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Mini Review

Chemistry of thermally stable bis(amino)silylenes

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Abstract

This paper provides a comprehensive review of the chemistry of the thermally stable bis(amino)silylenes $Si[(NCH_2Bu^t)_2C_6H_4$-1,2] [abbreviated as Si(NN)] **1** and $Si[N(Bu^t)CH]_2$ [abbreviated as Si(N′N′)] **2** and the somewhat less stable $Si[N(Bu^t)CH_2]_2$ [abbreviated as Si(N″N″)] **3**. In a brief introduction, comments are made on the importance of transient silylenes in organosilicon chemistry and on thermally stable mononuclear silicon(II) compounds having a coordination number greater than two for silicon. The chemistry of **1**–**3** is discussed under the headings: synthesis, molecular and electronic structures, and reactions. The latter are classified into eight categories: (i) nucleophilic additions to an unsaturated organic substrate; (ii) insertions (oxidative addition reactions to the silylene) into a compound containing an O–H, C–Cl, C–Br, C–I or B–C bond; (iii) insertions into a main group element compound having a M–N (M = Li, Na, K), Li–C, Li–Si, or M′(II)–X (M′ = Ge, Sn or Pb; X = C, N, O or Cl) bond; (iv) insertions into a transition metal–X bond; (v) further (see ii) oxidative addition reactions of a chalcogen or Bu^tNC; (vi) reduction reactions; (vii) silylenes as ligands in transition or 4f block metal chemistry, and (viii) silylenes as electrophiles. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silylenes; Organosilicon chemistry; Coordination chemistry; Silylene transition metal complexes; Application in organic synthesis

1. Introduction

A silylene may be defined as a mononuclear, divalent, silicon(II) compound of general formula SiX_2, in which either X^- is a monoanionic, unidentate ligand or $[X_2]^{2-}$ is a bidentate chelating ligand. Thus silicon is in a two-coordinate environment.

Transient silylenes have an important role in synthetic organosilicon chemistry. Atwell and Weyenberg made the seminal discovery that heating the disilane $MeO(SiMe_2)_2OMe$ at the relatively low temperature of 225°C led to a 1,2-shift of a methoxy group, the products being $SiMe_2(OMe)_2$ and $MeO(SiMe_2)_nOMe$ ($n = 3, 4, 5$); the formation of the latter was attributed to the reaction of the transient $SiMe_2$ with the initial disilane [1]. Related thermolyses are used not only in synthetic organosilicon chemistry, but also in fundamental physicochemical studies on gaseous silylenes such as SiH_2 and $SiMe_2$ [2].

The most recent comprehensive review of silylenes is by Gaspar and West [3]. Earlier reviews of transient silylenes, referred to therein, include those by Atwell and Weyenberg [4], Gaspar [5], Liu and Hwang on SiX_2 (X = H, F or Cl) [6] and Weidenbruch on SiX_2 (X = Bu^t, adamantyl or $C_6H_2Me_3$-2,4,6) [7] (see also Section 5).

Two notable examples of thermally stable mononuclear silicon(II) compounds related to silylenes but having multidentate X^- ligands have been reported. The first, by Karsch, et al., is $Si[(PMe)_2C(SiMe_3)]_2$ (**I**), which has a distorted pseudo-trigonal bipyramidal structure with silicon as the spiro centre [8]. The second, decamethylsilicocene, $Si(\eta^5\text{-}C_5Me_2)_2$, has two molecules in the unit cell, one (**II**) with Si at the inversion centre and the other with an angle of 25.3° between the two C_5Me_5 planes [9]; its wide ranging chemistry has been extensively studied by Jutzi and co-workers and is summarised in a recent review [10].

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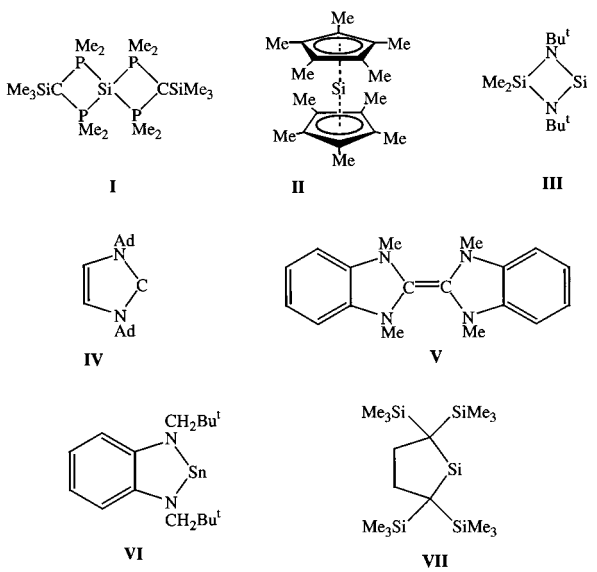
The first bis(amino)silylene $Si[(NBu^t)_2SiMe_2]$ (**III**), stable however only up to 77 K, was obtained by Veith, Schnöckel and co-workers in 1992, by photolysis of the azide $(N_3)_2Si[(NBu^t)_2SiMe_2]$ in benzene in an argon matrix [11]. For the labile $Si(NPr^i_2)_2$ (see Section 4.2).

The major breakthrough in the chemistry of thermally stable silylenes was the report by Denk, West, Haaland and their collaborators in 1994 of the synthesis and gas phase structure of $Si[N(Bu^t)CH]_2$ [12]. Their use of a 1,4-diazabuta-2,3-diene ligand [13] had received a new lease of life by the discovery in 1991 by Arduengo and co-workers of the thermally stable carbene $C[N(Ad)CH]_2$ (Ad = adamantyl) (**IV**) [14].

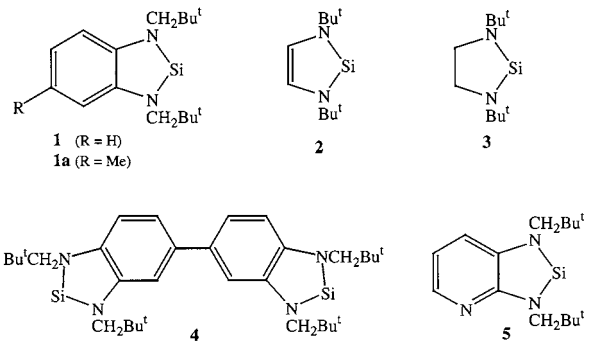
Our entry into the field was disclosed in a 1995 paper on the synthesis and the first X-ray structure of a thermally stable bis(amino)silylene, namely *N,N′*-dineopentyl-1,2-phenylenediaminosilylene $Si[(NCH_2Bu^t)_2C_6H_4\text{-}1,2]$ [15]. Our interest in developing this chemistry has the following antecedents. On the one hand, the Lappert group has a long standing interest in bis(amino)metallenes $E(N<)_2$ of the Group 14 elements. These have included bis(amino)carbenes such as $C[N(R)CH_2]_2$ as ligands [16], and their dimers, including **V** [17]; and thermally stable, monomeric divalent Ge(II), Sn(II) and Pb(II) compounds $M[N(SiMe_3)_2]_2$, which were the first heavier Group 14 metal carbene analogues to be characterised [18]. More recently, the stannylene **VI** has been reported [19] and the isoleptic Ge(II) and Pb(II) compounds have also been obtained [20]. On the other hand, Dr Gehrhus had a useful background in studying the chemistry of various transient silylenes [21].

An important contribution on thermally stable silylenes was the report by Kira and co-workers on the first isolable dialkylsilylene **VII**, which slowly isomerised at ambient temperature in solution to yield $Si(SiMe_3){:}C(SiMe_3)(CH_2)_2C(SiMe_3)_2$ [22].



2. Synthesis

The thermally stable silylenes which have been prepared are **1**–**5**. The saturated compound **3** is less stable, but sublimes as a monomer, although it was initially thought to dimerise (but see Section 4.1) in the solid state [23]. Molecular structural data are available for **1**–**4** (Section 3); evidence for **5** rests on microanalytical and spectroscopic results [24]; in view of the fact that **1** reacts with pyridine (Section 4.1), its stability is surprising.



The general method of synthesis involves the dehalogenation of the appropriate dihalogenosilane. This was first employed for the generation of **2** from the dichlorosilane of Eq. (1), potassium and tetrahydrofuran (THF) at 65°C [12]; full details are in Ref. [25]. Compound **3** was originally obtained from the difluorosilane of Eq. (2) and Rieke magnesium in THF [23]; treatment of the corresponding dibromide (but less successfully the dichloride) with potassium in THF was later employed [26]. The use of potassium-graphite as reducing agent at ambient temperature was found to be more effective for the synthesis of **1** and **4** from the appropriate dichlorosilane (Eq. (3)) or tetrachlorodisilane (Eq. (4)) [27] than the reduction with potassium in THF at 70–80°C for 2 days [15]. The preparation of the precursor for **5** is shown in Eq. (5); the reducing agent was K in THF [24]. Some characterising data on **1**–**5** are in Table 1.

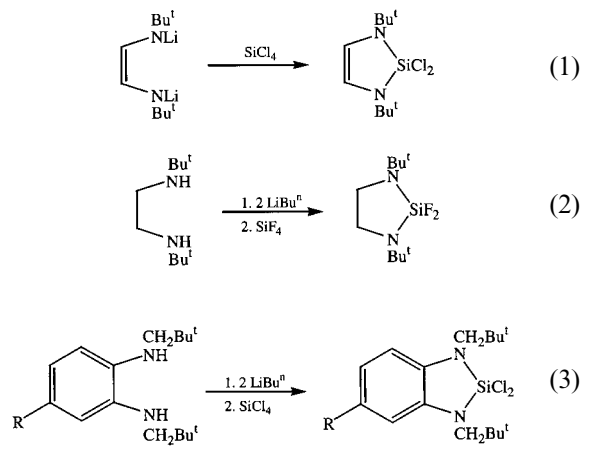


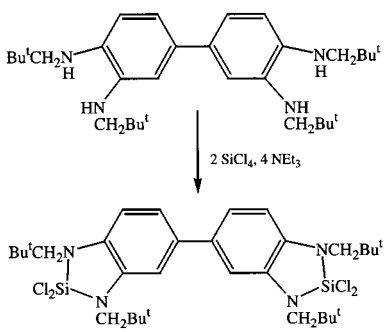
Table 1
Some data on the bis(amino)silylenes **1**–**5**

Silylene	M.p. (°C)	B.p. (°C/torr)	$\delta[^{29}Si\{^1H\}]$ (C_6D_6, 25°C)	Colour	Ref.
1	61–62	112–113/10^{-4}	96.9	Yellow	[15,28]
1a	88	(subl. <150/10^{-5})	97.7	Yellow	[15,28]
2	ca. 220 (decomp.)	70/10^{-1}	78.3	Colourless	[12,25]
3			119	Colourless	[23,26]
4	201–203 (decomp.)		96.6	Yellow	[27]
5	64–65	(subl. 105/10^{-5})	95.1	Yellow	[24]

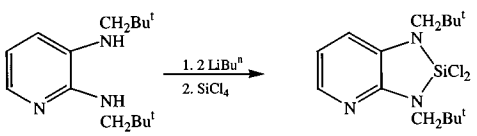
Table 2
Selected structural parameters for the bis(amino)silylenes **1**–**4**

Silylene	Si–N (Å)	C(1)–N (Å)	C_{sp2}–C_{sp2} (Å)	N–Si–N′ (°)	N–C–C (°) (endocyclic)	C–N–Si (°) (endocyclic)	C–N–Si (°) (exocyclic)	Ref.
1[a]	1.752(3)	1.385(5)	1.417(5)	88.2(1)	111.3(3)	114.1(2)	122.6(3)	[15,28]
	1.747(3)	1.380(5)			111.9(3)		123.7(3)	
2[b]	1.753(5)	1.400(9)	1.347(21)	90.5(10)	114.1(5)			[12]
3[a]	1.719(3)	1.489(6)		92.0(2)	106.2(7)	113.2(3)		[23,30]
4[a]	1.742(1)	1.395(4)	1.406(4)	89.02(12)	111.5(3)	113.5(2)	123.9(2)	[27]
	1.740(3)	1.396(4)			112.0(3)	113.8(2)	124.2(2)	

[a] X-ray.
[b] GED.



(4)



(5)

3. Molecular and electronic structures

X-ray data are available for the bis(amino)silylenes **1**, **3** and **4** and gas electron diffraction data on gaseous **2**. Selected geometric parameters are listed in Table 2. The saturated compound **3** has a puckered ring [3,23], whereas in the unsaturated analogue **2** the ring, as in **1** [15,28] is planar [12].

The electronic structures of the bis(amino)silylenes **1**–**3** have been probed by He(I) and He(II) photoelectron spectroscopy. The first of such studies was on **2** and **3** in 1994 [23,31] and was followed by data on **1** [32]. The highest occupied molecular orbitals were assigned with the aid of quantum mechanical calculations, as shown in Table 3. Such calculations were also reported on the isodesmic reactions of model compounds (in which for each of **1**–**3** the *N*,*N*′-substituents were replaced by hydrogen); for **2** and **3**, this was the reaction with H_2 [23,31], while for **1** and **2** it was for the reaction $2NH_3 + 2CH_4 + SiH_2$ [32]. Regarding **2** and **3**, the model hydrogenation reaction was calculated to be ca. 14 kcal mol^{-1} less exothermic for the unsaturated compound, indicative of a significant π-electron delocalisation in the five-membered ring of **2** [23,31]. For **1**, a 0.41 eV stabilisation of the HOMO from the silane $H_2Si[(NH)_2C_6H_4\text{-}1,2]$ to the silylene $Si[(NH)_2C_6H_4\text{-}1,2]$ was calculated, consistent with incorporation of the formally empty Si out-of-plane orbital with the π-system [32], a notion supported by the isodesmic reactions.

Aromatic delocalisation in **1** and **2** was further confirmed (see, however, Ref. [31]) by a number of theoretical studies, some of which have involved comparisons between **2** and the isoleptic carbene and germylene [33].

Table 3
Observed ionisation energies (eV) for the silylenes **1**–**3**

Photoelectron band	**1** [32]	**2** [31]	**3** [23]	Assignment
1st Band	7.32	6.96	7.54	b_1 ring π
2nd Band	7.91			a_2 phenyl π
3rd Band	8.55	8.21	8.11	a_1 Si lone pair

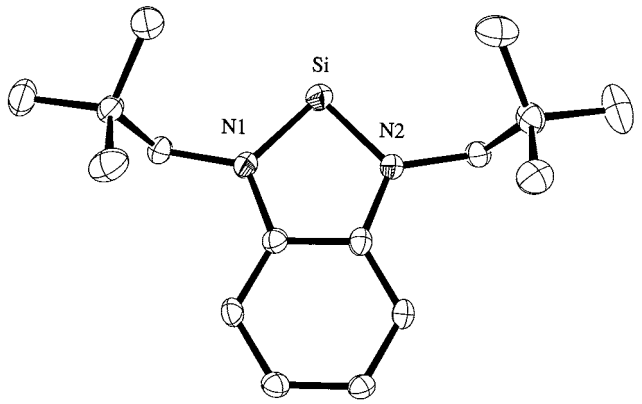


Fig. 1. The molecular structure of the crystalline silylene **1** [28].

Table 4
Observed chemical shift tensors for the silylenes **1**–**3** [34]

Silylene	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	CSA
1	92.5	316.4	21.1	−60.0	376.4	335.8
2	75.2	284.9	−16.1	−43.3	328.2	314.6
3	114.7	350.7	−2.1	−4.5	355.2	354.0

As well as electronic factors which influence the stability of **1**–**5**, it is clear that steric factors also have a role, the bulky substituents on the nitrogen atoms shielding the silylene atom from dimerisation (for **3**, however, see Section 4.1). This is illustrated by examining the molecular structure of the crystalline silylene **1**, shown in Fig. 1 [15,28].

Although, as will be illustrated in Section 4, the bis(amino)silylenes behave as both nucleophiles and (rarely) electrophiles, using the nomenclature based on carbenes, they may be described as nucleophilic silylenes. This is consistent with (i) the $^{29}Si\{^1H\}$-NMR spectroscopic chemical shift for the Si(II) nucleus being at much higher frequency in the dialkylsilylene **VII** (δ 567.4) [22] than in **1**–**5** (Table 1); and (ii) the n(Si) → $3p_\pi$(Si) band being at lower frequency in the red **VII** (λ_{max} 440 nm) [22] than in the yellow **1**, **4** or **5**: λ_{max} for **1**, 344 nm [28] and 302 nm for **5** [24].

The chemical shift tensors for **1**–**3** were determined from ^{29}Si CPMAS-NMR spectra and the results (Table 4) correlated reasonably with calculations using MO methods, as well as with DFT-GTAO, MP2/GIAO and IGLO calculations on models for **2** and **3** in which the *N*,*N′*-substituents were taken as hydrogen [34]. The data were supportive of π-delocalisation in each of **1** and **2**, with some degree of aromatic character.

4. Reactions

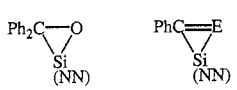
The first reports (in 1994) of the chemical behaviour of a stable bis(amino)silylene dealt with compound **2**; it was unreactive towards each of $HSiEt_3$, NEt_3, C_5H_5N, or THF but with $[Ni(CO)_4]$ formed the silylene complex $[Ni(CO)_2(\mathbf{2})_2]$, which was X-ray characterised [35]; with Me_3SiN_3 or Ph_3CN_3 in THF, $\mathbf{2}(N_3)N(SiMe_3)_2$ and the X-ray characterised $[\mathbf{2}(NCPh_3)(THF)]$ complexes were obtained [36]. A year later it was shown that **1** formed the oxidative adducts **1**(H)OEt and **1**(I)Me with EtOH and MeI, respectively [15,28]. In the intervening years the chemistry of **1**–**3** has been elaborated further, as described in Sections 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8.

4.1. Nucleophilic addition reactions of a bis(amino)silylene to an unsaturated organic compound

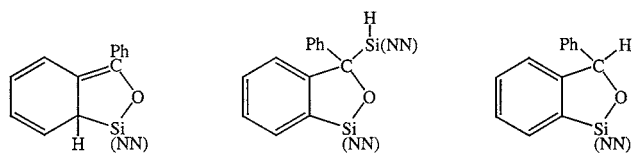
The unsaturated substrates which have proved to be reactive are a diene, an alkyne and various carbonyls, imines and azides, a nitrile, an isonitrile, pyridine, quinoline and a triphosphabenzene.

Some reactions of **1** [abbreviated as Si(NN)] were briefly summarised in a preliminary publication [37]. These included those shown in Scheme 1, for which full details have not been published, yielding the crystalline tetravalent silicon compounds **6**–**11** (Ad = adamantyl). X-ray data are available for **7**, **8** and **9** and ^{29}Si-NMR spectral chemical shifts were recorded: δ −9.11 (**6**), 19.02 and 26.33 (**7**), −17.84 (**8**), −15.96 and −39.31 (**9**), −28.49 (**10**) and −38.13 (**11**). Similarly, a review article referred to the reactions of **2** [abbreviated as Si(N′N′)] shown in Scheme 2 [38], giving rise to compounds **12**–**15**. Compounds **13** ($\delta[^{29}Si]$ −46.9) and the X-ray-characterised **15** ($\delta[^{29}Si]$ −66.6) had been published earlier [36]. It is likely that a common intermediate in the azide reactions is the appropriate iminosilane >Si=NR, which with **1** → **10**, with AdN_3 → **11** or **14** and with Me_3SiN_3 → **13**.

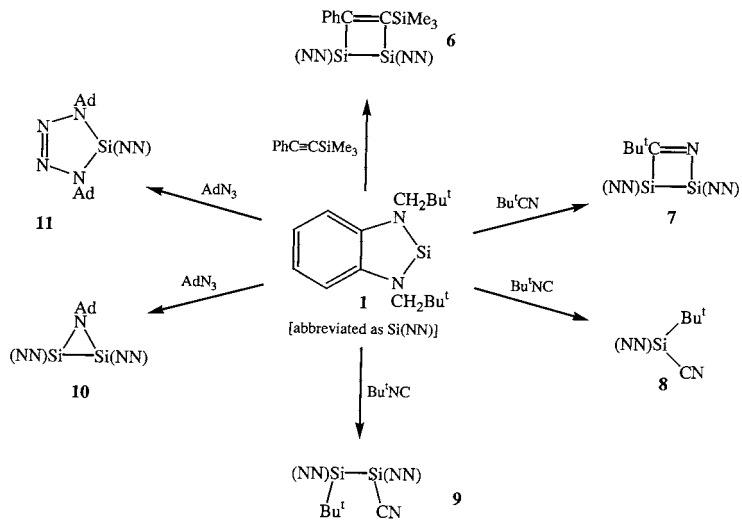
The reactions of **1** with various carbonyl compounds, summarised in Scheme 3, yielded the tetravalent silicon compounds **16**–**19** [39]. The diverse X-ray characterised products **16a** or **17** (a single diastereomer) from **1** and benzophenone (dependent on the reaction conditions employed) are particularly noteworthy. Compounds **16a**, **6** and **7** (Scheme 1) were believed to have arisen via a three-membered ring intermediate **VIIIa** or **VIIIb**, which readily underwent Si(NN) insertion into the Ph_2C–Si or PhC–Si bond, respectively. The formation of **17** was interpreted as involving successive intermediates **VIIIa**,



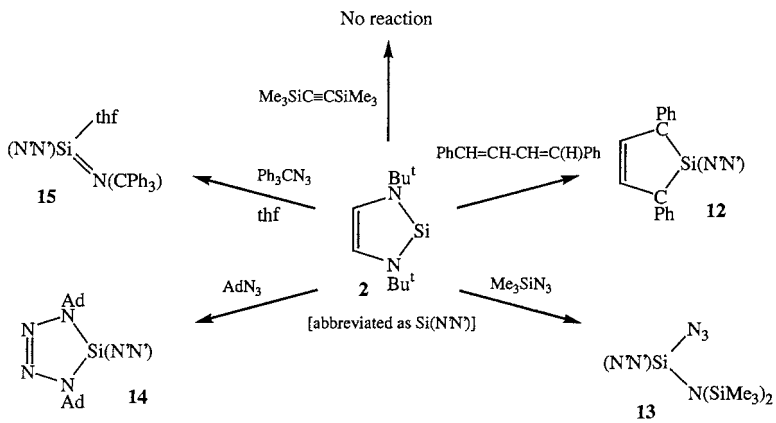
VIIIa VIIIb



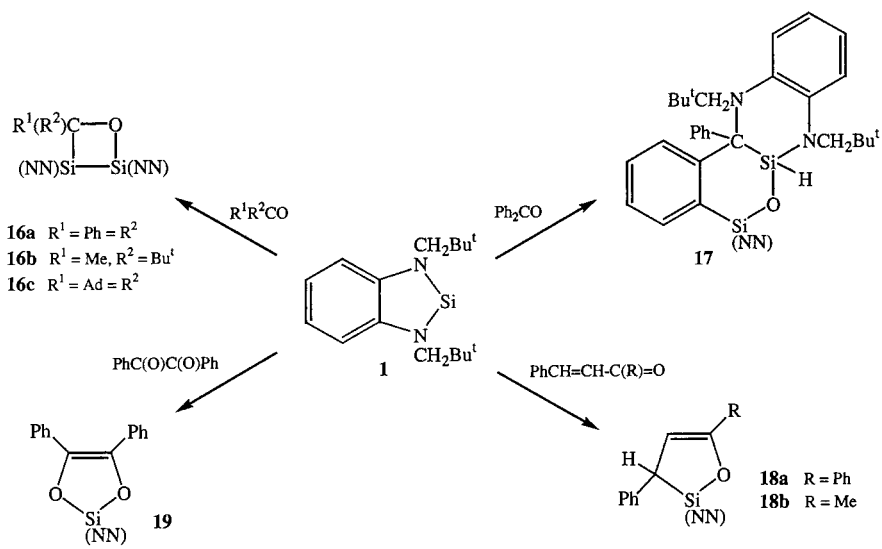
IX X XI



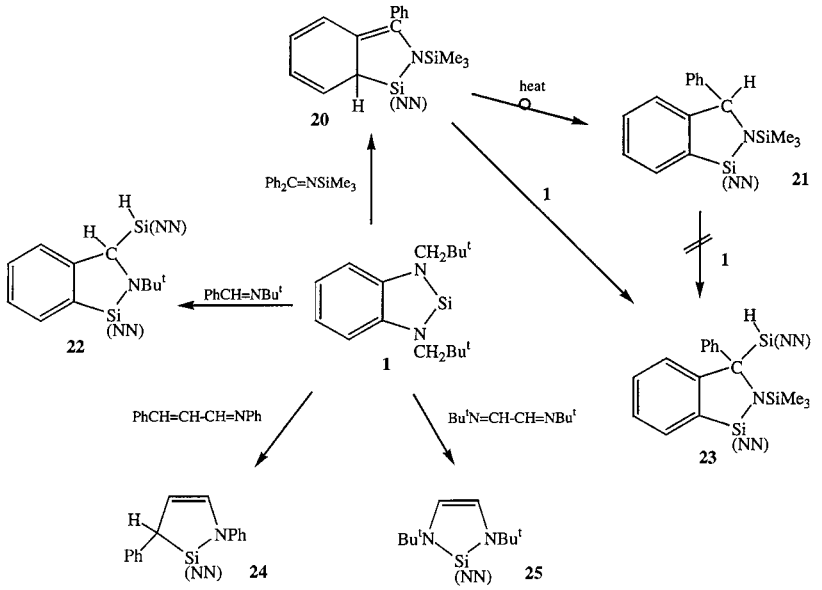
Scheme 1.



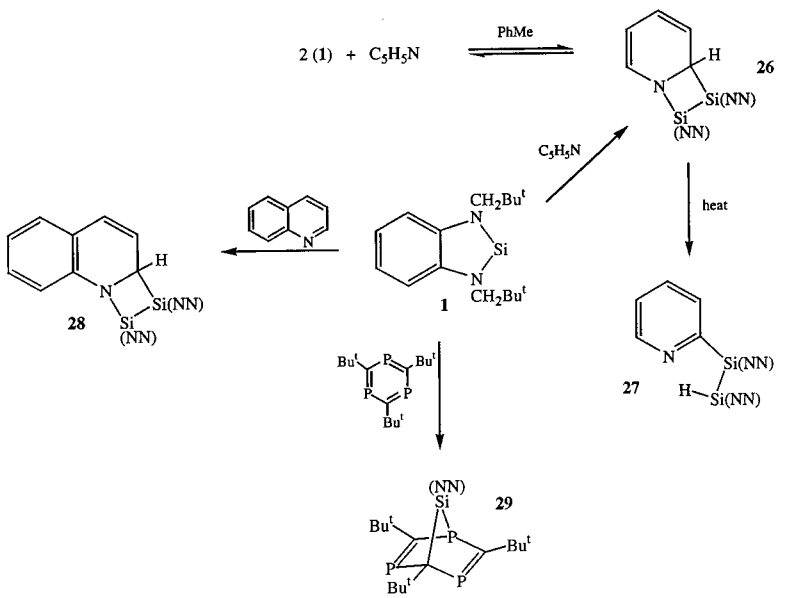
Scheme 2.



Scheme 3.



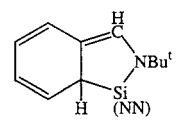
Scheme 4.



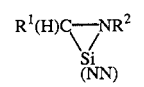
Scheme 5.

its rearranged dearomatised product **IX** and **X**; a possible intermediate along the pathway **IX** → **X** may have been **XI**.

The reactions of **1** with various imines, summarised in Scheme 4, yielded the tetravalent silicon compounds **20**–**25**; X-ray data were provided for **22** [40]. Thus, **1** with $Ph_2C=NSiMe_3$ at ambient temperature gave **20**, which slowly, or more rapidly on heating, afforded the thermodynamic rearranged product **21**. In contrast, under similar conditions, **1** and $PhCH=NBu^t$ furnished the X-ray-characterised 2:1 adduct **22**. A similar 2:1 adduct **23** from **1** and $Ph_2C=NSiMe_3$ required that the reagents be mixed in appropriate proportions, but **21** was not an intermediate along the pathway to **23** as it failed to react with **1**. Although an intermediate in the conversion of $\mathbf{1} + PhCH=NBu^t \rightarrow \mathbf{22}$ was not detected, it was suggested that a compound **XII** related to **20** may have played a role. An intermediate **XIII** along the pathway to **24** and **25** was proposed (analogous to **VIIIa** and **VIIIb**).



XII



XIIIa $R^1 = (CH)_2Ph$, $R^2 = Ph$
XIIIb $R^1 = (CH)NBu^t$, $R^2 = Bu^t$

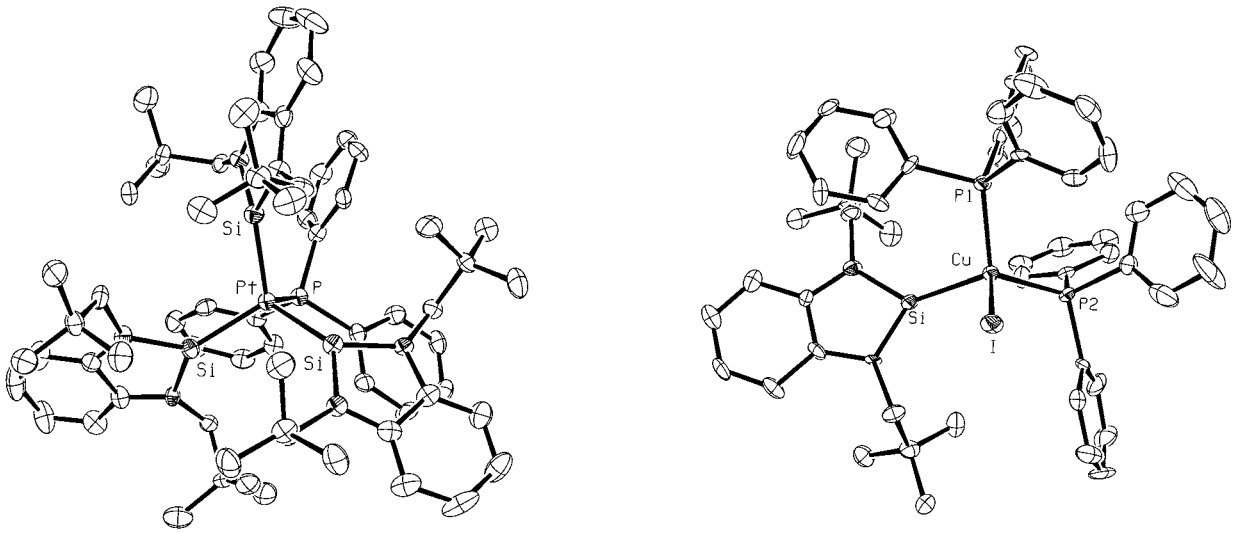
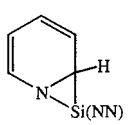


Fig. 2. The molecular structures of the Pt-silylene complex **70** [71] and the Cu–silylene complex **71** [27].

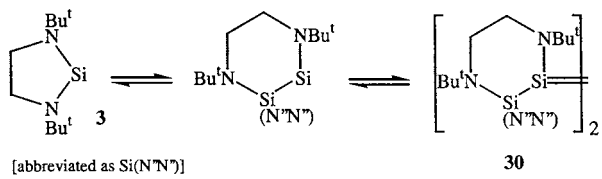
The reactions of **1** with pyridine and quinoline [27] and 2,4,6-tri-*t*-butyl-1,3,5-triphosphabenzene [41], summarised in Scheme 5, yielded the crystalline compounds **26**–**29**. Compound **26** in solution was partially dissociated. Compounds **26**, **27** and **29** (Fig. 2) were X-ray characterised. The formation of the bi- (**26**) or tricyclic (**28**) compounds probably proceeded via a three-membered intermediate **XIV**, or its quinoline-based analogue, (similar to **VIIIa**, **VIIIb** and **XIII**) followed by insertion of **1** into the C–Si or N–Si bond. Compound **29** is particularly interesting, being an example of a [1 + 4]-cycloaddition of a silylene to the triphosphabenzene [41].



XIV

An aspect regarding complexes **6**–**29** that may be worth exploring is to ascertain whether the (NN) or (N′N′) substituents may be regarded as protecting groups.

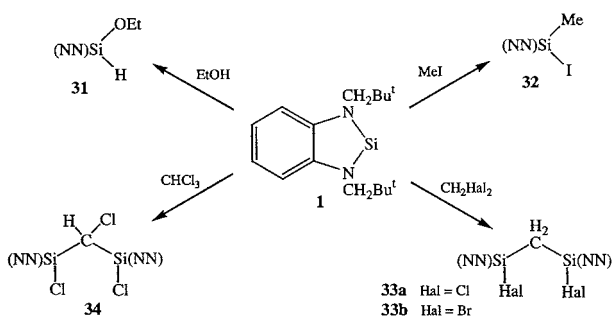
Some, but not all, of the tetravalent silicon-containing heterocycles **6**–**29** have skeletal precedents. Thus, various cyclic Si(IV) compounds have been obtained from transient silylenes or a disilene [42]. Of the former, among such silylenes have been $SiBu^t_2$ (generated photolytically from its trimer) [43], $SiMe_2$ or SiMe(OMe) (generated thermally) [44], Si(Me)Ph [45], $Si(C_6H_2Me_3\text{-}2,4,6)_2$ [46], $Si(C_6H_3Pr^i_2\text{-}2,6)_2$ [47], or $Si(C_6H_4CH_2NMe_2\text{-}2)_2$ [48]. The bis(diisopropylamino)silylene was trapped by triethyl(vinyl)silane or 2,3-dimethylbuta-1,3-diene [49]. Although it showed some stability at ambient temperature, it was believed to be in equilibrium in toluene solution with its dimer $[Si(NPr^i_2)_2]_2$ [49]. The latter was also generated photolytically from the [1 + 2] cycloadduct of $Si(NPr^i_2)_2$ and $Me_3SiC{\equiv}CSiMe_3$ in 3-methylpentane; its structure was based on UV–vis bands at 335 and 438 nm. However, the X-ray-characterised, crystalline tetramer **30** of the silylene **3** [abbreviated as Si(N″N″)] was a component of the dynamic equilibrium shown in Eq. (6), and **30** in hexane had similar absorption bands at 360 and 476 nm [50].



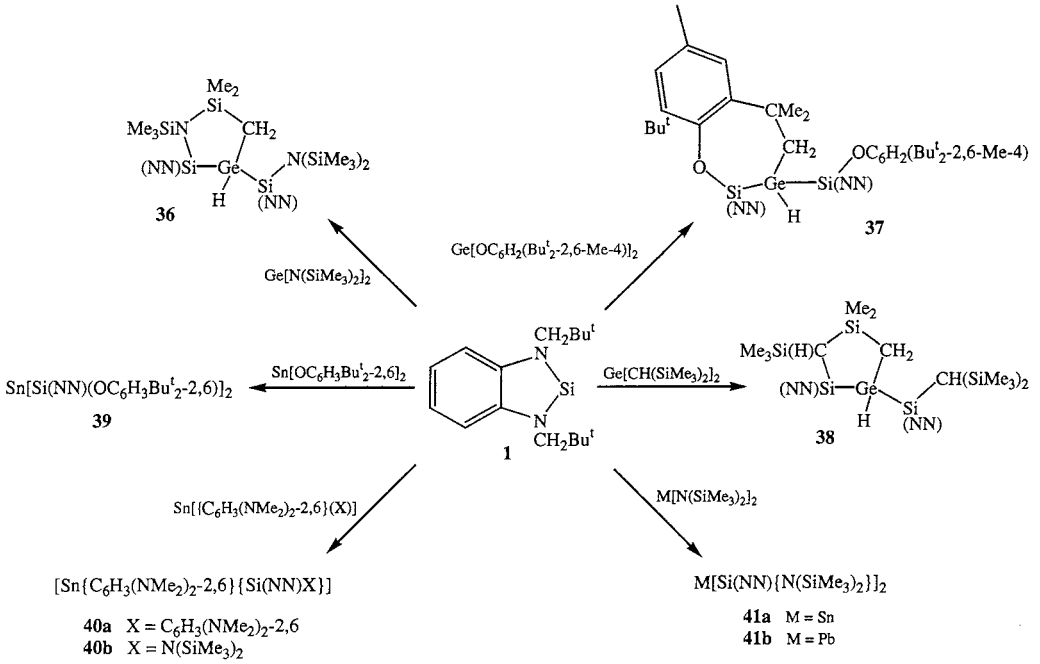
(6)

4.2. Insertion of a bis(amino)silylene into a compound containing an O–H, C–Cl, C–Br, C–I or B–C bond

The first oxidative addition reactions of an organic compound A-B to a stable bis(amino)silylene, yielding the adducts =Si(A)B (**31** and **32**), were those with EtOH and MeI [15,28]. Reactions with a chloro- or bromoalkane were later elaborated to include the adducts **33** and **34**, with CH_2Cl_2, CH_2Br_2 and $CHCl_3$ (Scheme 6)

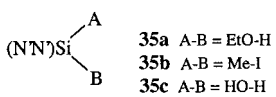


Scheme 6.



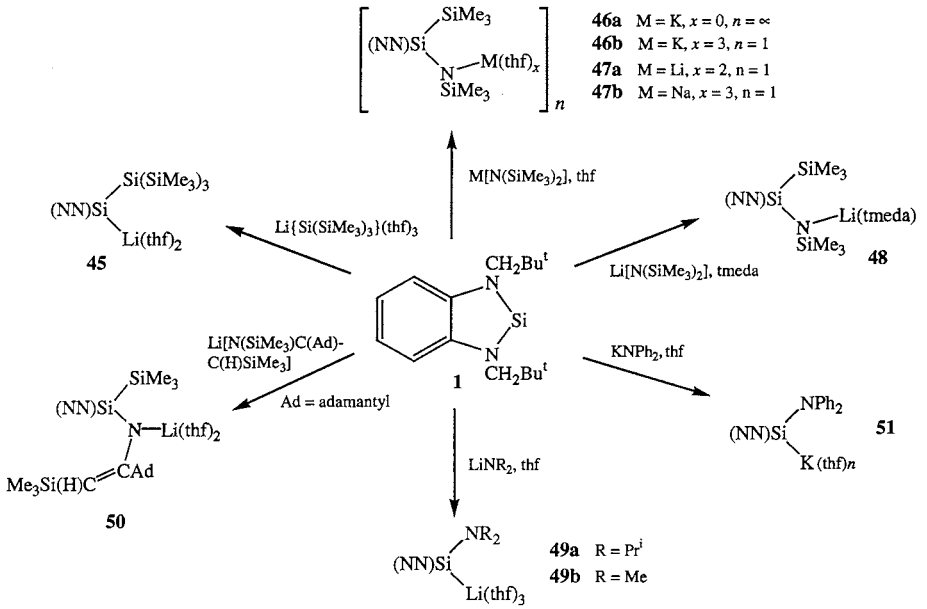
Scheme 7.

[27]. The mechanism of at least some of the C-Hal insertions may well be free radical, involving transient radical pairs $^{\bullet}$Si(NN)Hal/B$^{\bullet}$ (B = Me, CH_2Cl, CH_2Br or $CHCl_2$), by analogy with related reactions of $Sn[N(SiMe_3)_2]_2$/RHal which had been studied mechanistically [51]. Similar reactions of the silylene Si(N′N′) (**2**) with EtOH or MeI generated the adducts **35** [25]. The X-ray characterised disiloxane $O[Si(N'N')H]_2$ was isolated from **2** and water, presumably via **35c** as an intermediate. The reaction of the silylene **2** with $B(C_6F_5)_3$ yielded a 1:1 adduct which rearranged slowly in toluene solution, with a half-life of about 1 month at ambient temperature to yield the oxidative adduct $[(N'N')Si\{B(C_6F_5)_2\}(C_6F_5)]$ [52].

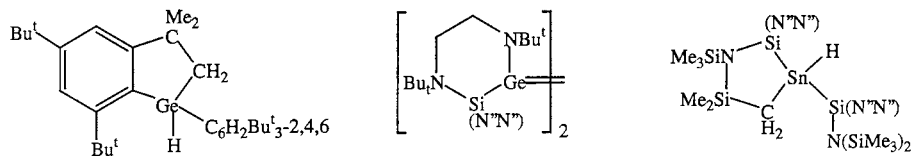


4.3. Insertions of a bis(amino)silylene into a compound having an M–N (M = Li, Na, K), Li–C, Li–Si, or M′(II)–X (M′ = Ge, Sn or Pb; X = C, N, O or Cl) bond

Attempts to make heterobimetallic unsaturated compounds by coupling the bis(amino)silylene with a different Group 14 element carbene analogue (or for a carbene, see Section 4.8) led to the chemistry summarised in Scheme 7. Each of the new compounds **36**–**41**, except **40b**, has been X-ray characterised, although data on **36**–**39** [27] are not yet published [53,54]. The reactions leading to **36** [53], **40b** [54], **41a** [53] and **41b** [53] are insertions into an M(II)–N bond (M = Ge, Sn or Pb), those for **37** and **39** involve an M′(II)–O bond (M′ = Ge or Sn) [27] and those for **38** [27] and **40a** [54] implicate an M′(II)–C bond. The reactions leading to **36**–**38**, which are not only insertions but also oxidative cyclometallations probably proceeded via the homoleptic Ge(II) silyl-amide, -aryl or -alkyl intermediate $Ge[Si(NN)X]_2$ [$X = N(SiMe_3)_2$, $OC_6H_2Bu^t_2$-2,6-Me-4 or $CH(SiMe_3)_2$] **XV**, by analogy with the reactions of **1** and the corresponding stannylene. A compound **XV** may have been formed from an initial 1:1 adduct; such silylene adducts are known for **1** and a carbene (Section 4.8) [55,56] and **2** and $B(C_6F_5)_3$ (Section 4.2) [52]. The formation of the germanium(IV) hydrides **36**–**38** from the appropriate compound **XV** as precursor was attributed to greater steric strain in **XV** compared with its isoleptic Sn(II) compound **39** or **41**, causing **XV** to insert into a C–H bond of the group X. Precedents for such a C–H activation include the formation of **XVI** from its isomer $Ge[C_6H_2Bu^t_3$-2,4,6$]_2$ [57]. The reaction of the silylene **2** with two equivalents of $SnCl_2$ yielded the X-ray characterised compound $Sn\{Si(N'N')Cl\}_3Cl$ (**42**) and elemental tin; thermolysis of **42** gave **2**, $Si(N'N')Cl_2$ and $[Si(Cl)(N'N')]_2$ [58]. The silylene **3** with a germylene or stannylene gave the X-ray characterised compounds **43** (the Ge analogue of **30**) and **44**, respectively [59].



Scheme 8.

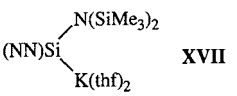


XVI 43 44

The diverse reaction of the silylene **1** with $LiSi(SiMe_3)_3(THF)_3$ and $K[N(SiMe_3)_2]$ yielded the new silyllithium compound **45** and the unusual potassium amide **46**, respectively [60]. In the former case, the product **45** arose from insertion of **1** into an Li–Si bond. In the latter case, a related product **XVII** of insertion of **1** into a K–N bond may have been an intermediate, but if so then it rapidly underwent a rearrangement to yield the isomer **46**. These and further reactions of **1** with other alkali metal amides or a 1-azaallyl, leading to the new compounds **47**–**51** [61], are summarised in Scheme 8. The crystalline complexes **45** and **46a** [60], as well as **46b**, **48**–**50** [61], have been X-ray characterised. The fact that the lithium bis(trimethylsilyl)amide [61], like its potassium analogue [60], gave the metal amide shows that the rearrangements of the type **XVII** → **46** are not metal-dependent.

The insertions of **1** into three compounds containing Li–C bonds yielding the new silyllithium compounds **52** and **53** are illustrated in Scheme 9 [61]. The compound **53** in C_6D_6-(THF-d_8) slowly decomposed to give the disilane **54**. Each of the crystalline compounds **52a**, **53a**, **53b** and **54** was X-ray characterised.

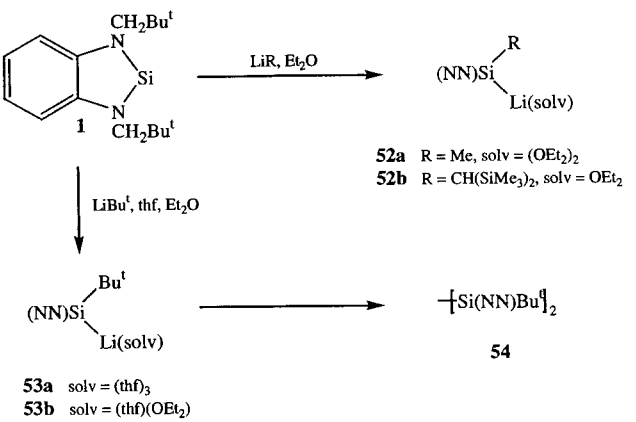
Insertions of a transient silylene into an M–N or Li–C bond of an alkali metal (M) amide or lithium alkyl do not appear to have been reported. The compounds **45**–**53** are promising precursors to new silyl or amido complexes of a wide range of metals.



XVII

4.4. Insertion of a bis(amino)silylene into a transition metal–X bond

Treatment of $[PtCl_2(PPh_3)_2]$ with the silylene **1** in benzene at ambient conditions afforded the X-ray au-



Scheme 9.

thenticated, crystalline *trans*-platinum(II) complex **55** (Eq. (7)) [62,63]. The $^{29}Si\{^1H\}$-NMR spectrum of **55** showed that in solution (at 213 K) **55** was in equilibrium not only with its *cis*-isomer **55a** but also a third minor isomer **55b** (Eq. (8)) [62]. The ^{29}Si-NMR spectral chemical shifts assigned to the $[Si(NN)Cl]^-$ ligand in **55** and **55a** were at δ 53.7 and δ 57.3 with $^1J(^{29}Si–^{195}Pt) =$ 934 and 957 Hz, respectively; while those assigned to the Si(NN) ligand were at δ 142.5 and 146.9 (**55**, **55a**) with $^1J(^{29}Si–^{195}Pt) = 2265$ and 2259 Hz, respectively; and for the minor (**55b**) at δ 143 and 146.5 (coupling not resolved) [62]. The major $^{195}Pt\{^1H\}$-NMR spectral signals in $CDCl_3$/PhMe at 213 K were at δ −5474 and δ −5497 (**55**, **55a**) with a minor signal attributed to **55b** at δ −5540. In the original publication [62], the minor isomer **55b** was suggested to be the six-coordinate, 20-electron platinum(II) complex *cis*-$[PtCl_2\{Si(NN)\}_4]$. However, the similarity of the NMR parameters for **55b** to those of **55** and **55a** and its diamagnetism makes it more likely that **55** and **55b** are the conformers shown in **XVIII** (major, *trans*, symmetric) and **XIX** (minor, *trans*, asymmetric), respectively [63]. The dynamic processes are those between **55** and **55b** only at 213 K, while the slower (starting at 243 K) higher energy process is that between **55** and its *cis*-isomer, which may be catalysed by a trace of free silylene (by analogy with similar *cis* ⇌ *trans* isomerisations of bis(tertiary phosphine)platinum(II) chlorides).

From **1** and $[PdCl_2(PPh_3)_2]$ there was similarly obtained the crystalline *trans*-palladium(II) complex **56**, which is isomorphous with its isoleptic Pt(II) complex **55** [63]. In both complexes, the neopentyl substituents in each silylene ligand adopt a *trans*-configuration, probably so as to accommodate the mutually *trans*-chlorines on the $[Si(NN)Cl]^-$ ligands.

Some other silylene-based platinum(II) complexes are known: *trans*-$[PtH\{Si(SEt)_2\}\{P(C_6H_{11}\text{-c})_3\}_2][BPh_4]$ [64a], $[PtH\{PPr^i_2CH_2CH_2PPr^i_2\}\{Si(C_6H_2Me_3\text{-2,4,6})_2\}]$ [64b] and $[Pt(PR_3)\{Si(C_6H_2Me_3\text{-2,4,6})_2\}]$ ($R = C_6H_{11}$-c or Pr^i) [64c]; however, **56** is the first palladium analogue.

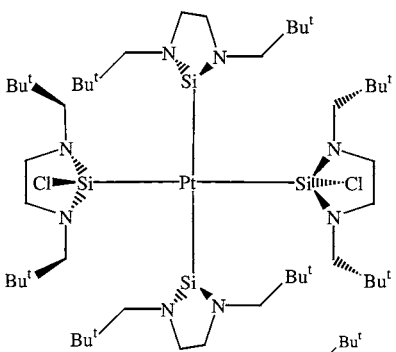
The reaction between the silylene **2** and $[M(\eta^5\text{-}C_5H_5)_2H_2]$ (M = Mo or W) yielded the insertion product **57**, which for M = Mo was X-ray-characterised [65]. An indirect insertion reaction product was **58**, obtained from $[Mo(\eta^5C_5H_5)_2\{Si(N'N')\}]$ and water; its structural assignment was based on NMR and IR spectra [65]. For Ru(II)Si(N′N′) complexes see Section 5.

$$[PtCl_2(PPh_3)_2] + 4\ (\mathbf{1}) \rightarrow \underset{\mathbf{55}}{trans\text{-}[Pt\{Si(NN)Cl\}_2\{Si(NN)\}_2]} \quad (7)$$

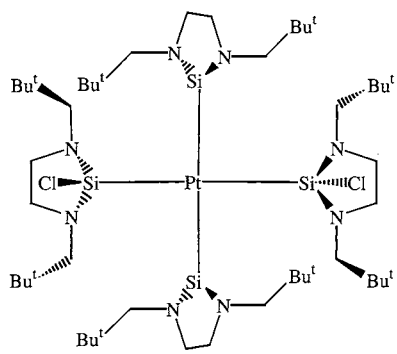
$$\mathbf{55} \overset{fast}{\rightleftharpoons} \underset{\mathbf{55b}}{\text{Minor isomer}} \overset{slow}{\rightleftharpoons} \underset{\mathbf{55a}}{cis\text{-}[Pt\{Si(NN)Cl\}_2\{Si(NN)\}_2]} \quad (8)$$

4.5. Further (see Section 4.2) oxidative addition reactions of a chalcogen or Bu^{t}NC to a bis(amino)silylene

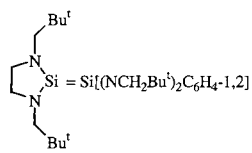
We showed in 1996 that the silylene **1** readily underwent oxidative addition with two equivalents of a chalcogen in toluene yielding the crystalline dinuclear silicon(IV) cyclochalcogenide **59**–**61**, Eq. (9) [28]; X-ray data for **60** and **61** were provided. Similarly, it was later demonstrated that the silylene **2** reacted with the appropriate portion of S or Se to give analogous X-ray authenticated cyclochalcogenides **62** and **63** [25]; the former with an excess of sulfur was shown (in an NMR



XVIII



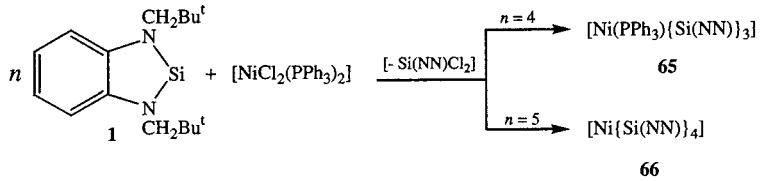
XIX



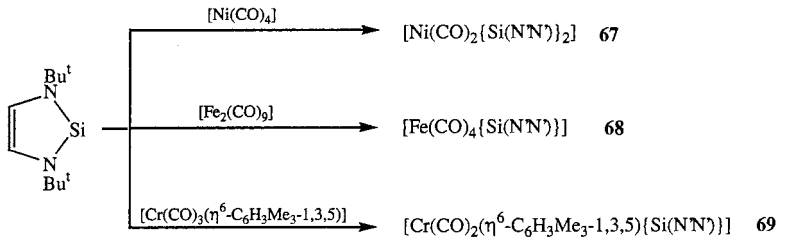
trans-$[Pd\{Si(NN)Cl\}_2\{Si(NN)\}_2]$ **56**

$[MH(\eta^5\text{-}C_5H_5)_2\{Si(N'N')H\}]$ **57** M = Mo or W

$[MoH(\eta^5\text{-}C_5H_5)_2\{Si(N'N')OH\}]$ **58**

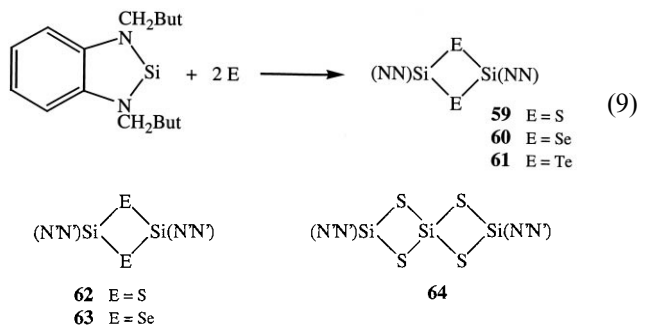


Scheme 10.



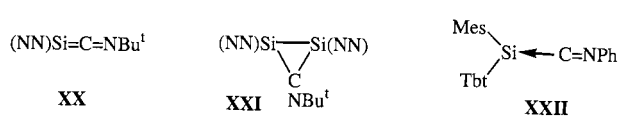
Scheme 11.

tube experiment) to yield **2** and a polysulfide formulated as **64**. The oxygen analogue of **64** was believed to be a minor product of the reaction of **2** with O_2 in toluene-d_8 which probably yielded SiO_2 and **2** [25].



(9)

The reactions of **1** with Bu^{t}NC in benzene, yielding the crystalline oxidative adducts Si(NN)(Bu^t)CN (**8**) and Bu^{t}Si(NN)Si(NN)CN (**9**), were mentioned in Section 4.1 and Scheme 1 [37]. The nature of the product depended on the order of addition rather than stoichiometry, since the binuclear disilane **9** was obtained by adding the isonitrile to **1** even when the reagents were mixed in 1:1 proportions. Furthermore, **8** is not an intermediate along the pathway to **9** because **8** did not react with **1**. A common intermediate to both **8** and **9** may be the simple 1:1 adduct **XX**, which either undergoes a 1.3-shift of Bu^t from N → Si to give **8** or undergoes insertion of **1** into the Si–C bond to yield **XXI** which isomerises to give **9**. A compound **XXII** related to **XX** was obtained from the thermally generated silylene [Si{$C_6H_2Me_3$-2,4,6}{C_6H_2-(CH[$SiMe_3$]$_2$)$_3$-2,4,6}[≡ Si(Mes)Tbt] from its dimer and PhNC [66].

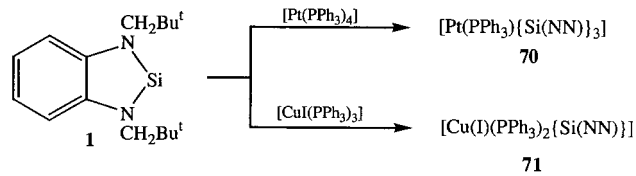


4.6. Reduction reactions of bis(amino)silylenes

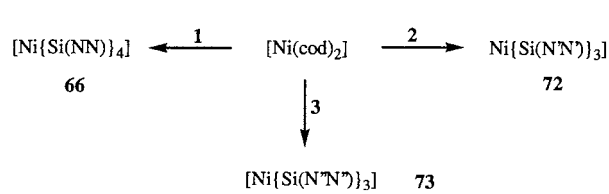
The insertions of Sections 4.1, 4.2 and 4.5, which are effectively oxidative additions to silylenes yielding tetravalent silicon(IV) products, may be regarded as reactions in which the silylenes function as reducing agents. By contrast, those insertions described in Sections 4.3 and 4.4 differ in that the products contain a formally four-coordinate silicon(II)-centred ligand [Si(NN)X]$^-$.

Although reactions of bis(amino)silylenes with other (e.g. chalcogen) oxidising agents such as Cl_2, Br_2, I_2, a peroxide or disulfide have not yet been reported (perhaps because the derived dihalogeno-, dialkyloxy- or dimercapto-silanes would be of limited interest), it is likely that they would proceed readily.

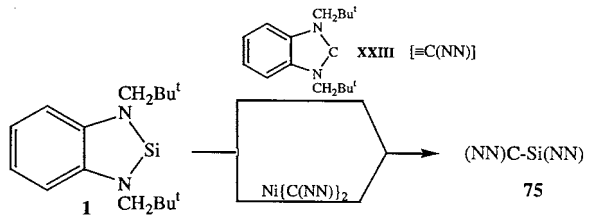
It is also probable that a bis(amino)silylene will reduce various halogenometal complexes. However, thus far the only such halogen-abstraction reactions to have been reported relate to [$NiCl_2(PPh_3)_2$], which with the silylene **1** in benzene under ambient conditions yielded the silylenenickel(0) complex **65** or **66**, depending on stoichiometry (Scheme 10) [62]. For both the crystalline



Scheme 12.



Scheme 13.



Scheme 14.

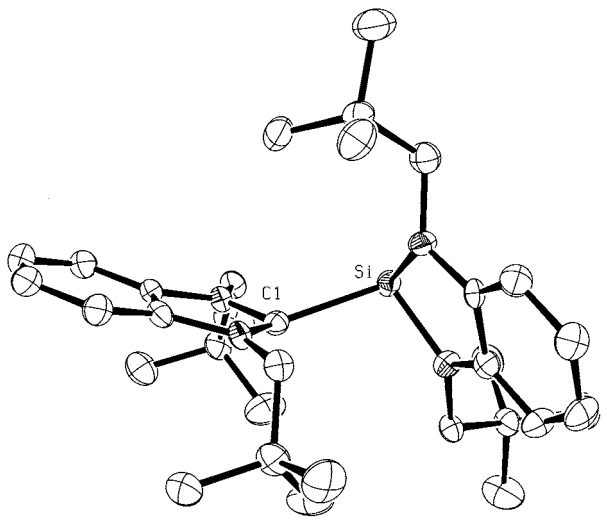


Fig. 3. Molecular structure of the carbene-silylene adduct **75**.

complexes **65** [62] and **66** [63], X-ray data are available. It is interesting that under similarly mild conditions the heavier Group 10 isoleptic complexes $[MCl_2(PPh_3)_2]$ (M = Pd or Pt) were not reduced, cf. **55** and **56** (Section 4.4) [62,63].

4.7. Bis(amino)silylenes in d and f metal chemistry

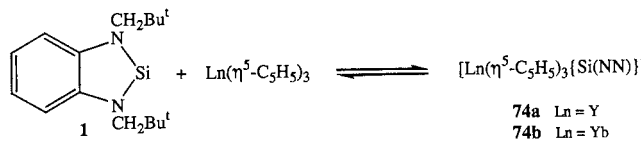
Several reviews concerning silylene transition metal complexes have been published in recent years [67–70].

The first example (in 1994) of a bis(amino)silylene behaving as a ligand relates to the formation of the X-ray characterised carbonylnickel(0) complex **67** [35]. Similar carbonyl displacement reactions were mentioned in a review [38] concerning an iron(0) (**68**) and a chromium(0) (**69**) complex (Scheme 11).

Complexes of nickel(0) (**65**, **66**), palladium(II) (**56**) and platinum(II) (**55**) bearing silylene ligands **1** have already been mentioned. A Pt(0) complex $[Pt(PPh_3)\{Si(NN)\}_3]$ (**70**) [71] and the first Cu-silylene complex $[CuI(PPh_3)_2\{Si(NN)\}]$ (**71**) [27] were obtained by reaction of **1** with $[Pt(PPh_3)_4]$ and $[CuI(PPh_3)_3]$, respectively (Scheme 12). Both complexes have been X-ray structurally characterised and show the metal to be in a tetrahedral environment (Fig. 2). The nickel(0) complex **66** was also accessible from $[Ni(cod)_2]$ and **1** [62,63] and a similar methodology led to the equally X-ray characterised complexes **72** and **73** (Scheme 13) [72]. These results may imply that the steric demands of the silylenes **2** and **3** are greater than those of **1**.

The data cited above and also in Sections 4.4 and 4.6 demonstrate that in their transition metal chemistry silylenes are not only able to displace carbonyl, tertiary phosphine or alkene ligands from a metal, but also that they can insert into M–Cl bonds (**55**, **56**) and/or act as chlorine atom abstractors (**65**, **66**). A similar diversity of bis(amino)-carbene [73], -germylene [16] or -stannylene [16] behaviour is known. For each MX_2 ligand (M = C, Si, Ge or Sn) including **1**–**3**, it appears that in its ligand behaviour in transition metal chemistry it is a strong σ-donor and weak π-acceptor, i.e. more like PR_3 than CO. Another example of a phosphine displacement reaction is the formation of the X-ray characterised molybdenum(II) complex $[Mo(\eta^5\text{-}C_5H_5)_2\text{-}\{Si(N'N')\}]$ from $[Mo(\eta^5\text{-}C_5H_5)_2(PEt_3)]$ and **2** [65].

It is also possible for a silylene to behave simply as a Lewis base. Thus, treatment of each of the tri(cyclopentadienyl)metal complexes $Ln(\eta^5\text{-}C_5H_5)_3$ (Ln = Y or Yb) with **1** in toluene at ambient temperature afforded the appropriate X-ray characterised, crystalline complex **74a** or **74b** [74]. Using variable temperature $^{29}Si\{^1H\}$-NMR spectroscopy, it was shown that in toluene-d_8 each complex readily dissociated into its factors (**74a** > **74b**) (Eq. (10)). This trend reflects the relative Ln–Si bond lengths: 3.038(2) Å (**74a**) and 2.984(2) (**74b**).



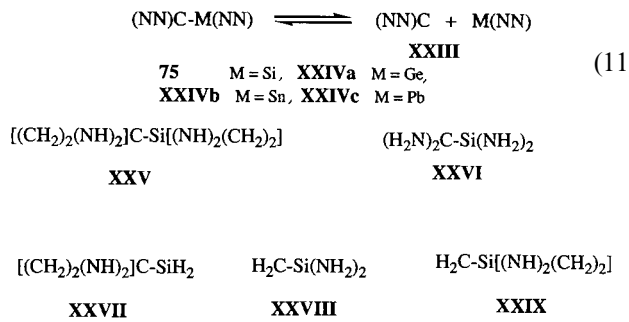
(10)

4.8. Bis(amino)silylenes as electrophiles

In all the reactions described in the preceding sections it appears that the bis(amino)silylene behaves at least initially as a nucleophile. With the exception of complex **75**, discussed below, there appear to be no examples as yet of simple adducts between any one of **1**–**3** and a Lewis base such as a tertiary amine or phosphine, a dialkyl sulfide or one of their bi- or tridentate analogues.

The crystalline carbene–silylene adduct **75** was prepared from the silylene **1** and the carbene **XXIII** [≡C(NN)] or $Ni\{C(NN)\}_2$ (Scheme 14) [55,56]. The X-ray structure of crystalline **75** (Fig. 3) shows it to possess an exceptionally long C–Si bond of 2.162(5) Å, with the ligating carbon atom in an almost trigonal planar and the silicon atom in a pyramidal environment [55]. The corresponding isoleptic carbene-M(NN) adducts (M = Ge **XXIVa**, Sn **XXIVb** or Pb **XXIVc**) were also prepared [56]. Each of the crystalline adducts **XXIV** has a similar geometry. The C–M distance (M =

Si, Ge, Sn or Pb) for each of the adducts **75** and **XXIV** is more than 10% longer than in a corresponding divalent Group 14 element(II) hydrocarbyl reference compound; the sum of the angles at C and M is 351.4 and 291.6° (**75**) [55], 347.7 and 287.9° (**XXIVa**), 351.4 and 277.3° (**XXIVb**) and 350.3 and 274.5° (**XXIVc**). Variable temperature ^{13}C-, ^{29}Si-, ^{119}Sn- and ^{207}Pb-NMR spectral data showed that in solution each of the complexes was in equilibrium with its precursors (Eq. (11)). The stability with respect to dissociation decreased in the sequence **XXIVb** > **XXIVc** > **75** > **XXIVa**, i.e. Sn > Pb > Si > Ge. Regarding the nature of the C–M bonds in **75** and **XXIV**, both the crystallographic and spectroscopic data point to the following conclusions: (i) the C–M bonds are weak; (ii) the attractive force between C and M is electrostatic, and (iii) the M atom in **75** or **XXIV** is the negative end of the CM dipole, the carbon in each case being the donor site [56]. For the case of the silylene adduct **75**, these conclusions were placed on a more quantitative basis by molecular orbital calculations on model compounds [55]. In summary, DFT calculations at the B3LYP/6-311 + G** level on **XXV** or **XXVI**, or even **XXVII**, but not **XXVIII** or **XXIX**, showed good agreement with the experimentally observed molecular geometry, the C–Si bond length and the weak and dipolar $C^{\delta+}$–$Si^{\delta-}$ bond. Related calculations on $H_2X{=}YH_2$ (X = Ge or Sn; Y = C, Si, Ge, or Pb) have been reported [75]. Bis(amino)carbene adducts of GeI_2 [76a], $SnCl_2$ [76b], $Sn(C_6H_2Pr^i_3\text{-}2,4,6)_2$ [76c] and $Pb(C_6H_2Pr^i_3\text{-}2,4,6)_2$ [76d] have revealed rather similar geometric and bonding features.



(11)

5. Concluding remarks

Despite the fact that the thermally stable bis(amino)-silylenes have been known for less than a decade, we trust that this account shows that this area of chemistry may now reasonably be described as mature.

6. Note added in proof

(i) An important review (stable silylenes) has appeared [77]; (ii) Ru(II) complexes derived from **2** have been described [78].

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