Sandwich Complexes

Ansa-Cycloheptatrienyl–Cyclopentadienyl Complexes[**]

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Group 4 *ansa*-metallocenes are among the most important compounds in homogeneous transition-metal-based catalysis.[1,2] In contrast, *ansa*-complexes containing a bridging unit between a cycloheptatrienyl (Cht) and a cyclopentadienyl (Cp) unit are virtually unknown.[3] During the course of our studies on complexes containing linked cycloheptatrienyl-phenolate[4] and -phosphane ligands,[5] we became interested in the preparation of bridged Cht–Cp sandwich complexes, in which the ligand can be regarded as a Cp-donor-functionalized cycloheptatrienyl ligand. For this purpose, we have chosen the 16-electron titanium complex [(η-C_7H_7)Ti(η-C_5H_5)] (troticene)[6] as a suitable starting material, as double-lithiation of troticene can be achieved with *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) resulting in the formation of the tmeda-stabilized complex [(η-C_7H_6Li)Ti(η-C_5H_4Li)].[7] In our hands, the reaction of the dilithio complex with Me_2SiCl_2 afforded the silicon-bridged *ansa*-Cht–Cp complex or [1]silatroticenophane **1** which can be isolated as blue-green crystals in 30–40% yield after crystallization from hexane (Scheme 1).[8]

Whereas the C_7H_7 and C_5H_5 rings in troticene give rise to only two resonance signals in the ^1H and ^{13}C NMR spectra,[9] the introduction of the Me_2Si bridge results in a splitting pattern which is in agreement with the formation of a C_s-symmetric complex. In the ^1H NMR spectrum (Figure 1), one broad signal is observed for the α and β C_5H_4 protons which is only marginally shifted in comparison to the corresponding troticene resonance ($\delta = 4.90$ ppm, C_5H_5). In contrast, the signal for the protons of the seven-membered ring in troticene ($\delta = 5.42$ ppm) is now split into a downfield multiplet ($\delta = 5.96$–5.84 ppm) for the β and γ hydrogen atoms and into a

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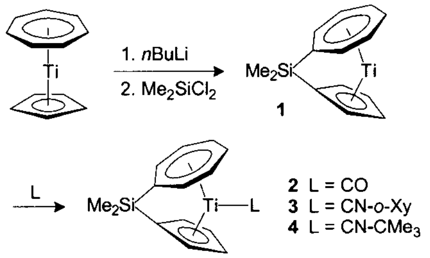


Scheme 1. Synthesis of [1]silatroticenophanes (o-Xy = 2,6-dimethylphenyl).

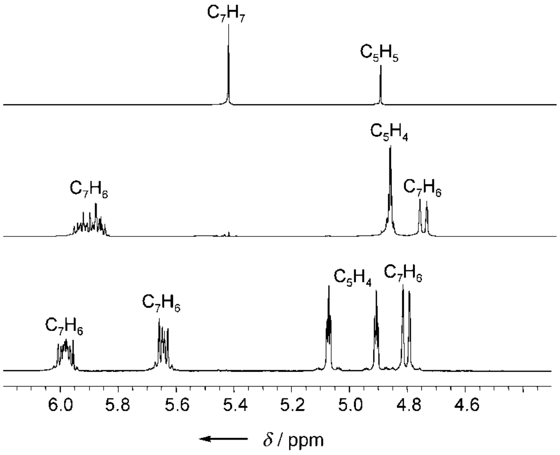


Figure 1. Excerpts from the ^1H NMR spectra of troticene (top), [1]silatroticenophane **1** (middle), and the 2,6-dimethylphenyl isocyanide complex **3** (bottom) in [D_6]benzene at 25 °C.

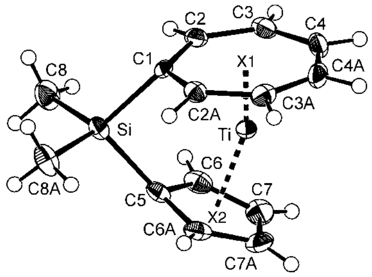
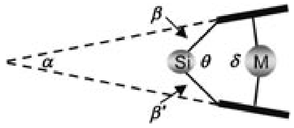


Figure 2. Molecular structure of **1**.[31] Selected bond lengths [Å]; calculated values are given in square brackets: Ti-C1 2.170(3) [2.168], Ti-C2 2.195(2) [2.205], Ti-C3 2.229(2) [2.250], Ti-C4 2.256(2) [2.269], Ti-C5 2.294(3) [2.308], Ti-C6 2.316(2) [2.330], Ti-C7 2.353(3) [2.385], C1-C2 1.436(3) [1.437], C2-C3 1.425(3) [1.425], C3-C4 1.409(3) [1.420], C4-C4a 1.413(3) [1.416], C5-C6 1.435(3) [1.434], C6-C7 1.411(3) [1.417], C7-C7a 1.410(5) [1.416], Si-C1 1.890(3) [1.908], Si-C5 1.894(4) [1.899], Ti-X1 1.496, Ti-X2 1.988 (X = centroid). Symmetry operation to equivalent positions a: A, 1/2−y, z.

Table 1: Distortions in silicon-bridged *ansa*-complexes.



Compound	α [°]	β [°], β' [°]	θ [°]	δ [°]
1	24.1	41.1, 28.7	95.6	160.5
$[Me_2Si(\eta\text{-}C_5H_4)_2Fe]$	20.8	37.0	95.7	164.7
$[Me_2Si(\eta\text{-}C_6H_5)_2Cr]$	16.6	38.2, 37.9	92.9	167.6

upfield doublet at $\delta = 4.75$ ppm which can be assigned to the α CH group next to the bridging Me_2Si moiety. As expected, the ^{13}C NMR spectrum of **1** has five resonance signals for the ring CH carbon atoms (between $\delta = 101.2$ and 87.6 ppm) together with two upfield signals which can be unambiguously assigned to the *ipso*-C_5H_4 carbon atom ($\delta = 83.6$ ppm) and to the *ipso*-C_7H_6 carbon atom ($\delta = 61.6$ ppm). This remarkably large upfield shift is characteristic for highly strained sandwich complexes, such as [1]ferrocenophanes,[10] and clearly reflects a strong structural distortion, in particular of the Si–C_7H_6 site (see below).

To confirm the formation of an *ansa*-Cht-Cp complex, the molecular structure of **1** was determined by X-ray diffraction (Figure 2). In agreement with the molecular structure of $[(\eta\text{-}C_7H_7)Ti(\eta\text{-}C_5H_5)]$,[11] the metal–carbon bonds to the seven-membered ring [2.170(3)–2.256(2) Å] are significantly shorter than those to the five-membered ring [2.294(3)–2.353(3) Å] revealing a much stronger interaction to the seven-membered ring. Despite the considerable strain imposed by the introduction of the Me_2Si bridge, both rings are virtually planar and can still be regarded as being essentially η^7- or η^5-coordinated, respectively. The deviation from an unstrained sandwich structure with an ideal coplanar ring orientation, as observed in troticene,[11] can be described with the angles α, β, θ, and δ presented in Table 1. Comparison with the structural data of related silicon-bridged *ansa*-complexes, such as the [1]ferrocenophane $[Me_2Si(\eta\text{-}C_5H_4)_2Fe]$[12] and the [1]chromarenophane $[Me_2Si(\eta\text{-}C_6H_5)_2Cr]$,[13] suggests that **1** can be regarded as the most strongly distorted sandwich complex in this series. Accordingly, **1** exhibits the largest tilt angle α (24.1 versus 20.8 and 16.6°) together with the smallest angle δ at the metal atom defined by the ring centroids (160.5 versus 164.7 and 167.6°). In all the complexes, the link between the two carbon rings results in a significant distortion from planarity at the *ipso*-carbon atoms bonded to silicon, with the largest angle β being observed between the C_7 plane and the C1−Si bond in **1** ($\beta = 41.1°$). In addition, all interior angles θ at the bridging silicon atoms are substantially smaller than expected for an ideally sp^3-hybridized atom (Table 1). These results indicate that **1** is a highly strained molecule which should be strongly susceptible to strain release by undergoing ring-opening polymerization (ROP) reactions.[14] A differential scanning calorimetry (DSC) study of **1** suggests that the compound polymerizes exothermically at about 140–160 °C without showing a melt endotherm at lower temperature. Integration of the exotherm gives an estimate of the strain energy of **1** of approximately 36 kJ/mol.[15] This is substantially lower than the values found for [1]ferrocenophanes,[10b,16] however, it can not be excluded that the compound melts and polymerizes simultaneously which would lead to an underestimation of the enthalpy of the ROP process. The characterization of the resulting poly(troticenylsilanes), which is hampered by their air- and moisture-sensitivity, is under investigation.

Herein, however, we wish to concentrate on another reactivity conferred by the introduction of the silicon bridge and distortion of the sandwich structure. Since both complexes, troticene and its *ansa*-derivative **1**, have 16 electrons, coordination of an additional two-electron-donor ligand should be possible. Whereas such adduct formation has never been observed for troticene, the bending of the two rings in **1** creates a gap at the titanium center, which might thereby become accessible to "slender" monodentate ligands, such as carbon monoxide or isocyanides. In addition, these ligands give rise to strong, diagnostic IR absorptions for the CO and CN stretching vibrations, respectively, which can be used to probe the electronic structure of the sandwich complex.

To assess the differences in the electronic structures of bridged and unbridged troticene derivatives and to identify suitable frontier orbitals in **1** for metal–ligand interaction, the structures of $[(\eta\text{-}C_7H_7)Ti(\eta\text{-}C_5H_5)]$ and of **1** have been optimized with DFT methods employing the B3LYP functional. The calculated geometry of **1** is in good agreement with the structure determined by X-ray diffraction analysis (see caption of Figure 2). For both complexes, contour plots of relevant molecular orbitals together with their eigenvalues are given in Figure 3. In agreement with other theoretical and experimental investigations of the bonding in mixed Cht–Cp sandwich molecules,[17,18] the LUMO in troticene is essentially titanium localized and consists of the $3d_{z^2}$ orbital with a small contribution from the C_7H_7 a_1 molecular orbital, in a coordinate system, in which the metal–ring axis is defined as the *z* axis. The degenerate set of the highest occupied molecular orbitals (HOMOs) stems from δ bonding between the metal center and the cycloheptatrienyl ring, and the strong contribution from both titanium and the C_7H_7 e_2 MOs indicates a significant degree of covalency.[17] In contrast, the next two levels representing the π bond to the cyclopentadienyl ring are made up predominantly of the C_5H_5 e_1 orbitals, and the interaction between the metal center and the Cp ring can thus be regarded as being mainly ionic. Owing to bridging of the two rings and distortion of the sandwich structure, the occupied molecular orbitals in **1** have given up their degeneracy, their energy positions are nonetheless very close to those in unbridged troticene. A closer inspection reveals that the tilting results in a small increase of the HOMO–LUMO gap. In principle, this difference could be qualitatively probed by UV/Vis spectroscopy, as the lowest energy band in the optical absorption spectrum of troticene has been assigned to a one-electron HOMO–LUMO transition, which is partly d–d and partly ligand-to-metal charge transfer (LMCT) in nature.[19] In our hands, the UV/Vis spectrum of troticene in CH_2Cl_2 exhibits a visible band at 696 nm ($\varepsilon = 31\ \text{L mol}^{-1}\text{cm}^{-1}$), which is blue-shifted to 663 nm ($\varepsilon = 105\ \text{L mol}^{-1}\text{cm}^{-1}$) in **1** (Figure 4). The greater intensity of the band in **1** can be explained by relaxation of the Laporte selection rule as the symmetry is lowered.[10]

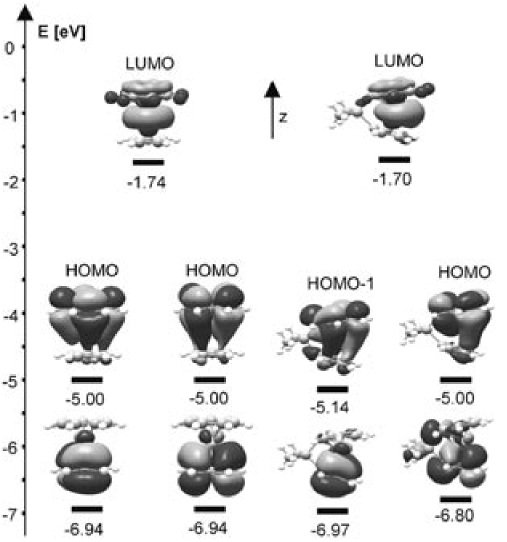


Figure 3. Contour plots and eigenvalues of valence molecular orbitals in $[(\eta\text{-}C_7H_7)Ti(\eta\text{-}C_5H_5)]$ (left) and **1** (right).[31]

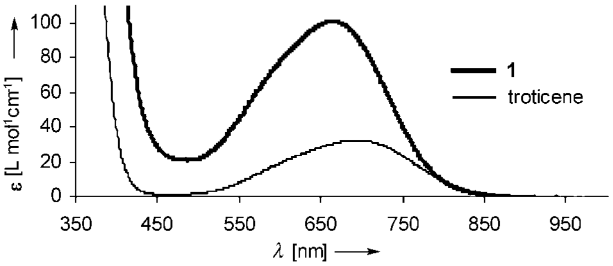


Figure 4. UV/Vis spectra of troticene and **1** in CH_2Cl_2.

The calculation additionally reveals that the 16-electron complex **1** contains a LUMO and a HOMO, which are suitably oriented for σ and π interaction with one additional ligand. Carbon monoxide (a σ-donor/π-acceptor ligand) was passed through a solution of **1** in THF. However, the formation of a stable carbonyl complex of type **2** (see Scheme 1) could not be detected at ambient pressure. An NMR spectroscopy study of **1** under elevated CO pressure reveals a gradual change of the chemical shifts with increasing gas pressure, as shown for the protons of the five- and seven-membered rings in Figure 5. No additional change in the resonance signals is observed between −70 and 20 °C indicating that CO is quickly exchanged on the NMR time scale. Further experiments are required to quantify the interaction between **1** and CO and to produce kinetic and thermodynamic data for this equilibrium reaction in a similar fashion as described for instance for the reaction of CO with decamethylcalciocene, $[(\eta\text{-}C_5Me_5)_2Ca]$,[20] and chromocene, $[(\eta\text{-}C_5H_5)_2Cr]$.[21,22]

The weak propensity to form the carbonyl complex **2** can be attributed to the low σ-donor capacity of CO as well as to the weak π-electron-donor ability of **1**. Consequently, the use of ligands with stronger σ-donor and weaker π-acceptor characteristics could lead to the formation of isolable complexes. Addition of 2,6-dimethylphenyl isocyanide or *tert*-butyl isocyanide to a blue-green solution of **1** in THF resulted

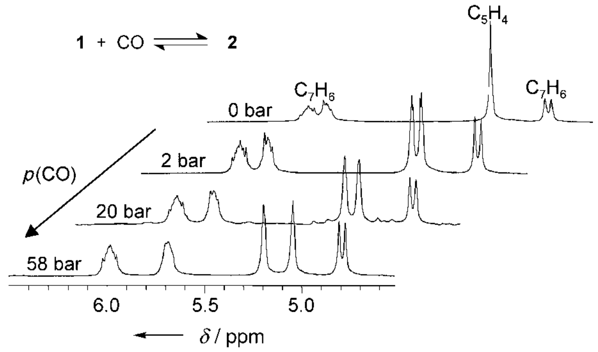


Figure 5. Excerpts from the ^1H NMR spectra of **1** in [D_8]THF under variable CO pressure at −20°C.

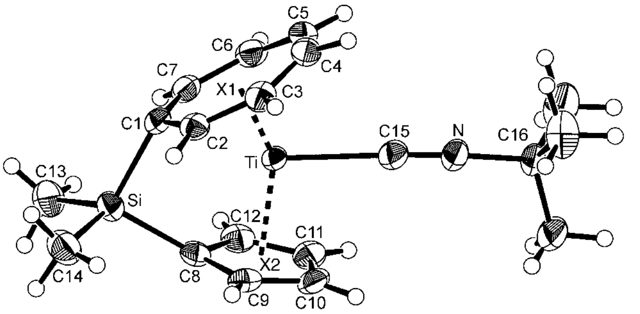


Figure 6. Molecular structure of **4**.[31] Selected bond lengths [Å] and angles [°]: Ti-C1 2.311(2), Ti-C2 2.248(2), Ti-C3 2.309(2), Ti-C4 2.412(3), Ti-C5 2.384(3), Ti-C6 2.289(2), Ti-C7 2.268(2), Ti-C8 2.380(2), Ti-C9 2.392(2), Ti-C10 2.421(2). Ti-C11 2.407(2), Ti-C12 2.368(2), Ti-C15 2.223(2), C1-C2 1.432(3), C1-C7 1.429(3), C2-C3 1.413(3), C3-C4 1.411(3), C4-C5 1.397(3), C5-C6 1.411(3), C6-C7 1.412(3), C8-C9 1.430(3), C8-C12 1.432(3), C9-C10 1.398(3), C10-C11 1.404(3), C11-C12 1.398(3), Si-C1 1.875(3), Si-C8 1.869(2), C15-N 1.153(3), N-C16 1.461(3), Ti-X1 1.649, Ti-X2 2.070; Ti-C15-N 177.0(2), C15-N-C16 175.5(2), X1-Ti-X2 147.6 (X = centroid).

in an instantaneous color change, and the isocyanide complexes **3** and **4** could be isolated in almost quantitative yield as brownish crystals (Scheme 1).[8] Coordination of the isocyanides is clearly demonstrated by the splitting patterns for the NMR resonances signals of the C_7H_6 and C_5H_4 hydrogen atoms (Figure 1). In the IR spectrum the CN stretching vibrations are at 2112 cm^{-1} (**3**) and at 2153 cm^{-1} (**4**), which is only slightly shifted compared to the values for the free isocyanides.[23] These observations indicate that metal-to-ligand π backbonding in **3** and **4** is significantly less pronounced than in related *ansa*-chromocene derivatives. For instance, $\nu_{CN} = 1835\ cm^{-1}$ for the tetramethylethylene-bridged complex $[Me_4C_2(\eta\text{-}C_5H_4)_2Cr(CNCMe_3)]$.[24] Considerably lower stretching frequencies are also observed for titanium isocyanide complexes, such as $[Me_2Si(\eta\text{-}C_5H_4)_2Ti(CN\text{-}o\text{-}Xy)_2]$ ($\nu_{CN} = 2044,\ 1938\ cm^{-1}$),[25] in which the titanium center is formally considered to be in the +II oxidation state. On the other hand, for typical so-called titanium(IV) complexes, values above 2200 cm^{-1} are found (e.g. the dimeric $[\{TiCl_4(CN\text{-}o\text{-}Xy)\}_2]$ ($\nu_{CN} = 2210\ cm^{-1}$)[26] and *ortho*-$[TiCl_4(CNCMe_3)_2]$ ($\nu_{CN} = 2226\ cm^{-1}$).[27])

The molecular structure of complex **4** was determined by X-ray diffraction analysis (Figure 6). Apparently, coordination of the *tert*-butyl isocyanide ligand leads to a pronounced elongation of the metal–carbon bonds, in particular of those to the seven-membered ring [2.248(2)–2.412(3) Å versus 2.170(3)–2.256(2) Å in **1** (Figure 2)]. The largest separations are observed between the titanium center and the carbon atoms C4 and C5, and this puckering of the seven-membered ring can be described as a moderately developed distortion from a symmetric η^7- towards an open η^5-bonding mode.[28] In the future, the use of stronger coordinating ligands might enforce the cycloheptatrienyl ring to undergo a complete η^7-η^5 hapticity interconversion giving a titanocene-like chemistry for the [1]silatroticenophane **1**.

A tentative comparison of the Ti-C-N bond lengths in **4** (Ti−C15 2.223(2), C15−N 1.153(3) Å) with those in representative titanium isocyanide complexes shows that the mixed carbonyl–isocyanide complex $[(\eta\text{-}C_5H_5)_2Ti(CO)(CNCMe_3)]$ has a shorter Ti−C (2.112(9) Å) and a longer C−N bond, (1.161(12) Å)[29] whereas the reverse order is observed for the diisocyanide complex *ortho*-$[TiCl_4(CNCMe_3)_2]$ (Ti−C 2.240(8), 2.256(6), C−N 1.145(10), 1.137(8) Å).[27] These results might suggest that **4** adopts an intermediate position between these Ti^{II} and Ti^{IV} complexes with respect to the strength of the titanium–isocyanide interaction. However, both shorter Ti−C and C−N bonds are found for cationic Ti^{IV} isocyanide complexes, such as $[(\eta\text{-}C_5H_5)_2Ti(CNCMe_3)(\eta^2\text{-}MeC{=}NCMe_3)]BPh_4$ (Ti−C 2.192(6), C−N 1.150(6) Å).[30]

In this contribution, we have reported on the synthesis and structural characterization of the highly strained [1]silatroticenophane **1**, which is the first example of an *ansa*-cycloheptatrienyl–cyclopentadienyl complex. Its reactivity towards σ-donor/π-acceptor ligands, such as carbon monoxide or isocyanides reveals that **1** does not behave like a complex containing titanium in a lower oxidation state but rather bears a closer resemblance to Lewis acidic Ti^{IV} complexes. Based on the theoretical calculations, this behavior can be attributed to the strong and appreciably covalent titanium–cycloheptatrienyl interaction leading to highly stabilized frontier orbitals and consequently to a diminishing π-electron release ability.

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[31] Details of the electronic structure calculations and of the X-ray crystal structure determinations can be found in the Supporting Information. CCDC-237472 (**1**) and CCDC-237473 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).