Ansa Complexes

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Selective Dimetalation of [Mn(η^5-C_5H_5)(η^6-C_6H_6)]: Crystal Structure and Conversion to Strained [*n*]Metalloarenophanes**

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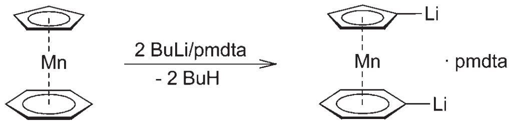
During the last 15 years the chemistry of strained ansa complexes has been of growing interest as a result of their unique structure, bonding, and reactivity patterns.[1] In general, this class of organometallic compounds is prepared by stoichiometric salt-elimination reactions of dimetalated metallocenes with element dihalides. Hence, the application of a selectively dimetalated and well-defined sandwich precursor is essential for this reaction and for the functionalization of metallocene complexes in general. By employing alkyl lithium bases in the presence of a coordinating amine such as *N,N,N′,N′*-tetramethylethylenediamine (tmeda) or *N,N′,N′,N″,N″*-pentamethyldiethylenetriamine (pmdta) the double deprotonation of the homoleptic sandwich complexes [M(η^5-C_5H_5)$_2$] (M = Fe,[2] Ru[3]) and [M(η^6-C_6H_6)$_2$] (M = V,[4] Cr[5]), as well as the heteroleptic species [M(η^5-C_5H_5)(η^7-C_7H_7)] (M = Ti,[6] V,[7] Cr[1f]), has been accomplished. However, except for the dilithiated ferrocene derivatives [Fe(η^5-C_5H_4Li)$_2$]·pmdta[8] and [Fe(η^5-C_5H_4Li)$_2$]$_3$·(tmeda)$_2$[9] structural data of dimetalated metallocenes are acutely rare to date. Very recently Mulvey and co-workers reported on the selective tetrametalation of ferrocene and its higher homologues,[10] the synergic monodeprotonation of bis(benzene)chromium,[11] and the selective dimetalation of ferrocene[12] by mixed alkali-metal–magnesium amide bases along with the corresponding crystal structure analyses.

In the course of our recent studies on strained metalloarenophanes, we became interested in manganese-containing ansa complexes. Since manganocene [Mn(η^5-C_5H_5)$_2$] cannot be metalated without decomposition, the number of known ansa complexes is limited to one structurally characterized example.[13] Therefore, we focused mainly on the heteroleptic sandwich complex [Mn(η^5-C_5H_5)(η^6-C_6H_6)] (**1**) originally reported by Fischer and Breitschaft in 1966.[14] This compound has been the subject of several spectroscopic[15] and theoretical investigations,[16] however, the reactivity has not been investigated in detail so far, most probably because of the interminable low-yield synthesis (2–4%). It should be noted, though, that a few earlier studies indicated the susceptibility of **1** towards deprotonation upon reaction with BuLi in the presence of tmeda.[17] The material thus obtained was not characterized but quenched in situ with various element halides. From the nature of the trapping products, including a proposed [2]silamanganoarenophane,[17b,c] the formation of a dilithiated metallocene intermediate appears plausible. The constitution of the trapping products, however, was deduced solely from NMR data, and owing to incomplete metalation of the starting material, inseparable product mixtures were obtained in various cases.[17b]

Herein we report on the facile and selective deprotonation of **1**, leading to a structurally characterized dimetalated species, and its conversion to the first structurally characterized boron- and silicon-bridged [*n*]manganoarenophanes (*n* = 1, 2).

Selective double deprotonation of **1** was achieved by employing a mixture of 2.7 equivalents of butyllithium and pmdta in aliphatic solvents at room temperature to afford the base-stabilized complex [Mn(η^5-C_5H_4Li)(η^6-C_6H_5Li)]·pmdta (**2**). Compound **2** can be isolated as a pale-brown, pyrophoric powder in high yields up to 85% (Scheme 1).[18]



1 **2**

Scheme 1. Selective dimetalation of **1**.

The ^{1}H NMR spectrum of **2** in [D$_8$]THF is consistent with the proposed structure and indicates the incorporation of one coordinating pmdta molecule. In agreement with a C_s-symmetric complex in solution, the aromatic protons of the C_5H_4 ring (δ = 3.94 and 4.18 ppm) and the C_6H_5 ring (δ = 4.44 and 4.47–4.53 ppm) feature two distinct signals each, with a relative intensity of 2:2:2:3. Moreover, the aromatic ring CH carbon atoms give rise to five signals (between δ = 71.2–83.3 ppm) in the ^{13}C NMR spectrum, whereas two broad downfield-shifted resonances can be unambiguously assigned to the *ipso* carbon atoms bound to lithium (δ = 88.7 and 100.7 ppm).

To confirm the selectivity of the dimetalation, the molecular structure of **2** was determined by crystal structure analysis (Figure 1).[19] In the solid state, **2** exhibits a dimeric structure in which both molecules are connected by two bridging lithium atoms (Li2 and Li3) bound to the *ipso* carbon atoms of both C_5H_4 rings and to one *ipso* carbon atom of the C_6H_5 ring. In contrast, the terminal lithium atoms (Li1 and

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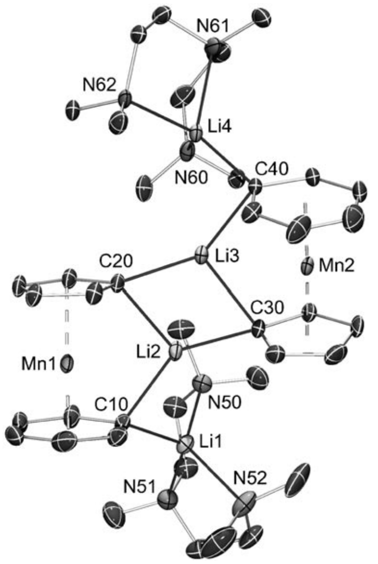
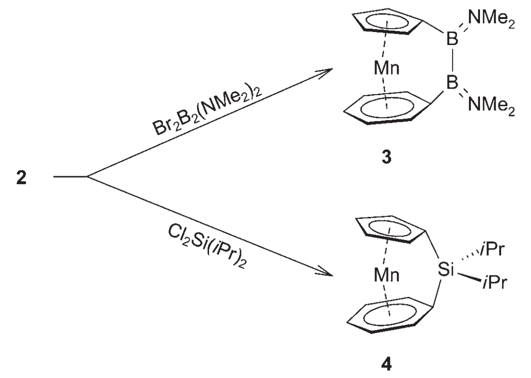


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Mn1···Li2 2.732(4), Mn2···Li3 2.686(4), Li1···Li2 2.782(6), Li2···Li3 2.385(6), Li3···Li4 2.793(6), Li1-C10 2.141(5), Li2-C10 2.127(5), Li2-C20 2.182(4), Li2-C30 2.118(5), Li3-C20 2.121(4), Li3-C30 2.174(4), Li3-C40 2.174(4), Li4-C40 2.149(5), Mn1-C_{Ph} 2.044(3)–2.160(2) [av 2.084(3)], Mn1-C_{Cp} 2.101(2)–2.191(2) [av 2.124(2)], Mn2-C_{Cp} 2.076(3)–2.184(3) [av 2.111(3)], Mn2-C_{Ph} 2.069(3)–2.169(2) [av 2.100(3)], Mn1-X_{Ph} 1.561, Mn1-X_{Cp} 1.787, Mn2-X_{Cp} 1.751, Mn2-X_{Ph} 1.604; C10-Li2-C20 101.44(17), C10-Li2-C30 142.79(23), C20-Li2-C30 111.62(20), C20-Li3-C30 111.81(20), C20-Li3-C40 143.01(22), C30-Li3-C40 102.50(17), X_{Ph}-Mn1-X_{Cp} 178.2, X_{Ph}-Mn2-X_{Cp} 177.7 (X_{Ph}, X_{Cp} = centroids of the C_6H_5 and C_5H_4 rings).

Li4) are stabilized by the coordination of the pmdta nitrogen atoms. In agreement with the molecular structure of **1**,[17a] the Mn−C(H) bond lengths for the five-membered rings (2.076(3)–2.117(3) Å) are comparable to those for the six-membered rings (2.044(3)–2.101(4) Å). However, the Mn−C_{ipso} bonds are significantly elongated for both the C_5H_4 (2.184(3) and 2.191(2) Å) and the C_6H_5 rings (2.160(2) and 2.169(2) Å).

As expected, the two aromatic rings of each manganese unit are arranged almost parallel; angles between the planes of the five- and six-membered rings amount to 2.05(16)° and 2.66(19)°, respectively. The bridging Li atoms display a distorted trigonal-planar environment (ΣLi2 = 356°, ΣLi3 = 357°), whereas the terminal lithium atoms adopt a distorted tetrahedral geometry. The Li−C bond lengths (2.118(5)–2.182(4) Å) as well as the Li−N bond lengths (2.096(5)–2.164(5) Å) lie within previously reported ranges.[8,9] The Li···Li separations (Li1···Li2 2.782(6), Li2···Li3 2.385(6), Li3···Li4 2.794(6) Å) are similiar to those found in the corresponding ferrocene derivative [Fe(η^5-C_5H_4Li)$_2$]·pmdta.[8] The relatively short distance between Li2 and Li3 (2.385(6) Å), which is comparable to that found in cyclohexyllithium (2.397 Å),[20] might suggest a direct lithium–lithium interaction in terms of stabilizing the unsaturated lithium centers. Also, the Mn···Li separations (Mn1···Li2 2.732(4) and Mn2···Li3 2.686(4) Å) are comparable to the sum of their covalent radii (Li 1.34 Å, Mn 1.37 Å)[21] and might indicate a stabilizing manganese–lithium interaction. However, DFT calculations of the entire molecule of **2** using crystallographic coordinates, and subsequent Wiberg bond-order calculations, as well as the topological analysis of the ELF function, do not reveal any evidence for a stabilizing metal–metal interaction.[22]

With this reactive species in hand, a selective route for the preparation of strained ansa complexes was achieved. Stoichiometric treatment of **2** with $Br_2B_2(NMe_2)_2$ or $Cl_2Si(iPr)_2$ in aliphatic solvents at −78 °C resulted in the formation of the [2]borametalloarenophane **3** and the [1]silametalloarenophane **4**, respectively. These compounds were isolated after work up as red crystalline solids in good yields (50–60 %; Scheme 2).[18]



Scheme 2. Syntheses of the ansa complexes **3** and **4**.

The introduction of a diborane bridge between the aromatic rings in **3** results in a splitting of the corresponding signals in the ^{1}H NMR spectrum in comparison to **1**.[17a,18] The α- and β-hydrogen atoms of the C_5H_4 ring show two distinct pseudotriplets (δ = 4.10 and 4.20 ppm), which appear downfield with respect to the resonance in **1** (δ = 3.83 ppm). Similarly, the benzene ring protons are split into a pseudodoublet at δ = 4.62 ppm, which can be assigned to the *ortho* CH group adjacent to the bridging boron center, and into two well-separated pseudotriplets (δ = 4.78 and 4.86 ppm) for the *meta* and *para* protons, respectively, with a relative intensity of 2:2:1. These findings are in excellent agreement with the results reported for the corresponding [2]boratrochrocenophane.[1f]

According to a single-crystal X-ray diffraction analysis (Figure 2),[19] compound **3** crystallizes in the orthorhombic space group *Pbca* with two independent molecules in the asymmetric unit, whereby the structural parameters of the two moieties differ only marginally. Hence, for simplicity reasons only one of the molecular structures is discussed below. The incorporation of an ansa diborane bridge results in a substantial deviation of the aromatic rings from the ideal coplanar arrangement observed in the unstrained sandwich complexes **1**[17a] and **2**. However, both rings are virtually planar and can be described as primarily η^5- and η^6-coordinated, respectively. This distortion imposes moderate molecular ring strain, which is best reflected by the tilt angle α = 11.26(12)°. Moreover, the angle δ (defined by the ring centroids and the metal center) is essentially reduced to a

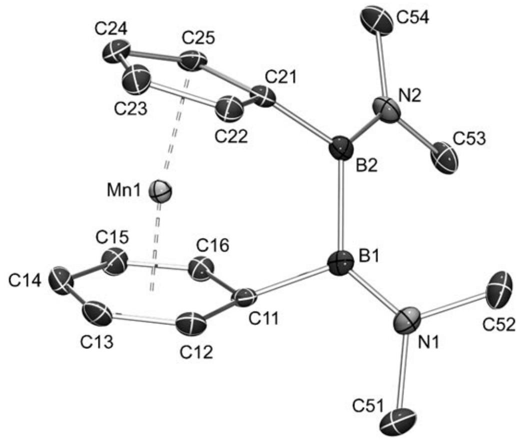


Figure 2. Molecular structure of **3**. Only one molecule of the asymmetric unit is shown for clarity. Selected bond lengths [Å] and angles [°]: Mn1-C11 2.062(2), Mn1-C12 2.074(2), Mn1-C13 2.086(2), Mn1-C14 2.100(2), Mn1-C15 2.101(2), Mn1-C16 2.066(2), Mn1-C21 2.094(2), Mn1-C22 2.076(2), Mn1-C23 2.126(2), Mn1-C24 2.128(2), Mn1-C25 2.102(2), B1-C11 1.596(3), B2-C21 1.588(3), B1-B2 1.727(3), B1-N1 1.387(3), B2-N2 1.393(3), Mn1-X_{Ph} 1.524, Mn1-X_{Cp} 1.721; C11-B1-B2 107.63(10), C21-B2-B1 110.30(18), C11-B1-B2-C21 42.91(23), X_{Ph}-Mn1-X_{Cp} 171.3.

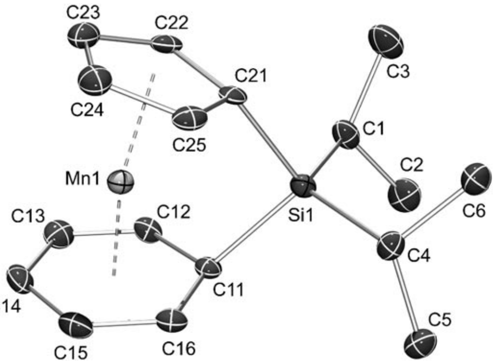


Figure 3. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Mn1-C11 2.040(3), Mn1-C12 2.059(2), Mn1-C13 2.100(3), Mn1-C14 2.119(3), Mn1-C15 2.109(3), Mn1-C16 2.069(3), Mn1-C21 2.075(2), Mn1-C22 2.089(3), Mn1-C23 2.118(3), Mn1-C24 2.127(3), Mn1-C25 2.085(3), Si1-C11 1.902(3), Si1-C21 1.889(3), Si1-C1 1.886(3), Si1-C4 1.883(3), Mn1-X_{Ph} 1.527, Mn1-X_{Cp} 1.715; C11-Si1-C21 95.00(11), C1-Si1-C4 115.85(12), X_{Ph}-Mn1-X_{Cp} 167.4.

value of 171.3° (versus 177.7 and 178.2° in **2**), and the C-B-B angles are considerably smaller than expected for an ideally sp^2-hybridized boron atom (C11-B1-B2 107.63(10) and C21-B2-B1 110.30(18)°). These values suggest a slightly higher ring strain present in **3** compared to the previously reported [2]borametalloarenophanes of chromium and vanadium.[1f,23,24]

The introduction of the smaller silicon bridge in **4** leads to significant differences in the ^1H NMR spectrum compared to **3**. In agreement with a more distorted molecular structure, the resonances of the α- and β-hydrogen atoms of the C_5H_4 ring are clearly more separated ($\delta = 3.70$ and 4.15 ppm) than in **3**. A similiar correlation between the degree of distortion and the separation of the aromatic Cp ring protons in the ^1H NMR spectrum has been observed for ansa ferrocenophanes.[1d,25] Moreover, the pseudodoublet assigned to the *ortho* CH group of the benzene ring next to the bridging silicon center ($\delta = 4.21$ ppm) is essentially shifted to higher field with respect to the *meta* and *para* hydrogen atoms ($\delta =$ 4.78 and 4.96 ppm). Such a large separation of the *ortho* and the *meta* protons within the C_6H_5 moiety ($\Delta\delta = 0.57$ versus 0.10 ppm in **3**) is characteristic for highly strained sandwich complexes and has previously been described for the corresponding [1]- and [2]bora derivatives of bis(benzene)-chromium.[23]

To confirm the formation of a strained ansa complex, a crystal structure analysis of **4** was carried out (Figure 3).[19] In accordance with the NMR spectroscopic data, the introduction of a monoatomic silicon bridge results in a more distorted geometry in **4** than in **3**. Whereas the Mn−C bond lengths are not affected by the smaller bridge (2.040(3)–2.127(3) Å), the higher ring strain is manifested by a larger tilt angle $\alpha =$ 16.97(14)°. This value is comparable to those previously described for the corresponding [1]silatrochrocenophanes (15.6–16.3°),[26] but significantly smaller than that for the appropriate troticene derivative ($\alpha = 24.1°$).[27] As expected, the angle δ (see above) is decreased to a value of 167.4° compared to 171.3° found in **3**. The molecular strain is also reflected by the C_{Ph}-Si-C_{Cp} angle ($\theta = 95.00(11)°$), which deviates significantly from the tetrahedral angle for an sp^3-hybridized silicon atom.

Detailed theoretical studies on the electronic structure of the strained ansa complexes **3** and **4** are currently ongoing and will be reported elsewhere. The reactivity of **3** and **4** towards low-valent transition-metal compounds is under investigation. Owing to their intrinsic molecular ring strain, these complexes should be susceptible to strain release by undergoing ring-opening polymerization. According to NMR spectroscopy, preliminary polymerization experiments employing a [1]silamanganoarenophane in the presence of Karstedt's catalyst indicate the formation of organometallic oligomers or polymers, respectively. The characterization of the resulting materials, which is hampered by their low solubility in common organic solvents, is the purpose of present studies.[18]

In this contribution, we have reported on the selective dilithiation of [Mn(η^5-C_5H_5)(η^6-C_6H_6)] to afford the highly reactive species **2**. The crystal structure of **2** represents one of the rare examples of dimetalated sandwich complexes described in the literature. Accordingly, the syntheses of the strained ansa complexes **3** and **4** were accomplished by salt-elimination reactions of **2** with the appropriate element dihalides. The ring strain present in **3** and **4** was confirmed by X-ray diffraction analyses. These compounds have the potential to undergo ring-opening polymerization (ROP) to yield manganese-containing oligomers and polymers.

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[18] The experimental section, including the syntheses, full characterization, and spectroscopic data of all new compounds, can be found in the Supporting Information.

[19] Experimental details of all X-ray crystal structure determinations can be found in the Supporting Information. CCDC-625069 (**2**), CCDC-625068 (**3**), and CCDC-625070 (**4**) contain the supplementary crystallographic data for 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.

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