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Communications

Synthesis and Characterization of the First Aluminum-Bridged [1]Ferrocenophane[†]

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Summary: The first example of a [1]ferrocenophane with a heavier group 13 element in the bridging position is described. The [1]aluminaferrocenophane, with the aluminum atom equipped with a bulky and intramolecularly stabilizing ligand, has been synthesized and structurally characterized by NMR spectroscopy and single-crystal X-ray analysis.

In 1975 Osborn and Whiteley described the first [1]ferrocenophane, a strained organometallic compound that contained silicon in the bridging position (ER$_x$ = SiPh$_2$; Figure 1).[1] Three decades later, Manners et al. discovered that ring-opening polymerization (ROP) of [1]silaferrocenophanes provides access to poly(ferrocenylsilanes) with high molecular weights.[2] Today, [1]-ferrocenophanes with main-group elements in the bridging position are known from group 16 (S, Se),[3,4] 15 (P, As),[5−8] 14 (Si, Ge, Sn),[1,2,5,6,9−11] and 13 (B)[12,13] elements, with the [1]boraferrocenophanes being the most recent examples in this series (ER$_x$ = BN(SiMe$_3$)$_2$, BN(SiMe$_3$)-*t*Bu, BN*i*Pr$_2$). However, [1]ferrocenophanes with heavier bridging group 13 elements are unknown today. Surprisingly, even simpler compounds such as ferrocenylalanes[14,15] or gallanes are very rare, with some interesting ferrocenylgallanes being characterized recently.[16−18] Within this report we describe the synthesis and structural characterization of the first [1]aluminaferrocenophane.

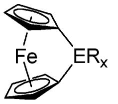

Figure 1. ER$_x$-bridged [1]ferrocenophane.

On the basis of our experience with organic ligands that are capable of intramolecular donation,[19−21] we decided to attach a trisyl ligand[22] in which one of the methyl groups is replaced by a 2-pyridyl group to aluminum (trisyl = tris(trimethylsilyl)methyl, C(SiMe$_3$)$_3$; commonly denoted as Tsi). The ligand C(SiMe$_3$)$_2$-(SiMe$_2$C$_5$H$_4$N-2) was described for the first time in 2000,[23] and since then, investigations have been published dealing with new compounds equipped with this ligand.[23−27] Very recently, the first compounds with group 13 elements containing this unique ligand were reported, including the two alanes (Pytsi)AlCl$_2$ and (Pytsi)AlMe$_2$ (Pytsi = C(SiMe$_3$)$_2$(SiMe$_2$C$_5$H$_4$N-2)).[28] In-

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[†] Dedicated to Professor Peter Paetzold on the occasion of his 70th birthday.

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dependent from this publication, we had started to exploit the chemistry of "pytrisyl" alanes recently.

A slurry of dilithioferrocene·$^2/_3$(TMEDA)[29] in toluene was slowly added to a solution of (Pytsi)$AlCl_2$ to a give the aluminum-bridged ferrocenophane **1**. Compound **1** was isolated from hexane solution as red crystals in a moderate yield of 31% (eq 1).[30] Suitable single crystals for X-ray structural analysis of compound **1** were grown from hexane solutions at ambient temperatures.[31]

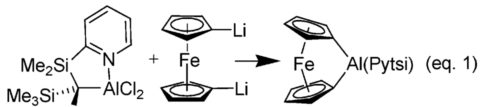

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Figure 2 shows the molecular structure of compound **1** in the crystal lattice. The aluminum-bridged ferrocenophane **1** crystallizes in the space group $P2_1/c$ with half of a molecule of $FeCp_2$ in the asymmetric unit. However, we could not find any unusually short intermolecular distances in the lattice that would indicate additional chemical interactions. Aluminum is distorted tetrahedrally surrounded by C7, N1, C16, and C21. The "tetrahedral" angles cover a wide range, with the smallest angle of 95° dictated by the ferrocene moiety (C16−Al1−C21) and the largest with 125° for C21−Al1−C7 (see Figure 2). As expected, the five-membered ring exhibits an envelope conformation, with C7 being 0.613(5) Å away from the least-squares plane Si1−C6−N1−Al1. The four bonds around the aluminum atom are very similar in length, and the values of 1.981(4) Å for Al1−N1 and 2.026(5) Å for Al1−C7 are slightly larger than those of 1.94 and 1.98 Å determined for the respective bonds in (Pytsi)$AlCl_2$.[28] Commonly, key structural features of a [1]ferrocenophane are described by a set of different angles, as illustrated in Figure 3.

The ferrocenophane **1** is a strained compound with the tilt angle $\alpha = 14.9(3)°$ (Figure 3). On the basis of pure geometric considerations, one would expect that a [1]aluminaferrocenophane would exhibit ring tilt values that are between those of germanium- and tin-bridged species.[32] One of the first structurally characterized ferrocenophanes was a germanium compound with $GePh_2$ as the bridging unit.[5,6] A few years later, a ferrocenophane bridged by $GeMe_2$ was characterized, followed by a report of the first [1]stannaferrocenophane. The tilt angles α were determined to be 16.6(15)° ($GePh_2$),[5,6] 19.0(9)° ($GeMe_2$),[9] 14.1(2)° (Sn*t*Bu_2),[10] and 15.2(2)° ($SnMes_2$),[11] illustrating that the [1]aluminaferrocenophane **1** with $\alpha = 14.9(3)°$ falls in the expected range.

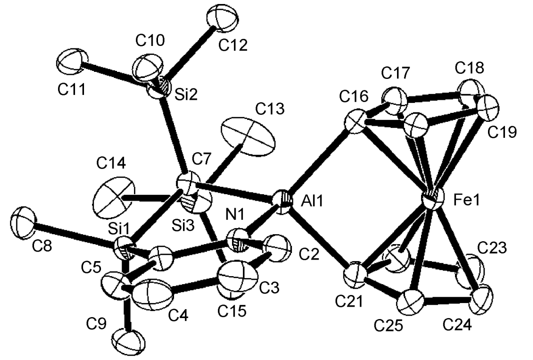

Figure 2. Molecular structure of **1** with thermal ellipsoids drawn at the 30% probability level. H atoms and $^1/_2$ $FeCp_2$ are omitted for clarity (see the Supporting Information for details).

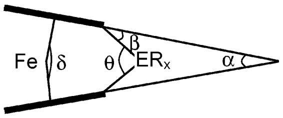

Figure 3. Common set of angles to describe [1]ferrocenophanes (data for **1**: $\alpha = 14.9(3)°$, $\beta = 43.1°$, $\gamma = 167.9°$, $\theta = 94.7(2)°$).

The ^1H NMR spectrum of the isolated product **1** clearly reveals a 1:1 ratio between a 1,1′-ferrocenyl moiety and a $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$ ligand, plus the presence of a 2-fold symmetry element. For example, the Cp range of the spectrum consists of four pseudo-triplets between δ 3.91 and 4.68. In addition, the sharp singlet at δ 3.99 indicates the presence of $^1/_2$ equiv of $FeCp_2$. Differences between the pseudo-triplets are commonly taken as an indication for a [1]ferrocenophane, and one might interpret the large splitting of $\Delta\delta = 0.77$ in **1** as being due to a highly strained ferrocenophane. However, the lower symmetry of **1** compared to that of ferrocenophanes with ER_2 bridging units (E = group 14 element) might contribute to the large splitting. In ^{13}C NMR spectra of [1]ferrocenophanes, the most informative chemical shifts are those of the *ipso*-C atoms of the Cp rings. It is known that their ^{13}C NMR values are shifted upfield with respect to the parent ferrocene (δ 68) with typical values of δ 33.1 ($SiMe_2$), 30.0 ($GeMe_2$), 34.9 (Sn*t*Bu_2), and 38.2 ($SnMes_2$).[11] Boron-bridged [1]ferrocenophanes are the highest strained ferrocenophanes known today, but surprisingly their *ipso*-C atoms resonate at relatively low field (δ 44−45; B(NRR′)).[12,13] This effect was attributed to the electropositive nature of the

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[30] Synthesis of **1**: $Cl_2AlC(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$ (1.49 g, 3.80 mmol) was dissolved in toluene (30 mL) and chilled to −10 °C. A suspension of $[Fe(\eta^5\text{-}C_5H_4Li)_2]\cdot{}^2/_3$TMEDA (1.05 g, 3.81 mmol) in toluene (30 mL) was added dropwise via tubing. After the solution was stirred for 16 h, the color changed to purple. After filtration, the solvent was removed under high vacuum (25 °C/0.01 mbar) to yield a dark purple, viscous oil. The residue was extracted with hexane (2 × 10 mL). After removal of some hexane, product **1** was obtained as $\mathbf{1}\cdot{}^1/_2FeCp_2$ as red crystals at room temperature (0.701 g, 31% with respect to (Pytsi)$AlCl_2$). NMR spectra in C_6D_6 at 25 °C, unless noted differently: ^1H NMR (500 MHz; C_6D_6 at 25 °C) δ 0.41 (s, 18H, $SiMe_3$), 0.45 (s, 6H, CH_3), 3.91, 4.31, 4.64, 4.68 (pst, 8H, C_5H_4), 3.99 (s, 5H, $FeCp_2$), 6.44, 6.84 (t, 2H, C_6H_4N), 6.98, 8.73 (d, 2H, C_6H_4N); ^{13}C NMR (125.8 MHz) δ 0.71 (Si-*C*$(SiMe_3)_2$−Al, −40 °C, C_7D_8), 3.67 (Si−*C*H_3), 6.52 ($SiMe_3$), 52.92 (*ipso*-C of C_5H_4−Al, −40 °C, C_7D_8), 68.30 ($FeCp_2$), 75.64, 75.69, 76.94, 77.27 (C_5H_4−Al), 124.18, 129.50, 138.93, 147.48 (2-C_6H_4N), 174.54 (*ipso*-C of 2-C_6H_4N); ^{27}Al NMR (130.3 MHz, C_7D_8, 60 °C): δ 141 ($h_{1/2}$ = 2000 Hz); MS (70 eV) *m/z* (%) 295 (35) $[C_{14}H_{29}Si_3N^+]$, 280 (100) $C_{13}H_{26}Si_3N^+]$, 264 (6) $[C_{12}H_{22}Si_3N^+]$, 186 (12) $[Cp_2Fe^+]$, 73 (9) $[SiMe_3^+]$. Anal. Calcd for $C_{29}H_{41}AlFe_{1.5}NSi_3$ (598.66): C, 58.18; H, 6.90; N, 2.34. Found: C, 58.81; H, 7.52; N, 2.39.

[31] Crystal data for $\mathbf{1}\cdot{}^1/_2FeCp_2$: $C_{29}H_{41}AlFe_{1.5}NSi_3$; monoclinic; space group $P2_1/c$; unit cell dimensions a = 19.3070(5) Å, b = 11.8720(4) Å, c = 13.5850(3) Å, α = 90°, β = 94.113(2)°, γ = 90°; V = 3105.83(15) Å^3; Z = 4; calculated density 1.280 mg/m^3; T = 173(2) K; λ = 0.710 73 Å; 18 974 reflections collected; 5488 independent reflections (R_{int} = 0.1079); completeness to θ of 25.03°, 99.9%; no absorption correction; refinement method, full-matrix least squares on F^2; no. of data/restraints/parameters = 5488/61/372; GOF = 1.072; final R1 = 0.0678, wR2 = 0.1347 ($I > 2\sigma(I)$) and R1 = 0.1166, wR2 = 0.1530 (all data).

[32] Covalent radii: Al (1.25 Å for CN = 3), Ge (1.22 Å for CN = 4), Sn (1.40 Å for CN = 4). Taken from: Holleman-Wiberg. *Inorganic Chemistry*, 1st English ed.; Academic Press: San Diego, London, 2001.

boron atom. The ^{13}C NMR spectrum of **1** can be rationalized by assuming a C_s-symmetrical compound. NMR peaks of ^{13}C atoms which are directly bound to Al are often broad and sometimes difficult to detect, which is caused by the electric quadrupole moment of aluminum. A broad peak for **1** at δ 53 measured at ambient temperature sharpens at −40 °C, clearly indicating the vicinity of aluminum. The signal unequivocally is due to the *ipso*-C atoms of the Cp rings. The value of δ 53 is shifted downfield in comparison with those *ipso*-C resonances of the known [1]ferrocenophanes mentioned before, but it is still shifted significantly upfield with respect to the parent ferrocene (δ 68). The detected ^{27}Al NMR resonance of δ 141 is in the expected range for tetracoordinated aluminum species.[33,34]

It seems that the "pytrisyl" ligand shields the Al center through the bulky $C(SiMe_3)_2$ unit and stabilizes it by the pyridine donor and presumably through α-silyl effects. We started to change the stabilizing ligand systematically to illuminate the factors that are important to obtain [1]ferrocenophanes with bridging heavier group 13 elements. Further investigations are underway to find out if one can take advantage of the strain in compound **1** to get access to new polymers via ROP. We will report on the results shortly.

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Supporting Information Available: Text detailing the instruments and techniques used for the experimental preparation and structural determination of $\mathbf{1}\cdot{}^1/_2FeCp_2$ and crystallographic data as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for $\mathbf{1}\cdot{}^1/_2FeCp_2$ have also been deposited with the Cambridge Crystallographic Data Centre (CCDC-253088) and can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44)-1223-336-033; deposit@ccdc.cam.ac.uk).

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