Five-Membered Titanacyclocumulenes that Contain Linked Amido−Cyclopentadienyl Ligands

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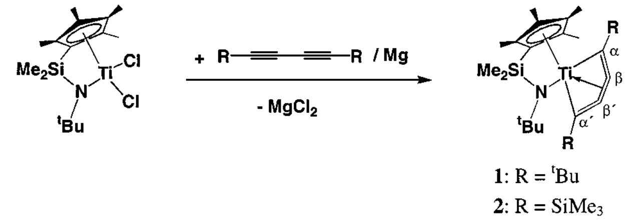
*Summary: The first non-metallocene five-membered titanacyclocumulene complexes (titanacyclo-2,3,4-trienes, η^4-1,2,3,4-butadiyne complexes) that contain linked amido−cyclopentadienyl ligands ($(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Ti(\eta^4\text{-}RC_4R)$ (**1**, R = ^{t}Bu; **2**, R = SiMe$_3$) were prepared by reaction of the dichloride $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)TiCl_2$ with magnesium in the presence of the corresponding disubstituted 1,3-butadiynes. The insertion of carbon dioxide into complexes **1** and **2** was achieved, forming the dinuclear complexes $\{(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Ti[-OC(=O)C(C\equiv CR)=C(R)-]\}_2$ (**3**, R = ^{t}Bu; **4**, R = SiMe$_3$). The structures of complexes **1**, **3**, and **4** were determined by X-ray diffraction.*

For titanocene complexes as well as zirconocene and also permethylzirconocene complexes some examples of stable five-membered metallacyclocumulenes (metallacyclopenta-2,3,4-trienes, η^4-1,2,3,4-butadiyne complexes) were prepared by different methods and investigated by selected reactions.[1] Recently also the first non-metallocene example of such zirconacyclocumulenes was published by Ashe et al., who used boratabenzene zirconium derivatives.[2]

We report here two examples of five-membered titanacyclocumulenes that contain linked amido−cyclopentadienyl ligands. Such complexes of “constrained geometry” type are of particular catalytic interest.[3]

Reaction of the dichloride $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)TiCl_2$ with magnesium in the presence of the corresponding disubstituted 1,3-butadiyne in THF at room temperature gave the complexes $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N\text{-}{}^tBu)Ti(\eta^4\text{-}RC_4R)$ (**1**, R = ^{t}Bu; **2**, R = SiMe$_3$) (Scheme 1).

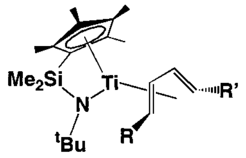
Scheme 1



The yellow complex **1** and the red-orange complex **2** are very soluble in *n*-hexane, THF, and aromatic solvents. The structure of cumulene **1** was confirmed by X-ray diffraction. Its molecular structure is depicted in Figure 1 together with selected bond lengths and angles.

The atoms C7, C8, C11, C12, and Ti form a nearly planar ring system (mean deviation from this plane is 0.054 Å). This feature in complex **1**, $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Ti$(1,3-diyne), considered as a titanacyclopenta-2,3,4-triene (η^4-1,2,3,4-butadiyne complex), differs from that in the corresponding $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NR)Ti$(1,3-diene) complexes, which are described as diolefinic π-complexes or titanacyclopent-3-enes (s-cis complexation, envelope-like structure, Scheme 2).[4] Both contain linked amido−cyclopentadienyl ligands.

Scheme 2



As found so far in all other five-membered metallacyclocumulenes, the ring in **1** contains three C−C double bonds, the middle one of which is elongated by coordination to the titanium atom (C7−C8 1.279(8), C7−C12 1.358(8), C11−C12 1.270(8) Å). According to detailed theoretical calculations of Jemmis et al., this interaction is essential for the stability of these complexes.[5] The corresponding titanocene complex, $Cp_2Ti(\eta^4\text{-}{}^tBuC_4{}^tBu)$,[6] shows very similar structure features ($C\alpha-C\beta$ 1.243(13), $C\beta-C\beta'$ 1.339(13), $C\beta'-C\alpha'$ 1.276(11) Å), so there is no significant influence of the different ligands $\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu$ and Cp. A further argument for the interaction between the metal and the C_β atoms is that the Ti−C_β distances (for **1**: Ti−C7 2.159(5); Ti−C12 2.169(5) Å) are shorter compared to the Ti−C_α (for **1**: Ti−C8 2.228(5); Ti−C11 2.209(6) Å) bonds.

On the basis of NMR investigations, the molecular structure of **2** is similar to that of **1**. Both are titanacyclocumulenes with characteristic ^{13}C NMR data for the metallacyclic carbon atoms. The metal-bonded α carbon atoms’ signals are seen at low field (about 190 ppm), whereas the shift of the β carbon atoms appears at higher field, responding sensitively to changes of the diyne substituents and the ligand sphere. For **1**, the C_β signal is found at 142.6 ppm but appears at 168.9 ppm in the ^{13}C NMR spectrum of **2**. This low-field shift in **2** is due to the SiMe$_3$ substituent, and such an effect was found earlier for the metallocene−cumulene $Cp^*_2Zr(\eta^4\text{-}Me_3SiC_4SiMe_3)$.[7] The influence of the ligands and the interaction between the metal atom and the $\beta\beta'$ double

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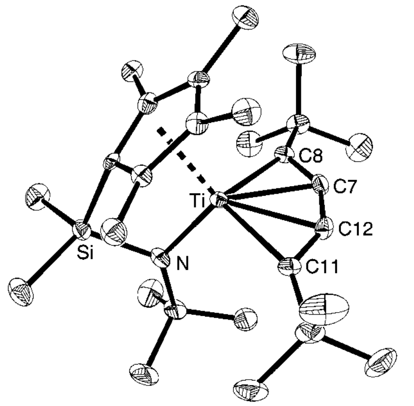
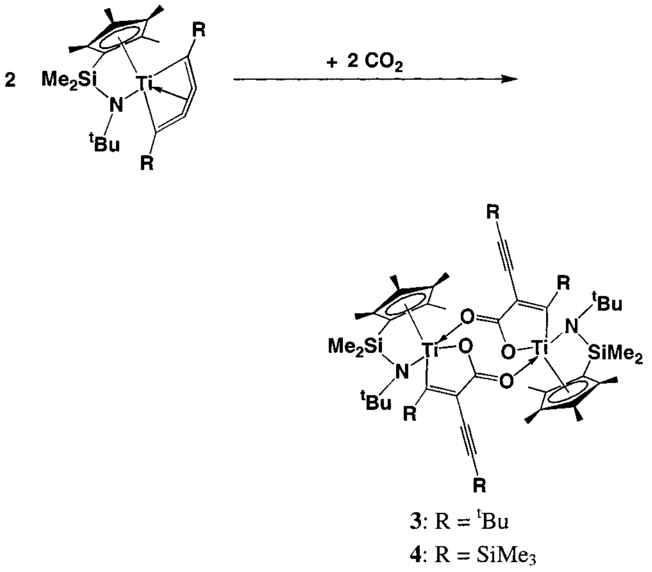


Figure 1. Crystal structure of **1**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C7−C8 1.279(8), C7−C12 1.358(8), C11−C12 1.270(8), C8−Ti 2.228(5), C7−Ti 2.159(5), C12−Ti 2.169(5), C11−Ti 2.209(6), C8−Ti−C11 103.7(2), C8−C7−C12 147.7(5), C7−C12−C11 145.8(5).

Scheme 3



bond is indicated also by differences in the chemical shift of the β atoms. The 18-electron metallocene−cumulene Cp$_2$Ti(η^4-^{t}BuC$_4$^{t}Bu)[6] exhibits this ^{13}C NMR signal at 94.7 ppm, almost 50 ppm upfield from that of the 14-electron cumulene **1**.

Carbon dioxide underwent insertion into complexes **1** and **2** (Scheme 3). Such an insertion of only one carbon dioxide molecule is typical for η^2-butadiyne complexes of titanocenes, whereas five-membered zirconacyclocumulenes can insert two CO$_2$ molecules.[7] The titanafuranone thus obtained is stabilized by dimerization.

The yellow complexes **3** and **4** are poorly soluble in common nonprotic organic solvents. The solubility is not sufficient to allow satisfactory ^{13}C NMR spectra to be obtained, but the proton spectra clearly indicate a lack of symmetry of each of the titanafuranone subunits (four signals for cyclopentadienyl methyl groups, two for silyl methyl groups, two for diyne substituents, but only one for the *N*-^{t}Bu groups).

The crystal structures of dinuclear complexes **3** and **4**, determined by X-ray crystallography, confirmed that they are isostructural. The structure of **3** is depicted in Figure 2. The central structural element of compounds **3** and **4** is the eight-membered ring [−Ti−O−C−O−]$_2$, which is already known for the reaction product of [*rac*-(ebthi)Zr(2-vinylpyridine)], ebthi = 1,2-ethylene-1,1′-bis-(η^5-tetrahydroindenyl), and carbon dioxide.[8] Interestingly, most zirconafuranones give by dimerization four-membered ring systems [−O−Zr−]$_2$, whereas the corresponding titanafuranones yield the above-mentioned larger ring systems.

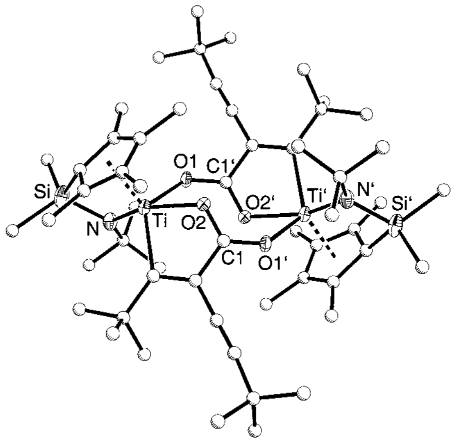


Figure 2. Crystal structure of **3**. For clarity hydrogen atoms and one position of disordered groups are omitted and only non-carbon atoms are drawn as ellipsoids corresponding to 30% probability. Selected bond lengths (Å) and angles (deg): O1−Ti 2.070(3), O2−Ti 2.094(3), C1−O2 1.278(5), C1−O1′ 1.274(5), C1−C2 1.472(6), C2−C3 1.359(5), C3−Ti 2.294(5), O1−Ti−O2 75.3(1), Ti−O2−C1 115.7(3), O2−C1−O1′ 122.0(5), C1−O1′−Ti′ 127.3(3).

Experimental Section:

Dimethylsilyl[(*tert*-butylamido)(tetramethylcyclopentadienyl)]titanium dichloride was obtained commercially (Witco GmbH) and used as supplied. All operations were carried out under an inert atmosphere (argon) using standard Schlenk techniques. Prior to use, solvents were dried and freshly distilled under argon. NMR spectra were recorded on a Bruker ARX 400 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to the solvent resonances and reported relative to tetramethylsilane. Melting points were determined in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were performed with a Leco CHNS-932 elemental analyzer. X-ray data of compounds **1**, **3**, and **4** were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[9] and refined by full matrix least-squares techniques against F^2 (SHELXL-93).[10] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

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Crystal data for **1**: crystal dimensions 0.4 × 0.3 × 0.2, yellow prisms, space group $P2_1/n$, monoclinic, $a = 11.233(2)$ Å, $b = 11.790(2)$ Å, $c = 20.887(4)$ Å, $\beta = 98.65(3)°$, $V = 2734.7(9)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.116$ g cm^{-3}, 6573 reflections measured, 3567 were independent of symmetry and 2533 were observed $(I > 2\sigma(I))$, R1 = 0.071, wR2 (all data) = 0.224, 271 parameters.

Crystal data for **3**: crystal dimensions: 0.3 × 0.2 × 0.1, yellow-orange prisms, space group $P\bar{1}$, triclinic, $a = 10.382(2)$ Å, $b = 11.219(2)$ Å, $c = 12.817(3)$ Å, $\alpha = 85.00(3)$, $\beta = 79.14(3)$, $\gamma = 83.65(3)°$, $V = 1453.8(5)$ Å^3, $Z = 1$, $\rho_{\text{calcd}} = 1.151$ g cm^{-3}, 3612 reflections measured, 3612 were independent of symmetry and 1624 were observed $(I > 2\sigma(I))$, R1 = 0.048, wR2 (all data) = 0.151, 295 parameters.

Crystal data for **4**: crystal dimensions 0.3 × 0.2 × 0.1, yellow prisms, space group $P2_1/c$, monoclinic, $a = 10.382(2)$ Å, $b = 11.598(2)$ Å, $c = 26.650(5)$ Å, $\beta = 96.56(3)°$, $V = 3188(1)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.116$ g cm^{-3}, 4307 reflections measured, 2329 were independent of symmetry and 1534 were observed $(I > 2\sigma(I))$, R1 = 0.050, wR2 (all data) = 0.121, 295 parameters.

(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)Ti(η^4-$^tBuC_4{}^tBu$) (1) or **(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)Ti(η^4-$Me_3SiC_4SiMe_3$) (2)**. 1,4-Bis(*tert*-butyl)butadiyne (162 mg, 1 mmol) or 1,4-bis(trimethylsilyl)butadiyne (194 mg, 1 mmol) was dissolved in 10 mL of THF. The solution was added to (η^5:η^1-$C_5Me_4SiMe_2N^tBu$)$TiCl_2$ (368 mg, 1 mmol) and magnesium turnings (24 mg, 1 mmol). The mixture was stirred for 5 h. The color of the solution changed to yellow-brown/red-brown, the solvent was evaporated to dryness, and the residue was extracted with *n*-hexane. The extracts were filtered and concentrated in vacuo. At −30 °C yellow **1** or red-orange **2** crystallized. The product was filtered and dried under vacuum.

1: yield 253 mg (55%), mp 153 °C. Anal. Calcd for $C_{27}H_{45}NSiTi$ (459.63): C, 70.56; H, 9.87; N, 3.05. Found: C, 70.72; H, 9.96; N, 3.23. ^{1}H NMR (toluene-d_8, $T = 240$ K): δ [ppm] 0.69 (s, 6H, $SiMe_2$, $^2J_{H,Si} = 6.5$ Hz), 0.72 (s, 9H, N-^{t}Bu), 1.15 (s, 6H, β-Me), 1.43 (s, 9H, ^{t}Bu), 2.67 (s, 6H, α-Me). ^{13}C NMR (toluene-d_8, $T = 240$ K): δ [ppm] 7.5 ($^1J_{C,H} = 118$ Hz, $SiMe_2$), 11.5 ($^1J_{C,H} = 126$ Hz, C_5Me_4/β-Me), 17.7 ($^1J_{C,H} = 126$ Hz, C_5Me_4/α-Me), 33.3 ($^1J_{C,H} = 129$ Hz, $^3J_{C,H} = 4$ Hz, C-^{t}Bu), 33.6 ($^1J_{C,H} = 127$ Hz, N-^{t}Bu), 38.0 ($^2J_{C,H} = 4$ Hz, C-^{t}Bu/$C_{\text{quart.}}$), 54.1 (N-^{t}Bu/$C_{\text{quart.}}$), 101.9 (C_5Me_4/C−Si), 123.2 (C_5Me_4/$C_{\text{quart.}}$), 124.4 (C_5Me_4/$C_{\text{quart.}}$), 142.6 (β-C_{cumulene}), 190.9 ($^3J_{C,H} = 5$ Hz, α-C_{cumulene}). ^{29}Si NMR (toluene-d_8, $T = 240$ K): δ [ppm] −24.6. MS (70 eV) *m*/*z*: 459 (M^+).

2: yield 192 mg (39%), mp 167 °C. Anal. Calcd for $C_{25}H_{45}NSi_3Ti$ (491.78): C, 61.06; H, 9.22; N, 2.85. Found: C, 61.20; H, 9.13; N, 2.87. ^{1}H NMR (toluene-d_8, $T = 300$ K): δ [ppm] 0.35 (s, 18H, $SiMe_3$, $^2J_{H,Si} = 6.7$ Hz), 0.59 (s, 9H, ^{t}Bu), 0.67 (s, 6H, $SiMe_2$, $^2J_{H,Si} = 6.6$ Hz), 1.01 (s, 6H, β-Me), 2.67 (s, 6H, α-Me). ^{13}C NMR (toluene-d_8, $T = 300$ K): δ [ppm] 1.4 ($^1J_{C,H} = 120$ Hz, $SiMe_3$), 7.5 ($^1J_{C,H} = 118$ Hz, $SiMe_2$), 11.2 ($^1J_{C,H} = 126$ Hz, C_5Me_4/β-Me), 17.4 ($^1J_{C,H} = 126$ Hz, C_5Me_4/α-Me), 33.7 ($^1J_{C,H} = 128$ Hz, $^3J_{C,H} = 4$ Hz, ^{t}Bu), 53.6 ($^2J_{C,H} = 4$ Hz, ^{t}Bu/$C_{\text{quart.}}$), 103.8 (C_5Me_4/C-Si), 123.7 (C_5Me_4/$C_{\text{quart.}}$), 124.1 (C_5Me_4/$C_{\text{quart.}}$), 168.9 (β-C_{cumulene}), 193.2 ($^3J_{C,H} = 2$ Hz, α-C_{cumulene}). ^{29}Si NMR (toluene-d_8, $T = 300$ K): δ [ppm] −7.2 ($SiMe_3$), −25.1 ($SiMe_2$). MS (70 eV) *m*/*z*: 491 (M^+).

{(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)Ti[−OC(=O)C(C≡C^{t}Bu)=C(^{t}Bu)−]}$_2$ (3) or **{(η^5:η^1-$C_5Me_4SiMe_2N^tBu$)Ti[−OC(=O)C(C≡CSiMe$_3$)=C(SiMe$_3$)−]}$_2$ (4)**. Compound **1** (138 mg, 0.3 mmol) or **2** (148 mg, 0.3 mmol), respectively, was dissolved in 10 mL of *n*-hexane. Argon was carefully removed in a vacuum, and the flask was filled with carbon dioxide. During 1 h crystals appeared in the solution. These were separated by fitration and dried under vacuum.

3: yield 101 mg (67%), mp 265 °C (dec). Anal. Calcd for $C_{56}H_{90}N_2O_4Si_2Ti_2$ (1007.27): C, 66.78; H, 9.01; N, 2.78. Found: C, 66.81; H, 9.07; N, 2.87. ^{1}H NMR (toluene-d_8, $T = 343$ K): δ [ppm] 0.64 and 0.79 (s, 3H each, $SiMe_2$); 1.23, 1.44 and 1.45 (s, 9H each, ^{t}Bu); 1.75 and 1.79 (s, 3H each, C_5Me_4), 2.29 (s, 6H, C_5Me_4). MS (70 eV) *m*/*z*: 503.

4: yield 76 mg (47%), mp 248 °C (dec). Anal. Calcd for $C_{52}H_{90}N_2O_4Si_6Ti_2$ (1071.57): C, 58.29; H, 8.47; N, 2.61. Found: C, 58.55; H, 8.60; N, 2.80. ^{1}H NMR (toluene-d_8, $T = 297$ K): δ [ppm] 0.20 and 0.39 (s, 9H each, $SiMe_3$); 0.64 and 0.81 (s, 3H each, $SiMe_2$); 1.44 (s, 9H, ^{t}Bu); 1.74, 1.75, 2.29, and 2.30 (s, 3H each, C_5Me_4). MS (70 eV) *m*/*z*: 535.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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