

[1 + 4]-Cycloadditions of silylenes to 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene

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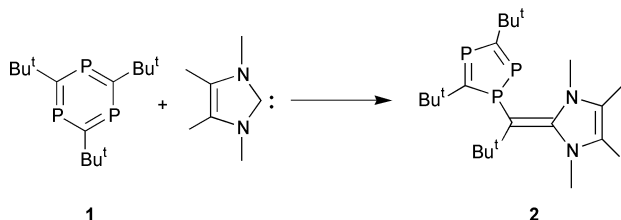
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2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene **1** undergoes [1 + 4]-cycloaddition with the stable bis(amino)silylenes Si[(NCH₂Bu^t)₂C₆H₄-1,2] **3**, Si[(NBu^t)₂C₂H₂] **4** and Si[(NBu^t)₂C₂H₄] **7** to afford the structurally characterised **5**, **6** and **11**. The intermediate aminosilylsilylene resulting from the dissociation of the disilene [Si{(NBu^t)₂C₂H₄}]₂ **9** was trapped as its [1 + 4]-cycloadduct with **1**, which was also structurally characterised. The reversibility of the cycloaddition was demonstrated for **5** through reaction with [Mo(CO)₄(nbd)] to afford [Mo(CO)₃(η⁶-P₃C₃Bu^t₃)] (**13**) and a mixture of *cis*- (**14a**) and *trans*-[Mo(CO)₄(**3**)] (**14b**) of which **14b** has been structurally characterised by a single crystal X-ray diffraction study.

Introduction

Along with the recent flurry of activity in the field of stable 'Arduengo'-type carbenes¹⁻³ (imidazol-2-ylidenes) there is considerable current interest in their heavier silicon analogues.^{4,5} We recently reported⁶ on a remarkable carbene-induced ring contraction of the aromatic 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene⁷⁻⁹ **1** to an aromatic five-membered 1,2,4-triphosphole **2** (Scheme 1) and we were also interested in

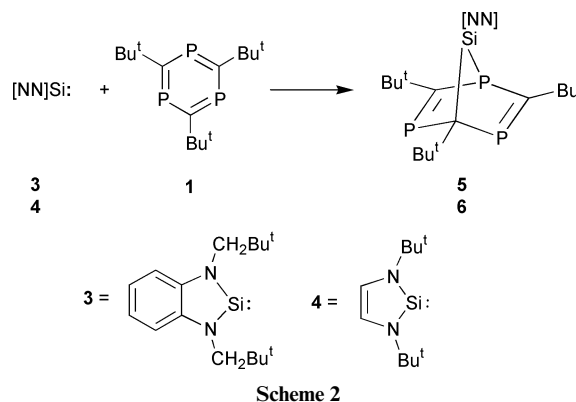


exploring the reactivity of **1** with stable silylenes. To date only a handful of reactions of transient silylenes, R₂Si:, with CP multiple bonds have been reported.¹⁰ Photolytically generated Bu₂Si: undergoes [1 + 2]-cycloaddition with the CP triple bond of phosphalkynes to afford three-membered phosphasilacycloprenes¹¹ whereas Me₂Si: yields four-membered phosphadisilacyclobutenes by insertion of a second silylene moiety into the initially formed phosphasilacycloprenes.¹² Germynes also react with phosphalkynes. A three-membered germaphosphacycloprenes has been isolated from the combination of Ge[CH(SiMe₃)₂]₂ and Bu^tC≡P¹³ whereas reaction of the same phosphalkyne with Ar₂Ge (Ar = 2-Bu^t-3,4,5-Me₃C₆H) unexpectedly affords a four-membered germadiphosphacyclobutene with an exocyclic C=Ge double bond.¹⁴ On the other hand, a solution monomer/dimer mixture of R₂Sn: and R₂Sn=SnR₂ [R = CH(SiMe₃)₂] reacts with the same phosphalkyne to afford the phosphadistannacyclobutene.¹⁵ In this case, there is no NMR spectroscopic evidence for the formation of an initial phosphastannacycloprenes. The isoelectronic stannylene Sn[N(SiMe₃)₂]₂, which exists solely as the monomer, fails to react with Bu^tC≡P. Consequently, this reaction most likely occurs *via* a [2 + 2]-cycloaddition of the distannene rather than

through a [1 + 2]-cycloaddition of R₂Sn: followed by an insertion. In a recent communication¹⁶ we reported the first reaction of a stable silylene, Si[(NCH₂Bu^t)₂C₆H₄-1,2] (**3**),¹⁷ with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**) to afford the [1 + 4]-cycloadduct. We now wish to give a full report on this work as well as its extension to the [1 + 4]-cycloaddition of other stable bis(amino)silylenes and a transient aminosilylsilylene. Evidence for the thermal reversibility of the cycloaddition will also be presented.

Results and discussion

The stable bis(amino)silylenes Si[(NCH₂Bu^t)₂C₆H₄-1,2] **3**¹⁷ and Si[(NBu^t)₂C₂H₂] **4**¹⁸ undergo smooth [1 + 4]-cycloaddition with P₃C₃Bu^t₃ (**1**) to afford **5** and **6** (Scheme 2), respectively, which



have been characterised by analytical and spectroscopic techniques and whose structures were confirmed by single crystal X-ray diffraction studies. Thus, treatment of the pale yellow bis(amino)silylene **3** with the triphosphabenzene in benzene at room temperature afforded the [1 + 4]-cycloadduct **5** as an orange solid in 66% yield after removal of the solvent and recrystallisation from hexane. Similarly, addition of a colourless solution of Si[(NBu^t)₂C₂H₂] **4** to a yellow toluene solution of **1** afforded the [1 + 4]-cycloadduct **6** as dark purple crystals in 80% yield following recrystallisation from hexane.

Table 1 Selected bond lengths (Å) and angles (°) for **6**

Si–N(1)	1.7481(15)	N(1)–C(16)	1.414(2)
Si–N(2)	1.7507(14)	N(2)–C(17)	1.410(2)
Si–C(1)	1.9730(16)	C(16)–C(17)	1.328(3)
Si–P(2)	2.3082(6)		
P(1)–C(2)	1.6874(17)	N(2)–Si–N(1)	92.94(7)
P(3)–C(3)	1.6855(17)	C(1)–Si–P(2)	88.80(5)
P(2)–C(2)	1.8528(17)	C(2)–P(2)–C(3)	98.82(8)
P(2)–C(3)	1.8544(18)	P(3)–C(1)–P(1)	108.38(8)
C(1)–P(1)	1.8550(17)	C(2)–P(1)–C(1)	102.51(8)
C(1)–P(3)	1.8529(17)	P(2)–C(2)–P(1)	119.39(9)

The ^{31}P , ^{29}Si , ^{13}C and ^1H NMR spectroscopic data are in agreement with the proposed [1 + 4]-cycloaddition products. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit the expected doublet and triplet patterns consistent with a plane of symmetry bisecting both the triphosphabenzene and silylene moieties. The doublets at δ 320.4 (**5**) and δ 328.4 (**6**) are characteristic of an unsaturated P environment, while the triplets at δ –63.8 (**5**) and δ –53.9 (**6**) are typical of a saturated P centre. These values compare favourably with those of δ 324.1 and –87.0 reported by Binger *et al.*¹⁹ for the *tert*-butyl substituted tetraphosphabarrelene resulting from the [2 + 4]-cycloaddition of $\text{Bu}^t\text{C}\equiv\text{P}$ and $\text{P}_3\text{C}_3\text{Bu}^t_3$ (**1**). As expected, the ^{29}Si NMR spectra each exhibit a doublet, with chemical shifts of δ 3.8 (**5**) and 2.8 (**6**), which is consistent with a tetravalent Si centre. The $^1J_{\text{SiP}}$ couplings of 7.1 (**5**) and 17.7 Hz (**6**) to the bridgehead P lie within the expected range. Furthermore, the $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra are in accord with the proposed structures with the ^1H NMR spectrum of **6** exhibiting a small four bond coupling of $^4J_{\text{HP}}$ 2.6 Hz to phosphorus between the two vinylic protons in the silylene moiety and the bridgehead P atom. This coupling disappears in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum.

The molecular structure of **5**, full details of which are reported in our initial communication,¹⁶ clearly reveals it to be the [1 + 4]-cycloaddition product of the silylene across the triphosphabenzene ring. The average P=C distance of 1.683 Å and the longer average P–C bond distances of 1.854 Å to the bridgehead P atom and 1.856 Å to the bridgehead C atom are appropriate for this formulation. Likewise, the molecular structure of **6** was confirmed by a single crystal X-ray diffraction study (Fig. 1, Table 1). Similar average bond distances of 1.6865 Å

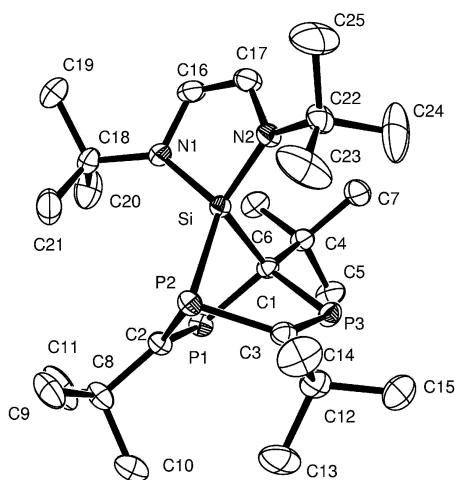
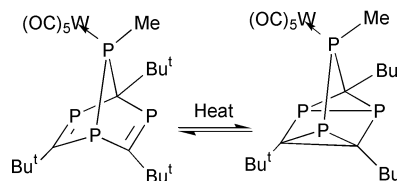


Fig. 1 Molecular structure of **6** (ORTEP without hydrogen atoms, thermal ellipsoids at 20% probability level). Relevant bond lengths and angles are summarised in Table 1.

for the P=C phosphalkene moieties and 1.8536 Å to the bridgehead P atom and 1.8540 Å to the bridgehead C atom for the P–C single bonds were found. X-Ray crystallography confirms that the silylene moieties maintain their planarity in both cases with an average sum of the angles about nitrogen of 359.2° for **5** and 359.7° for **6**. The most significant changes to the silylene-derived fragments in the [1 + 4]-cycloadducts are

summarised in Table 2 and arise due to the formation of a tetravalent Si centre. As a result, the average Si–N bond distance decreases marginally from 1.750 Å in **3** to 1.737 Å in **5** and from 1.753 Å in **4** to 1.749 Å in **6**. Although somewhat counterintuitive, this follows the same trend observed for the pairs (**3**)/[(Si{NCH₂Bu^t}₂C₆H₄-1,2)(μ-Se)]₂ and (**3**)/[(Si{NCH₂Bu^t}₂C₆H₄-1,2)(μ-Te)]₂ in which a decrease to 1.720 and 1.730 Å, respectively, was found for the Si–N bonds.¹⁷ This shortening is in accord with theoretical predictions that bonds to divalent silicon are generally longer than those to tetravalent silicon due to the large p character in the bonding MO.²⁰

NMR scale reactions indicated that these reactions went to completion in under ten minutes at ambient temperature and no intermediates were observed by NMR spectroscopy. Consequently, any discussion of a mechanism for the formal [1 + 4]-cycloaddition, be it concerted or the result of a stepwise process, would be pure conjecture. Lastly, although the [1 + 4]-cycloadduct **5** still contains two P=C double bonds, it failed to undergo any further reaction with excess Si[(NCH₂Bu^t)₂C₆H₄-1,2] (**3**) after heating the reaction mixture at 80 °C for three days as monitored by ^{31}P NMR spectroscopy. Furthermore, heating **5** in *d*₈-toluene at 80 °C for three days gave no ^{31}P NMR spectroscopic evidence for a formal intramolecular [2 + 2]-cycloaddition of the phosphalkene moieties to afford a cage compound analogous to that found to be in equilibrium with the [1 + 4]-cycloadduct of the electrophilic phosphinidene complex [MePW(CO)₅] and $\text{P}_3\text{C}_3\text{Bu}^t_3$ (Scheme 3).²¹



Scheme 3

The silylene Si[(NBu^t)₂C₂H₄] (**7**) with a saturated backbone is less robust in comparison to its unsaturated analogue **4**. West *et al.* have recently shown that **7** reacts with itself *via* insertion into a Si–N bond to form an intermediate aminosilylsilylene dimer **8** which couples to afford a disilene tetramer **9** (Scheme 4).^{22,23} By varying the reaction conditions, it has proven possible to isolate and fully characterise the [1 + 4]-cycloadducts of both the silylene monomer **7** and the intermediate silylene dimer **8** with the triphosphabenzene **1** (Scheme 4).

Under an inert atmosphere, colourless crystals of **7** slowly convert to the red powdery tetramer **9** which has been structurally characterised.²² Dissolution of **9** into an inert solvent yields a concentration dependent mixture of monomeric silylene **7** and disilene **9** with dilution favouring the silylene. The intermediate aminosilylsilylene **8** cannot be observed by NMR spectroscopy but has been trapped as its methanol adduct **10** and characterised by multinuclear NMR spectroscopy.²² Thus by allowing the disilene **9** to dissociate in a THF solution prior to the addition of the triphosphabenzene **1** it was possible to isolate the [1 + 4]-cycloadduct **11** with the monomeric silylene in 19% yield as an orange crystalline solid. On the other hand, the transient aminosilylsilylene was trapped in 17% yield as its yellow [1 + 4]-cycloadduct **12** with $\text{P}_3\text{C}_3\text{Bu}^t_3$ by combining the two solids, adding toluene precooled to –40 °C and allowing the reaction mixture to slowly warm to ambient temperature.

The [1 + 4]-cycloadduct with the monomeric silylene **11** was fully characterised and its properties closely resemble those of the [1 + 4]-cycloadducts **5** and **6**. The ^{31}P , ^{29}Si , ^{13}C and ^1H NMR spectroscopic data are in accord with the proposed structure. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits the expected doublet at δ 340.1 and triplet at δ –48.1. Both of these signals are noticeably deshielded with respect to those of the [1 + 4]-cycloadducts with the aromatic bis(amino)silylenes. As

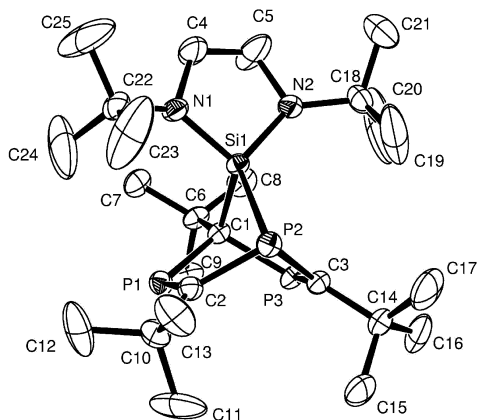
Table 2 Structural data (Å, °) for [1 + 4]-cycloadducts of stable bis(amino)silylenes with P₃C₃Bu^t₃

	Silylene 3 ¹⁶	[1 + 4] 5	Silylene 4 ¹⁷	[1 + 4] 6	Silylene 7 ^{21,22}	[1 + 4] 11
Si–N	1.752(3) 1.747(3)	1.736(3) 1.738(3)	1.753(5)	1.7481(15) 1.7507(14)	1.72	1.739(2) 1.748(2)
N–C(bb)	1.385(5) 1.380(5)	1.408(5) 1.417(5)	1.400(9)	1.414(2) 1.410(2)	1.49	1.449(4) 1.438(4)
C(bb)–C'(bb)	1.417(5)	1.417(5)	1.347(21)	1.328(3)		1.391(5)
N–Si–N	88.2(1)	91.71(14)	90.5(10)	92.94(7)	92.0	94.34(10)
N–C(bb)–C(bb)	111.9(3) 111.3(3)	112.7(3) 112.1(3)	114.1(5)	115.30(17) 115.38(16)		113.4(3) 114.0(3)

bb = silylene backbone.

anticipated, the ²⁹Si NMR spectrum exhibits a doublet at δ 6.7 with a ¹J_{SiP} coupling of 17.0 Hz to the bridgehead P atom.

The molecular structure of **11** (Fig. 2, Table 3) clearly reveals

**Fig. 2** Molecular structure of **11** (ORTEP without hydrogen atoms, thermal ellipsoids at 20% probability level). Relevant bond lengths and angles are summarised in Table 3.

it to be the [1 + 4]-cycloaddition product of the silylene across the triphosphabenzene ring; the average P=C bond distance of 1.684 Å and the longer average P–C bond distances of 1.854 Å to the bridgehead P atom and 1.853 Å to the bridgehead C atom are appropriate for this formulation. X-Ray crystallography confirms that the silylene moiety maintains the puckered ring structure reported for the free silylene. The most significant changes to the silylene-derived fragments in the [1 + 4]-cycloadducts are summarised in Table 2 and arise due to the formation of a tetravalent Si centre. Contrary to the case with the aromatic bis(amino)silylenes **3** and **4**, the average Si–N

Table 3 Selected bond lengths (Å) and angles (°) for **11**

Si(1)–N(1)	1.748(2)	N(1)–C(4)	1.449(4)
Si(1)–N(2)	1.739(2)	N(2)–C(5)	1.438(4)
Si(1)–C(1)	1.982(2)	C(4)–C(5)	1.391(5)
Si(1)–P(2)	2.3249(9)		
P(1)–C(2)	1.685(2)	N(2)–Si(1)–N(1)	94.34(10)
P(3)–C(3)	1.682(2)	C(1)–Si(1)–P(2)	87.74(7)
P(2)–C(2)	1.853(3)	C(2)–P(2)–C(3)	98.40(11)
P(2)–C(3)	1.855(3)	P(3)–C(1)–P(1)	107.47(12)
C(1)–P(1)	1.849(2)	C(2)–P(1)–C(1)	102.71(11)
C(1)–P(3)	1.857(2)	P(2)–C(2)–P(1)	118.96(14)

bond distance increases marginally from 1.72 Å in **7** to 1.744 Å in **11**. A similar lengthening was observed in the structurally characterised 2,3-dimethyl-1,3-butadiene trap of **7**.²³

By allowing the disilene **9** to react directly with P₃C₃Bu^t₃ (**1**) it was possible to catch its dissociation product, the transient aminosilylsilylene **8**, as the [1 + 4]-cycloadduct **12** whose properties vary from those of the previously discussed cycloadducts due to its lower symmetry.

The ³¹P, ²⁹Si, ¹³C and ¹H NMR spectroscopic data support the proposed structure of **12**. The ³¹P{¹H} NMR spectrum reveals three doublets of doublets at δ 367.5, 318.1 and –22.6, the second of which appears as a pseudo-triplet. Once again, these signals are considerably downfield shifted with respect to those of the [1 + 4]-cycloadducts with the aromatic bis(amino)silylenes. The two bond coupling constants of ²J_{PP} 28.1 and 24.1 Hz are similar to those for **5**, **6** and **11**. As expected, the ²⁹Si NMR spectrum exhibits two doublets at δ 38.6 and –30.5, the first of which is assigned to the Si atom straddling the triphosphabenzene moiety on the basis of its larger coupling constant of ¹J_{SiP} 35.6 Hz in comparison to that of ²J_{SiP} 26.3 Hz for the other doublet. These values may be compared to those of δ –24.77 and –34.41 reported for the methanol adduct of **8**.²²

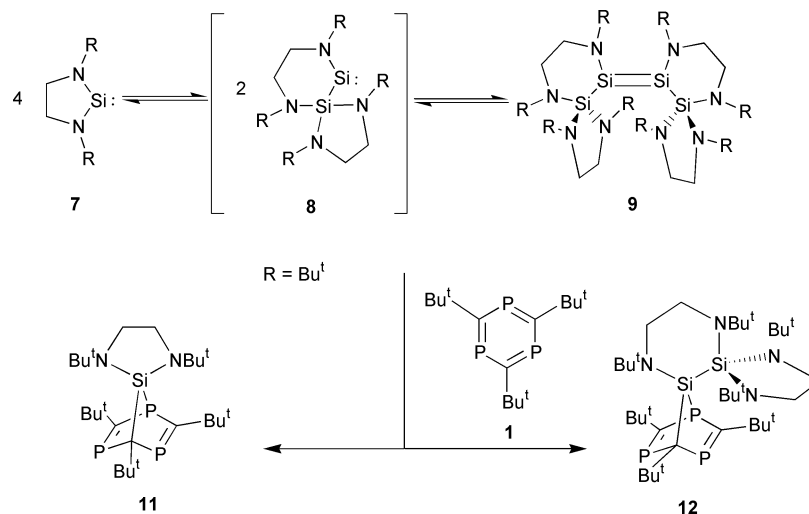
**Scheme 4**

Table 4 Selected bond lengths (Å) and angles (°) for **12**

Si(1)–N(4)	1.7601(15)	Si(2)–N(1)	1.7365(16)
Si(1)–Si(2)	2.4658(7)	Si(2)–N(2)	1.7457(17)
Si(1)–C(1)	2.0258(19)	N(1)–C(16)	1.466(3)
Si(1)–P(1)	2.3055(7)	N(2)–C(17)	1.477(3)
P(2)–C(2)	1.673(2)	C(16)–C(17)	1.509(3)
P(3)–C(3)	1.683(2)		
P(1)–C(2)	1.861(2)	Si(2)–Si(1)–N(4)	97.86(6)
P(1)–C(3)	1.856(2)	N(1)–Si(2)–N(2)	92.99(8)
C(1)–P(2)	1.863(2)	N(3)–Si(2)–Si(1)	97.14(6)
C(1)–P(3)	1.8650(19)	C(1)–Si(1)–P(1)	87.32(6)
Si(2)–N(3)	1.7324(17)	C(2)–P(1)–C(3)	98.34(9)
N(3)–C(26)	1.471(2)	P(3)–C(1)–P(2)	108.52(10)
C(26)–C(27)	1.524(3)	C(2)–P(2)–C(1)	104.29(9)
N(4)–C(27)	1.477(3)	P(2)–C(2)–P(1)	117.51(11)

The previously reported methanol adduct of the aminosilylsilylene (**10**) was only characterised by ^{29}Si and ^1H NMR spectroscopy. As a result, the structurally characterised **12** (Fig. 3,

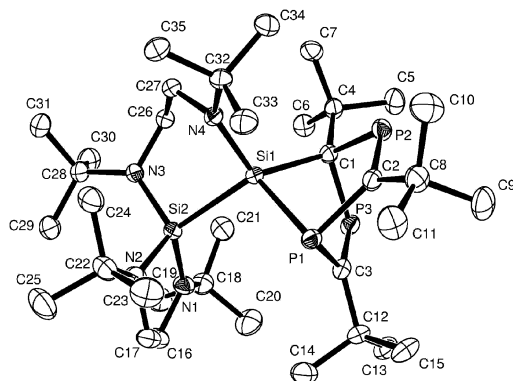
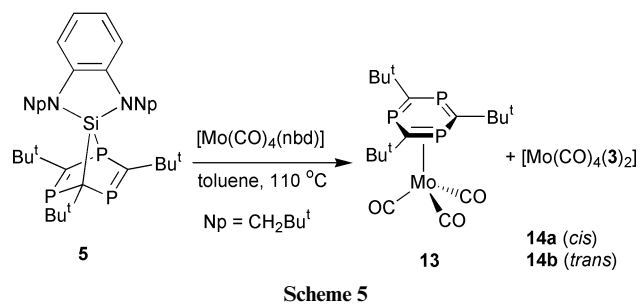


Fig. 3 Molecular structure of **12** (ORTEP without hydrogen atoms, thermal ellipsoids at 20% probability level). Relevant bond lengths and angles are summarised in Table 4.

Table 4) provides definitive proof of the aminosilylsilylene structure. First of all, inspection of the triphosphabenzene moiety reveals small but important differences with the bis(amino)silylene [1 + 4]-cycloadducts. Due to the lack of symmetry of the silylene fragment, the P=C bond distances of 1.673(2) Å and 1.683(2) Å are no longer the same within experimental error. Similar small but real differences are observed for the longer P–C single bonds to the bridgehead P atom: 1.856(2) and 1.861(2) Å. The structural data for the aminosilylsilylene moiety in **12** must be compared with those of both the free monomeric silylene **7** and its disilene tetramer **9**. Firstly, the bond lengths in the silylene unit which has inserted into the Si–N bond of the second are similar to those of the free monomer with the expected increase in the Si–N bond length from 1.72 Å in **7** to an average value of 1.741 Å in **12**. This increase is the same as that found in the [1 + 4]-cycloadduct **11** of the monomeric saturated silylene with the triphosphabenzene (1.744 Å). It is more interesting to look at the structural changes between the trapped aminosilylsilylene fragment and the disilene. To begin with, the Si–Si single bond in **12** is significantly longer than that found in the disilene [2.4658(7) versus 2.2890(14) Å]. Secondly, the Si–N bond length in the six membered ring is longer in **12** [1.7601(15) Å] than in the disilene [1.746(3) Å]. Thirdly, there is a noticeable decrease in the N–Si–Si angle in the six-membered ring of **12** at 97.86(6)° compared to that of 104.27° in the disilene. These structural changes can be rationalised in terms of a change from an sp^3 -hybridised Si centre in the [1 + 4]-cycloadduct to an sp^2 -hybridised centre in the disilene.

Many cycloadditions of silylenes are reversible²⁴ and the cycloaddition of $\text{Si}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4-1,2]$ (**3**) to $\text{P}_3\text{C}_3\text{Bu}_3^t$ (**1**) is another example. The thermal reversibility of the cycloaddition

was shown through two independent trapping experiments. A recrystallised sample of the [1 + 4]-cycloadduct **5** was refluxed in d_8 -toluene in the presence of benzophenone, $\text{Ph}_2\text{C}=\text{O}$, which is known to trap the silylene **3**.²⁵ After two days a small singlet for the free triphosphabenzene at δ_{p} 232.6 had appeared in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum thereby suggesting the thermal reversibility of the silylene addition. In a corroborating experiment, a pure sample of **5** and $[\text{Mo}(\text{CO})_4(\text{nbd})]$ were refluxed in d_8 -toluene in a sealed NMR tube over nine days. This led to the consumption of ca. 60% of **5** and the formation of $[\text{Mo}(\text{CO})_3(\eta^6\text{-P}_3\text{C}_3\text{Bu}_3^t)]$ (**13**) along with a mixture of *cis*- and *trans*- $[\text{Mo}(\text{CO})_4(\mathbf{3})_2]$ (**14a** and **14b**) as revealed by ^{31}P and ^1H NMR spectroscopy (Scheme 5). While **13** is a known com-



ound,^{26,27} **14a** and **14b** were not previously known and were identified on the basis of identical ^1H NMR and mass spectra with an independently prepared sample. The *cis* and *trans* isomers of **14** were assigned from the ^{13}C NMR spectrum of this sample. Thus, **14a** and **14b** were synthesised as a pale yellow powder in 55% yield by the addition of two equivalents of **3** to $[\text{Mo}(\text{CO})_4(\text{nbd})]$ in toluene and were characterised by ^{29}Si , ^{13}C and ^1H NMR and infrared spectroscopies, mass spectrometry and a single crystal X-ray diffraction study in the case of **14b**.

The ^1H NMR spectrum of **14a** and **14b** was particularly revealing. In order to have a singlet for the methylene protons in the neopentyl groups in both the *cis* and *trans* complexes, free rotation must occur around the Mo–Si bonds as well as the N–neopentyl bonds. As it turns out, these processes are slow on the NMR timescale at ambient temperature as evidenced by the very broad singlets for the methylene protons between δ 4.0 and 3.6 which meet in the middle at half height. The methyl protons, however, appear as sharp singlets at this temperature and their integrals indicate that the mixture consists of ca. 70% *trans* isomer (**14b**) and 30% *cis* isomer (**14a**). This ratio is maintained upon heating up to 100 °C at which point the methylene protons appear as sharp singlets at δ 3.88 for the *trans* isomer and δ 3.64 for the *cis* isomer, respectively. The room temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the mixture shows distinct resonances for the *cis* and *trans* isomers with the less intense silylene signals of the *cis* isomer upfield shifted by approximately 0.2 ppm. More importantly, it was possible to observe the ^{13}C NMR carbonyl resonances for both isomers. The *trans* isomer gives one strong resonance at δ 211.5 while the *cis* isomer gives two weaker singlets at δ 212.9 and 211.2 in the expected 1 : 1 ratio. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **14a** and **14b** reveals singlets at δ 156.5 for *trans*- $[\text{Mo}(\text{CO})_4(\mathbf{3})_2]$ (**14b**) and δ 153.7 for *cis*- $[\text{Mo}(\text{CO})_4(\mathbf{3})_2]$ (**14a**), respectively, assigned on the basis of the relative intensities of the signals. These downfield shifts in the ^{29}Si NMR signals from δ 96.9 reported for the free silylene **3**¹⁷ were also found for $[\text{Ni}(\text{PPh}_3)(\mathbf{3})_3]$ (δ 136.2) and $[\text{Ni}(\mathbf{3})_4]$ (δ 145.9)²⁸ and are comparable to that of δ 78.3 for $[\text{Si}(\text{NBU}^t)_2\text{C}_2\text{H}_2]$ (**4**)¹⁸ and δ 119.3 for *trans*- $[\text{Mo}(\text{CO})_4(\mathbf{4})_2]$ (**15**)⁵, δ 97.5 for $[\text{Ni}(\text{CO})_2(\mathbf{4})_2]$,²⁹ δ 110.6 for $[\text{Ni}(\mathbf{4})_3]$ ³⁰ and δ 139.3 for $[\text{Mo}(\text{Cp})_2(\mathbf{4})]$.³¹ Lastly, it should be noted that **14a** is the first example of an octahedral bis[bis(amino)silylene] metal carbonyl complex with the *cis* ligand disposition. It was previously thought that steric constraints would preclude this arrangement, however, **3** is estimated to have a considerably smaller cone angle of 81.3° in

Table 5 Selected bond lengths (Å) and angles (°) for **14b**

Mo–Si	2.4472(6)	N(1)–C(3)	1.405(3)
Mo–C(1)	2.029(2)	C(3)–C(4)	1.411(3)
Mo–C(2)	2.049(2)		
C(1)–O(1)	1.150(3)	C(1)–Mo–C(2)	90.42(8)
C(2)–O(2)	1.139(3)	C(1)–Mo–C(2')	89.58(8)
Si–N(1)	1.732(2)	N(1)–Si–N(2)	90.84(8)
		N(1)–C(3)–C(4)	112.10(18)

comparison to **4** with 118.8° which would reduce the steric repulsion in the *cis* isomer.³⁰

A Nujol mull of the mixture of **14a** and **14b** was analysed by IR spectroscopy and revealed carbonyl stretching frequencies at 1958 (m), 1932 (s), 1910 (s), 1895 (s) and 1873 (sh) cm⁻¹ all of which lie in the expected range for terminally bound CO ligands. One can tentatively assign the strong stretch at 1910 cm⁻¹ to **14b** by comparison with the carbonyl stretch at 1904 cm⁻¹ reported for *trans*-[Mo(CO)₄(**4**)₂] (**15**).³² This stretching frequency would be very similar to that of 1902 cm⁻¹ found for *trans*-[Mo(CO)₄(PPh₃)₂]³³ thereby indicating that silylene **3** and triphenylphosphine exhibit similar overall electronic behaviour as ligands in this case.

It proved possible to grow a single crystal of *trans*-[Mo(CO)₄(**3**)₂] (**14b**) suitable for X-ray diffraction analysis from a saturated toluene solution of the two isomers. The molecular structure shown in Fig. 4 reveals a *trans* disposition of the

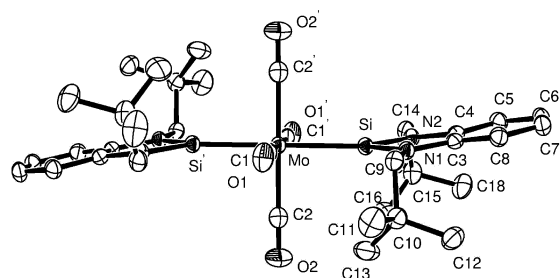


Fig. 4 Molecular structure of **14b** (ORTEP without hydrogen atoms, thermal ellipsoids at 20% probability level). Relevant bond lengths and angles are summarised in Table 5.

silylene ligands which describe a near perfect octahedral environment around the Mo centre with the carbonyl ligands. There are virtually no structural changes in the silylene ligands when compared to the free entity (Table 5). This has been previously observed in the structurally characterised nickel complexes [Ni(PPh₃)(**3**)₃], [Ni(**3**)₄],²⁸ [Ni(CO)₂(**4**)₂]²⁹ and [Ni(**7**)₃].³⁰ Finally, the Si–Mo bond length of 2.4472(6) Å is almost identical to that of 2.471 Å reported for *trans*-[Mo(CO)₄(**4**)₂] (**15**)⁵ and 2.413 Å for [Mo(Cp)₂(**4**)].³¹

It is interesting to note that it was also possible to prepare the [1 + 4]-cycloaddition product **5** along with [Mo(CO)₄(**3**)₂] (**14**) by heating a benzene solution of [Mo(CO)₃(η⁶-P₃C₃Bu^t₃)] (**13**) and the silylene **3** (Scheme 6). There was no evidence in the ³¹P{¹H} NMR or mass spectra for the presence of a molybdenum carbonyl fragment ligated to the [1 + 4]-cycloadduct.

Finally, our attempts to extend the [1 + 4]-cycloaddition to the heavier congeners of the silylenes were unsuccessful. Thus, no reaction was observed on treatment of **1** with M[(NCH₂-Bu^t)₂C₆H₄-1,2] [M = Ge,³⁴ Sn,³⁵ Pb³⁴] or Ge[(NBu^t)₂C₂H₄],³⁶ even at higher temperatures. This general lack of reactivity may be a combination of electronic factors and decreasing bond energies to group 14 elements as one descends the group.

Conclusions

The present work clearly shows the ability of 2,4,6-tri-*tert*-

butyl-1,3,5-triphosphabenzene (**1**) to act as a diene in [1 + 4]-cycloadditions with stable bis(amino)silylenes. Moreover, the transient aminosilylsilylene resulting from the dissociation of [Si{(NBu^t)₂C₂H₄}]₄ (**9**) has been structurally characterised for the first time as its [1 + 4]-cycloadduct with the 1,3,5-triphosphabenzene P₃C₃Bu^t₃ (**1**). The thermal reversibility of the cycloaddition was demonstrated in the case of [(P₃C₃-Bu^t₃)Si{(NCH₂Bu^t)₂C₆H₄-1,2}] (**5**). This reactivity is in stark contrast to the carbon extrusion reaction observed with the imidazol-2-ylidene, C[(NMe)₂C₂Me₂].

Experimental

All experiments were carried out under an inert atmosphere of Ar or N₂ using standard Schlenk and glove-box techniques. Solvents were pre-dried and distilled from appropriate drying agents under an inert atmosphere. Unless otherwise stated, ¹H, ¹³C and ³¹P NMR spectra were acquired on a Bruker Avance 300DPX spectrometer operating at 300.13 MHz for ¹H, 75.47 MHz for ¹³C and 121.49 MHz for ³¹P measurements. ²⁹Si NMR spectra were acquired on a Bruker AMX500 spectrometer operating at 99.33 MHz for ²⁹Si measurements. NMR spectra were referenced to the residual proton/carbon shifts in the internal deuterated solvent (¹H and ¹³C), TMS (²⁹Si) or external H₃PO₄ (³¹P). Unless otherwise stated, NMR spectra were acquired at 25 °C. Mass spectra were acquired on a VG Auto-Spec mass spectrometer operating in EI mode. X-Ray crystal data were collected on an Enraf-Nonius CAD4 (**5**) or an Enraf-Nonius κCCD (**6**, **11**, **12**, **14b**) diffractometer. All structures were refined using full-matrix least-squares refinement on *F*² using SHELXL-97 as included in the WINGX program package. Elemental analysis was performed by MEDAC LTD., UK. 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**),⁸ [Mo(CO)₃(η⁶-P₃C₃Bu^t₃)] (**13**),²⁶ [Mo(CO)₄(nbd)],³⁷ Si[(NCH₂-Bu^t)₂C₆H₄-1,2] (**3**),¹⁷ Si[(NBu^t)₂C₂H₄] (**4**)¹⁸ and [Si{(NBu^t)₂C₂H₄}]₄ (**9**)²² were prepared in accordance with the literature.

[(P₃C₃Bu^t₃)Si{(NCH₂Bu^t)₂C₆H₄-1,2}] (**5**)

P₃C₃Bu^t₃ (**1**) (200.0 mg, 0.666 mmol) and Si[(NCH₂Bu^t)₂C₆H₄-1,2] (**3**) (182.8 mg, 0.666 mol) were dissolved in benzene (20 mL) to afford an orange solution which was stirred for 15 h. Removal of the solvent *in vacuo* gave an orange powder from which a saturated *n*-hexane solution was made. Cooling to -45 °C afforded orange crystals of **5** which were washed with *n*-pentane at -78 °C and dried *in vacuo* (251.3 mg, 66%). Anal. Found: C, 64.08; H, 8.99; N, 5.03. P₃SiN₂C₃₁H₅₃ requires: C, 64.78; H, 9.29; N, 4.87%. ¹H NMR (C₆D₆): δ 6.73–6.79 (m, phenyl, 2H), 6.63–6.69 (m, phenyl, 2H), 3.23 (AB-type, CH₂Bu^t, 4H), 1.55 (s, Bu^t, 18H), 1.38 (s, Bu^t, 9H), 0.95 (s, Bu^t, 18H). ¹³C{¹H} NMR (C₆D₆): δ 218.3 (m, P=C), 111.6, 118.4 and 138.1 (phenyl), 103.1 (td, ¹J_{CP} 64.8, ³J_{CP} 8.4, CSi), 54.1 (s, NCH₂Bu^t), 43.3–43.9 (m, C(CH₃)₃), 36.9 (t, ²J_{CP} 16.2, C(CH₃)₃), 35.4 (d, ⁴J_{CP} 0.4, C(CH₃)₃), 34.5 (dd, ³J_{CP} 14.0, 7.0, C(CH₃)₃), 33.8 (t, ³J_{CP} 9.2, C(CH₃)₃), 29.5 (d, ⁵J_{CP} 2.7, C(CH₃)₃). ²⁹Si{¹H} NMR (99.33 MHz, C₆D₆): δ 3.8 (d, ¹J_{SiP} 7.1). ³¹P{¹H} NMR (C₆D₆): δ 320.4 (d, ²J_{PP} 30.7), -63.8 (t, ²J_{PP} 30.7). MS (EI+): *m/z* 574 (M⁺, 75%), 517 (M⁺ - Bu^t, 25), 300 (P₃C₃Bu^t₃⁺, 10), 274 (silylene⁺, 100), 217 (silylene⁺-Bu^t, 90).

(i) **Reaction of 5 with benzophenone.** A recrystallised sample of [(P₃C₃Bu^t₃)Si{(NCH₂Bu^t)₂C₆H₄-1,2}] (**5**) (5.0 mg, 0.0086 mmol) and benzophenone, Ph₂C=O (6.3 mg, 0.035 mmol), in *d*₈-toluene (0.5 mL) was heated at 110 °C for 2 d in an NMR tube. A singlet at δ_p 232.6 appeared and slowly grew in the ³¹P{¹H} NMR spectrum indicating the formation of P₃C₃Bu^t₃.

(ii) **Reaction of 5 with [Mo(CO)₄(nbd)].** An NMR scale reaction of [Mo(CO)₄(nbd)] (11.5 mg, 0.038 mmol) and

$[(P_3C_3Bu^t_3)Si\{(NCH_2Bu^t)_2C_6H_4-1,2\}]$ (**5**) (22.1 mg, 0.038 mmol) in d_8 -toluene (0.5 mL) was monitored by 1H and $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry as the solution was heated at 110 °C for 9 d. On the basis of the $^{31}P\{^1H\}$ NMR integrals, ca. 60% of **5** was consumed to form $[Mo(CO)_3(\eta^6-P_3C_3Bu^t_3)]$ (**13**), as seen by δ_P 56.0,²⁶ and $[Mo(CO)_4\{Si\{(NCH_2Bu^t)_2C_6H_4-1,2\}_2\}]$ (**14**), on the basis of an identical 1H NMR spectrum in comparison to an independently prepared sample (*vide infra*). Strong molecular ions and the expected fragmentation signals for **13** and **14** were also present in the MS (EI+) of the reaction mixture.

$[(P_3C_3Bu^t_3)Si\{(NBu^t)_2C_2H_2\}]$ (**6**)

A yellow solution of $P_3C_3Bu^t_3$ (225.6 mg, 0.751 mmol) in toluene (5 mL) was added to a colourless solution of $Si\{(NBu^t)_2C_2H_2\}$ (**4**) (147.5 mg, 0.751 mmol) in toluene (5 mL) to afford a dark red solution which was stirred at RT for 17 h. The solvent was removed *in vacuo* yielding **6** as a dark red powder. The [1 + 4]-cycloadduct was recrystallised from a saturated hexane solution at -45 °C as dark purple crystals which were isolated by filtration at -50 °C and washed with hexane (1 mL) at the same temperature (299.9 mg, 80%). Anal. Found: C, 60.21; H, 9.67; N, 5.85. $C_{25}H_{47}N_2P_3Si$ requires: C, 60.46; H, 9.54; N, 5.64%. 1H NMR (C_6D_6): δ 5.61 (d, $^4J_{HP}$ 2.6, $HC=CH$, 2H), 1.75 (s, Bu^t , 9H), 1.55 (s, Bu^t , 18H), 1.17 (s, Bu^t , 18H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 221.2–219.4 (m, P=C), 114.3 (d, $^3J_{CP}$ 1.4, NC=CN), 103.9 (td, $^1J_{CP}$ 63.2, $^3J_{CP}$ 7.4, P=C), 53.7 (s, NC(CH₃)₃), 44.0–43.1 (m, C(CH₃)₃), 38.3 (t, $^2J_{CP}$ 17.1, C(CH₃)₃), 34.7–34.3 (m, C(CH₃)₃), 31.7 (s, C(CH₃)₃). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 2.8 (d, $^1J_{SiP}$ 17.7). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 328.4 (d, $^2J_{PP}$ 28.3), -53.9 (t, $^2J_{PP}$ 28.3). MS (EI+): m/z 496 (M^+ , 80%), 439 ($M^+ - Bu^t$, 35), 396 (5), 383 ($M^+ - 2Bu^t$, 10), 358 (10), 300 ($P_3C_3Bu^t_3^+$, 30), 196 (silylene⁺, 100).

Crystal data. $C_{25}H_{47}N_2P_3Si$, $M = 496.65$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.0847(4)$, $b = 17.7623(5)$, $c = 14.7350(4)$ Å, $\alpha = 90$, $\beta = 101.718(2)$, $\gamma = 90^\circ$, $U = 2840.71(15)$ Å³, $Z = 4$, $D_c = 1.16$ Mg m⁻³, crystal dimensions $0.2 \times 0.2 \times 0.2$ mm, $F(000) = 1080$, $T = 173(2)$ K, Mo-K α , radiation ($\lambda = 0.71073$ Å). Data collection: Kappa CCD. Of the total 8244 independent reflections measured, 6202 having $I > 2\sigma(I)$ were used in the calculations. The final indices [$I > 2\sigma(I)$] were $R1 = 0.047$, $wR2 = 0.103$ and $R1 = 0.072$, $wR2 = 0.114$ (for all data).

CCDC reference number 171464.

$[(P_3C_3Bu^t_3)Si\{(NBu^t)_2C_2H_4\}]$ (**11**)

The disilene $[Si\{(NBu^t)_2C_2H_4\}]_4$ (**9**) (99.9 mg, 0.126 mmol) was dissolved in THF (10 mL) to afford a red solution and stirred at RT for 48 h. The resulting murky yellow mixture was filtered prior to addition to a yellow solution of $P_3C_3Bu^t_3$ (75.6 mg, 0.252 mmol) in THF (5 mL). The resulting red solution was stirred for 72 h at RT. Removal of the solvent afforded a red-brown solid which was extracted with hexane (2×3 mL) to yield a red filtrate that was concentrated and slowly cooled to -25 °C. In addition to yellow needles of unreacted $P_3C_3Bu^t_3$, a dirty brown solid had precipitated after 24 h. The red supernatant was isolated by filtration at -40 °C, concentrated, and

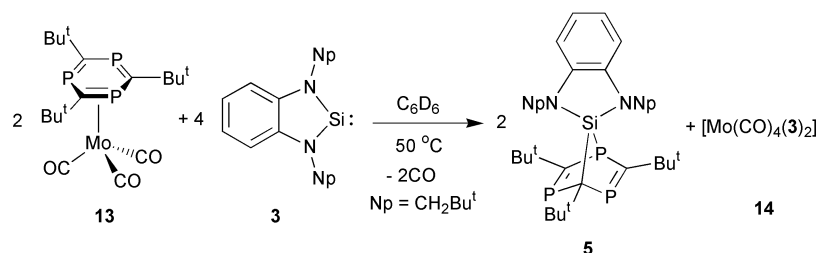
stored at -45 °C. The same process was repeated a second time. The [1 + 4]-cycloadduct **11** was then isolated as an orange crystalline solid by filtration at -65 °C and was washed with hexane (1 mL) at the same temperature (24.4 mg, 19% with respect to $P_3C_3Bu^t_3$). Anal. Found: C, 60.12; H, 10.02; N, 5.79. $P_3SiN_2C_{25}H_{49}$ requires: C, 60.21; H, 9.90; N, 5.62%. 1H NMR (C_6D_6): δ 2.81–2.68 (AA'BB' pattern, CH_2CH_2 , 4H), 1.81 (s, Bu^t , 9H), 1.56 (s, Bu^t , 18H), 1.14 (s, Bu^t , 18H). $^{13}C\{^1H\}$ NMR (125.76 MHz, C_6D_6): δ 222.2–221.1 (m, P=C), 101.5 (td, $^1J_{CP}$ 63.8, $^3J_{CP}$ 7.3, ring C), 53.3 (s, NC(CH₃)₃), 44.9 (s, NCH₂-CH₂N), 43.5–43.2 (m, C(CH₃)₃), 37.9 (t, $^2J_{CP}$ 17.6, C(CH₃)₃), 34.9 (t, $^3J_{CP}$ 9.7, C(CH₃)₃), 34.5–34.2 (m, C(CH₃)₃). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 6.7 (d, $^1J_{SiP}$ 17.0). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 340.1 (d, $^2J_{PP}$ 28.0), -48.1 (t, $^2J_{PP}$ 28.0). MS (EI+): m/z 498 (M^+ , 55%), 483 ($M^+ - CH_3$, 25), 441 ($M^+ - Bu^t$, 5), 426 (5), 383 (95), 345 (45), 300 ($P_3C_3Bu^t_3^+$, 20), 198 (silylene⁺, 20), 183 (silylene⁺-Me, 100).

Crystal data. $C_{25}H_{49}N_2P_3Si$, $M = 498.66$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.0980(3)$, $b = 17.8562(6)$, $c = 14.7586(4)$ Å, $\alpha = 90$, $\beta = 100.983(2)$, $\gamma = 90^\circ$, $U = 2871.11(15)$ Å³, $Z = 4$, $D_c = 1.15$ Mg m⁻³, crystal dimensions $0.4 \times 0.4 \times 0.4$ mm, $F(000) = 1088$, $T = 173(2)$ K, Mo-K α , radiation ($\lambda = 0.71073$ Å). Data collection: Kappa CCD. Of the total 6821 independent reflections measured, 5243 having $I > 2\sigma(I)$ were used in the calculations. The final indices [$I > 2\sigma(I)$] were $R1 = 0.057$, $wR2 = 0.137$ and $R1 = 0.079$, $wR2 = 0.150$ (for all data). One *tert*-butyl group was disordered over two positions.

CCDC reference number 171465.

$[(P_3C_3Bu^t_3)Si\{Si\{(NBu^t)_2C_2H_4\}N(Bu^t)C_2H_4N(Bu^t)\}]$ (**12**)

The disilene $[Si\{(NBu^t)_2C_2H_4\}]_4$ (**9**) (197.0 mg, 0.248 mmol) and $P_3C_3Bu^t_3$ (149.1 mg, 0.497 mmol) were combined. The addition of toluene (8 mL) precooled to -40 °C led to a brown reaction mixture which was allowed to warm to RT overnight with stirring in an acetone bath initially cooled to -40 °C. The reaction mixture was filtered leaving behind **12** as a fine yellow powder which was washed with toluene (2×3 mL) and dried *in vacuo* (55.0 mg, 16%). Crystals suitable for X-ray diffraction study were grown from a saturated hexane solution slowly cooled to -25 °C. Anal. Found: C, 60.23; H, 10.38; N, 7.96. $C_{35}H_{71}N_4P_3Si_2$ requires: C, 60.31; H, 10.27; N, 8.04%. 1H NMR (500.13 MHz, C_6D_6): δ 3.47–3.29 (AA'BB' pattern, 1H), 3.04–3.00 (AA'BB' pattern, 1H), 2.86–2.76 (AA'BB' pattern, 5H), 2.69–2.66 (AA'BB' pattern, 1H), 1.82 (s, Bu^t , 9H), 1.63 (s, Bu^t , 9H), 1.62 (s, Bu^t , 9H), 1.43 (s, Bu^t , 9H), 1.40 (s, Bu^t , 9H), 1.30 (s, Bu^t , 9H), 1.20 (s, Bu^t , 9H). $^{13}C\{^1H\}$ NMR (125.76 MHz, C_6D_6): δ 222.4–221.3 (m, P=C), 103.2 (td, $^1J_{CP}$ 68.5, $^3J_{CP}$ 9.0, P=C), 56.2 (s, NC(CH₃)₃), 55.0 (s, NC(CH₃)₃), 52.1 (s, NC(CH₃)₃), 51.7 (s, NC(CH₃)₃), 51.3 (s, NCH₂CH₂N), 43.9 (t, $^2J_{CP}$ 20.5, C(CH₃)₃), 43.1 (s, NCH₂CH₂N), 42.3 (s, NCH₂CH₂N), 42.2 (s, NCH₂CH₂N), 42.2 (t, $^2J_{CP}$ 20.0, C(CH₃)₃), 38.7 (t, $^2J_{CP}$ 18.9, C(CH₃)₃), 36.2 (dd, $^3J_{CP}$ 11.8, 8.4, C(CH₃)₃), 35.7 (dd, $^3J_{CP}$ 11.3, 8.3, C(CH₃)₃), 33.4 (dd, $^3J_{CP}$ 12.6, 7.3, C(CH₃)₃), 31.0 (s, C(CH₃)₃), 30.7 (d, $^4J_{CP}$ 6.6, C(CH₃)₃), 29.9 (s, C(CH₃)₃), 29.0 (s, C(CH₃)₃). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 38.6 (d, $^1J_{SiP}$ 35.6), -30.5 (d, $^2J_{SiP}$ 26.3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 367.5 (dd, $^2J_{PP}$ 28.1, 24.1), 318.1 (pseudo-t, $^2J_{PP}$ 24.1), -22.6 (dd, $^2J_{PP}$ 28.1, 24.1).



Scheme 6

MS (EI+): m/z 697 (M^+ , 25), 498 ($M^+ - \{\text{Si}(\text{NBU}^t)_2\text{C}_6\text{H}_4\}$, 15), 396 (70), 345 (20), 300 ($\text{P}_3\text{C}_3\text{Bu}_3^+$, 10), 199 (45), 183 (100).

Crystal data. $\text{C}_{35}\text{H}_{71}\text{N}_4\text{P}_3\text{Si}_2$, $M = 697.05$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.3052(3)$, $b = 17.7570(3)$, $c = 21.9827(7)$ Å, $\alpha = 90$, $\beta = 94.840(1)$, $\gamma = 90^\circ$, $U = 4008.3(2)$ Å³, $Z = 4$, $D_c = 1.16$ Mg m⁻³, crystal dimensions $0.4 \times 0.4 \times 0.4$ mm, $F(000) = 1528$, $T = 173(2)$ K, Mo-K α , radiation ($\lambda = 0.71073$ Å). Data collection: Kappa CCD. Of the total 7042 independent reflections measured, 5735 having $I > 2\sigma(I)$ were used in the calculations. The final indices [$I > 2\sigma(I)$] were $R1 = 0.038$, $wR2 = 0.086$ and $R1 = 0.052$, $wR2 = 0.093$ (for all data).

CCDC reference number 171463.

[Mo(CO)₄{Si((NCH₂Bu^t)₂C₆H₄-1,2)}₂] (14)

A yellow solution of Si((NCH₂Bu^t)₂C₆H₄-1,2) (3) (276.5 mg, 1.007 mmol) in toluene (8 mL) at 0 °C was added with stirring to a yellow solution of [Mo(CO)₄(nbd)] (151.2 mg, 0.504 mmol) in toluene (8 mL). The yellow solution was warmed to RT over 14 h in the dark then decanted, due to the presence of a small amount of colourless, clear solid, and concentrated before slowly cooling to -85 °C. [Mo(CO)₄{Si((NCH₂Bu^t)₂C₆H₄-1,2)}₂] (14) precipitated as a pale yellow crystalline solid which was isolated by decantation of the supernatant and washed with pentane (2 × 3 mL) at -80 °C before drying *in vacuo* (209.5 mg, 55%). Single crystals suitable for X-ray diffraction were grown by slowly cooling a saturated toluene solution to -25 °C. The integrals of the ¹H NMR spectrum of the isolated solid indicated that the mixture consisted of ca. 70% *trans*-[Mo(CO)₄{Si((NCH₂Bu^t)₂C₆H₄-1,2)}₂] (14b) and 30% *cis*-[Mo(CO)₄{Si((NCH₂Bu^t)₂C₆H₄-1,2)}₂] (14a). This ratio did not change upon heating the sample up to 100 °C as monitored by variable temperature ¹H NMR spectroscopy. The following data were obtained for the mixture (14a and 14b): Anal. Found: C, 57.16; H, 6.92; N, 7.47. $\text{C}_{36}\text{H}_{52}\text{MoN}_4\text{O}_4\text{Si}_2$ requires: C, 57.12; H, 6.92; N, 7.40%. IR (Nujol mull): ν_{CO} (cm⁻¹) 1958 (m), 1932 (s), 1910 (s), 1895 (s), 1873 (sh). MS (EI+): m/z 758 (M^+ , 10%), 702 ($M^+ - 2\text{CO}$, 40), 646 ($M^+ - 4\text{CO}$, 30), 566 (100), 509 (85).

(i) *cis*-[Mo(CO)₄{Si((NCH₂Bu^t)₂C₆H₄-1,2)}₂] (14a). ¹H NMR (d_8 -toluene, 80 °C): δ 7.09–6.79 (m, phenyl, 8H), 3.63 (s, CH₂Bu^t, 8H), 0.94 (s, Bu^t, 36H). ¹³C{¹H} NMR (125.76 MHz, C₆D₆): δ 212.9 (s, CO), 211.2 (s, CO), 140.6, 118.8 and 110.8 (s, phenyl), 52.5 (s, NCH₂Bu^t), 34.0 (s, C(CH₃)₃), 28.9 (s, C(CH₃)₃). ²⁹Si{¹H} NMR (d_8 -toluene, -25 °C): δ 153.7 (s).

(ii) *trans*-[Mo(CO)₄{Si((NCH₂Bu^t)₂C₆H₄-1,2)}₂] (14b). ¹H NMR (d_8 -toluene, 80 °C): δ 7.09–6.79 (m, phenyl, 8H), 3.86 (s, CH₂Bu^t, 8H), 1.06 (s, Bu^t, 36H). ¹³C{¹H} NMR (125.76 MHz, C₆D₆): δ 211.5 (s, CO), 140.8, 118.8 and 111.3 (s, phenyl), 52.7 (s, NCH₂Bu^t), 34.1 (s, C(CH₃)₃), 29.1 (s, C(CH₃)₃). ²⁹Si{¹H} NMR (d_8 -toluene, -25 °C): δ 156.5 (s).

Crystal data. $\text{C}_{36}\text{H}_{52}\text{MoN}_4\text{O}_4\text{Si}_2$, $M = 756.94$, specimen $0.3 \times 0.2 \times 0.2$ mm, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.1949(3)$, $b = 7.0615(1)$, $c = 26.7601(9)$ Å, $\alpha = 90$, $\beta = 90.555(1)$, $\gamma = 90^\circ$, $U = 1926.40(9)$ Å³, $Z = 2$, $\mu = 0.44$ mm⁻¹, $T = 173(2)$ K, $D_c = 1.31$ Mg m⁻³, $F(000) = 796$, Mo-K α , radiation ($\lambda = 0.71073$ Å). Data collection: Kappa CCD. Of the total 3368 independent reflections measured, 3009 having $I > 2\sigma(I)$ were used in the calculations. The final indices [$I > 2\sigma(I)$] were $R1 = 0.029$, $wR2 = 0.071$ and $R1 = 0.035$, $wR2 = 0.074$ (for all data).

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See <http://www.rsc.org/suppdata/dt/b1/b108020m/> for crystallographic data in CIF or other electronic format.

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