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Visiting the limits between a highly strained 1-zirconacyclobuta-2,3-diene and chemically robust dizirconacyclooctatetraene

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Dedicated to the memory of Prof. Dr. h. c. mult. Günther Wilke in recognition of his contributions to the development of LIKAT.

ABSTRACT: The reaction of the allene precursor Li₂(Me₃SiC₃SiMe₃) with Cp₂ZrCl₂ was examined. We observed selective formation of hitherto unknown linear allene bridged dizirconocene complexes [(Cp₂ZrCl)₂{-µ-(Me₃Si)C₃(SiMe₃)-}] and [(Cp₂Zr)₂{-µ-(Me₃Si)C₃(SiMe₃)-}₂]. Upon σ coordination of the allenediyl unit to [Cp₂Zr] pyrophoric Li₂(Me₃SiC₃SiMe₃) is tamed stepwise, yielding a surprisingly robust 1,5-dizirconacyclooctatetra-2,3,6,7-ene with cumulated double bonds. This complex is unexpectedly inert against moisture, air, water and acetone. Surprisingly it degrades under MS conditions to give the highly strained 1-zirconacyclobuta-2,3-diene. All isolated compounds were fully characterised and the molecular structures are discussed. The stability and reactivity of these complexes are rationalised by DFT computations.

1a) containing cumulated double bonds is not reported to date. Computational studies on biradicaloids (**B**, E = CH₂, NH, O and S; R = H)^[7] and beryllium analogues (**B**, E = Be; R = H)^[8] shed light on the theoretical stability and the singlet-triplet states of this class of compounds. In the synthesis of 1,3,4,6-tetrakis(*t*butylthio)thieno[3,4-c]thiophene a dithiocyclooctatetraene (**B**, E = S, R = *t*-Bu-S) was mentioned as an intermediate which shows a C-C coupling of the central allene carbon atoms.^[9] To the best of our knowledge, the disilacyclooctatetraene (structure of type **B**, E = SiMe₂, R = SiMe₃), which was described by Barton in 1993, using *in situ* generated Li₂(Me₃SiC₃SiMe₃) (1) and Me₂SiCl₂, is the only example of this class of compounds that has been fully characterised and structurally investigated to date.^[10]

Introduction

As early as 1911 Willstätter isolated cyclooctatetra-1,3,5,7-ene (COT, A, Figure 1a) for the first time in a multi-step synthesis starting from pseudopelletierine¹ which was later confirmed by Cope's repetition of the original protocol.^[2] Later, Reppe developed a nickel catalysed process for the synthesis of COT from acetylene.^[3] COT is unstable and easily forms explosive organic peroxides. However, stabilization of this compound is possible by coordination to transition metal centres to yield COT complexes. With respect to the four C-C double bonds it shows a broad chemistry with η^2 , η^4 , η^6 and η^8 π -type coordination modes and can be regarded as classical olefin ligand.^[4] COT itself is a non-aromatic species in contrast to the cyclooctatetraenide $[C_8H_8]^{2-}$ dianion, which is a classical Hückel system and forms sandwich like complexes analogous to cvclopentadienvl ligands.^[5] Seminal work by Wilke established this chemistry as he described a series of M_m[COT]_n derivatives using disodium cyclooctatetraenide Na₂[C₈H₈] and metal halides as starting materials (e.g. M[COT]: M = V, Ni, Co; M[COT]₂: M = Ni, Ti, Zr; M₂[COT]₃: M = Cr, Mo, W).^[6]

In contrast to the well examined and versatile chemistry of **A**, its derivative cyclooctatetra-1,2,5,6-ene (**B**, $E = CH_2$; R = H, Figure

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Supporting information for this article is given via a link at the end of the document.



Figure 1. a) Willstätter's COT (A), COT containing cumulated double bonds (B). b) Schematic representation of selected exotic stable metallacycles of group 4 metals.

In analogy to π complexation in Wilke's $M_m[COT]_n$ compounds σ coordination of unsaturated substrates was also found to result in the formation and stabilization of unusual cyclic structures, which can formally be regarded as the products of isolobal ring-substitution of a CH₂ group in hypothetical highly ring-strained compounds by a group 4 metal fragment.^[11] In this regard, Erker and Suzuki as well as our group have reported on the stabilization of a variety of exotic structural motifs such as 1-metallacyclopent-3-ynes, 1-metallacyclopenta-2,3,4-trienes, and 1-metallacyclopenta-3,4-dienes (Figure 1b).^[12] Very recently, Beckhaus reported on the stabilization of a hexapentaene unit as a binuclear zig-zag titanium complex.^[13]

As a part of our long-standing interest in the realization of unusual metallacycles of Ti, Zr, and Hf we have very recently attempted to access a hitherto unknown four-membered 1-titanacyclobutadi-2,3-ene (**C**, Scheme 1)^[14] following up on theoretical studies of these structures.^[15]

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Scheme 1. Possible products of a reaction of $Li_2R_2C_3$ and $[M]Cl_2$.

In this context, as all previous attempts to access structures of type **C** failed, we investigated alternative allene precursors. In this contribution, we present the synthesis of a dilithioallene precursor and its reactions with Cp_2ZrCl_2 to evaluate possible reaction pathways to 1-metallacyclobutadi-2,3-ene (**C**) or dimetallacyclooctatetraene (**D**) (Scheme 1).

Results and Discussion

Motivation. To get a deeper insight into the chemistry of these zirconacyclobuta-2,3-dienes (**C**) we considered a simple isodesmic equation between the Cp'_2ZrMe_2 complex ($Cp'=Cp = \eta^5$ -cyclopentadienyl, $Cp'=Cp^*=\eta^5$ -pentamethylcyclopentadienyl) and the allene precursors Me(Me_3Si)C=C=C(SiMe_3)Me as well as Me(*t*-Bu)C=C=C(*t*-Bu)Me for comparison (Scheme 2).



Scheme 2. Isodesmic equation to zirconacyclobuta-2,3-dienes.

Furthermore we considered the corresponding metallacyclopenta-2,3,4-trienes for the analogue isodesmic equation (Table 1). The metallacyclopenta-2,3,4-trienes $Cp_2Zr(\eta^2-t\cdot BuC_4t-Bu)^{[16a]}$ and $Cp^*_2Zr(\eta^2-Me_3SiC_4SiMe_3)^{[16b]}$ are experimentally accessible, nicely expressed by their exergonic Gibbs Free Energy of -18.94 kcal·mol⁻¹ and -14.55 kcal·mol⁻¹, therefore we chose theses as benchmark values.

A

syntheses of 1-zirconacyclobuta-2,3-dienes and zirconacyclopenta-2,3,4-trienes.							
precursor	Cp ₂ ZrMe ₂	Cp* ₂ ZrMe ₂					
Me(Me ₃ Si)C ₃ (SiMe ₃)Me	-8.97	+3.87					
Me(Me ₃ Si)C ₄ (SiMe ₃)Me	-22.06	-14.55					
Me(<i>t</i> -Bu)C ₃ (<i>t</i> -Bu)Me	+0.74	+22.24					
Me(<i>t</i> -Bu)C ₄ (<i>t</i> -Bu)Me	-18.94	-3.55					

The calculations clearly reveal the combination of the zirconocenes and *t*-butyl substituents at the allene unit as inappropriate due to the endergonic Gibbs Free Energies for the considered reactions (Table 1). With a closer look to the computed values, $Cp_2Zr(\eta^2-Me_3SiC_3SiMe_3)$ appeared as the most promising candidate for the formation of a 1-metallacyclobuta-2,3-diene structure with the Gibbs Free Energy for its formation of -8.97 kcal-mol⁻¹ being exergonic but challenging and compared to the corresponding 1-titanacyclobuta-2,3-diene (-11.8 kcal-mol⁻¹) this value is slightly lower.^[14b]

Synthesis of the dilithioallene precursor Li₂(Me₃SiC₃SiMe₃). Although propargylic metalation^[17] as well as structures of organolithium compounds^[18] have been well studied and understood for decades, no structural investigation of a suitable dilithioallene precursor is known to date. Based on our experience with trimethylsilyl substituted substrates, supported by the aforementioned theoretical studies of the stability of corresponding derivatives of C,^[14b] we decided to focus on the synthesis of Li₂(Me₃SiC₃SiMe₃) (1). In two previous studies, the synthesis of 1 was performed by deprotonation of 1,3bis(trimethylsilyl)prop-1-yne in Et₂O and THF with *n*-BuLi^[19] (Scheme 3). Compound 1 was not isolated, however, its presence was confirmed by addition of chlorosilanes and subsequent analysis of the residues obtained. From analogous reactions we have attempted to isolate 1 as a solid material, but only colourless to yellowish oils were obtained. For this reason, we modified the procedure and tested deprotonation of 1,3bis(trimethylsilyl)prop-1-yne using Lochmann-Schlosser Base^[20], but were only able to isolate the potassium salt [K(THF)₂(Me₃SiC(H)C₂SiMe₃)] which forms a linear coordination polymer in the solid state as confirmed by X-ray analysis.^[21] West et al. reported the synthesis of Li₄C₃ in n-hexane with n-BuLi;^[22] we thus revisited the lithiation of 1,3-bis(trimethylsilyl)prop-1-yne with n-BuLi in aprotic, non-polar solvents toluene, nhexane, and benzene. Eventually, benzene was the solvent of choice; after a reaction time of one week we obtained 1 in good yields (62 %) as an analytically pure white pyrophoric solid which decomposes at 239 °C under Ar atmosphere (Scheme 3).



Scheme 3. Optimised synthesis of 1 in benzene.

The NMR characterization of **1** was done at ambient temperature in $[D_6]$ benzene solution (data see below). Whereas the tetrameric aggregate completely lacks symmetry in the crystal (eight inequivalent lithium sites and SiMe₃ groups, Figure 2), higher symmetry is found in solution. There are two silyl groups and (at least) two lithium sites. This does not necessarily imply dissociation of the aggregates but indicates a dynamic behaviour which is also obvious from the ¹³C and ²⁹Si NMR

spectra (broad resonances for the methyl groups and the metalised quart. carbon atom, lack of spin-spin coupling fine structure, Figure S20). The strongest broadening is found for the metalised allene carbon atoms whose signals hardly show up in the 1D spectra but were identified by indirect detection (Figure S19) with remarkable chemical shifts of δ = 44.6 and 37.8 ppm at much lower frequency than expected for metalised sp² carbon atoms (cf. phenyllithium, δ (CLi) 176 to 198 ppm depending on conditions: data compiled in ref. 23). Although we did not attempt to investigate the dynamics, we find it remarkable that it does not lead to a complete signal averaging (for the monomeric entity one would expect only one set of signals). Usually, organolithium compounds in solution undergo fast inter- and intra-aggregate exchange processes that require NMR investigations to be done at very low temperatures^[24] if structural features such as symmetry, coordination behaviour and degree of association are to be determined. This aggregation behaviour was however not further studied. The signal for the central carbon atom is found downfield at 174.1 ppm. Furthermore we detected a weak antisymmetric C=C=C vibration at 1751 cm⁻¹ in the Raman spectrum which is in agreement with the calculated frequency ($\tilde{v}_{calc./uncor.} = 1802 \text{ cm}^{-1}$).

The molecular structure of 1 is shown in Figure 2 and reveals the connectivity in this allene precursor. It should be mentioned that 1 dissolves moderately in benzene and very well in THF, the molecular structures obtained after crystallization from these solvents differ considerably, but reveal in both cases the formation of a tetramer in the solid state.^[21] In THF solvate (1thf), the peripheral lithium atoms are saturated by THF coordination. In benzene solvate (1benz) there is no direct interaction with the solvent but we detected short contacts between Li atoms and SiCH₃ groups of neighboring tetramers (cf. Li4-C23A 2.450(3) and Li7-C32B 2.438(4) Å). The benzene solvate crystallises in the triclinic space group $P\bar{l}$ and thus we found four slightly different C₃ units in the tetramer which forms the asymmetric unit. In each C=C=C group two different C-C bonds are found, one shorter (e.g. C2-C3 1.304(2) Å) and one slightly longer (e.g. C1-C2 1.323(2) Å).





Both values clearly indicate double bond character (*cf.* Σr_{cov} C=C 1.34; C=C 1.20 Å)^[25] and correspond well to data reported by Schleyer for a dilithiobutatriene dimer structure {(Li•THF)₂(*t*-BuC₄*t*-Bu)}₂ (*cf.* C=C=C=C: 1.321(5), 1.292(5) and 1.336(5) Å).^[26] For **1benz** angles between the planes defined by Si,C,C/C,C,Si of the SiC₃Si units indicate roughly orthogonality of the cumulated double bonds (64.7(2)-72.7(2)°, Table S4). Notably, in **1thf** one of the two allenediyl ligands in the asymmetric unit deviates significantly from this behaviour with a surprisingly small value (26.0(4)° vs. 83.7(2)°).

We conceived **1** as an ideal stoichiometric synthon for inorganic as well as organic reactions, were lithium halide elimination at compounds like R-EX₂ (R = substituent; E = element e.g. B, P, S, Sn; X = halogen) can be used as driving force leading to a series of interesting, new allenediyl bearing organoelement and/or organometallic compounds.

Reactions of the dilithioallene precursor Li₂(Me₃SiC₃SiMe₃) with Cp2ZrCl2. With compound 1 in hand we evaluated its reaction with Cp₂ZrCl₂ using different stoichiometric ratios of dilithioallene and zirconocene precursor. In a first experiment with 1:1 stoichiometry in benzene we observed formation of some by-products but good turnover into a main component which shows two resonances in the ¹H NMR spectrum in 18:10 ratio at 0.39 and 6.04 ppm. This corresponds exactly to the expected ratio for a hypothetic 1-zirconacyclobutadi-2,3-ene (C) or a dizircona-cyclooctatetraene (D) (Scheme 1). With the help of ¹³C NMR analysis, which shows four resonances, we could exclude the presence of a compound of type C since the resonance for the central carbon atom was found at 171.4 ppm and thus only slightly deviates from the value of linear 1. In comparison, the only reported examples of 1-metallacyclobutadi-2,3-enes show ¹³C resonances of the central carbon atom that are shifted to much lower field (cf. 257 ppm in (i-PrO)₂(pyridine)₂Mo(t-BuC₃t-Bu),^[27] 220 ppm in Cp(Cl)W(t-BuC₃t-Bu)^[28] and 205 ppm in (Ph₃SiO)₂(phen)Mo(p-MeOPhC₃-Ph-p-OMe)^[29]).

Since it was difficult to separate the by-products and obtain suitable crystals for X-ray diffraction analysis of the assumed product, we then performed the reaction of **1** with Cp_2ZrCl_2 in 1:2 stoichiometry. After reaction in benzene at ambient temperature clean conversion into a single main product was observed (Scheme 4).



Scheme 4. Optimised synthesis of 2.

The bright orange solid of **2** is highly air and moisture sensitive, decolourises upon decomposition and degrades at 161 °C under Ar atmosphere. The ¹H NMR spectrum of **2** in [D₆]benzene shows three resonances in 18:10:10 ratio, one for the Me₃Si

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group (0.37 ppm) and two signals for inequivalent Cp ligands (6.08, 6.16 ppm). ¹³C NMR analysis reveals a signal for the central allene carbon atom at 174.7 ppm which is in the same range as for the linear dilithioallene **1**. In addition we detected the antisymmetric C=C=C vibration as strong resonance at 1776 cm⁻¹ in the IR spectrum and as weak signal at 1781 cm⁻¹ in the Raman spectrum which is in agreement with the calculated frequency ($\tilde{v}_{calc./uncor.} = 1806 \text{ cm}^{-1}$). On the basis of these data in combination with the molecular mass of *m*/*z* 697 we assume **2** as an allenediyl bridged dinuclear zirconocene monochloride complex. This is confirmed by X-ray analysis (Figure 3). It should be noted that similar compounds with bent C₃ units were reported, e.g. Jensen and Messerle described on the formation of a dinuclear Ta allenediyl complex via double C-H activation of an allene ligand.^[30]



Figure 3. Molecular structure of compound 2. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms and the second molecule of the asymmetric unit were omitted for clarity.

We used this unusual complex 2 as synthon for the formation of the dizirconacyclooctatetraene which was postulated after initial experiments described above. After optimization of the reaction procedure we observed full conversion in a cooled diethyl ether solution (-30 °C) that can be followed by a slow colour change from bright orange to deep red within a reaction time of one day (Scheme 5). After separation of LiCl, NMR spectra exclusively showed the resonances that were assigned to structure **D** before after reaction of 1 and Cp₂ZrCl₂ in 1:1 stoichiometry in benzene. We thus assign this compound as a 1,5-dizirconacyclooctatetra-2,3,6,7-ene (3) which to the best of our knowledge represents the first dimetallacyclooctatetraene. The presence of an antisymmetric C=C=C vibration is illustrated by strong signals in the IR spectrum at 1784 and 1772 cm⁻¹ and weak signals at 1787 and 1774 cm⁻¹ in the Raman spectrum which is in good agreement with the calculated frequencies ($\tilde{v}_{\text{calc./uncor.}}$ = 1811 and 1794 cm⁻¹).



Scheme 5. Optimised synthesis of 3.

Notably, the MS-Cl⁺ spectrum of **3** shows the $[M+H]^+$ at m/z 807 as well as an intense peak at m/z 403 which suggests the presence of the corresponding 1-metallacyclo-butadi-2,3-ene (**C**) or a dicationic dimetallacyclooctatetraene $[3]^{2+}$. ESI-TOF/HRMS analysis unambiguously confirmed the presence of a 1-zirconacyclo-butadi-2,3-ene which formed under MS conditions $(m/z \ 403 \ [M+H]^+)$ (Figure 4).



Figure 4. HRMS spectra for the peaks at m/z 403 of the 1-zirconacyclo-butadi-2,3-ene (top) and for the peak at m/z 807 of compound 3 (bottom).

The low Gibbs free energy of a dimerization process from two molecules of type **C** to give **3** supports this observation (-2.4 kcal-mol⁻¹). However, attempts to sublime a compound of this type from **3** in vacuo at 207 °C failed.^[21] Nevertheless, this, and the stability towards the eluent (MeOH/0.1% HCOOH in H₂O 90:10) during the ESI-TOF/HRMS experiment demonstrates the impressive stability of **3** ($T_{dec.}$ = 315 °C under Ar). The molecular structure of **3** confirms the unusual dimetallacyclooctatetraene motif (Figure 5).

Discussion of structural data. Both complexes **2** and **3** can be crystallised from saturated solutions at ambient temperature. While compound **2** crystallises from benzene (Figure 3), crystals of **3** were grown from toluene (Figure 5). In **2** and **3** the Zr1-C1 distances are in the range of Zr-C σ bonds (Table 2) which corresponds to the data reported for Cp₂ZrMe₂ (*cf.* 2.280(5)/2.273(5) Å).^[31] The Zr-Cl distances in **2** are in the range 2.4432(11) to 2.4562(11) Å, which is in excellent agreement to values found for Cp₂ZrCl₂ (*cf.* 2.446(5)/2.436(5) Å).^[32] It should be mentioned that on the basis of quantum chemical calculations, the inner/outer orientation of the Cl atoms found in the molecular structure of **2** does not correspond to the thermodynamically most favorable orientation.

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Figure 5. Molecular structure of compound 3. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms were omitted for clarity.

We found that orientation of both CI atoms towards the centre of the molecule (inner/inner) is preferred; compared to this, the inner/outer and the outer/outer orientations are endergonic by 1.48 kcal·mol⁻¹ and 3.43 kcal·mol⁻¹, respectively.^[21] In contrast to 1benz, all C-C distances in the allenediyl units in complexes 2 and 3 are almost identical (1.303(6) to 1.319(6) Å) and are best described as slightly shortened C-C double bonds (cf. C=C 1.34 Å).^[25] This is in agreement with the C1-C2 distance found in Barton's disilacyclooctatetraene (E) (1.311(3) Å).^[10] A closer look at the C-C-C angle shows that the C₃ units in 2 and 3 do not differ considerably. The dilithioallene is significantly more bent, most likely as a consequence of its tetrameric structure (Table 2). For both zirconocene complexes the angles between the planes defined by Si,C,C/C,C,Si of the SiC₃Si units suggest almost orthogonal orientation of the cumulated double bonds (2: 71.8(2)/69.8(2)°). As 86.9(3)° 3: in Barton's disilacyclooctatetraene E)^[10] the allenediyl units in 3 are twisted about 61.8(4)°, as defined by the planes C1-C2-C3 and C4-C5-C6 (cf. 78.1° in E).

Table 2. Selected bond distances in Å and angles in °.

Compound	E-C _{all.}	C1-C2	C2-C3	C1-C2-C3
$E (E = Si)^{[a]}$	1.881(2)	1.311(3)	_ [b]	175.2(2)
1benz (E = Li)	2.189(3) 2.220(3) ^[c]	1.323(2)	1.304(2)	173.65(15) ^[d] 174.80(15)
2 (E = Zr) ^[e]	2.265(4)- 2.288(4)	1.306(6) 1.303(6)	1.310(6) 1.319(6)	176.8(4) 178.0(4)
3 (E = Zr) ^[f]	2.283(3)- 2.306(3)	1.313(4) 1.309(4)	1.310(4) 1.306(4)	176.7(3) 177.3(3)

[a] Data taken from ref. [10]; [b] Data not reported; [c] Shortest Li-C1 bonds, for a detailed bond analysis see Table S5; [d] Only the largest and smallest value is given here; [e] Two different molecules in the asymmetric unit; [f] Values of both allenediyl units are reported, second set Zr2-C4-C5-C6.

To gain a deeper insight into the bonding situations of 2 and 3 we calculated the Natural Localised Molecular Orbitals (NLMOs) with the NBO6.0 package.^[33] In the calculated gas phase the structure of complex 3 is C2 symmetric and 2 is C1 symmetric, therefore we observed for 3 a set of degenerated NLMOs from which only one part of these pairs is shown in Figure 6. With a closer look to the HOMO-1 orbitals of 3 these are best described as classical C-C π-bonds which mainly consist of two pure porbitals of the allenediyl carbon atoms with just a small contribution of about 4 % from the d orbitals of the zirconium centre. The HOMO orbitals show nearly a rectangular arrangement to the HOMO-1 orbitals and have lower zirconium contribution. In contrast to this the LUMOs are best described as empty d orbitals of the zirconium centre with minor antibonding contributions from the Cp and allenediyl units. The NLMOs of complex 2 show almost the same features and can be found in the Supporting Information (Figure S45).



Figure 6. Representation of NLMOs of compound 3.[34]

General comments on the reactivity of complexes 2 and 3. The structural features of the central allenediyl units in complexes 2 and 3 are almost identical; however their thermal and chemical behaviour differs considerably. Compound 2 decolourises within a few minutes when exposed to air. The colourless powdery decomposition product can be dissolved in benzene and two different crystal types were obtained from this solution. Both crystal types were analysed by X-ray diffraction (unit cell determination) and were both identified as (μ_2 -oxo)bis(chloro-(ŋ⁵-cyclopentadienyl)-zirconium) [Cp₂Zr(Cl)-O-(Cl)-ZrCp₂] in two different literature known unit cells.^[35] Furthermore we identified [Cp₂Zr(Cl)-O-(Cl)-ZrCp₂] by mass spectrometry, IR and NMR spectroscopy. In addition to this we identified 1,3-bis-(trimethylsilyl)prop-1-yne as second product of this decomposition reaction via ^1H and ^{13}C NMR spectroscopic analysis of the benzene solution. In contrast, the dizirconacyclooctatetraene 3 is stable for hours under these conditions. During analysis of compound 3 we noticed its remarkable stability to air and humidity. For this reason we have decided to carry out some stability tests. For this purpose, a small amount of compound 3 was mixed with an excess neat acetone, water and dichloromethane. After an exposure time of 24 hours, ¹H and ¹³C NMR spectra of the dried solids were collected in [D6]benzene (Figures 7 and S2). As can be seen from the ¹H NMR spectra, **3** is completely inert. It dissolves well in dichloromethane, moderately in acetone and hardly in water. In addition to this neat acetone, water and dichloromethane VIANUSCI

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This behaviour is very unusual for metallacycles of early transition metals as with these substrates typically formation of oxido or chlorido complexes is observed.^[36] Also, with carbonyl compounds, facile insertions into the M-C bonds are a common reactivity motif.^[37] Complex **3** is highly non-polar; as a consequence it floats on water and is difficult to wet. This is nicely expressed by the space filling model of **3** which shows, in contrast to **1** and **2**, the metal centre perfectly shielded by the Cp and Me₃Si groups (Figures S8/S11/S14). Having this in mind, the decreasing reactivity of these compounds towards air (**1** > **2** > **3**) can be rationalised.

Conclusion

In summary, we have revisited the chemistry of the previously described, yet in our eyes very interesting and underrated allene precursor **1**. Upon reaction of **1** with Cp_2ZrCl_2 hitherto unknown unusual linear allenediyl bridged dizirconocene complexes, namely a dinuclear monochlorido complex **2** as well as the first dimetallacyclooctatetraene **3** are formed. Initial reactivity test showed that exchange of Li for $[Cp_2Zr]$ results in a remarkable stabilization of the highly reactive C_3 precursor. As stepwise synthesis of **3** from **1** and **2** was successful we are currently investigating the reactivity of **2** to explore the frontiers of the chemistry of more strained allenediyl bridged dizirconocenes. Furthermore we are evaluating the potential of the highly unusual dimetallacyclooctatetraene **3**. In this report we show the unexpected degradation of **3** under MS conditions to the highly strained 1-zirconacyclobuta-2,3-diene.

Experimental Section

General: All manipulations were carried out in an oxygen- and moisturefree argon atmosphere using standard Schlenk and drybox techniques. The solvents were purified with the Grubbs-type column system "Pure Solv MD-5" and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Commercially available n-BuLi solution (1.6 M and 2.5 M in n-hexane, Acros), chlorotrimethylsilane (Me₃SiCl, 98 %. Acros), bis(cyclopentadienyl)zirconium(IV) dichloride (Cp2ZrCl2, >98 %, Aldrich), and trimethylsilylacetylene (98 %, TCI) were transferred in Schlenk Tubes stored under argon and used as received. N,N,N',N'-Tetramethylethylenediamine (99 %, Acros) was pre-dried over molecular sieves (4 Å) and dried by sodium/benzophenone distillation. Potassium tert-butanolate (KOtBu) [38] and lithium diisopropylamine (LDA) [39] were freshly prepared according to literature procedures and isolated as white solids. 1,3-bis(trimethylsilyl)prop-2-yne was synthesised according to modified literature procedure (see above). NMR spectra were determined on Bruker AV300 and AV400. ¹H and ¹³C chemical shifts were referenced to the solvent signal: $[D_6]$ benzene (δ_H 7.16, δ_C 128.06)^[40] and [D₈]toluene ($\delta_{\rm H}$ 2.09, $\delta_{\rm C}$ 20.4)^[41] Chemical shifts of ⁷Li are given relative to a reference frequency calculated from the actual ¹H reference frequency and $\Xi(^{7}Li) = 38.863797 \text{ MHz}^{[42]}$ (which corresponds to LiCl in D₂O, 9.7 mol/kg, at 0 ppm). Accordingly, chemical shifts of ²⁹Si are given relative to SiMe₄, Ξ ⁽²⁹Si) = 19.867 187 MHz. Raman spectra were recorded on a LabRAM HR 800 Raman Horiba spectrometer equipped with an Olympus BX41 microscope with variable lenses was used. The samples were excited by different laser sources: 633 nm (17 mW, air cooled). 784 nm Laser diode (100 mW, air-cooled) or 473 nm Ar+ Laser (20 mW, air-cooled). All measurements were carried out at ambient temperature. IR spectra were recorded on a Bruker Alpha FT-IR, ATR Spectrometer, spectra are not corrected. MS analysis was done using a Finnigan MAT 95-XP (Thermo-Electron), Cl⁺/Cl⁻ Isobutane. The measurement of the ESI-TOF/HRMS of 3 was carried out at a 6210 Agilent Tec. device equipped with a 1200 HPLC system using MeOH/0.1 % HCOOH in H₂O 90:10 as eluent. CHN analysis was done using a Leco Tru Spec elemental analyser. Melting points are uncorrected and were determined in sealed capillaries under Ar atmosphere using a Mettler-Toledo MP 70. Diffraction data for [K(THF)₂(Me₃SiC(H)C₂SiMe₃)], 1benz, 1thf, 2 and 3 were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F² with the SHELXTL software package. [43] XP (Bruker AXS) and Diamond^[44] were used for graphical representations. All calculations were carried out with the Gaussian 09 package of molecular orbital programs.^[45] In our calculations, we have used the real-size molecules at the BP86 level with the TZVP basis set for non-metal elements and the effective core potential LANL2DZ basis set for Zr. Vibrational frequencies were also computed, to include zero-point vibrational energies in thermodynamic parameters and to characterise all structures as minima on the potential energy surface.

Synthesis of [K(THF)2(Me3SiC(H)C2SiMe3)]: The mixture of potassium tert-butanolate (2.46 g, 22 mmol) and LDA (2.32 g, 22 mmol) was dispersed in 70 mL of benzene and stirred for two hours at ambient To the resulting pale yellow temperature. suspension bis(trimethylsilyl)propyne (2.00 g, 10.8 mmol) was added dropwise within 15 minutes and stirred for further 18 hours. The viscous yellow mixture was freed of the supernatant by filtration and the solid was washed with benzene (2 x 10 mL). The resulting solid was dried in vacuo for three hours, redispersed in cooled THF (-78 °C, approx. 10 mL), filtered through celite, concentrated to approximately 4 mL and stored at -78 °C for three days. Colourless crystals of [K(THF)₂(Me₃SiC(H)C₂SiMe₃)] thus obtained were washed with a minimum of cooled THF and dried in vacuo for three hours. m.p. (dec. Ar): 178 °C. ¹H NMR (25 °C, [D8]THF, 400.13 MHz): $\delta = 0.62$ (s, 1H, ${}^{1}J_{H,C} = 142$ Hz), -0.07 (s, 9H, CSi(CH₃)₃, ${}^{1}J_{H,C} =$

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117 Hz, ${}^{2}J_{H,Si} = 7$ Hz), -0.11 ppm (s, 9H, CHSi(CH₃)₃, ${}^{1}J_{H,C} = 117$ Hz, ${}^{2}J_{H,Si} = 6$ Hz). 13 C{¹H} NMR (25 °C, [D8]THF, 100.63 MHz): $\delta = 150.1$ (s, CCCH), 78.1 (s, CCCH), 18.0 (s, CCCH), 3.3 (s, CSi(CH₃)₃), 2.4 ppm (s, CHSi(CH₃)₃). 29 Si-inept NMR (25 °C, [D8]THF, 79.49 MHz): -9.3 (dec), -26.4 (ddec). IR (Nujol, 64 scans): 1996 (s), 1245 (m), 837 (s), 682 (w), 664 (w), 641 cm⁻¹ (w). MS-CI⁺ (*isobutene*): 364 (100) [(Me₃Si)₄C₆]⁻, 184 (5) [(Me₃Si)₂C₃H]⁻.

Synthesis of {Li₂(Me₃SiC₃SiMe₃)}₄ (1): To a colourless solution of 1,3bis-(trimethylsilyl)prop-1-yne (1.89 g, 10.3 mmol) in 30 mL of benzene a n-BuLi solution in n-hexane (2.5 M, 8.64 mL, 21.6 mmol) was added dropwise within 20 minutes at ambient temperature. The clear champagne coloured solution was cooled to -78 °C, degassed and heated to 60 °C for one week. The resulting solution was then freed of all volatile components and dried in vacuo for three hours. The colourless solid was washed with pentane (3 x 7 mL) and dried in vacuo to obtain 1 (1.26 g, 1.6 mmol (Tetramer), 62 %). m.p. (dec. Ar): 239 °C. ¹H NMR (25 °C, [D6]benzene, 400.13 MHz): $\delta = 0.31$ (s, 18H, CSi(CH₃)₃, ¹J_{H,C} = 117 Hz, ²J_{H,Si} = 6 Hz). ¹³C{¹H} NMR (25 °C, [D6]benzene, 100.63 MHz): $\delta = 174.1$ (s, C=C=C), 44.6, 37.8 (br, C=C=C), 3.7, 3.3 (br, SiCH₃).²⁹Siinept NMR (25 °C, [D6]benzene, 79.49 MHz): $\delta = -9.3$, -14.3. ⁷Li{¹H} NMR (25 °C, [D6]benzene, 155.5 MHz) δ = 1.6, 2.6 (Figure S21). MS-CI⁺ (*isobutene*): [M⁺] 785 (100), [(Me₃Si)₄C₆⁺] 365 (5), [(Me₃Si)₂C₃H₃⁺] 185 (5). IR (Nujol, 64 scans): decomposition while measuring. RAMAN (632nm, 10 sec, 20 scans): 2952 (m), 2890 (s), 1751 (vw), 1408 (w), 1262 (vw), 1246 (vw), 1237 (w), 1214 (vw), 831 (w), 754 (vw), 677 (w), 628 (vs), 565 (w), 535 (w), 423 (vw), 386 (w), 344 (vw), 283 (vw), 221 cm⁻¹ (w). Elemental analysis calcd (%) for $M(C_{36}H_{72}Li_8Si_8) = 785.17 \text{ g mol}^{-1}$: C 55.07, H 9.24; found: C 55.09, H 9.00.

Synthesis of [(Cp2ZrCl)2{-µ-(Me3Si)C3(SiMe3)-}] (2): The colourless solids Cp₂ZrCl₂ (1.6 mmol, 0.464 g) and 1 (0.2 mmol, 0.157 g) were mixed, dissolved in benzene (10 mL) and stirred for 12 hours. The resulting orange mixture was cannula filtered and the colourless precipitate was washed with benzene (3 x 2 mL). The combined solutions were concentrated and stored at ambient temperature. Fractional crystallization and drying in vacuo yields orange crystals of 2 (0.412 g, 75 %). m.p. 161 °C (dec. Ar). ¹H NMR (25 °C, [D6]benzene, 300.20 MHz): δ = 0.37 (s, 18H, CH₃, ¹J(¹H-¹³C) = 118.4 Hz, ²J(¹H-²⁹Si) = 6.3 Hz), 6.08 (s, 10H, Cp), 6.16 (s, 10H, Cp). ¹³C NMR (25 °C, [D6]benzene, 75.49 MHz): δ = 174.7 (s, C=C=C), 113.8 (s, Cp), 113.3 (s, Cp), 106.5 (s, C=C=C), 3.2 (s, SiCH₃). ²⁹Si-inept NMR (25 °C, [D6]benzene, 79.49 MHz): $\delta = -5.41$ (dec, Si(CH₃)₃, ²J(¹H-²⁹Si) = 6.3 Hz). **MS-CI**⁺ (*isobutane*): $\label{eq:main_state} [M^{+}] \ 697 \ (4), \ [M-Cp^{+}] \ 627 \ (95), \ [Cp_{2}Zr(Me_{3}SiC_{3}SiMe_{3})^{+}] \ 403 \ (100). \ IR$ (ATR, 16 scanns): 3105 (w), 2948 (w), 2891 (w), 1776 (s), 1438 (m), 1399 (w), 1364 (w), 1254 (m), 1236 (m), 1128 (w), 1066 (w), 1013 (m), 830 (m), 795 (s), 738 (s), 677 (m), 622 (m), 520 (m), 508 (w), 400 cm⁻¹ (m). RAMAN (632 nm, 10 sec, 20 scans): 3110 (vw), 2964 (vw), 2948 (vw), 2902 (vw), 1781 (vw), 1439 (vw), 1363 (vw), 1126 (vs), 1064 (vw), 843 (vw), 816 (vw), 779 (w), 676 (vw), 624 (w), 522 (vw), 507 (vw), 361 (w), 317 (w), 292 cm⁻¹ (m). Elemental analysis calcd (%) for $M(C_{29}H_{38}Cl_2Si_2Zr_2) = 696.14 \text{ g mol}^{-1}$: C 50.04, H 5.50; found: C 48.82, H 5.46 (best value of six measurements).

Synthesis of $[(Cp_2Zr)_2(-\mu-(Me_3Si)C_3(SiMe_3)-\}_2]$ (3): The solids of 2 (0.3 mmol, 210 mg) and 1 (0.075 mmol, 60 mg) were mixed as powders, dissolved in Et₂O (10 mL) at -78 °C, stirred for one hour at this temperature and for additional 24 hours at -30 °C. The solvent was then removed *in vacuo*, the resulting red raw product was dissolved in toluene (10 mL) and cannula filtered. The solution were concentrated and stored at -78 °C. After fractional crystallization and drying the red crystals of 3 *in vacuo* yield (0.183 g, 75 %). m.p. (Ar, dec): 315 °C. ¹H NMR (25 °C, [D6]benzene, 300.20 MHz): δ = 0.39 (s, 36H, CH₃, ¹J(¹H-¹³C) = 118.2 Hz, ²J(¹H-²⁹Si) = 6.2 Hz), 6.04 (s, 20H, Cp). ¹³C NMR (25 °C, [D6]benzene,

75.49 MHz): δ = 171.4 (s, C=C=C), 110.1 (s, Cp), 105.4 (s, C=C=C), 3.5 (s, SiCH₃). ²⁹Si-inept NMR (25 °C, [D6]benzene, 79.49 MHz): δ = -8.16 (dec, Si(CH₃)₃, ${}^{2}J({}^{1}H-{}^{29}Si) = 6.2$ Hz). **MS-CI**⁺ (*isobutane*): [M+H⁺] 806 (28), $[\text{M-4} \text{ methane}^+] \quad 741 \quad (24), \quad [\text{Cp}_2\text{Zr}(\text{Me}_3\text{Si}\text{C}_3\text{Si}\text{Me}_3) + \text{H}^+] \quad 403 \quad (100),$ ESI-TOF/HRMS: $[(Me_3Si)_2C_3H_2^+]$ 185 (20). $[M+H^+]$ 807. [Cp₂Zr(Me₃SiC₃SiMe₃)+H⁺] 403. IR (ATR, 16 scanns): 3095 (w), 2950 (w), 2895 (w), 1784 (s), 1772 (s), 1444 (w), 1397 (w), 1370 (w), 1240 (m), 1132 (w), 1015 (m), 834 (s), 781 (s), 740 (s), 675 (s), 618 (m), 538 (w), 483 cm⁻¹ (m). RAMAN (784 nm,50 sec, 10 scans): 3104 (vw), 2961 (vw), 2896 (vw), 1786 (vw), 1443 (vw), 1371 (vw), 1362 (vw), 1259 (vw), 1246 (vw), 1226 (vw), 1131 (vs), 1124 (m), 1072 (w), 893 (vw), 848 (w), 831 (w), 806 (w), 774 (m), 728 (w), 679 (w), 620 (w), 538 (w), 502 (w), 387 (w), 366 (m), 311 (s), 291 cm⁻¹ (s). Elemental analysis calcd (%) for $M(C_{38}H_{56}Si_4Zr_2) = 807.65 \text{ g mol}^{-1}$: C 56.24, H 7.03; found: C 56.51, H 6.99.

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Keywords: metallacycles • X-ray analysis • bridging ligands • zirconium • cyclopentadienyl ligands

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FULL PAPER



The taming of a shrew: Reaction of a pyrophoric dilithioallene with zirconocene results in a remarkable stabilisation and stepwise formation of a highly unusual dizirconacyclooctatetraene species.

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