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The Instability of Ni{N(SiMe₃)₂}₂: A Fifty Year Old Transition Metal Silylamide Mystery

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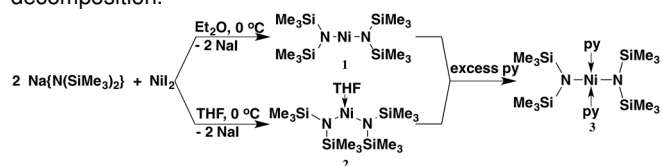
Dedicated to the memory of Prof. G. L. Hillhouse, maker of many fine contributions to nickel chemistry.

Abstract: The characterization of the unstable Ni(II) bis(silylamide) Ni{N(SiMe₃)₂}₂ (**1**), its THF complex Ni{N(SiMe₃)₂}₂(THF) (**2**), and the stable bis(pyridine) derivative trans-Ni{N(SiMe₃)₂}₂(py)₂ (**3**), are described. Both **1** and **2** decompose at ca. 25 °C to a tetrameric Ni(I) species, [Ni{N(SiMe₃)₂}]₄ (**4**), also obtainable from LiN(SiMe₃)₂ and NiCl₂(DME). Experimental and computational data indicate that the instability of **1** is likely due to ease of reduction of Ni(II) to Ni(I) and the stabilization of **4** via London dispersion forces.

In the early 1960s, Bürger and Wannagat reported that the bis(trimethylsilyl)amido ligand -N(SiMe₃)₂ stabilized the first 2- and 3-coordinate, open shell transition-metal complexes.^[1, 2] These included the M(II) species Mn{N(SiMe₃)₂}₂,^[2] Co{N(SiMe₃)₂}₂,^[1] and Ni{N(SiMe₃)₂}₂.^[2] The corresponding Fe(II) derivative, Fe{N(SiMe₃)₂}₂, was described in 1988.^[3] Uniquely, the Ni(II) amide was reported to be unstable, decomposing to a black solid at room temperature.^[2] The Mn, Fe, and Co silylamides are thermally stable and have proven to be valuable synthons in diverse applications,^[4-13] but the unstable nature of Ni{N(SiMe₃)₂}₂ has hindered its further use. Its instability is especially striking because several other stable, homoleptic Ni(II) amides are known. These include [(Ni(NPh₂)₂)₂]₂,^[14] the borylamides Ni{N(R)BMe₂}₂ (R = Ph or Mes),^[15,16] the primary terphenyl amides Ni{N(H)Ar^{Me6}}₂,^[17] Ni{N(H)Ar^{iPr4}}₂,^[18] and Ni{N(H)Ar^{iPr6}}₂,^[17] (Ar^{Me6} = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂, Ar^{iPr4} = C₆H₃-2,6-(C₆H₃-2,6-ⁱPr₂)₂, Ar^{iPr6} = C₆H₃-2,6-(C₆H₂-2,4,6-ⁱPr₃)₂), and Ni{N(SiMe₃)Dipp}₂ (Dipp = C₆H₃-2,6-ⁱPr₂).^[19,20] Computations indicated that the latter and its Fe and Co analogues are probably stabilized by attractive interligand dispersion forces.^[21,22]

We showed recently^[23] that the earlier reports on Co{N(SiMe₃)₂}₂^[1,10] actually described its THF complex Co{N(SiMe₃)₂}₂(THF).^[23,24] This prompted us to re-investigate the synthesis of the elusive Ni{N(SiMe₃)₂}₂ (**1**). We found that the addition of two equivalents of Na{N(SiMe₃)₂} to a THF slurry of NiI₂ at ca. 0 °C gave a red solution which upon workup gave a red oil (Scheme 1; see Supporting Information). Distillation yielded Ni{N(SiMe₃)₂}₂(THF) (**2**) instead of the earlier reported Ni{N(SiMe₃)₂}₂,^[2] as a mobile red liquid. Storage at ca. -18 °C gave green crystals of **2** suitable for X-ray diffraction. The THF free Ni{N(SiMe₃)₂}₂ (**1**) was obtained using diethyl ether as a

solvent. It distilled as a red vapor which condensed to give a yellow crystalline solid which has not yet proved amenable to X-ray crystallography. Crystals of **1** and **2** become black at room temperature and must be stored below -18 °C. ¹H NMR spectroscopy in C₇D₈ indicated that both **1** and **2** are paramagnetic and display a broad singlet at ca. 11 ppm due to the -N(SiMe₃)₂ protons. Complex **2** also features downfield THF proton signals which shift upfield at higher temperatures (Figure S5), consistent with dissociation of THF, as also seen for its Mn and Co analogs.^[23,25] Treatment of **1** or **2** with excess pyridine gave the diamagnetic bis(pyridine) complex trans-Ni{N(SiMe₃)₂}₂(py)₂ (**3**) as gold crystals. Complex **3** is stable as a crystalline solid or in pyridine solution at 25 °C, but dissociation of pyridine ligands in NMR solvents results in rapid decomposition.



Scheme 1. Summary of the synthesis of Ni{N(SiMe₃)₂}₂ (**1**) and its THF and pyridine complexes **2** and **3**.

For the structures of **2** and **3** (Figure 1), **2** has essentially trigonal planar geometry at Ni (Σ° Ni 359.86°) and it narrowly misses having a C₂ axis along the Ni-O bond, like its Fe and Co analogs.^[12,23,24] The Ni-N (1.8646(2) and 1.8570(2) Å) and Ni-O (2.0143(2) Å) bonds in **2** are shorter by ca. 0.05 and 0.02 Å than the Co-N and Co-O bonds in its Co analog (Table S2). However, the Ni-N bond lengths are similar to those in Ni{N(Mes)BMe₂}₂ (avg. 1.865 Å).^[15,16] The bis(pyridine) complex **3** has nearly ideal square planar coordination at Ni with interligand angles near 90°. The Ni-N(SiMe₃)₂ bond lengths (1.9394(4) and 1.9449(4) Å) are longer than those in **2** by ca. 0.08 Å, which is likely due to the higher coordination number and increased steric crowding in **3**. The Ni-N bonds are longer than those in Ni{N(Mes)BMe₂}₂, (avg. 1.884 Å),^[16] Ni{N(SiMe₃)Dipp}₂ (1.8029(9) Å),^[21] {Ni(NPh₂)₂}₂ (avg. 1.828 Å for terminal Ni-N bonds),^[14] and Ni{N(H)Ar}₂ (Ar = terphenyl) (avg. 1.821 Å).^[17,18]

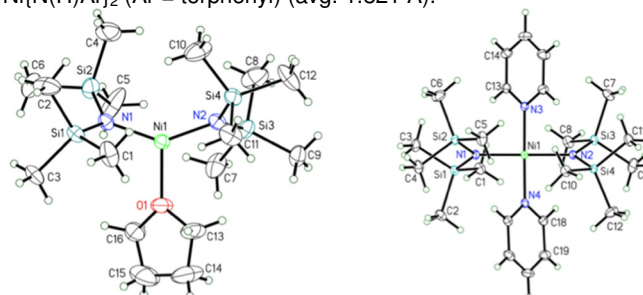


Figure 1. Thermal ellipsoid (50%) plots of Ni{N(SiMe₃)₂}₂(THF) (**2**, left) and Ni{N(SiMe₃)₂}₂(py)₂ (**3**, right). Selected bond lengths (Å) and angles (°) for **2**: Ni1-N1 1.8646(2), Ni1-N2 1.8570(2),

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Ni1-O1 2.0143(2), N1-Ni1-N2 140.664(5), N1-Ni1-O1 109.42(19), N2-Ni1-O1 109.78(19); **3**: Ni1-N1 1.9394(4), Ni1-N2 1.9449(4), Ni1-N3 1.9305(4), Ni1-N4 1.9314(4) Å, N1-Ni1-N2 179.2607(3), N3-Ni1-N4 179.0992(2).

Originally, Bürger and Wannagat reported that blood red $\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}_2$ (probably $\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})$) turned black after a short time at room temperature.^[2] We also found that **1** and **2** became black within 30 minutes at ca. 25 °C, but had greater stability as hydrocarbon solutions, whose red colors persist for 2–3 days at ca. 25 °C. A sample of **1** in toluene decomposed over 4–5 weeks during which time the red solution became black and precipitated black crystals that were shown to be $[\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}_4]$ (**4**) by X-ray crystallography. ¹H NMR spectroscopy of **2** in C_6D_6 indicated that decomposition to **4** yielded a second product which is $\text{HN}(\text{SiMe}_3)_2$ based on the observed singlet at ca. 0.1 ppm (Figure S7). Compound **4** can also be synthesized from $\text{LiN}(\text{SiMe}_3)_2$ and $\text{NiCl}_2(\text{DME})$ in Et_2O .^[25] Workup of the dark amber solution afforded black crystals of **4** suitable for X-ray crystallography.

The structure of **4** (Figure 2) has four Ni(I) ions in an approximate square plane and bridged by four $\text{N}(\text{SiMe}_3)_2$ ligands. A C_2 axis bisects the N(1) and N(3) atoms, to give two crystallographically unique Ni(1) sites on adjacent edges of the Ni_4 square. The N-Ni-N units deviate from linearity such that the Ni nuclei are displaced toward each other with Ni...Ni distances of 2.4328(4) and 2.4347(5) Å (cf. sum of single bond covalent radii for two Ni atoms = 2.20 Å).^[27] The Ni...Ni distances in **4** are ca. 0.25 Å shorter than the $\text{Cu}\cdots\text{Cu}$ separations in $[\text{Cu}\{\text{N}(\text{SiMe}_3)_2\}_4]$,^[2,25,28] 2.6770(7) and 2.6937(7) Å. Consistent with its bridging character, the average Ni-N bond length in **4** (1.916 Å) is longer than those in two-coordinate Ni(II) amides (1.803(9)–1.885(4) Å)^[15,18–20] and in the three-coordinate Ni(I) amides $(\text{Ph}_3\text{P})_2\text{NiN}(\text{SiMe}_3)_2$ (1.88(1) Å),^[29] $[\{\text{CHN}(\text{Dipp})\}_2\text{C}]\text{NiN}(\text{SiMe}_3)_2$ (1.865(2) Å),^[30] and $(\text{Bu}^t_2\text{PCH}_2\text{CH}_2\text{P}^t\text{Bu}^t)_2\text{Ni}\{\text{N}(\text{H})\text{Dipp}\}$ (1.882(2) Å).^[31]

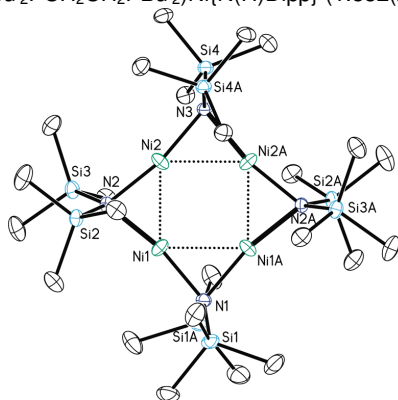


Figure 2. Thermal ellipsoid (50%) plot of $[\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}_4]$ (**4**, without H atoms). Ni1-N1 1.9127(2) Å, Ni1-N2 1.9151(2) Å, Ni2-N1 1.9166(2) Å, Ni2-N2 1.9189(2) Å, Ni1...Ni2 2.4328(4) Å, Ni1...Ni1A 2.4347(5) Å, Ni1-N2-Ni2 78.77(1)°, N1-Ni1-N2 168.80(4)°, N2-Ni2-N3 168.90(4)°

Magnetic studies of **4** yielded a χT vs. T plot (Figure S14) indicative of antiferromagnetic exchange between Ni(I) centers. Since the coordination of the four nickels is essentially the same, the magnetic data were fit with the Hamiltonian $H = -2J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1)$, assuming a single exchange coupling constant, J , for the Ni(I)-Ni(I) exchange. The best fit was obtained with $S_i = 1/2$ and $g = 2$ for the Ni ions, and yielded $J = -102(2) \text{ cm}^{-1}$, a value typical for the exchange pathways involved. The singlet ground state of **4** is well reproduced by calculations

at the CASSCF/NEVPT2 level of theory (see SI), but there are low-lying triplet and quintet states whose population at higher temperatures accounts for the μ_{eff} value of 2.70 μ_B measured for **4** at 300 K. The only other Ni(I) species similar to **4** is $[\text{Ni}(\text{NP}^t\text{Bu}_3)]_4$.^[32] However, the two complexes differ structurally and magnetically. The N-Ni-N angles in $[\text{Ni}(\text{NP}^t\text{Bu}_3)]_4$ are 180°, and the Ni_4N_4 core is folded along one of the $\text{N}\cdots\text{N}$ axes to yield a Ni...Ni separation of 2.375(3) Å (ca. 0.06 Å shorter than **4**). The magnetic moment of $[\text{Ni}(\text{NP}^t\text{Bu}_3)]_4$ at 27 °C is 4.40 μ_B and indicates a higher contribution from higher spin states.

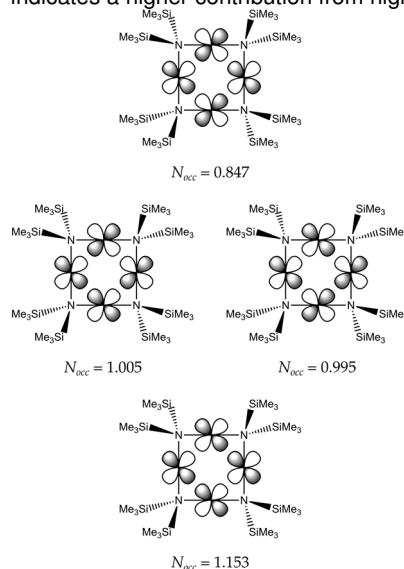


Figure 3. Schematic illustration of important natural orbitals from a CASSCF[4,4] calculation on **4**.

The ground state wave function for **4** is strongly multiconfigurational in character, as is evident from the CASSCF CI-vector or from the CASSCF natural orbital occupation numbers (Figure 3). Four electrons occupy four natural orbitals, roughly one each, that are composed of a set of nickel d-orbitals in four possible combinations. The natural orbitals show both bonding and anti-bonding Ni...Ni character. However, since the occupancies of the fully bonding (1.153) and anti-bonding (0.847) combinations deviate significantly from 1, there remains some very weak metal...metal bonding character in **4**. More detailed magnetic and computational studies of **4** are in hand.

The experimental data clearly show that the stability of **1** is far lower than its Mn, Fe, or Co analogs. The decomposition of **1** into **4** involves cleavage of Ni-N bonds with reduction of Ni(II) to Ni(I), the exact mechanism of which is unknown. The energetics of the decomposition process can, however, be evaluated at dispersion corrected DFT level (LC- ω PBE-D3/def-TZVP) by making the assumption that the formation of $\text{HN}(\text{SiMe}_3)_2$ involves hydrogen abstraction from the solvent (ether). The results show that homolytic cleavage of one of the Ni-N bonds in **1** has a high energetic penalty, and the formation of **4**, $\text{HN}(\text{SiMe}_3)_2$ and ether radical is only barely exergonic, -2 kJ mol^{-1} . We note that the dispersion correction plays in this instance a major role by lowering the calculated reaction energy as much as 85 kJ mol^{-1} . In contrast, similar calculations for the Co analog of **1** show that the formation of $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_4]$ is endergonic by as much as 154 kJ mol^{-1} even with dispersion. It should be noted that the calculations do not take solvent effects into account nor is the fate of the ether radical modelled in any way. The predicted qualitative trend should, however, be unaffected by these, and indicates significant differences in the stability of the Ni(I) and Co(I) products. Additional support for the

large energy difference comes from the M(I/II) oxidation potentials of the related amido M(I) monoanions $[M\{N(SiMe_3)_2Dipp\}_2]^-$ (-0.152 and -1.082 V for Co and Ni, respectively),^[33] which indicate that with amido ligands the process $Ni(II) \rightarrow Ni(I)$ is more favored than $Co(II) \rightarrow Co(I)$.

Indirect evidence for homolytic Ni-N dissociation comes from the reaction of $Na\{N(SiMe_3)_2\}$ and NiI_2 in pyridine which yielded an orange solution. Workup gave two crystalline products: orange blocks of $Ni\{N(SiMe_3)(SiMe_2CH_2)\}(py)_2$ (**5**) and gold needles of the aforementioned **3** in a ca. 3:1 ratio. In **5** (Figure 4), Ni is bound to two *cis*-oriented pyridines, an amido nitrogen (N1), and the carbon from a deprotonated Si2 methyl group. The C-H activation of methyl substituents in sterically crowded trimethylsilylamido transition metal complexes is well-known,^[21,34-38] but **5** is apparently the first example for nickel. Complex **5** has distorted square planar geometry at Ni ($\Sigma^\circ Ni = 360.07^\circ$) and a lengthening of the Ni-py bond *trans* to the deprotonated methyl group, Ni1-N2 = 1.9992(15) Å (*cf.* 1.9197(14) and 1.9119(15) Å for Ni1-N1 and Ni1-N3). At 1.8329(17) Å, the Si2-C6 bond is shorter than the other Si-C bonds in **5** (avg. 1.883 Å). Another interesting feature of **5** is its slightly pyramidal geometry at N1 ($\Sigma^\circ N1 = 353.74^\circ$), whereas **2** and **3** have planar geometry at the amido nitrogens.

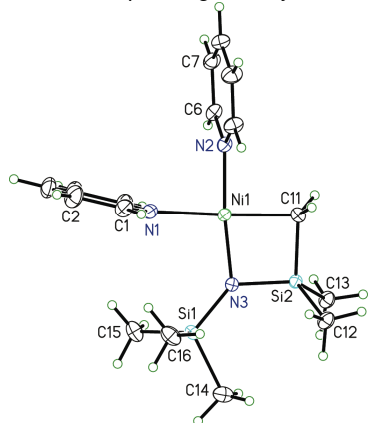


Figure 4. Thermal ellipsoid (50%) drawing of $Ni\{N(SiMe_3)(SiMe_2CH_2)\}(py)_2$ (**5**). Ni1-N1 1.9197(14) Å, Ni1-N2 1.9992(15) Å, Ni1-N3 1.9119(15) Å, Ni1-C6 1.9707(17) Å, Si2-C6 1.8329(17) Å, N2-Ni1-N3 87.51(6)°, N3-Ni1-C6 89.72(6)°, C6-Ni1-N1 84.41(6)°, N1-Ni1-N2 98.42(6)°.

In conclusion, we have described the unstable Ni(II) bis-silylamides $Ni\{N(SiMe_3)_2\}_2$ (**1**) and $Ni\{N(SiMe_3)_2\}_2(THF)$ (**2**) as well as the pyridine complex $Ni\{N(SiMe_3)_2\}_2(py)_2$ (**3**). We showed that **1** and **2** decompose to the tetrameric Ni(I) amide $[Ni\{N(SiMe_3)_2\}]_4$ (**4**). The tetramer **4**, along with $Ni\{N(SiMe_3)(SiMe_2CH_2)\}(py)_2$ (**5**), suggest that the decomposition of **1** and **2** formally occurs via homolytic fission of a Ni-N bond but the mechanistic details of this process are unknown. Computations indicate that the instability of **1** and **2** in comparison to their Mn, Fe, and Co analogs may be due to the greater tendency of Ni(II) to be reduced as the energies of the d-electrons decrease across the 3d-series.^[39] However, the quasi-stability of **1** and **2** in solution should permit their use as synthons, a use that is currently being investigated.

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- [40] CCDC 1401113, 1401114, 1401115, and 1401116 contain the supplementary crystallographic data for compounds **2-5** in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.