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Synthesis, Molecular Structure, and Reactivity of the First Strained [2]Silanickelocenophane

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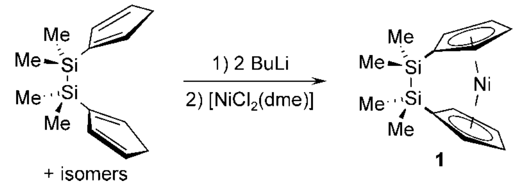
Summary: The strained ansa-complex [($Me_2Si)_2Cp_2Ni$] was synthesized by dilithiaton of 1,2-bis(cyclopentadienyl)-1,1,2,2-tetramethyldisilane with BuLi and subsequent reaction with [$NiCl_2$(dme)]. The molecular structure was confirmed by X-ray diffraction analysis. Reaction of the ansa-complex with nickeltetra(tert-butylisonitrile) leads to rearrangement of the ligand framework to form a dinuclear compound.

Over the past 15 years strained metallocenophanes have received great attention because of their structural and electronic properties as well as their reactivity. Iron complexes with different number and kind of bridging elements connecting the cyclopentadienyl rings constitute classical examples of strained metallocenophanes. Most commonly, strained *ansa*-complexes are synthesized by salt elimination reactions from dimetalated metallocenes and suitable element dihalides.[1] Strained *ansa*-complexes with π-aromatic five-, six-, or seven-membered rings and different bridging elements can also be obtained via this general synthetic route and have been reported for various transition metals of groups 4 to 8 (Ti, V, Cr, Mo, Mn, Fe, Ru).[2]

For nickel, however, this synthetic access via dimetalated nickelocene is precluded, due to loss of one Cp ring upon treatment of [Cp_2Ni] with organolithium or -magnesium compounds and subsequent formation of polynuclear species.[3] Consequently, knowledge on *ansa*-nickelocenes is severely restricted, and only very recently the first nonstrained [*n*]carbanickelocenophanes ($n = 4, 6$) were prepared by ring-closing metathesis of 1,1′-bis(alkenyl)-substituted nickelocenes.[4] Corresponding strained *ansa*-complexes, however, remained unknown.

Scheme 1. Synthesis of 1



In cases where metallocenes are not susceptible to dimetalation, *ansa*-complexes can be obtained from suitable ligand precursors of the type $R_nE(\eta^1\text{-}C_5H_5)_2$, subsequent to deprotonation and reaction with transition metal halides, a method successfully employed particularly for metallocenophanes of group 4 elements[5] and to a much lesser extent for metallocenophanes of late transition metals (Fe, Ru, Co).[2n,6] Here we report the synthesis and molecular structure of the first strained [2]nickelocenophane and its conversion to a novel dinuclear diamagnetic half-sandwich species.

The title compound **1** was synthesized in a straightforward two-step procedure, by deprotonation of 1,2-bis(cyclopentadienyl)-1,1,2,2-tetramethyldisilane with BuLi at −78 °C in toluene/ether (1:1) and subsequent reaction of the dilithiated intermediate with [$NiCl_2$(dme)] at −78 °C in THF (Scheme 1). After workup the product was isolated as a green, highly air- and moisture-sensitive solid in 64% yield.

Single crystals suitable for X-ray diffraction studies could be obtained by crystallization from hexane at −30 °C (Figure

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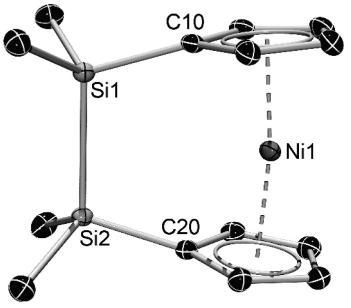
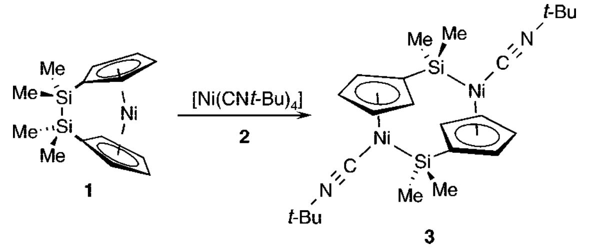


Figure 1. Molecular structure of **1a**. Selected bond lengths [Å] and angles [deg]: Si1−Si2 2.3638(4), $X_{Cp}1-X_{Cp}2$ 3.606, Ni1−$X_{Cp}1$ 1.808, Ni1−$X_{Cp}2$ 1.808, C10−Si1−Si2−C20 2.17, $X_{Cp}1$−Ni1−$X_{Cp}2$ 171.40 ($X_{Cp}1$, $X_{Cp}2$ = centroids of the C_5H_4 rings).

1).[7] Compound **1** crystallizes in the monoclinic space group $P2_1/c$ and contains two independent molecules in the asymmetric unit. These molecules differ primarily in the dihedral angle C10−Si1−Si2−C20, and thus, one molecule (**1a**) displays an almost eclipsed (2.17°) arrangement of the cyclopentadienyl rings, while the second (**1b**) is characterized by a larger dihedral angle (13.46°). All other pertinent structural parameters are almost identical, and hence, only the structure of **1a** will be discussed in detail.

The most significant structural feature is the tilt angle (α = 9.37(8)°), which indicates a more pronounced molecular strain than reported for the corresponding [2]silaferrocenophane (α = 4.19(2)°)[8] or related Si_2-bridged metallocenophanes.[2c,f] Likewise, the deformation angle δ (defined by the ring centroids and the metal center) of **1a** (δ = 171.40°) shows a greater deviation from linearity than in the analogue iron complex (δ = 176.48(3)°), thus providing further evidence for an increased molecular strain in the former compound. These findings can tentatively be ascribed to the increased separation of the cyclopentadienyl ring centroids in **1a** (3.606 Å) in comparison to the corresponding disilaferrocenophane (3.286 Å), thus reflecting the significant difference in the parent compounds nickelocene (3.633 Å)[9] and ferrocene (3.295 Å).[10] The overall geometry of the Si_2Me_4 bridge, such as the Si−Si distance of 2.3638(4) Å, is unobtrusive and matches those of related [2]silametallocenophanes, which due to the eclipsed disposition of the cyclopentadienyl rings often display elongated Si−Si separations compared to typical (exocyclic) Si−Si bond distances (approximately 2.34 Å).[2c,f,8]

Scheme 2. Synthesis of 3.



In solution, complex **1** was analyzed by ^{1}H NMR spectroscopy, revealing two broad and strongly shielded resonances at δ = −229.79 and −254.96 that can be assigned to the α- and β-protons of the cyclopentadienyl rings, thus being in the typical range of silylated paramagnetic nickelocene species.[11] The additional sharp signal at δ = 15.34 can be assigned to the methyl groups.

To provide initial information on the influence of the *ansa*-bridge on the reactivity of the title compound, **1** was treated with [Ni(CN*t*-Bu)$_4$] (**2**) at room temperature to afford [(Me$_2$Si)(η^5-C_5H_4)Ni(CN*t*-Bu)]$_2$ (**3**) as an orange solid in 24% yield (Scheme 2). Despite the low yield, no other byproducts could be detected by ^{1}H NMR spectroscopy because of paramagnetic impurities in solution.

The formation of **3** is in sharp contrast to the corresponding reaction of parent [Cp_2Ni] with **2** that leads to a dinuclear species with a CN*t*-Bu-bridged Ni−Ni bond.[12] Here, however, the Si_2 bridge is cleaved with formation of two Si−Ni bonds, thus leading to a structural motif that is unprecedented for Ni half-sandwich complexes, but has been observed for Fe, Ru, Mo, and W.[13] It should be noted, though, that these species were not obtained from corresponding [2]silametallocenophanes.

Single crystals suitable for X-ray diffraction analysis were obtained from hexane at room temperature. **3** crystallizes in the triclinic space group *P*-1 and the molecule adopts C_i symmetry (Figure 2).[7] All pertinent structural parameters, particularly the Ni1−Si1 (2.2458(3) Å)[14] and average Ni1−C(Cp) distances (2.0409(11)−2.1589(12) Å)[15] are unobtrusive and in the expected range. Likewise, the Si centers adopt an only slightly distorted tetrahedral geometry (C1−Si1−Ni1 107.48(4)°), and the isonitrile ligands display the expected almost linear arrangement (C8−N1−C9 167.17(13)°).

The diamagnetic compound **3** was also characterized by multinuclear NMR spectroscopy. The ^{1}H NMR spectrum reveals two virtual triplets at δ = 5.77 and 5.60 for the α- and β-protons of the cyclopentadienyl rings, and two single resonances can be assigned to the CMe_3 (δ = 0.89) and the $SiMe_2$ groups (δ = 0.81), respectively. The Ni-bound carbon atoms of the isonitrile ligands are characterized by a resonance at δ = 108.16

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(7) The crystal data of **1** and **3** were collected at a Bruker X8APEX diffractometer with CCD area detector and multi-layer mirror monochromated Mo Kα radiation. The structures were solved using direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen, 1997), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for **1**: $C_{14}H_{20}NiSi_2$, M_r = 303.19, green block, 0.29 × 0.23 × 0.11, monoclinic space group $P2_1/c$, a = 8.1406(2) Å, b = 16.7750(4) Å, c = 21.4929(5) Å, β = 90.5000(10)°, V = 2934.93(12) Å^3, Z = 8, ρ_{calcd} = 1.372 g·cm^{-3}, μ = 1.462 cm^{-1}, $F(000)$ = 1280, T = 100(2) K, R_1 = 0.0412, wR_2 = 0.0755, 11 632 independent reflections [$2\theta \le 76.62°$] and 307 parameters. Crystal data for **3**: $C_{24}H_{38}N_2Ni_2Si_2$, M_r = 528.16, yellow block, 0.31 × 0.26 × 0.16, triclinic space group $P\bar{1}$, a = 6.5827(2) Å, b = 8.7450(3) Å, c = 11.4819(3) Å, α = 100.3620(10)°, β = 90.3490(10)°, γ = 93.1940(10)°, V = 649.09(3) Å^3, Z = 1, ρ_{calcd} = 1.351 g·cm^{-3}, μ = 1.556 mm^{-1}, $F(000)$ = 280, T = 100(2) K, R_1 = 0.0249, wR_2 = 0.0624, 3612 independent reflections [$2\theta \le 66.04°$] and 136 parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-659559 (**1**) and CCDC-659560 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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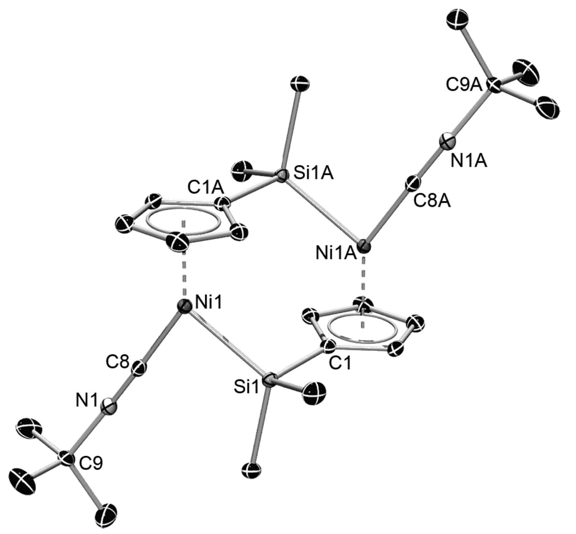

Figure 2. Molecular structure of **3**. Selected bond lengths [Å] and angles [deg]: Si1−Ni1 2.2458(3), Ni−X_{Cp}1 1.747, Si1−C1 1.8686(13), C8−N1−C9 167.17(13).

in the ^{13}C NMR spectrum, while the ^{29}Si NMR spectrum displays a single resonance at $\delta = 16.6$ for the bridging Si atoms.

We reported the first strained [2]silanickelocenophane, which was obtained from a dianionic ligand precursor and [$NiCl_2$(dme)]. Reaction of the title compound with [Ni(CN*t*-Bu)$_4$] furnished a novel dinuclear half-sandwich species, thus proving the decisive influence of the *ansa*-bridge on the reactivity of this species.

Experimental Section. All manipulations were carried out under a dry argon atmosphere with common Schlenk techniques. Solvents were dried with a solvent purification system (SPS) from M. Braun and stored under argon over molecular sieves; reagents were dried and purified by standard procedures. [$NiCl_2$(dme)],[16] [Ni(CN*t*-Bu)$_4$],[17] and 1,2-bis(cyclopentadienyl)-1,1,2,2-tetramethyldisilane[18] were synthesized according to literature procedures. BuLi was obtained commercially and used without further purification. NMR spectra were recorded on a Bruker Avance 500 (400) at 500.13 MHz (400.13 MHz) (^{1}H, internal standard TMS), 125.77 MHz (^{13}C{^{1}H}, internal standard TMS), and 99.36 MHz (^{29}Si, internal standard TMS). Elemental analyses (C, H, N) were obtained from a Leco Instruments elemental analyzer, type CHNS 932.

[(Me$_2$Si)$_2$(η^5-C$_5$H$_4$)$_2$Ni] (1). A solution of 0.57 g (2.32 mmol) of 1,2-bis(cyclopentadienyl)-1,1,2,2-tetramethyldisilane in 10 mL of toluene/ether (9:1) was cooled to −78 °C, and a solution of *n*-BuLi in hexane (2.90 mL, 4.64 mmol, 1.6 mol L^{-1}) was added dropwise over 30 min. After warming to room temperature, the mixture was allowed to stir for 18 h. The white precipitate was filtered, washed with hexane, dried *in vacuo*, and dissolved in 30 mL of THF. The solution was cooled to −78 °C, and 0.51 g (2.32 mmol) [$NiCl_2$(dme)] was added. The dark green reaction mixture was allowed to warm to room temperature and stirred for 18 h. All volatiles were removed *in vacuo*, the residue was dissolved in 30 mL of hexane, and the insoluble components were filtered off. After removing the volatiles *in vacuo*, the dark green residue was purified by sublimation. Yield: 0.45 g (1.48 mmol, 64%) of **1** as a green solid. ^{1}H NMR (400.13 MHz, C_6D_6): δ 15.34 (s, 12 H, SiMe$_2$), −229.79 (br, 4 H, Cp*H*), −254.96 (br, 4 H, Cp*H*) ppm. Anal. Calcd (%) for $C_{12}H_{20}Si_2Ni$: C 55.46, H 6.65. Found: C 55.56, H 6.72.

[(Me$_2$Si)(η^5-C$_5$H$_4$)Ni(CN*t*-Bu)]$_2$ (3). A mixture of 0.081 g (0.268 mmol) of **1** and 0.105 g (0.268 mmol) of [Ni(CN*t*-Bu)$_4$] (**2**) was stirred in 15 mL of hexane at room temperature for 18 h. The suspension was filtered, and the red-brown solution concentrated to 3 mL. After 2 days at room temperature, orange crystals could be isolated. Yield: 0.034 g (0.064 mmol, 24%) of **3** as orange crystals. ^{1}H NMR (500.13 MHz, C_6D_6): δ 5.77 (vt, 4 H, Cp*H*), 5.60 (vt, 4 H, Cp*H*), 0.89 (s, 18 H, *t*-Bu), 0.81 (s, 12 H, SiMe$_2$) ppm. ^{13}C NMR (125.77 MHz, C_6D_6): δ 108.16 (N*C*), 95.98 (*C*Cp), 93.71 (*C*Cp), 56.15 (*C*(CH$_3$)$_3$), 30.19 (C(*C*H$_3$)$_3$), 8.16 (SiMe$_2$) ppm. ^{29}Si NMR (99.36 MHz, C_6D_6): δ 16.64 ppm. Anal. Calcd (%) for $C_{24}H_{38}N_2Si_2Ni_2$: C 54.58, H 7.25, N 5.30. Found: C 53.31, H 7.21, N 5.48.

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Supporting Information Available: X-ray structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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