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Selective Dilithiation of [Ti(η^5-C_5H_5)(η^8-C_8H_8)] and Subsequent Conversion into Neutral and Cationic *ansa*-Complexes

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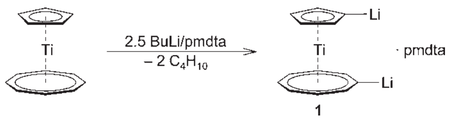
Supporting Information

ABSTRACT: Selective dimetalation of a sandwich complex featuring the cyclooctatetraene ligand has been accomplished for the first time. The isolation of the dilithiated species **1** subsequently enabled the isolation of a paramagnetic [2]stannatitanoarenophane (**2**) via salt elimination reaction. Chemical oxidation resulted in the formation of a rare example of a cationic *ansa*-complex (**3**).

During the past two decades, the number of sandwich complexes employed in the synthesis of *ansa*-complexes has increased substantially. Without any doubt, ferrocene represents by far the best-investigated system. Numerous [*n*]ferrocenophanes with either main group elements[1] or transition metals[2] in bridging positions have been realized to date. Stimulated by the initial findings, subsequent work successfully transferred this structural motif to other metallocene systems such as ruthenocene,[1a,f,3] cobaltocene,[1a,4] and nickelocene.[5] The group of Elschenbroich synthesized the first *ansa*-complex not derived from a metallocene precursor in the early 1990s, [Cr(η^6-C_6H_5)$_2$SiPh$_2$]. Related metalloarenophanes of the bis-benzene-based precursors [M(η^6-C_6H_6)$_2$] (M = V, Cr, Mo) have been accessed in different laboratories.[6] However, the focus of recent research in this area has shifted to heteroleptic species such as [Co(η^4-C_4Me_4)(η^5-C_5H_5)],[7] [Mn(η^5-C_5H_5)(η^6-C_6H_6)],[6p,8] and [M(η^5-C_5H_5)(η^7-C_7H_7)] (M = Ti, V, Cr)[6p,9] with two different carbocyclic ligands attached to the metal center. The most common strategy toward the synthesis of such *ansa*-species is the salt elimination reaction of a dilithiated sandwich precursor with appropriate element dihalides. Thus, the availability of selectively dimetalated sandwich complexes is considered essential for this approach. These highly reactive species are usually obtained by double deprotonation employing alkyllithium bases in the presence of chelating amines such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdta).

As part of our longstanding interest in metalloarenophane systems featuring π-ligands with different numbers of carbon atoms, i.e., cyclopentadienyl (Cp), benzene (Bz), and cycloheptatrienyl (Cht) ligands, we became interested in cyclooctatetraene (Cot)-based sandwich compounds. Since facile deprotonation of Cot is hampered by its favored reduction chemistry to afford the corresponding dianion,[10] the generation of Cot derivatives that act as C_8H_7-nucleophiles is only possible by halogen−metal exchange of halogenated Cot compounds with magnesium or alkyllithium reagents.[11] However, a closer look at the literature suggested that the paramagnetic sandwich complex [Ti(η^5-C_5H_5)(η^8-C_8H_8)] might be a promising candidate for the preparation of *ansa*-species. [Ti(η^5-C_5H_5)(η^8-C_8H_8)] was first described by Van Oven and Meijer in 1969,[12] and has been the subject of several theoretical,[13] spectroscopic,[12,14] synthetic,[12,15] and electrochemical[14g,16] investigations. Furthermore, the related system [Ti(η^5-C_5H_5)(η^7-C_7H_7)] has already proven its suitability as an efficient precursor for the syntheses of troticenophanes.[9a,d,e,i] To the best of our knowledge, examples of *ansa*-complexes featuring the Cot ligand are limited to [U(η^8-$C_8H_7SiMe_2$)$_2$$C_2H_4$], which was obtained following an alternative approach and has not yet been structurally characterized.[17] Herein, we report on the selective dilithiation of [Ti(η^5-C_5H_5)(η^8-C_8H_8)] to afford the highly reactive species [Ti(η^5-C_5H_4Li)(η^8-C_8H_7Li)]·pmdta (**1**), and its subsequent conversion into the [2]stannatitanoarenophane **2**. Oxidation of **2** with [Fe(η^5-C_5H_5)$_2$]-[PF$_6$] enabled the isolation of the cationic *ansa*-complex **3**.

Scheme 1. Dilithiation of [Ti(η^5-C_5H_5)(η^8-C_8H_8)]



Selective dimetalation of [Ti(η^5-C_5H_5)(η^8-C_8H_8)] is readily accomplished by reaction with BuLi and pmdta in hexane at 0 °C. After workup, **1** can be isolated as a yellow pyrophoric powder in excellent yields of 98% by simple gravity filtration (Scheme 1).[18] The selectivity of the deprotonation reaction was ascertained by means of X-ray diffraction and microanalysis, which also suggested the coordination of one pmdta molecule per sandwich unit.

Suitable crystals of **1** were obtained by recrystallization from a saturated thf solution at −70 °C. **1** crystallizes in the triclinic space group $P\bar{1}$ and exhibits a dimeric structure in the solid state (Figure 1).[18] Thus, the structural motif is consistent with those found for related dilithiated systems such as [Fe(η^5-C_5H_4Li)$_2$]·pmdta,[19] [Mn(η^5-C_5H_4Li)(η^6-C_6H_5Li)]·pmdta,[8] and [Ti(η^5-C_5H_4Li)(η^7-C_7H_6Li)]·pmdta.[9g] Consequently, two different coordination environments are observed for the lithium centers: (i) two terminal lithium atoms attached to one C_5H_4 residue, which are further stabilized by coordination to one pmdta ligand, and (ii) two bridging lithium atoms bound to the *ipso*-carbons of one C_5H_4 and both C_8H_7 moieties. The Ti−CH distances to the five- and eight-membered rings are comparable [C_5H_4, 2.3258(15)−2.3701(16) Å; C_8H_7, 2.3102(17)−2.3398(16) Å] and strongly resemble those found for the parent sandwich complex [Ti(η^5-C_5H_5)(η^8-C_8H_8)].[20] The Ti−C$_{ipso}$ bond within the Cot fragment [2.3634(17) Å] is slightly elongated with respect to its Ti−CH bonds, whereas this is not the case for the Ti−C$_{ipso}$ bond [2.3737(14) Å] within the Cp moiety.

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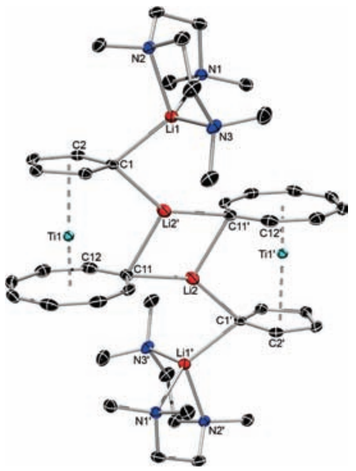
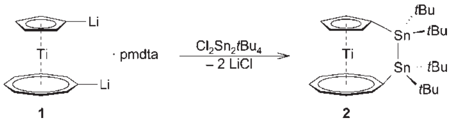


Figure 1. Molecular structure of $[Ti(\eta^5\text{-}C_5H_4Li)(\eta^8\text{-}C_8H_7Li)]\cdot$pmdta (**1**). Thf molecules incorporated in the crystal lattice and hydrogen atoms are omitted for clarity. Symmetry-related positions ($-x$, $-y$, $-z+2$) are labeled with ′. Thermal ellipsoids are set at the 30% probability level.

Scheme 2. Synthesis of $[Ti(\eta^5\text{-}C_5H_4)(\eta^8\text{-}C_8H_7)Sn_2tBu_4]$ (2)



Accordingly, the Ti−centroid separation distances differ substantially for the two carbocyclic ring systems [$Ti-X_{Cp}$, 2.0197(8) Å; $Ti-X_{Cot}$, 1.4315(7) Å]. The anticipated unstrained character of **1** is highlighted by the tilt angle α = 2.83(11)° and the deformation angle δ = 178.0°, which confirm an almost coplanar arrangement of the aromatic π-ligands. The geometry of the bridging lithium atoms Li2 and Li2′ is best described as highly distorted trigonal-planar (Σ = 359°) with angles [104.30(13)−145.66(16)°] significantly deviating from the expected value of 120° for ideally sp^2-hybridized lithium centers. By contrast, the terminal lithium centers feature highly distorted tetrahedral environments. The C1−Li1 [2.174(3) Å] and N−Li1 distances [2.110(3)−2.143(3) Å] are unremarkable and lie within previously reported ranges.[8,9g] Even though the Li2−Li2′ separation distance [2.514(6) Å] is notably shorter than the Li1−Li2′ distance [2.835(4) Å], recent studies suggest that a stabilizing lithium−lithium interaction has to be considered weak at best.[8,21]

Isolation of the well-defined precursor **1** provided convenient access to *ansa*-complexes by simple salt elimination reactions. Thus, reaction of **1** with 1 equiv of $Cl_2Sn_2tBu_4$ in hexane at −70 °C enabled the isolation of the [2]stannatitanoarenophane **2** after chromatography in good yield as a yellow, highly air-sensitive powder (Scheme 2).[18] The identity of this paramagnetic material was ascertained by mass spectrometry, which indicated the molecular ion (m/z = 683). This signal shows the characteristic isotopic pattern expected for a compound of the formula $C_{29}H_{47}Sn_2Ti$.

For structural characterization, single crystals of **2** were studied by X-ray diffraction (Figure 2).[18] **2** crystallizes in the monoclinic space group $P2_1/c$, with two independent molecules in the asymmetric unit whose structural parameters differ only marginally. Consequently, only one of the molecular structures is discussed below. The influence of the large diatomic *ansa*-bridge in **2** on the geometry of the sandwich unit is rather small. Thus, the corresponding bond lengths and angles are comparable to those observed in $[Ti(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)]$.[20] For instance, the Ti−C bonds to the C_5H_4 ring [2.3494(19)−2.3752(19) Å] are only marginally longer than those to the Cot moiety [2.3167(19)−2.3432(21) Å], whereas the Ti−centroid distances [$Ti-X_{Cp}$, 2.0293(9) Å; $Ti-X_{Cot}$, 1.4355(8) Å] differ significantly (Table 1). The lack of ring strain is further reflected by the small tilt angle α = 1.84(11)° and the large deformation angle δ = 178.9°. Similar to the solid-state structure of $[Ti(\eta^5\text{-}C_5H_4)(\eta^7\text{-}C_7H_6)Sn_2tBu_4]$,[9d] both tin atoms display a highly distorted environment, emphasized by $C_{ipso}-Sn-Sn$ angles of 98.11(5) and 94.48(5)°. In addition, deviations of the tin atoms from the ring planes of the Cp and Cot moieties (β_{Cp} = 3.9°; β_{Cot} = 22.0°) correlate with the ring size.

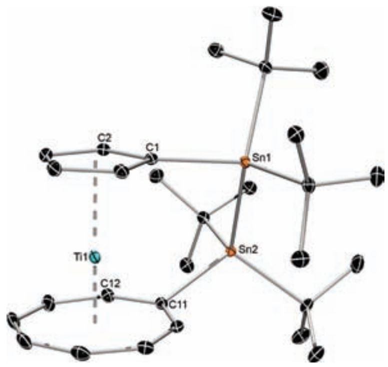


Figure 2. Molecular structure of $[Ti(\eta^5\text{-}C_5H_4)(\eta^8\text{-}C_8H_7)Sn_2tBu_4]$ (**2**). Only one of the molecules of the asymmetric unit is shown. Hydrogen atoms and hexane molecules incorporated in the crystal lattice are omitted for clarity. Thermal ellipsoids are set at the 30% probability level.

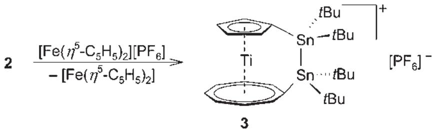
Table 1. Selected Bond Angles [°] and Lengths [Å] of 2, 3, and $[Ti(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)]$

	2	3	$[Ti(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)]^a$
α	1.84(11)	1.40(11)	1.90
δ	178.9	178.7	–
$Ti-C_{Cp}$ (av.)	2.3630	2.2924	2.353
$Ti-C_{Cot}$ (av.)	2.3344	2.2684	2.323
$Ti-X_{Cp}{}^b$	2.0293(9)	1.9487(10)	2.031
$Ti-X_{Cot}{}^c$	1.4355(8)	1.3188(8)	1.440

[a] Experimental values see ref 20. [b] X_{Cp} = centroid of the C_5H_4 or C_5H_5 ring. [c] X_{Cot} = centroid of the C_8H_7 or C_8H_8 ring.

It is well documented that ferrocene readily undergoes a reversible one-electron oxidation to afford the paramagnetic 17-electron ferrocenium cation, for which a wide range of different examples have been isolated to date.[22] While several bridged [n]ferrocenium species (n ≥ 2)[23] have already appeared in the literature, a strained [1]silaferrocenium ion remained unknown until very recently.[24] Manners and co-workers impressively demonstrated that this cationic species is even more strained than its neutral precursor, which results in enhanced reactivity. Cationic *ansa*-derivatives are also known for cobaltocene,[4a,b,23a,25] and in a few cases for other sandwich systems featuring chromium[26] or rhodium[27] as the metal center. However, no structurally characterized cationic metalloarenophane featuring the Cot ligand is known so far. It should be mentioned though that earlier studies indicated (i) the formation

Scheme 3. Preparation of [Ti(η^5-C_5H_4)(η^8-C_8H_7)$Sn_2t$$Bu_4$][$PF_6$] (3) by Oxidation of 2



of [Ti(η^5-C_5H_5)(η^8-C_8H_8)][X] (X = I, I_3) upon treatment of the neutral complex with iodine, and (ii) the generation of a diamagnetic species upon oxidation of [Ti(η^5-C_5Me_5)(η^8-C_8H_8)].[14g,15a]

In our hands, oxidation of **2** was readily achieved in CH_2Cl_2 by addition of [Fe(η^5-C_5H_5)$_2$][PF_6]. The transformation is accompanied by an immediate color change of the reaction mixture from yellow to deep red. After workup, diamagnetic **3** (16 valence electrons) can be isolated analytically pure in satisfying yields (Scheme 3).[18] Analysis by multinuclear NMR spectroscopy in solution is fully consistent with the presence of a cationic *ansa*-species. The most notable change in the ^{1}H NMR spectrum of **3** with respect to [Ti(η^5-C_5H_5)(η^8-C_8H_8)][PF_6][28] is given by the splitting of the resonances associated with the ring protons of the carbocyclic ligands into two multiplets each (C_5H_4, δ 5.62, 5.66; C_8H_7, δ 7.33, 7.50). Furthermore, due to chemical inequivalence of the *t*Bu groups, two singlets are detected at δ 1.44 and 1.72, flanked by characteristic ^{117}Sn ($^3J_{H,^{117}Sn}$ = 71.5 and 69.8 Hz) and ^{119}Sn ($^3J_{H,^{119}Sn}$ = 74.5 and 71.6 Hz) satellites. However, in contrast to [Ti(η^5-C_5H_4)(η^7-C_7H_6)$Sn_2t$$Bu_4$], no long-range $^4J_{H,Sn}$ coupling is observed.[9d] The ^{13}C{^{1}H} NMR spectrum shows the expected splitting pattern for the aromatic ring moieties, i.e., three resonances for the Cp ring [δ 109.2, 115.0, 128.2 (C_{ipso})] and five signals for the C_8H_7 ring [δ 100.2, 100.3, 103.6, 108.8, 124.7 (C_{ipso})]. The tin nuclei are found as two distinct singlets (δ −0.5, 41.7) in the ^{119}Sn NMR spectrum of **3**, surrounded by the expected ^{117}Sn ($^1J_{^{119}Sn,^{117}Sn}$ = 293.2 Hz, each) and ^{119}Sn ($^1J_{^{119}Sn,^{119}Sn}$ = 306.3 Hz, each) satellites.

The identity of **3** in the solid state was ascertained by X-ray diffraction. Again, two independent molecules are found in the asymmetric unit; however, for simplicity only one of the structures is discussed below (Figure 3).[18] One-electron oxidation of **2** exerts a substantial impact on the geometry of the sandwich unit, highlighted by a considerable shortening of the Ti−C bonds to the aromatic π-ligands [C_5H_4, 2.2860(20)−2.3067(20) Å; C_8H_7, 2.2478(20)−2.2823(21) Å] compared to **2**. Consequently, the Ti−centroid separations are notably contracted to 1.9487(10) and 1.3188(8) Å for the Cp (Ti−X_{Cp}) and Cot (Ti−X_{Cot}) ring systems, respectively (Table 1). In sum, the ring−ring distance is reduced by about 0.20 Å. Nevertheless, the tilt angle α =1.40(11)° and the deformation angle δ = 178.7° remain almost unaffected by these alterations. Decreased metal−carbon distances are also observed for related [*n*]cobaltocenophanium species (18 valence electrons),[4a,b,23a,25] which can be rationalized by the fact that the single electron in cobaltocene (19 valence electrons) occupies an antibonding orbital. However, former investigations suggest that the unpaired electron in [Ti(η^5-C_5H_5)(η^8-C_8H_8)] is located in an orbital that is mainly d_{z^2} in nature with no antibonding character.[13b,c,14b,c,g,15a] The related [1]silaferrocenophane/[1]silaferrocenophanium couple shows a completely different behavior upon oxidation to the cationic species, most likely a result of the removal of an electron from a binding orbital.[24] The influence of the one-electron oxidation on the *ansa*-bridge is considerably less pronounced, and all relevant bond lengths are similar to those found for **2**. In agreement with the smaller ring−ring separation in **3**, the deviations of the bridging Sn atoms from the ring planes are slightly reduced (β_{Cp} = 0.3°; β_{Cot} = 19.6°).

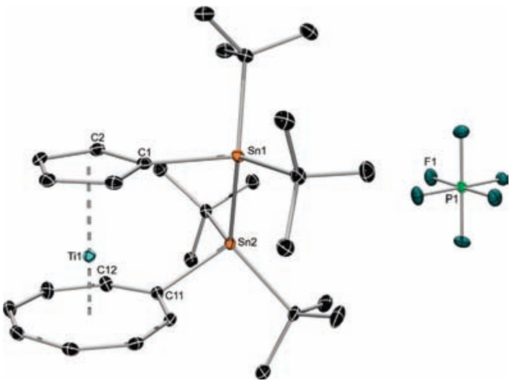


Figure 3. Molecular structure of [Ti(η^5-C_5H_4)(η^8-C_8H_7)$Sn_2t$$Bu_4$]-[$PF_6$] (**3**). Only one of the molecules in the asymmetric unit is shown. For clarity, hydrogen atoms and CH_2Cl_2 molecules incorporated in the crystal lattice are omitted. Thermal ellipsoids are displayed at the 30% probability level.

In summary, we were able to selectively dilithiate [Ti(η^5-C_5H_5)(η^8-C_8H_8)] to afford the highly reactive precursor **1** in essentially quantitative yields, which was successfully converted to the neutral and cationic *ansa*-derivatives **2** and **3** in subsequent functionalization reactions. This system enables the convenient incorporation of the Cot motif into [*n*]metalloarenophane chemistry for the first time. While **1** features the well-known dimeric structure in the solid state with two sandwich units connected by bridging lithium atoms, the crystal structure of [2]stannatitanoarenophane **2** represents the first structurally characterized *ansa*-complex containing the Cot fragment. Chemical oxidation of **2** with [Fe(η^5-C_5H_5)$_2$][PF_6] resulted in clean conversion into **3**, another rare example of a cationic metalloarenophane, whose molecular structure revealed a remarkable decrease in the interannular ring−ring distance.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures; spectroscopic and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Oxidation of $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)]$ with $[\mathrm{Fe}(\eta^5\text{-}C_5H_5)_2][\mathrm{PF}_6]$ provided the following chemical shifts for $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)][\mathrm{PF}_6]$: ^{1}H NMR (500 MHz, CD_3NO_2) δ 5.53 (C_5H_5), 7.52 (C_8H_8); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3NO_2) δ 102.1 (s, C_8H_8), 107.2 (C_5H_5); $^{31}P\{^1H\}$ NMR (202 MHz, CD_3NO_2) δ −144.7 (sept, PF_6, $J_{^{31}P,^{19}F}$ = 707.0 Hz).