

Serendipitous syntheses and structures of $[\text{Cp}_2\text{Nb}(\text{H})\{(\text{SiMe}_2)_2(\mu\text{-NR})\}]^{\dagger\ddagger}$ Georgii I. Nikonov,^{*a} Sergei F. Vyboishchikov,^{§b} Lyudmila G. Kuzmina^c and Judith A. K. Howard^d^a Chemistry Department, Moscow State University, Vorob'evy Gory, 119899 Moscow, Russia.

E-mail: nikonov@org.chem.msu.su

^b Humboldt-Universität zu Berlin, Institut für Chemie, Arbeitsgruppe Quantenchemie, Jägerstr. 10–11, D-10117 Berlin, Germany^c Institute of General and Inorganic Chemistry, RAS, Leninsky Prosp. 31, 117907 Moscow, Russia^d Chemistry Department, University of Durham, South Road, Durham, UK DH1 3LE

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The compound $[\text{Cp}_2\text{Nb}(\text{SiMe}_2\text{I})_2\text{H}]$ reacts with H_2NBu^t and HNEt_2 to afford the unexpected imido-bridged 1,3-disilaniobocyclobutanes $[\text{Cp}_2\text{Nb}(\text{H})\{(\mu\text{-SiR}_2)_2\text{NR}\}]$ ($\text{R} = \text{Bu}^t$ (**4**), Et (**5**)) exhibiting surprising structural and spectral properties.

1,3-Disilacyclobutanes $[(\mu\text{-X})\text{SiR}_2]_2$ (**1**) with electron-withdrawing bridges X ($\text{X} = \text{O}, \text{NR}$) exhibit unusually short Si–Si distances (2.25–2.57 Å),¹ which brought about a controversy regarding the nature of these Si–Si contacts. Although there was an attempt to rationalize bonding in **1** as ‘unsupported Si–Si π -bond’,² the conclusion of most studies was that this contact is non-bonding.³ Meanwhile, similar short Si–Si contacts observed in some 1,3-disiladimetallacyclobutanes $[(\mu\text{-SiR}_2)\text{ML}_n]_2$ (**2**) were explained in terms of residual bonding in coordinated disilenes.⁵ Mixed structures of the type $\text{L}_n\text{M}(\mu\text{-SiR}_2)_2\text{X}$ ($\text{X} = \text{O}, \text{NR}$) (**3**) are scarce⁶ and only few (for $\text{X} = \text{O}$) were characterised by X-ray study. Here we report the serendipitous synthesis, first crystal structure, and DFT calculations of nitrogen-bridged 1,3-disilaniobocyclobutanes $[\text{Cp}_2\text{Nb}(\text{H})\{(\mu\text{-SiR}_2)_2\text{NR}\}]$ ($\text{R} = \text{Bu}^t$ (**4**), Et (**5**)).

Addition of a 10-fold excess of H_2NBu^t to $[\text{Cp}_2\text{Nb}(\text{SiMe}_2\text{I})_2\text{H}]$ (**6**) afforded, after separation of $[\text{H}_3\text{NBu}^t]\text{I}$ and work-up, a light yellow crystalline complex **4**. Its ¹H NMR is surprising in that the hydride resonance is observed at very high field (−7.79 ppm), far away from the normal trisubstituted niobocene range (−2 to −5 ppm). The ²⁹Si NMR spectrum shows singlets at 14.0 and 10.5 ppm broadened due to coupling to ⁹⁶Nb nucleus (spin 9/2).

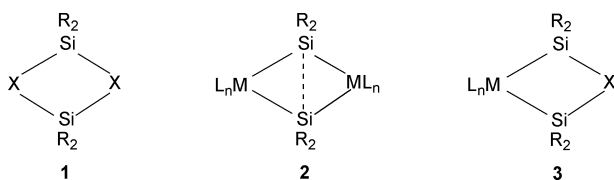
X-Ray study[†] established that in **4** the silyls are bridged by an imido group (Fig. 1). This result is amazing on its own right since it implies (i) silyl/hydride position exchange and (ii) that amination of the second silyl group by the initially formed $(\text{L}_n\text{M})\text{SiMe}_2\text{NHBu}^t$ (**7**) ligand is favoured over iodide substitution in SiMe_2I by an excess of the more nucleophilic amine H_2NBu^t . A thinkable pathway based on dehydroiodation of **7** to give a silylsilylene intermediate $\text{Cp}_2\text{Nb}(\text{SiMe}_2)(\text{SiMe}_2\text{NHBu}^t)$ can be safely ruled out, given the well-known basicity of neutral early-transition metal hydrides.⁷ A reaction of **6** with a secondary amine, HNEt_2 , led to a similar product **5** having non-equivalent SiMe_2 -group signals and hydride resonance at −8.11 ppm. This unexpected result means that activation of the N–C

bond occurred, which is a very rare process in organic chemistry. Moreover, addition of a tertiary amine, NEt_3 , to **6** also resulted in a facile reaction giving a mixture of products.

Our tentative rationale for the formation of **4** and **5** is that substitution of iodide in the second SiMe_2I ligand is made by the hydride, as a developing of interligand hypervalent interaction (IHI)⁸ between H and Si (Scheme 1). Then the first aminated silyl ligand in the resultant cationic complex $[\text{Cp}_2\text{Nb}(\text{SiMe}_2\text{NET}_2)(\text{SiMe}_2\text{H})]^+$ attacks *intramolecularly* the second SiMe_2H group ($\text{S}_{\text{N}}2$ substitution) with a concomitant migration of the hydride back to the metal but on the opposite side. The more accessible N–C bond (or N–H bond in the case of **4**) rather than the shielded N–Si bond is then split in an $\text{S}_{\text{N}}2$ attack of free amine on the disilylated ammonium salt to give eventually **5**. Indirectly supporting this mechanism is the reaction between **6** and a bulkier amine HNPr_2 which produces a mixture of hydrides, the ¹H NMR signals of which lie in the normal region (−4 to −5 ppm). Obviously, in this case the steric hindrance prevents attack of the silylated amine on the second silyl ligand.

Trisubstituted niobocenes commonly have one ligand in the central and two ligands in the lateral positions in the bisecting plane. In contrast, in **4** all the $(\text{SiMe}_2)_2\text{NBu}^t$ fragment, as a single unit, is shifted to the central position so that the effective symmetry is, with a very good accuracy, C_{2v} . Further structural data of **4** are also unusual. First of all, there is a short Si–Si contact of 2.654(2) Å, close to the upper end of single Si–Si bonds.⁹ Secondly, the Nb–Si bonds are unexpectedly long (2.680(2) and 2.685(1) Å), considering the presence of an electron-withdrawing nitrogen substituent, even longer than typical Nb–Si distances in trialkylsilyl derivatives (2.646–2.669(3) Å).¹⁰ In the related complexes $[\text{Cp}_2\text{W}\{(\text{SiMe}_2)_2(\mu\text{-O})\}]$ the W–Si bonds^{6d} of 2.547(4) and 2.559(4) Å are shorter than the W– SiMe_3 bonds in $\text{Cp}_2\text{W}(\text{SiMe}_3)\text{R}$ (range 2.591–2.602(4) Å).¹¹

To elucidate the structures of **4** and **5**, we performed DFT calculations on the model compounds $[\text{Cp}_2\text{Nb}(\text{H})\{(\text{SiH}_2)_2(\mu\text{-}$



[†] Electronic supplementary information (ESI) available: experimental section. Fig. 1S and Table 1S. See <http://www.rsc.org/suppdata/cc/b1/b111636c/>

[‡] Dedicated to Prof. Dr J. Lorberth on the occasion of his 65th birthday.

[§] Present address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany.

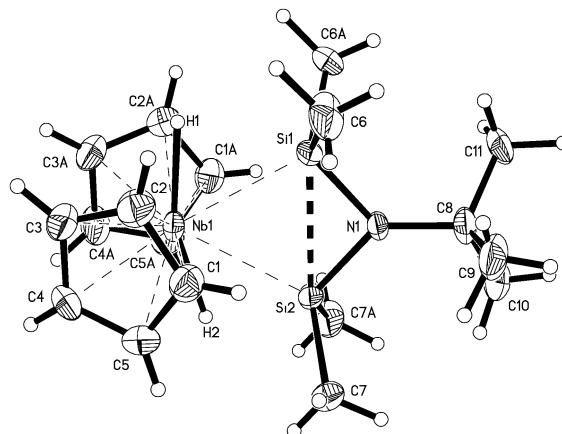
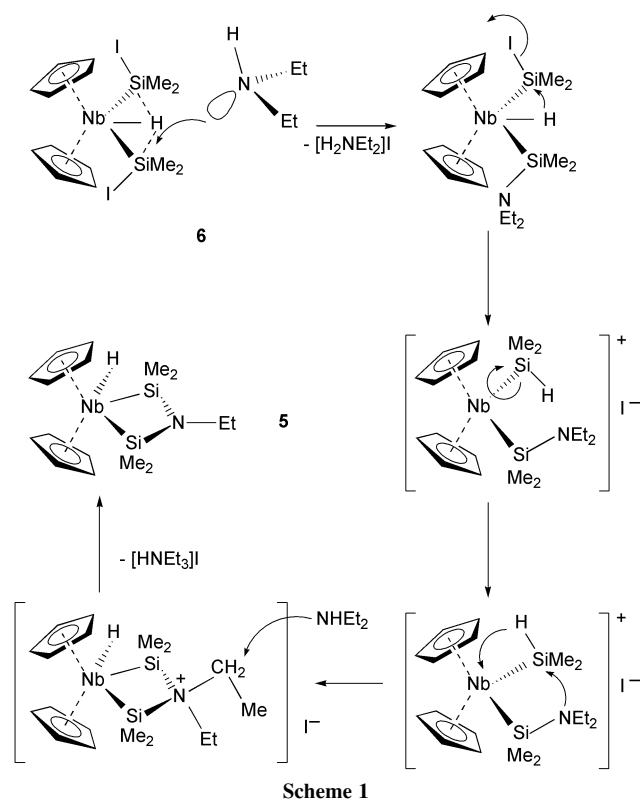


Fig. 1 Molecular structure of complex **4**. The hydride ligand is disordered.



NH)) (**8**) and $[\text{Cp}_2\text{Nb}(\text{H})\{\text{Si}(\text{Me}_2)_2(\mu\text{-NMe})\}]$ (**9**) and calculated the related bis(amidosilyl) derivative $[\text{Cp}_2\text{Nb}(\text{H})(\text{SiH}_2\text{NH}_2)_2]$ (**10**) with central position of the hydride for comparison. ^{††} The difference between **8** and **9** is minor and both satisfactorily reproduce the experimental geometry, thus establishing that steric factors are of *no importance* in this system. Although the calculated Nb–Si bonds are shorter than X-ray determined, comparison of **8** with **10** shows the relative lengthening of the Nb–Si bonds in the former. The hydride was optimised to a normal Nb–H distance of 1.772 Å.

Earlier, the classical nature of the 1,3-disilacyclobutanes $[(\mu\text{-X})\text{SiR}_2]_2$ (**1**) was established on the basis of low Wiberg bond indices (WBI) of 0.03.^{3b} The observed short Si–Si distances in **1** are believed to result from the X–X electrostatic repulsion.^{1a,3b} By way of contrast, in **8** the Nb and N atoms have opposite charges, which must lead to an attraction between these atoms and hence to the lengthening of the Si–Si distance. Nevertheless, this distance in **8** is short and high WBI (0.21) and NBO bond orders (0.33) were calculated for the Si–Si ‘bond’. These values are comparable with the corresponding parameters for the Nb–H bond and are only 1.5–2 times lower than those for the Nb–Si bonds. The exact reason for the shortening of the Si–Si distance and for the central shift of the $(\text{SiMe}_2)_2(\mu\text{-NMe})$ unit is not clear at the moment. However, long Nb–Si and short Si–Si distances, high-field shift of the hydride ¹H NMR signal which is close to that in d^2 $[\text{Cp}_2\text{Nb}(\text{PR}_3)\text{H}]$, suggesting that metal configuration is intermediate between d^0 and d^2 , and high Wiberg and NBO bond indices are consistent with the description of **4** as a stretched Si–Si σ -complex. Our calculations of the disilaaminocyclopropane $(\text{SiH}_2)_2(\mu\text{-NH})$ in its equilibrium configuration **A** and in a distorted form **B**, in which the Si–Si bond was forcibly elongated to the distance observed in **4**, show that this distortion requires only 17 kcal mol⁻¹ but there is a great difference in the electronic structure of both forms. The HOMO of **A** is the lone pair at nitrogen (pure p-orbital), below lies the outward inverted $sp^3\text{-}sp^3$ Si–Si bond. In contrast, the HOMO of **B** is a strained Si–Si bond, which according to the NBO analysis is $sp^{4.6}$ hybridised. Increased p-character makes this ‘banana-bond’ a good σ -donor. Thus $(\text{SiH}_2)_2(\mu\text{-NH})$ as a whole can act as a two-electron σ ligand,

amenable to σ -complexation to the $[\text{Cp}_2\text{NbH}]$ fragment. The residual Si–Si bonding will persist only if the back-donation from the metal is incomplete.¹³ In the case of **4** this could be due to small overlap of the $(\text{Si-Si})^*$ orbital with the niobocene orbital b_2 since the Si–Nb–Si angle of 59.3° is much less than the optimum value of 90°.

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Notes and references

† X-Ray structure analysis of **4**: $\text{C}_{18}\text{H}_{32}\text{NNbSi}_2$, $M = 411.54$, orthorhombic, space group $Pnma$, $a = 17.4105(4)$, $b = 13.2514(3)$, $c = 8.6175(2)$ Å, $V = 1308.6(12)$ Å³, $T = 150.0(2)$ K, (no. 62), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.724$ mm⁻¹. A total of 2151 reflections were measured (1993 observed). $R_1 = 0.0500$, $wR_2 = 0.1122$ and GOF = 1.246. CCDC reference number 157841. See <http://www.rsc.org/suppdata/cc/b1/b111636c/> for crystallographic data in CIF or other electronic format.

†† See Table 1S and Fig. 1S in ESI†† for details.

** The BP86 functional, which involves Becke’s exchange functional^{12a} in combination with Perdew’s correlation functional,^{12b} was employed. The (341/321/31) basis set with the ‘Los Alamos’ ECP^{12c} was used for niobium; (31/31/1) with the ‘Stuttgart’ ECP for silicon,^{12c} and 6-31G* for carbon and hydrogen were employed. The hydride H was supplemented by a set of polarization p functions.

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