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FULL PAPER

Crystalline (NN)C–M(NN) complexes: synthesis, structure, bonding and lability [M = Si, Ge, Sn or Pb; (NN) = 1,2-($Bu^tCH_2N)_2C_6H_4$]

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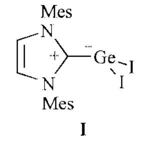
Each of the red-brown or red, isomorphous, crystalline adducts (NN)C–M(NN) [(NN) = 1,2-$(Bu^tCH_2N)_2C_6H_4$ and M = Si, Ge, Sn or Pb] has been obtained from the carbene (NN)C and the appropriate silylene, germylene, stannylene or plumbylene M(NN) in benzene and crystallisation from a hydrocarbon. They are monomeric, with the three-co-ordinate C_{carb} and M atoms in an almost planar (C) or pyramidal (M) environment. The C–M distances are more than *ca.* 10% longer than for a typical M^{II}–C bond in an MR_2 molecule. Variable temperature ^{13}C and ^xM NMR spectra (^xM = ^{29}Si, ^{119}Sn or ^{207}Pb) in toluene-d_8, as well as for the appropriate M(NN) and C(NN) precursors, have been recorded. The C_{carb} and M chemical shift data show that the compounds readily dissociate in solution, their stability decreasing in the sequence Sn > Pb > Si > Ge. From the magnitude of the chemical shifts, their conformation and C–M distances of the adducts, it is concluded that the C–M bond in each adduct is best formulated as being electrostatic in nature, with the carbene moiety as electron donor and the M(NN) fragment as acceptor.

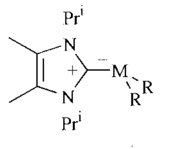
Introduction

Interest in thermally stable carbenes was triggered by the discovery about ten years ago of the first such compound, the chelating bis(amino)carbene $\overline{C[N(R)CHCHN}R]$ (R = adamantyl).[1] A major theme of the numerous subsequent publications has been their role as ligands in transition metal chemistry. Examples are [Ni{$\overline{CN(R)CHCHN}R$}$_2$] (R = C_6H_2-Me_3-2,4,6)[2] and [Pd{$\overline{CN(Me)CHCHN}$)$_2CH_2$-*cis*}(NCMe)$_2$]-$[BF_4]_2$ (which catalyses the copolymerisation of C_2H_4 and CO).[3] Related carbenemetal complexes, in which the carbene ring is saturated, are readily available from their dimers, the enetetramines, including [C{N(CH$_2$Ph)}$_2C_6H_4$-1,2]$_2$;[4] an example is [NiCl{$\overline{CN(Me)CH_2CH_2N}Me$}$_3$][$BF_4$].[5]

The thermally stable carbenes have also featured as ligands in main group element chemistry. Particularly relevant to the present study are the complexes **I**,[6] **II**,[7] **III**,[8] and **IV**,[9] having a Group 14 metal(II) complex as acceptor moiety.



I



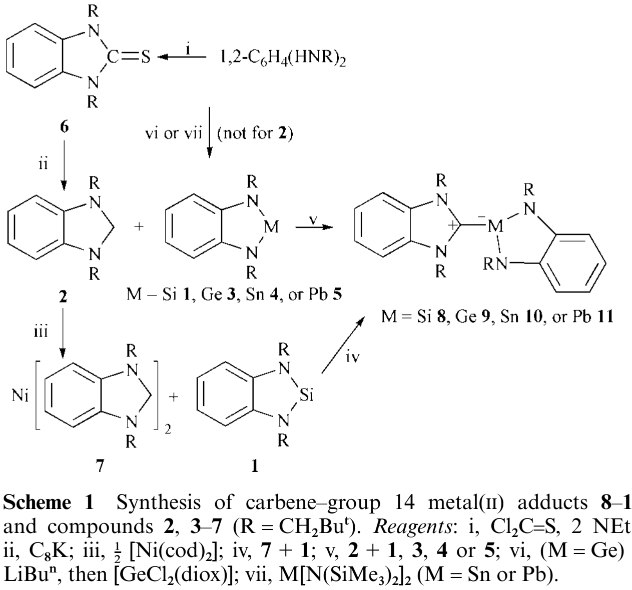
II M = Sn, R = $C_6H_2Pr^i_3$-2,4,6
III M = Pb, R = $C_6H_2Pr^i_3$-2,4,6
IV M = Sn, R = Cl

We have been actively engaged in exploring the chemistry of the thermally stable silylene Si[1,2-$(Bu^tCH_2N)_2C_6H_4$] [≡ Si(NN)] **1**. Recently we briefly communicated the synthesis, structure and bonding of its 1 : 1 adduct with the then newly prepared isoleptic carbene **2** (see Scheme 1).[10] (Compound **2** had independently been synthesised by Hahn *et al.*, who also described its crystal structure.[11]) We now provide full details of this study and extensions to the synthesis and structure of 1 : 1 adducts of **2** with the heavier Group 14 element(II) congeners M[1,2-$(Bu^tCH_2N)_2C_6H_4$] (M = Ge **3**,[12] Sn **4**,[13] or Pb **5**[12]).

Results and discussion

This study has its origins in an attempt to synthesize a heteroleptic nickel(0) complex Ni{Si(NN)}$_n${C(NN)$_m$} **V**, containing both the silylene Si(NN) **1** and the then unknown isoleptic carbene C(NN) **2** as ligands. It was prompted by our discovery of the related nickel(0) complexes [Ni{Si(NN)}$_4$] and [Ni(PPh$_3$){Si(NN)}$_3$], obtained from **1** and either [Ni(cod)$_2$] or [NiCl$_2$(PPh$_3$)$_2$].[14]

Accordingly, the first task was to prepare the carbene **2**, which was achieved (steps i and ii of Scheme 1) by a two step synthesis from $C_6H_4[N(H)CH_2Bu^t]_2$-1,2,[13] using the methodology pioneered by Kuhn and Kratz.[15] In the thiourea reduction step (step ii) we used potassium–graphite in thf; we found this to be much more reactive than the sodium–potassium alloy in toluene, used by Hahn *et al.*[11] The carbene **2** (clearly a monomer from the NMR spectroscopic data, as evident from



Scheme 1 Synthesis of carbene–group 14 metal(II) adducts **8**–**11** and compounds **2**, **3**–**7** (R = CH_2Bu^t). *Reagents*: i, Cl_2C=S, 2 NEt_3; ii, C_8K; iii, $\frac{1}{2}$ [Ni(cod)$_2$]; iv, **7** + **1**; v, **2** + **1**, **3**, **4** or **5**; vi, (M = Ge) 2 LiBu^n, then [GeCl$_2$(diox)]; vii, M[N(SiMe$_3$)$_2$]$_2$ (M = Sn or Pb).

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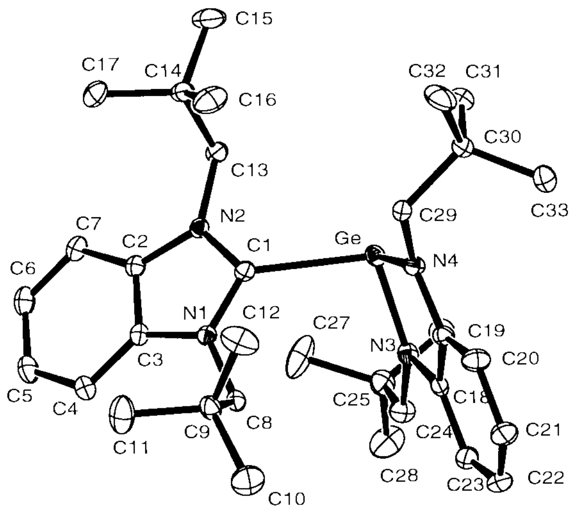


Fig. 1 Molecular structure of the adducts **9**–**11**, illustrated for the germanium compound **9**.

the X-ray analysis[11]) with [Ni(cod)$_2$] yielded (step iii in Scheme 1) the new (carbene)nickel(0) complex [Ni{C(NN)}$_2$] **7**. An attempt to use this as substrate for the target heteroleptic nickel(0) complex **V** by treatment with Si(NN) **1** led instead (step iv in Scheme 1) to the 1:1 carbene–silylene adduct **8**. Our initial rationalisation of this outcome was to consider that **V** may have been a labile intermediate, the nickel atom thus providing the template for an intramolecular ligand–ligand coupling and elimination to yield **8**. This remains a possibility; however **8** was also obtained (step v of Scheme 1) directly, by mixing **1** and **2** in benzene at ambient temperature. The related (NN)C–M(NN) adducts (M = Ge **9**, Sn **10** or Pb **11**) were obtained (step v of Scheme 1) from **2** and the germylene **3**, stannylene **4** or plumbylene **5**, in a similar fashion.

The solid adducts (NN)C–M(NN) were dark red-brown (M = Si **8**), red (M = Ge **9**), ruby dark red (M = Sn **10**), or dark red (M = Pb **11**). X-Ray quality crystals were obtained from pentane (**8**, 83%), hexane (**9**, 64%; or **11**, 71%), or toluene (**10**, 77%). Satisfactory microanalyses were recorded. Their EI-mass spectra showed the parent molecular cation in substantial (**8** or **10**) or low (**11**) intensity, or absent for **9**.

The crystal structure of crystalline **8** was described in our earlier communication;[10] those of **9**–**11** are presented herein. The four adducts **8**–**11** are isostructural and isomorphous. The ORTEP[16] diagrams are very similar; that for the germylene adduct **9** is illustrated in Fig. 1. Selected geometric parameters for the three adducts **9**–**11** are in Table 1; comparative values of the C–M bond lengths and the fold angles *Φ*1 and *Φ*2 (Fig. 2) at C and M, respectively, for **8**–**11** (also the N–C–M angles) and **I**–**IV** are shown in Table 2.

Each of the crystalline adducts **9**–**11**, like **8**,[10] is a monomer, having an exceptionally long central bond between the three-co-ordinate carbon [C(1)] and the M atoms. These C(1)–M distances (Table 2) may be compared with those (av.) in the following $\mathrm{M^{II}R_2}$ compounds: $\overline{\mathrm{SiC[C(SiMe_3)_2(CH_2)_2C}}\mathrm{(SiMe_3)_2]}$ [1.908(2) Å],[17] [M{CH(SiMe$_3$)$_2$}$_2$]$_2$ [M = Ge, 2.016; M = Sn, 2.216(6) Å],[18] and Pb[C$_6$H(Bu^t-2)Me$_4$-4,5,6]$_2$ [2.357(4) Å].[19] Thus, each C(1)–M distance in **8**–**11** is more than 10% longer than in the appropriate divalent Group 14 element(II) hydrocarbyl reference compound. The C(1)–M distances in **10** and **11** are closely similar to those in the corresponding (N″N″)C–MR$_2$ molecules **II**[7] and **IV**.[9] In **9**–**11**, like **8**,[10] C(1) is in an almost trigonal planar environment: the sum of the angles Σ at C(1) is 347.7 (**9**), 351.4 (**10**), or 350.3° (**11**) (*cf.*[10] 351.4° for **8**). By contrast, M is in a pyramidal environment [Σ = 287.9 (**9**), 277.3 (**10**), or 274.5° (**11**); *cf.*[10] 291.6° for **8**], attributed to the presence on M of a stereochemically active lone pair of electrons.

Table 1 Selected geometric data (bond lengths in Å and angles in °) for complexes **9**–**11**

	M = Ge	M = Sn	M = Pb
C(1)–M	2.339(3)	2.472(5)	2.586(7)
C(1)–N(1)	1.359(4)	1.349(6)	1.360(8)
C(1)–N(2)	1.360(4)	1.369(6)	1.364(8)
M–N(3)	1.906(2)	2.104(5)	2.218(5)
M–N(4)	1.889(3)	2.083(4)	2.167(5)
N(1)–C(3)	1.400(4)	1.401(6)	1.389(9)
N(2)–C(2)	1.397(4)	1.398(6)	1.391(9)
C(2)–C(3)	1.388(4)	1.385(7)	1.390(10)
N(3)–C(18)	1.398(4)	1.399(6)	1.386(9)
N(4)–C(19)	1.386(4)	1.387(6)	1.393(8)
C(18)–C(19)	1.424(4)	1.429(7)	1.419(9)
N(1)–C(1)–N(2)	105.7(2)	105.4(4)	104.7(6)
N(1)–C(1)–M	126.6(2)	129.0(4)	128.5(4)
N(2)–C(1)–M	115.4(2)	117.0(3)	117.1(4)
N(3)–M–N(4)	84.3(10)	79.30(16)	77.0(2)
N(3)–M–C(1)	101.26(10)	98.41(17)	97.1(2)
N(4)–M–C(1)	101.08(11)	99.60(16)	100.9(2)
C(3)–N(1)–C(8)	124.4(2)	123.8(4)	124.3(6)
C(1)–N(1)–C(2)	110.9(2)	111.8(4)	112.4(6)
C(1)–N(1)–C(8)	124.6(2)	124.3(4)	123.1(6)
C(13)–N(2)–C(1)	124.6(2)	125.6(4)	125.1(6)
C(13)–N(2)–C(2)	124.5(2)	123.9(4)	124.1(6)
C(1)–N(2)–C(2)	110.9(2)	110.61(2)	110.8(6)
C(18)–N(3)–M	113.30(2)	113.5(3)	112.4(4)
C(24)–N(3)–M	137.3(3)	116.3(6)	132.1(5)
C(18)–N(3)–C(24)	108.9(3)	126.5(6)	115.3(5)
C(19)–N(4)–M	114.3(2)	114.2(3)	114.3(4)
C(29)–N(4)–M	123.62(2)	124.7(3)	123.9(4)
C(19)–N(4)–C(29)	121.1(2)	120.8(4)	120.7(6)

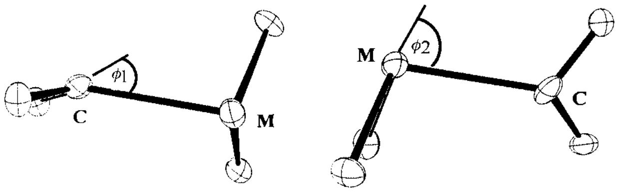


Fig. 2 The presentation illustrating the fold angles *Φ*1 and *Φ*2.

The geometric parameters of the (NN)C moiety in compounds **9**–**11** are closely similar to those in the parent carbene,[11] the only significant feature being a slight widening by *ca.* 1.5° of the N(1)–C–N(2) angle in the adducts from the 103.49(13) or 104.26(14)° in (NN)C; *cf.* 105.6(2)° in **8**.[10] However, the N(3)–M–N(4) angles in **8** [87.5(2)°][10] or **10** [79.30(16)°] differ little from those in their parent M(NN) molecules: 88.2(1) (M = Si)[20] or 78.5(2)° (M = Sn).[13] The fold angles at C1 (*Φ*1) and M (*Φ*2) in the four (NN)C–M(NN) crystalline adducts **8**–**11** do not show (Table 2) a monotonic trend as a function of M, being 29 ± 2° for *Φ*1 and 77.5 ± 2.5° for *Φ*2. There is a considerable torsion between the closely planar C(1)N(1)N(2)C(2)C(3) and MN(3)N(4)C(18)C(19) fragments, being 60.8(0.16) (**8**),[10] 56.71(0.26) (**9**), 56.89(0.19) (**10**) and 53.99(0.23)° (**11**).

Variable temperature (VT) ^{13}C and ^{x}M NMR spectral chemical shifts of each of the crystalline adducts (NN)C–M-(NN) **8**–**11** (for M = Ge only ^{13}C) in toluene-d$_8$ revealed the presence of the dissociative equilibrium (1), indicative of a labile C–M bond. These data are illustrated graphically in Figs. 3 (^{x}M = ^{29}Si), 4 (^{x}M = ^{119}Sn) and 5 (^{x}M = ^{207}Pb); the reference compounds, for which similar data are shown, are the free silylene **1** (Fig. 3), stannylene **4** (Fig. 4) and plumbylene **5** (Fig. 5). The VT ^{x}M NMR chemical shifts for **1**, **4** and **5** have not previously been reported. The VT ^{13}C NMR spectral chemical shifts for each of the adducts **8**–**11** are compared in Fig. 6.

$$\mathrm{(NN)C{-}M(NN)} \rightleftharpoons \underset{\mathbf{2}}{\mathrm{C(NN)}} + \mathrm{M(NN)} \qquad (1)$$

Table 2 Comparative C(1)–M bond lengths (Å) and angles (°) at C(1) and M

Complex	C(1)–M	N(1,2)–C(1)–M	Fold angle $\Phi 1^a$	Fold angle $\Phi 2^a$	Ref.
8 (NN)CSi(NN)	2.162(5)	129.3(3), 116.5(3)	28	77	10
9 (NN)CGe(NN)	2.339(3)	126.6(2), 115.40(19)	31	75	This work
10 (NN)CSn(NN)	2.472(5)	129.0(4), 117.0(3)	27	79	This work
11 (NN)CPb(NN)	2.586(7)	128.5(4), 117.1(4)	28	80	This work
I (N′N′)CGeI$_2$^{b}	2.102(12)				6
II (N″N″)CSn(C$_6$H$_2$Pr$^i_3$-2,4,6)$_2$^{c}	2.379(5)			69	7
III (N″N″)CPb(C$_6$H$_2$Pr$^i_3$-2,4,6)$_2$^{c}	2.290(5)				8
IV (N″N″)CSnCl$_2$^{c}	2.540(6)			70.5	9

^{a} Φ1 and Φ2 are defined in Fig. 2. ^{b} (N′N′) ≡ [2,4,6-Me$_3$C$_6$H$_2$NCH=]$_2$. ^{c} (N″N″) ≡ [Pr^{i}NCH=]$_2$.

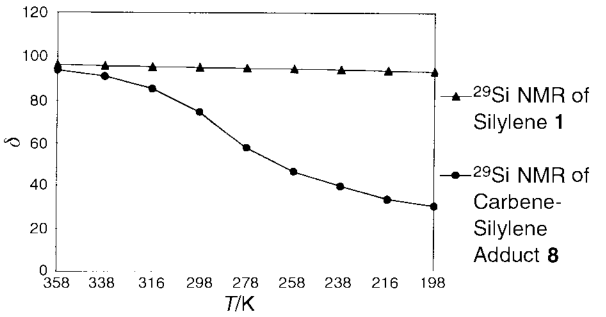


Fig. 3 Temperature dependence of ^{29}Si-NMR spectroscopic shifts (δ) of the carbene–silylene adduct **8**.

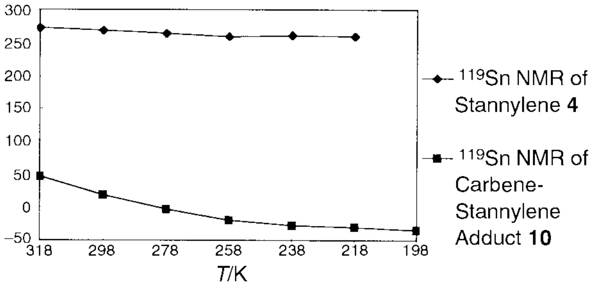


Fig. 4 Temperature dependence of ^{119}Sn-NMR spectroscopic shifts (δ) of the carbene–stannylene adduct **10**.

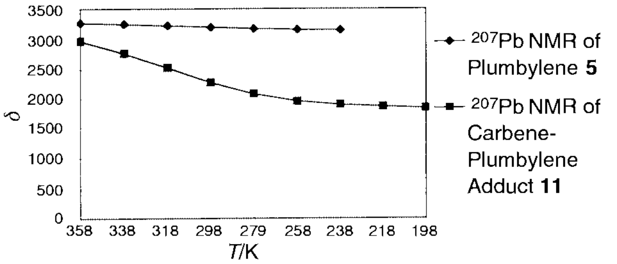


Fig. 5 Temperature dependence of ^{207}Pb-NMR spectroscopic shifts (δ) of the carbene–plumbylene adduct **11**.

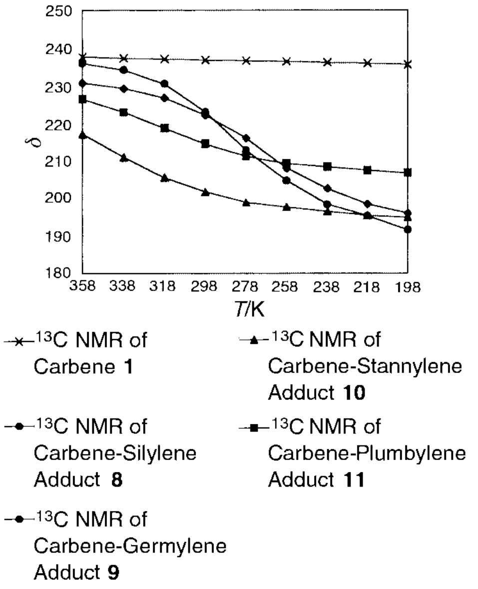


Fig. 6 Temperature dependence of ^{13}C-NMR spectroscopic shifts (δ) of the carbene **2** and the carbene–Group 14 metal(II) adducts **8**–**11**.

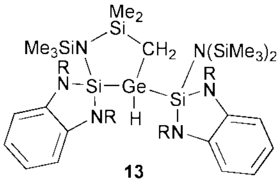
At 358 K it is evident (Fig. 6) that the stability of the adduct with respect to dissociation decreases in the sequence Sn (**10**) > Pb (**11**) > Ge (**9**) ≥ Si (**8**), the adduct **8** or **9** being essentially absent. This trend is confirmed by the δ[^{29}Si] (Fig. 3), δ[^{119}Sn] (Fig. 4) and δ[^{207}Pb] (Fig. 5) data. At 198 K, on the other hand, the presence of the largely undissociated adducts is indicated for **8**, **10** and **11** by the δ[^{x}M] (Figs. 3–5) and δ[^{13}C] (Fig. 6) data; Fig. 6 also shows that the in the wider temperature range **8** is more robust than **9**. The overall conclusion is that stability of the adducts in solution follows the sequence Sn > Pb > Si > Ge.

The ^{13}C or ^{x}M NMR (not **9**) spectral chemical shift of each adduct **8**–**11** is at lower frequency than that of the free carbene (Fig. 6) or metallene M(NN) (Figs. 3–5). We note that for carbene–transition metal complexes δ[^{13}C] is at lower frequency than for the free carbene, as illustrated in the present instance by comparing this parameter for the bis(carbene)nickel(0) complex Ni[C(NN)]$_2$ **7** of δ 208 with the δ 231.6 for the free carbene **2**, both at ambient temperature. On the other hand, when a stannylene behaves as a ligand, δ[^{119}Sn] is invariably at higher frequency for the complex than the "free" ligand, as shown (for example) for [Pt{Sn[N(SiMe$_3$)$_2$]$_2$}$_3$] (δ 885) and Sn[N(SiMe$_3$)$_2$]$_2$ (δ 775).[21] We conclude that in each adduct the carbene is the donor and the heavier homologue M(NN) is the acceptor.

We now turn to the nature of the C–M bond in each adduct **8**–**11**. Both the crystallographic and the spectroscopic data point to the same conclusion. First, that this bond is exceedingly weak and progressively so for M = Sn > Pb > Si > Ge. Secondly, that the attraction between C and M is electrostatic, with C and M being the positive and negative ends of the CM dipole, respectively. It is unprecedented for a divalent Group 14 element(II) bis(amide) to display acceptor properties and hence the weak nature of the CM bond in **8**–**11** is unsurprising. That the stannylene **4** is a better acceptor than the germylene **3** is consistent with the observation that Sn[CH(SiMe$_3$)$_2$]$_2$,[22] unlike its germanium analogue, forms a weak adduct with pyridine.

For the case of the silylene adduct **8** the above conclusions have been placed on a more quantitative basis by molecular orbital calculations on model compounds.[10] In summary, DFT calculations at the B3LYP/6-311+G** level on [(CH$_2$)$_2$(NH)$_2$]C–Si[(NH)$_2$(CH$_2$)$_2$] **12** or (H$_2$N)$_2$C–Si(NH$_2$)$_2$, or even [(CH$_2$)$_2$(NH)$_2$]C–SiH$_2$, but not H$_2$C–Si(NH$_2$)$_2$ or H$_2$C–Si[(NH)$_2$(CH$_2$)$_2$], showed good agreement with the experimentally observed molecular symmetry, the C–Si bond length and the weak C–Si bond. Thus, for the C_1-symmetric model compound **12** the computed C–Si bond length was 2.024 Å, the C–Si dissociation energy -13.4 kJ mol^{-1}, with a partial negative charge on the silicon atom [Mulliken charge $q[\mathrm{Si\{(NH)_2(CH_2)_2\}}]$ -0.072] and a torsion barrier of only *ca.* 4 kJ mol^{-1}, there being a significant twisted energy minimum. Related calculations on other $\mathrm{H_2X{=}YH_2}$ model compounds (X = Ge or Sn; Y = C, Si, Ge or Sn) have been made.[23]

The present results regarding formation of the adducts **8**–**11** by the reverse of eqn. (1) may be contrasted with the following observations. (i) The silylene $\overline{\mathrm{M[N(Bu^t)(CH)_2N}}\mathrm{Bu^t]}$ (M = Si) failed to react with the corresponding carbene (M = C), germylene (M = Ge) or CO.[24] (ii) The silylene **1** was found to react readily with the stannylene Sn(Ar)X [Ar = $\mathrm{C_6H_3(NMe_2)_2}$-2,6; X = Ar or $\mathrm{N(SiMe)_3}$],[25] or $\mathrm{M[N(SiMe_3)_2]_2}$ (M = Ge, Sn or Pb);[26] although 1 : 1 adducts may have been transient intermediates, the isolated crystalline products were Sn(Ar)[Si(N-N)X],[25] $\mathrm{M[Si(NN)N(SiMe_3)_2]_2}$ (M = Sn or Pb),[26] or **13**.[26] (iii) The labile adducts **I**,[6] **II**,[7] **III**[8] and **IV**[9] were formed from their appropriate carbene and $\mathrm{MX_2}$ precursors, each of which has a long and labile C–M bond (Table 2). (iv) Robust 1 : 1 adducts ⟩C–M⟨ (M = Ge or Sn) were obtained from the carbene $\mathrm{C[B(Bu^t)C(SiMe_3)_2BBu^t]}$ and $\mathrm{M[C_6H(Bu^t\text{-}2)Me_3\text{-}4,5,6]_2}$, having appreciably shorter C–M bonds than those listed in Table 2, of 1.845(10) or 1.773(14) (M = Ge) or 2.032(2) Å (M = Sn), respectively.[27] As for (ii), the contrast between the above cited insertion reactions[25,26] and the present results involving in both cases the silylene **1** is attributed to the fact that insertion is inhibited when the $\mathrm{MX_2}$ (M = Ge, Sn or Pb) moiety has the $\mathrm{X^-}$ ligands joined as a chelate, as in M(NN). In support, we note that each of the compounds $\mathrm{MAr_2}$ (M = Ge or Sn) forms a 1 : 1 adduct with the chelated tin(II) amide $\mathrm{Sn'[1,8\text{-}(SiMe_3N)_2\text{-}C_{10}H_6]}$, derived from 1,8-diaminonaphthalene; the Sn–Sn′ distance is exceptionally long [3.087(2) Å] and the pyramidal tin atom Sn′ is the acceptor.[28]



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R = $\mathrm{CH_2Bu^t}$

Experimental

General procedures

All operations and manipulations were carried out under purified argon, by conventional Schlenk techniques. Solvents were dried and degassed before use. Microanalyses were carried out by Medac Ltd. (Brunel University). The NMR spectra were recorded using Bruker instruments: DPX 300 (^{1}H and ^{13}C) and AMX 500 (^{29}Si, ^{119}Sn and ^{207}Pb), and referenced internally to residual solvent resonances (data in δ). Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were obtained in sealed capillaries and are uncorrected. The silylene **1** was synthesized by a published procedure,[20] germylene **3** was prepared from $\mathrm{C_6H_4[N(Li)CH_2Bu^t]_2}$-1,2 and $\mathrm{[GeCl_2(diox)]}$ (diox = 1,4-dioxane),[12] while the stannylene **4**[13] and plumbylene **5**[12] were prepared from $\mathrm{C_6H_4[N(H)CH_2Bu^t]_2}$-1,2 and $\mathrm{Sn[N(SiMe_3)_2]_2}$ or $\mathrm{Pb[N(SiMe_3)_2]_2}$, respectively.

Syntheses

$\mathrm{C[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]}$ 2 (see also ref. 11). A solution of the thiourea **6** (22.87 g, 0.082 mol) in thf (100 cm^{-3}) was added to a suspension of $\mathrm{C_8K}$ (prepared from K (6.4 g, 0.18 mol)) and graphite (17.3 g, 1.44 mol)) in thf (600 cm^{-3}) at 0 °C. The mixture was stirred for 1 d at ambient temperature, then filtered. The solvent was removed *in vacuo* from the filtrate. The remaining residue was distilled to yield compound **2** (16.6 g, 81.6%) (Found: C, 78.9; H, 9.99; N, 10.94. $\mathrm{C_{17}H_{26}N_2}$ requires C, 79.0; H, 10.14; N, 10.84%) as a colourless, viscous liquid, bp 98–100 °C at 0.05 Torr, which subsequently solidified. ^{1}H NMR (300.13 MHz, $\mathrm{CD_3C_6D_5}$, 293 K): δ 0.9 (s, 18 H, $\mathrm{CH_3}$), 3.89 (s, 4 H, $\mathrm{CH_2}$) and 6.92–7.01 (m, 4 H, phenyl). ^{13}C-{^{1}H} NMR (75.48 MHz, $\mathrm{CD_3C_6H_5}$, 293 K): δ 28.46 (C*Me*$_3$), 33.83 (*C*Me$_3$), 58.67 ($\mathrm{CH_2}$), 110.7, 120.71 and 136.33 (phenyl) and 231.63 (carbene C). MS: *m*/*z* 259 ([*M* + 1]$^+$, 47%).

$\mathrm{Ni[C\{1,2\text{-}(Bu^tCH_2N)_2C_6H_4\}]_2}$ 7. A solution of the carbene **2** (0.3 g, 1.16 mmol) in benzene (10 cm^3) was added to a solution of $\mathrm{[Ni(cod)_2]}$ (0.16 g, 0.581 mmol) in benzene (10 cm^3) at ambient temperature. There was an immediate change to dark violet. The mixture was stirred for 1 h, the solvent removed and the residue recrystallised from hexane at -25 °C to afford dark violet crystals of compound **7** (0.27 g, 82%) (Found: C, 70.4; H, 9.08; N, 9.62. $\mathrm{C_{34}H_{52}N_4Ni}$ requires C, 71.0; H, 9.11; N, 9.73%), mp 142–144 °C. ^{1}H NMR (300.13 MHz, $\mathrm{C_6D_6}$, 293 K): δ 0.89 (s, 18 H, $\mathrm{CMe_3}$), 4.42 (br s, 4 H, $\mathrm{CH_2}$) and 6.9–7.0 (m, 4H, phenyl). ^{13}C-{^{1}H} NMR (75.48 MHz, $\mathrm{C_6D_6}$, 293 K): δ 29.53 (C*Me*$_3$), 34.61 (*C*Me$_3$), 58.17 ($\mathrm{CH_2}$), 109.23, 119.54, 138.81 (phenyl) and 207.57 (carbene C). MS: *m*/*z* 574 (*M*$^+$, 8%).

$\mathrm{S{=}C[1,2\text{-}(Bu^tCH_2N)_2C_6H_4\}]}$ 6. A solution of thiophosgene $\mathrm{CSCl_2}$ (7.8 cm^3, 0.102 mol) in $\mathrm{Et_2O}$ (50 cm^3) was added to a solution of $\mathrm{C_6H_4[N(H)(CH_2Bu^t)]_2}$-1,2 (25.3 g, 0.102 mol) and $\mathrm{NEt_3}$ (28.4 cm^3, 0.204 mol) in $\mathrm{Et_2O}$ (300 cm^3) at -78 °C. The mixture was stirred for 16 h at ambient temperature and filtered. The solvent was removed *in vacuo* from the filtrate. The residual solid was sublimed at *ca.* 140 °C at 10^{-5} Torr to yield the colourless thiourea **6** (24.32 g, 83%), mp 92–93 °C. ^{1}H NMR (300.13 MHz, $\mathrm{C_6D_6}$, 293 K): δ 0.98 (s, 18 H, $\mathrm{CH_3}$), 4.08 (br s, 4 H, $\mathrm{CH_2}$) and 6.94–6.77 (m, 4 H, phenyl). ^{13}C NMR (75.48 MHz, $\mathrm{C_6D_6}$, 293 K): δ 29.17 (C*Me*$_3$), 35.47 (*C*Me$_3$), 55.07 ($\mathrm{CH_2}$), 110.33, 121.95 and 133.84 (phenyl) and 175.09 (C=S). MS: *m*/*z* 290 (*M*$^+$, 81%).

$\mathrm{[C_6H_4(NCH_2Bu^t)_2\text{-}1,2]C{-}Si[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]}$ 8 from compounds 1 and 7. A solution of the silylene **1** (0.18 g, 0.66 mmol) in benzene (20 cm^3) was slowly added to the carbene–nickel complex **7** (0.19 g, 0.33 mmol) in benzene (20 cm^3) at ambient temperature. There was a change from deep violet to brown. The mixture was stirred for 3 h, the solvent removed and the residue disolved in pentane and filtered. The filtrate was concentrated and at -25 °C red-brown crystals of **8** (0.3 g, 85%) were obtained. For characterisation, see below.

General procedure for the synthesis of the adducts $\mathrm{[C_6H_4(NR)_2\text{-}1,2]C{-}M[1,2\text{-}(RN)_2C_6H_4]}$ (M = Si 8, Ge 9, Sn 10 or Pb 11; R = $\mathrm{CH_2Bu^t}$). A solution of $\mathrm{M[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]}$ (M = Si **1**, Ge **3**, Sn **4** or Pb **5**) in benzene (20 cm^3) was added to a solution of the carbene $\mathrm{C[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]}$ **2** in benzene (20 cm^3). The mixture immediately turned red (Ge) or dark red-brown (Si, Sn or Pb). It was stirred for 4 h at ambient temperature; volatiles were removed *in vacuo*. The residue was dissolved in an appropriate solvent and filtered. The filtrate was concentrated to *ca.* 20 cm^3 for crystallisation.

$\mathrm{[C_6H_4(NCH_2Bu^t)_2\text{-}1,2]C{-}Si[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]}$ **8.** Using the carbene **2** (0.65 g, 2.52 mmol) and silylene **1** (0.69 g, 2.52 mmol) and crystallisation from pentane at -25 °C yielded dark red-brown crystals of compound **8** (1.11 g, 83%) (Found: C, 74.5; H, 9.91; N, 10.47. $\mathrm{C_{33}H_{52}N_4Si}$ requires C, 74.4; H, 9.84; N, 10.51%), mp 92–94 °C (decomp.). ^{1}H NMR (300.13 MHz, $\mathrm{CD_3C_6D_5}$, 293 K): δ 0.82 and 0.9 (2 s, $\mathrm{CH_3}$, 36 H), 3.39 and 3.93

Table 3 Crystal data and refinement for complexes **9**–**11**

	9	**10**	**11**
Formula	$C_{33}H_{52}GeN_4$	$C_{33}H_{52}N_4Sn$	$C_{33}H_{52}N_4Pb$
M	577.38	623.5	712.0
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)
a/Å	10.146(2)	10.396(3)	10.421(4)
b/Å	16.243(9)	16.059(5)	16.015(4)
c/Å	20.054(4)	20.198(36)	20.254(10)
β/°	101.85(2)	103.39(6)	102.61(4)
U/Å^3	3234(2)	3281(6)	3299(2)
Z	4	4	4
μ(Mo-Kα)/mm	0.97	0.81	5.14
T/K	173(2)	173(2)	173(2)
Total reflections	6018	6096	6112
Independent reflections	5683	5767	5784
Reflections with $I > 2\sigma(I)$	4370	4063	4274
$R1$ $[I > 2\sigma(I)]$	0.042	0.047	0.041
$wR2$ (all data)	0.104	0.108	0.086

(2 s, CH_2, 8 H) and 6.87–6.94 (m, phenyl, 8 H). $^{13}C\text{-}\{^1H\}$ NMR ($CD_3C_6D_5$, 75.48 MHz, 293 K): δ 28.34 and 28.91 (C*Me*$_3$), 55.08 and 57.53 (*C*Me$_3$), 109.73, 111.3, 117.6, 124.75, 135.78 and 142.61 (phenyl) and 216.46 (carbene C). $^{29}Si\text{-}\{^1H\}$ NMR (C_6D_6, 298 K): δ 77.14. MS: *m*/*z* 532 (M^+, 46%).

$[C_6H_4(NCH_2Bu^t)_2\text{-}1,2]C\text{–}Ge[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]$ **9**. From the carbene **2** (0.43 g, 1.66 mmol) and the germylene **3** (0.53 g, 1.66 mmol), after crystallisation from hexane first at room temperature and then at −25 °C, red crystals of compound **9** (0.61 g, 63.5%) were obtained (Found: C, 68.4; H, 8.77; N, 9.79. $C_{33}H_{52}GeN_4$ requires C, 68.7; H, 9.08; N, 9.70%), mp 110–112 °C. ^1H NMR (300.13 MHz, C_6D_6, 293 K): δ 0.91 and 0.92 (2 s, 36 H, CH_3), 3.68 and 3.96 (2 s, 8 H, CH_2), 7.0 and 7.05 (2 m, 8 H, phenyl). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.48 MHz, 293 K): δ 28.4 and 28.7 (C*Me*$_3$), 33.2 and 33.8 (*C*Me$_3$), 56.8 and 58.2 (CH_2), 110.0, 111.1, 117.4, 121.2, 136.1 and 143.7 (phenyl) and 224.9 (carbene C). MS *m*/*z* 320 ($[M - \text{carbene}]^+$, 23%).

$[C_6H_4(NCH_2Bu^t)_2\text{-}1,2]C\text{–}Sn[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]$ **10**. Using the carbene **2** (1.07 g, 4.147 mmol) and stannylene **4** (1.5 g, 4.147 mmol) and crystallisation from toluene at room temperature and then at −25 °C yielded dark red crystals of compound **10** (2.0 g, 77%) (Found: C, 63.7; H, 8.44; N, 9.11. $C_{33}H_{52}N_4Sn$ requires C, 63.6; H, 8.41; N, 8.98%), mp 168–170 °C. ^1H NMR (300.13 MHz, C_6D_6, 293 K): δ 0.739 and 1.06 (2 s, 36 H, CH_3), 3.57 and 3.89 (2 s, 8 H, CH_2), 6.88 and 7.01 (2 m, 8 H, phenyl).$^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.48 MHz, 293 K): δ 28.04 and 29.26 (C*Me*$_3$), 33.82 and 34.29 (*C*Me$_3$), 56.75 and 59.39 (CH_2), 109.46, 112.26, 115.2, 122.84, 135.0 and 148.41 (phenyl) and 200.83 (carbene C). $^{119}Sn\text{-}\{^1H\}$ NMR ($CD_3C_6D_5$, 298 K): δ 10.5. MS: *m*/*z* 623 (M^+, 3.7%).

$[C_6H_4(NCH_2Bu^t)_2\text{-}1,2]C\text{–}Pb[1,2\text{-}(Bu^tCH_2N)_2C_6H_4]$ **11**. From the carbene **2** (0.31 g, 1.2 mmol) and plumbylene **5** (0.54 g, 1.2 mmol) and crystallisation from hexane at room temperature and then at −25 °C there were obtained dark red crystals of compound **11** (0.85 g, 71%) (Found: C, 55.5: H, 7.30: N, 7.77. $C_{33}H_{52}N_4Pb$ requires C, 55.7; H, 7.36; N, 7.87%), mp > 60 °C (decomp.). ^1H NMR (300.13 MHz, $CD_3C_6D_5$, 293 K): δ 0.69 and 0.948 (2 s, 36 H, CH_3), 3.67 and 4.13 (2 s, 8 H, CH_2), 6.75 and 6.85 (2 m, 8 H, phenyl).$^{13}C\text{-}\{^1H\}$ NMR ($CD_3C_6D_5$, 293 K): δ 28.06 and 28.94 (C*Me*$_3$), 33.8 and 34.54 (*C*Me$_3$), 57.57 and 61.93 (CH_2), 111.83, 112.29, 115.38, 122.31, 137.43 and 155.86 (phenyl) and 211.49 (carbene C). MS: *m*/*z* 712 (M^+, 0.9%).

Crystal data and refinements details

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation, λ 0.71073 Å, with the crystals under a stream of cold nitrogen gas. Intensities were measured by an ω–2θ scan. Corrections were made for absorption using psi-scan measurements. The programs used for structure solutions and refinement were SHELXS 86[29] and SHELXL 97,[30] respectively. Further details are in Table 3.

CCDC reference number 186/2121.

See http://www.rsc.org/suppdata/dt/b0/b005216g/ for crystallographic files in .cif format.

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