great interest is the fact that the C1–N1 bond length of 1.171(4) Å in **3e** is considerably longer than that found in **5** (1.099(4) Å), indicating that there is more electron density on the molybdenum atom of **3e** available for back-donation. These observations seem to reflect a difference in the *trans*-influence of the silyl and the carbonyl ligand, although both are known to exhibit a strong *trans*-influence.<sup>5a</sup> As noted above, the *trans*-influence of the silyl ligand can be mainly interpreted in terms of its  $\sigma$ -donor ability. On the other hand, the carbonyl ligand behaves as a strong  $\pi$  acid causing reduction of  $d\pi$  electron density in the metal, and hence the M( $d\pi$ )–CN( $p\pi^*$ ) interaction in **5** would be weaker than that in **3e**. This also explains significant changes in IR C=N stretching frequencies for these complexes. Thus, the value of  $\nu(\text{CN})$  for **3e** (1979 cm<sup>-1</sup>) is considerably lower than that of **5** (2004 cm<sup>-1</sup>(av.)) and the Si ligand plays an important role in enabling the isocyanide function to accept electron density from the metal into the  $\pi^*$  antibonding orbital.

#### Synthesis of the carbonyl complex

To learn more about the properties of the Mo–Si fragment, we have examined the reaction of **1a** with carbon monoxide (Scheme 2). A pale yellow THF solution of **1a** turned green on exposure to 1 atm of carbon monoxide with stirring for 3 h at ambient temperature. The carbonyl complex **6** was obtained as a green powder in a good yield (91%). Coordination of the carbonyl ligand at the molybdenum centre was proved on the basis of the solid-state IR spectrum of **6** (KBr), which shows an intense absorption at 1885 cm<sup>-1</sup> for the CO stretch. The value is much lower than that found in free carbon monoxide (2143 cm<sup>-1</sup>), consistent with the view that the Mo–Si fragment participates in back-donation and can be an excellent  $\sigma$ -donor



Scheme 2

in accord with the results obtained for isocyanides. The  $^1\text{H}$  NMR spectrum of **6** displays a hydrido resonance at  $\delta -6.40$  as an apparent broad triplet  $^2J_{\text{HP}} = 23.3$  Hz. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum for **6** shows a pair of doublets at  $\delta 110$  and  $81$  with coupling constants  $^2J_{\text{PP}} = 58$  and  $61$  Hz in a 1 : 1 ratio.

## Experimental

### General

Unless otherwise noted, all manipulations were conducted using standard Schlenk techniques under purified argon or nitrogen. Commercially available reagent grade chemicals were used as such without any further purification. All solvents were dried by standard methods and were stored under argon. Complexes **1**, **2**<sup>1,2</sup> and phenyl isocyanide<sup>15</sup> were prepared as previously described. All NMR spectra were recorded on a JEOL-JNM-270 spectrometer.  $^{31}\text{P}\{^1\text{H}\}$  NMR peak positions were referenced to external  $\text{PPh}_3$ . Microanalyses were performed but none of the products analyzed properly; carbon percentage values were found to be approximately 2–4% below their calculated values, and reproducibility was poor on samples which were clean as determined by  $^1\text{H}$  NMR. In silicon compounds, carbon contents are occasionally too low due to formation of silicon carbide.<sup>16</sup>

### Synthesis of the isocyanide complexes

A typical procedure is as follows. A mixture of **1a** (88 mg, 0.088 mmol) and *tert*-butyl isocyanide (10  $\mu\text{L}$ , 0.088 mmol) was dissolved in toluene (10 mL) at room temperature. The mixture was stirred for 12 h at room temperature. Slow addition of hexane (about 2 mL) to the solution caused the separation of a precipitate, which was removed by filtration. The resultant filtrate was concentrated to dryness leaving a yellow powder. The crude product was washed with hexane and dried under reduced pressure. The complex **3a** thus obtained could be recrystallized from toluene–hexane to give yellow crystals (95 mg, 72% yield). This procedure is also applicable to the synthesis of the other isocyanide complexes. Experiments listed in Table 1 were carried out under essentially the same conditions.

### Synthesis of the carbonyl complex

A pale yellow solution of **1a** (120 mg, 0.120 mmol) in THF (15 mL) turned green on exposure to 1 atm of carbon monoxide, which was generated by conc.  $\text{H}_2\text{SO}_4$  and  $\text{HCOOH}$ ,<sup>17</sup> with stirring for 3 h at ambient temperature. Slow addition of hexane to the solution caused the separation of a precipitate, which was removed by filtration. The resultant filtrate was concentrated to dryness leaving a green powder. The crude product was washed with hexane and dried under reduced pressure to give **6** (112 mg, 91% yield). IR (KBr)  $\nu(\text{C}=\text{O})$ : 1885  $\text{cm}^{-1}$ ,  $\nu(\text{Mo}-\text{H})$ : 1715  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (270 MHz at 20  $^\circ\text{C}$ , in  $\text{C}_6\text{D}_6$ ):  $\delta -6.40$  (br t, 1H,  $J = 23.2$  Hz, Mo–H), 1.8–3.6 (m, 8H,  $\text{C}_2\text{H}_4$ ), 6.5–8.0 (m, 43H, aromatic).  $^{31}\text{P}\{^1\text{H}\}$  NMR (109.25 MHz at 20  $^\circ\text{C}$ , in  $\text{C}_6\text{D}_6$ ):  $\delta 81.4$  (d,  $J = 61.0$  Hz), 110.3 (d,  $J = 58.0$  Hz).

## X-Ray crystallographic study of **3a**, **3b** and **3e**

Crystals of complexes **3a**, **3b** and **3e** suitable for X-ray crystallography were grown in toluene–hexane at room temperature, and crystals thus obtained were mounted on a glass fiber. Measurement was made on a Rigaku AFC7R (for **3b** and **3e**) or a Rigaku RAXIS-IV (for **3a**) diffractometer by using Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) for data collection. The unit-cell parameters were determined by least-squares fitting of 25 reflections for **3b** and **3e** with ranges  $28.3^\circ < 2\theta < 30.0^\circ$  and  $20.4^\circ < 2\theta < 23.9^\circ$ , respectively. The parameters used during the collection of diffraction data are given in Table 4. The structure was solved and refined by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In compound **3a**, the solvent has been refined isotropically and with no hydrogens. As all the residuals in **3a** are high, there are large residual density peaks, all indicating that the data is poor for refinement.

CCDC reference numbers 194603–194605.

See <http://www.rsc.org/suppdata/dt/b2/b209624m/> for crystallographic data in CIF or other electronic format.

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