Formation of a 1-Zircona-2,5-disilacyclopent-3-yne: Coordination of 1,4-Disilabutatriene to Zirconocene?**

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Dedicated to Professor Günther Wilke on the occasion of his 85th birthday

The inherent instability of small cyclic alkynes has restricted attempts to isolate these strained structures. Nevertheless, their use as reactive in situ generated intermediates has been demonstrated in many synthetic applications.^[1] Significant advances in the synthesis of stable cycloalkynes have been achieved by Suzuki et al., who reported the first preparation of 1-zirconacyclopent-3-ynes in 2002.^[2] The success of this approach was based on the formation of metallacycles, in which a specific type of interaction with the metal center stabilizes the strained geometry of the cycloalkyne. Subsequently, analogous complexes containing titanium and hafnium were reported.^[3] A discussion about the structure and bonding nature of this class of compounds^[4–6] led to a better understanding of the uncommon bonding interactions of transition metals with unsaturated bonds.

Silicon-containing cycloalkynes have also been successfully isolated; the smallest structurally characterized species was the six-membered ring of a substituted tetrasilacyclohexyne.^[7] In addition, some metallacyclosilanes of Group 4 metals are also known.^[8] Considering these facts, we concluded that it should be possible to form a five-membered Sicontaining metallacycloalkyne that is analogous to the known metallacyclopentynes. It should be noted that Marschner et al. recently described an unsuccessful attempt to synthesize an analogous compound from a dipotassium bis(silyl)alkyne reagent.^[8b] Nevertheless, we were prompted to investigate pathways to the title compound, which was expected to exhibit interesting bonding properties. Furthermore, stable silicon-containing analogues of butatriene (even coordinated

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ones), which may exist in the target compound, have not been reported to date.

The synthesis of an unsubstituted 1-titanacyclopent-3-yne reported by our research group utilized the reaction of 1,4dichlorobut-2-yne with two equivalents of the titanocene alkyne complex $[Cp_2Ti(\eta^2-Me_3Si-C=C-SiMe_3)]$ ($Cp = \eta^5$ -cyclopentadienyl), which served simultaneously as a source of the " Cp_2Ti " fragment and as an acceptor of chlorine atoms (producing $[Cp_2TiCl_2]$ as a by-product).^[3b] We investigated the application of this procedure to the alkyne $ClMe_2Si-C=C-SiMe_2Cl$ (1). Surprisingly, the formation of $[Cp_2TiCl_2]$ was not observed and the isolated material was identified as complex **2**, which is a product of an alkyne-exchange reaction (Scheme 1). Similarly, by utilizing the zirconocene source,



Scheme 1. Formation of complexes **2** and **3** from alkyne-exchange reactions that occurred during attempts to prepare compound **4** from alkyne complexes.

 $[Cp_2Zr(\eta^2-Me_3Si-C=C-SiMe_3)(C_5H_5N)]$ ($C_5H_5N = pyridine$), we obtained the pyridine-stabilized alkyne complex **3**. Solid-state structures of both complexes were determined (see the Supporting Information), while the obtained structural parameters together with observed spectroscopic properties confirmed the expected metallacyclopropene structures and were comparable with known complexes of this type.^[9]

In contrast, an approach that parallels the reported procedure for the preparation of metallacyclopentynes utilizing magnesium reduction^[3a] led to the desired product: Stoichiometric amounts of $[Cp_2ZrCl_2]$ and **1** were treated with two equivalents of magnesium in tetrahydrofuran at room temperature. This procedure afforded the desired 1-zircona-2,5-disilacyclopent-3-yne derivative **4** (Scheme 2) as a crystalline solid in a rather low yield of 37 %.^[10] The occurrence of two singlet signals in the ¹H NMR spectrum

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Scheme 2. Synthesis of complex 4.

and three signals in the ¹³C NMR spectrum confirm a symmetrical structure; the C=C resonance appears at $\delta =$ 110.9 ppm, which is comparable to that of **1** ($\delta =$ 111.1 ppm), and is shifted downfield compared to that of $[Cp_2Zr(H_2C-C=C-CH_2)]$ ($\delta = 102.45 \text{ ppm}$).^[3a] The signal at $\delta = 58.2$ ppm in the ²⁹Si NMR spectrum lies in the range of Si= C unsaturated bonds,^[11] or Si-containing aromatic systems coordinated to transition metals,^[12] and the value is also comparable with that observed in zirconocene complexes of alkynylsilanes with an Si-H-M agostic interaction.^[13] Such a downfield shift can be explained by partial delocalization of the electron density along the ring.^[12c] The IR spectrum shows a band attributable to C=C bond stretching at $\tilde{\nu} = 1899 \text{ cm}^{-1}$, which is indicative of a weakening of the corresponding bond (cf. the value for the analogous 1-zirconacyclopent-3-yne, $\tilde{\nu} =$ 2018 cm^{-1}).^[14]

The X-ray diffraction analysis of **4** revealed the expected structure (Figure 1) of the five-membered planar zirconacycle, with two Si atoms and a C=C bond in the ring. The C1–C2 distance (1.240(3) Å) is longer, while the Si–C distances (1.83 Å on average) are only slightly shorter than those of free silyl-group-substituted alkynes (cf. the values in Me₃Si–C=C–SiMe₃,^[15] 1.208(3) Å for C=C and 1.844(1) Å for Si–C, respectively). Zr–Si distances (average 2.74 Å) are comparable with those of other zirconocene silyl complexes.^[8b,16] The strained geometry of the ring is demonstrated by acute Zr-Si-C angles (average 64.0°) and by average Si–C=C angles of 151.5° (cf. values in 1-zirconacyclopent-3-ynes prepared by



Figure 1. A view of the molecular structure of **4** perpendicular to the plane Zr-Si1-C1-C2-Si2. Thermal ellipsoids correspond to the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr–Si1 2.7395(7), Zr–Si2 2.7352(6), Zr–C1 2.538(2), Zr–C2 2.539(2), C1–Si1 1.827(2), C2–Si2 1.834(2), C1–C2 1.240(3); Si1-Zr-Si2 109.03(2), Zr-Si1-C1 63.91(7), Zr-Si2-C2 64.01(7), Si1-C1-C2 151.7(2), Si2-C2-C1 151.3(2).

Suzuki et al., range from 151 to 156°).^[2,3a] The average distance from the Zr center to the C=C carbon atoms (2.54 Å) is longer than that in 1-zirconacyclopent-3-ynes (2.29–2.32 Å); this value suggests only weak interaction of the unsaturated bond with the metal. Substitution of two carbon atoms with Si thus results in the triple bond being located further from the Zr center, thus reducing their mutual interaction.

Calculations performed by Lam and $\text{Lin}^{[4]}$ for 1-zirconacyclopent-3-yne $[\text{Cp}_2\text{Zr}(\text{H}_2\text{C}-\text{C}=\text{C}-\text{CH}_2)]$ suggested that both the metallacyclopentyne (analogous to structure **A** in Scheme 3) and a coordinated cumulene (analogous to struc-



Scheme 3. 1-Metalla-2,5-disilacyclopent-3-ynes (A) and their possible resonance forms $(B,\,C).$

ture **B**) resonance forms contribute to the bonding in this molecule. On the basis of an experimental electron density study, Hashizume et al. claimed that the cumulene structure is the dominant resonance form.^[5] On the other hand, Jemmis, Jiao, et al.^[6] concluded the existence of metal– π interaction of the metallocene core with the unsaturated bond (analogous to structure **C**). Such a coordination mode agrees better with the observed structural and spectral parameters and explains the enhanced stability.

For a better understanding of the bonding interaction in the novel complex 4, we carried out DFT computations with the B3LYP hybrid functional (see the Supporting Information for details). Compound 4 has C_2 symmetry and the computed structural parameters agree very well with those of the experimentally determined molecular structure. Natural localized molecular orbital (NLMO) analysis reveals a metallacvelopentyne complex with a C \equiv C bond (structure **A** in Scheme 3), rather than a 1,4-disilabutatriene complex (structure **B**). This C=C bond (1.246 Å) is longer than the corresponding bond in Me₃Si−C≡C−SiMe₃ (1.216 Å), and the Si-C bond of complex 4 (1.832 Å) is very slightly shorter than that in Me₃Si–C=C–SiMe₃ (1.848 Å), thus indicating a Si-C single bond. The Wiberg bond orders for the C=C and Si-C bonds are 2.431 and 0.793 for complex 4, and 2.888 and 0.787 for Me₃Si-C=C-SiMe₃, respectively. For comparison, the computed Si=C and C=C bond lengths for 1,4-disilabutatriene Me₂Si=C=C=SiMe₂ (D_{2h} symmetry) are 1.716 and 1.263 Å, and their corresponding Wiberg bond orders are 1.362 and 2.286, respectively.

In addition, NLMO analysis also shows the interaction between the Zr center and the C=C bond in **4** (corresponding to structure **C**), with a Zr–C distance of 2.580 Å; the computed Zr–C Wiberg bond order is 0.379, which might explain the slightly elongated C=C bond. However, the contribution of the Zr center to the C=C bond is about half the value of the contribution in $[Cp_2Zr(H_2C-C=C-CH_2)]$;^[6] this difference can be ascribed to the long Zr–C distance compared to that in $[Cp_2Zr(H_2C-C=C-CH_2)]$. On one hand, the metal–ligand interaction is shown by the negative value of the nucleus-independent chemical shifts (NICS). On the other hand, the lower NICS value at the center (NICS(0) = -40.6 ppm) of **4**, compared to the NICS value (-49.4 ppm) of complex $[Cp_2Zr(H_2C-C=C-CH_2)]$,^[6] indicates a weaker interaction between the Zr center and the C=C bond.

In conclusion, we have reported the preparation and characterization of a novel Zr complex. According to the observed structural and spectral parameters, as well as DFT calculations, the bonding situation in this compound is plausibly described by the 1-zircona-2,5-disilacyclopent-3-yne structure with a weak metal-triple-bond interaction (\mathbf{C}), rather than a zirconocene-stabilized 1,4-disilabutatriene complex (\mathbf{B}).

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove-box techniques. Prior to use, solvents were pre-dried, freshly distilled from sodium tetraethylaluminate, and stored under argon. [Cp₂ZrCl₂] was purchased from Sigma–Aldrich. **1**,^[17] $[Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)],^{[9a]}$ Alkvne and $[Cp_2Zr(\eta^2 Me_3SiC_2SiMe_3)(C_5H_5N)$ ^[9c] were synthesized according to published procedures. The following spectrometers were used: NMR: Bruker AV 400, AV 300; chemical shifts (¹H, ¹³C, ²⁹Si) given relative to SiMe₄ and referenced to residual solvent signals ([D₆]benzene: $\delta_{\rm H}$ = 7.16 ppm, $\delta_{\rm C} = 128.0$ ppm). IR: Bruker Alpha-P. Elemental analyses: Leco CHNS-932 analyzer. Melting points: Büchi 535 apparatus, capillaries sealed under Ar.

X-ray structure determination of **4**: Crystals suitable for measurement were obtained from *n*-hexane/toluene at -78 °C. Diffraction data were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo_{Ka} radiation. The structure was solved by direct methods (SHELXS-97)^[18] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).^[18] The crystal lattice contained disordered solvent molecules, which are not shown in the figures. The DIAMOND program was used for graphical representations.^[19] C₁₆H₂₂Si₂Zr, M_r = 361.74, space group $P2_1/n$, monoclinic, a = 7.9232(2), b = 10.4110(2), c = 23.9891(7) Å, $\beta = 96.180(2)^\circ$, V = 1967.3(1) Å³, Z = 4, $\rho_{calcd} = 1.377$ g cm⁻³, 32.926 reflections measured, 4700 were independent of symmetry, 4052 of which were observed ($I > 2\sigma(I)$), R1 = 0.028, wR2 (all data) = 0.077, 212 parameters.

Synthetic procedures, X-ray structure determination details, molecular structures of compounds 2 and 3, an alternative view of structure 4, and all computational details are given in the Supporting Information. CCDC 756947 (2), 756949 (3), and 756948 (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.

Synthesis of **4**: Alkyne **1** (107 mg, 0.51 mmol) was added to a stirred suspension of $[Cp_2ZrCl_2]$ (150 mg, 0.51 mmol) and magnesium turnings (25 mg, 1.07 mmol) in THF (10 mL) at room temperature. The color of the mixture turned to dark amber over a period of 30 min and the stirring was continued for further 18 h. All volatiles were subsequently removed under vacuum and the residue was extracted with *n*-hexane (2×10 mL) at 50°C and filtered. The solution was concentrated to ca. 5 mL, and upon standing at -78°C overnight, brown crystals of **4** were formed. Yield: 68 mg (37%); m.p. 180–185°C dec. without melting; anal. calcd. for C₁₆H₂₂Si₂Zr (361.74 gmol⁻¹) C 53.13, H 6.13; found: C 49.91, H 6.45 (better values could not be obtained probably because of a partial formation of SiC even in the presence of an additional chemical oxidant V₂O₅ in

the combustion process). NMR (297 K, [D₆]benzene): $\delta({}^{1}\text{H}) = 0.57$ (s, 12 H, SiMe₂), 4.88 ppm (s, 10 H, C₅H₅); $\delta({}^{13}\text{C}{}^{1}\text{H}]) = -0.2$ (SiMe₂), 96.8 (C₅H₅), 110.9 ppm (C=C); $\delta({}^{29}\text{Si}{}^{1}\text{H}]) = 58.2$ ppm; IR (Nujol): $\tilde{\nu} = 1899 \text{ cm}^{-1}$ (w, C=C); MS (CI, isobutane): m/z 360 [*M*]⁺.

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