Reactions of Hexatriynes with Permethyltitanocene and -zirconocene Complexes: First NMR Observation of a Metallocene Sliding along a Polyyne Chain

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Carbon-rich organometallics[1] have attracted increasing interest in recent years because of their novel features for carbon-rich networks,[2a−c] their nanoarchitectures for materials science,[2d−h] and their potential as special polymers.[2i−j] One or more triple bonds in the substrates are frequently used to realize such a chemistry.

For several years we have been interested in systematic studies of the interaction of different alkynes with titanocene and zirconocene, which is the basis for the above-mentioned chemistry. These investigations were not limited to simple alkynes $RC\equiv CR$[3a] but were also directed toward branched polyynes such as $1,3,5-(RC\equiv C-C\equiv C)_3C_6H_3$[3b] and $(RC\equiv C)_4Si$[3c] and to linear 1,3-butadiynes $R(C\equiv C)_2R$[3d] and octatetraynes $R(C\equiv C)_4R$.[3e] Additionally, reactions of some permethylmetallocene complexes of titanium and zirconium were included.[4] This work deals with novel reaction products of the hexatriyne $tBu(C\equiv C)_3tBu$ and permeth-
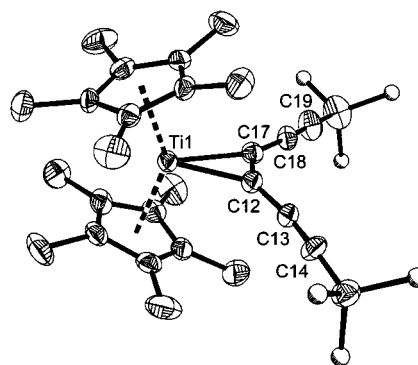

Figure 1. ORTEP diagram (30% probability) of one of two symmetry-independent molecules of the asymmetric unit of **1** (hydrogen atoms and disorders are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti1−C12 2.082(5), Ti1−C17 2.107(5), C12−C17 1.306(6), C13−C14 1.192(7), C18−C19 1.179(7), C12−C13 1.417(8), C17−C18 1.405-(7), C12−C17−C18 141.3(5), C17−C12−C13 144.0(5), C12−C13−C14 172.5(6), C17−C18−C19 173.3(6).

yltitanocene and -zirconocene in comparison to the products of the recently described reactions of $Me_3Si(C\equiv C)_2SiMe_3$[5a] and $1,2-(RC\equiv C)_2C_6H_4$.[5b] The reaction of $Cp*_2TiCl_2$ with magnesium in THF in the presence of $tBu(C\equiv C)_3tBu$ gives the η^2-complex $Cp*_2-Ti(tBuC\equiv C-C_2-C\equiv CtBu)$ (**1**) (eq 1, Figure 1).[6]

$$Cp*_2TiCl_2 \xrightarrow[\substack{+ \ tBu\text{-}C_6\text{-}tBu \\ + \ Mg \\ - \ MgCl_2}]{} Cp*_2Ti \quad (1)$$

1
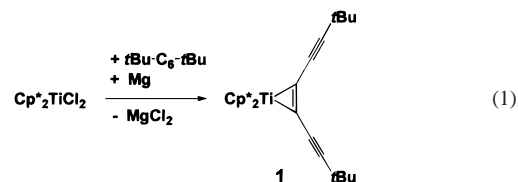
The absorption in the IR spectrum (1680 cm^{-1}) and the signals of the coordinated alkyne carbon atoms in the ^{13}C NMR spectrum[6] indicate a titanacyclopropene structure[3a] for complex **1**. This metallacycle is substituted symmetrically by two free alkynyl groups (2149 cm^{-1}). The carbon resonance of the titanacyclopropene unit (C12/C17) is found at rather high field (compare to $Cp*_2Ti(PhC_2Ph)$, 200.6 ppm,[7] for instance). This can be ascribed to the magnetic anisotropy of the attached triple bond. The low-field shift for C14 might be interpreted by an electronic interaction between the metallacycle (as a π acceptor) and the conjugated π system. The crystal structure of **1**[8,13] exhibits an almost symmetric cis configuration of the complexed hexatriyne in which the alkynyl substituents are directed away from the metal. The distances and angles of the two uncomplexed triple bonds are in the expected range. The connecting C−C single bonds are considerably shortened as is expected between a metalated and an sp-hybridized C atom.

To the best of our knowledge structural data of transition metal complexes of hexatriynes are only reported for dinuclear or cluster compounds.[9] A mononuclear structure as found for **1** was never described before and was proposed only by Choukroun for a vanadocene complex of a hexatriyne, but without an X-ray crystal structure analysis.[9e] Compared to the structure of the zirconocene complex of $1,2-(RC\equiv C)_2C_6H_4$,[5b] in which the two unsaturated

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(6) Green crystals, mp 168−169 °C. Anal. Calcd for $C_{34}H_{48}Ti$ (504.64): C, 80.92; H, 9.59. Found: C, 80.55; H, 9.72. MS (70 eV): *m/z* 504 (M$^+$). ^1H NMR (400.13 MHz, C_6D_6, 297 K): δ 1.16 (s, 18H, 2*t*Bu), 1.81 (s, 30H, 2Cp*). ^{13}C NMR (100.6 MHz, C_6D_6, 297 K): δ 11.5 (C_5Me_5), 29.1 (C*Me*$_3$), 31.6 (*C*Me$_3$), 79.3 (C13), 114.4 (C14), 122.0 (C_5Me_5), 181.2 (C12/C17).

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(8) Crystal data for **1**: triclinic, $P\bar{1}$, *a* = 12.866(3), *b* = 15.594(3), and *c* = 18.197(4) Å, α = 67.33(3), β = 76.78(3), and γ = 73.38(3)°, *V* = 3199(1) Å^3, *Z* = 4, ρ = 1.048 g cm^{-3}, 6470 measured reflections, 6470 were independent of symmetry, 3733 were observed (*I* > 2σ(*I*)), 619 refined parameters, R1 = 0.052, wR2 (all data) = 0.133.

(9) Selected examples for Co: (a) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 4966. Os, Ru: (b) Low, P. J.; Udachin, K. A.; Enright, G. D.; Carthy, A. J. *J. Organomet. Chem.* **1999**, *578*, 103. Ru: (c) Adams, R. D.; Bunz, U. H. F.; Fu, W.; Roidl, G. *J. Organomet. Chem.* **1999**, *578*, 55. Rh, Fe: (d) Etches, S. J.; Hart, I. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2281. V: (e) Choukroun, R.; Lorber, Ch.; Donnadieu, B.; Henner, B.; Frantz, R.; Guerin, Ch. *J. Chem. Soc., Chem Commun.* **1999**, 1099.
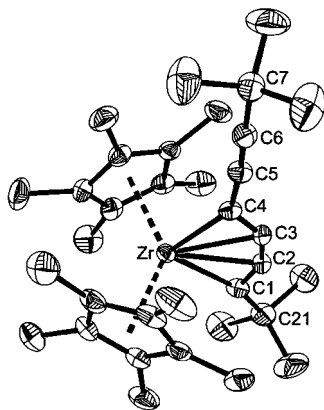
Figure 2. ORTEP diagram (30% probability) of **2** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr—C1 2.434(4), Zr—C2 2.319(4), Zr—C3 2.338(4), Zr—C4 2.324(4), C1—C2 1.285(6), C2—C3 1.325(6), C3—C4 1.282(6), C5—C6 1.192(6), C4—C5—C6 175.4(5), C5—C6—C7 179.6 (4).

units are directed to the metal and interact with zirconium, complex **1** indicates no such complexation.

When Cp*$_2$ZrCl$_2$ is reacted with magnesium in THF in the presence of tBu(C≡C)$_3t$Bu, the η^4-complex Cp*$_2$Zr(tBuC$_4$—C≡CtBu) (**2**) is generated in high yields (eq 2, Figure 2).[10]
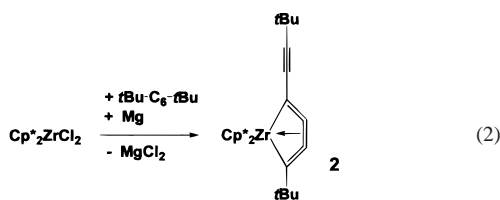
The IR absorptions (1865 and 1653 cm^{-1}) as well as signals in the ^{13}C NMR spectrum[10] are typical for five-membered zirconacyclocumulenes (zirconacyclo-2,3,4-pentatrienes).[4a] An uncomplexed alkynyl group is indicated by additional spectroscopic data (2149 cm^{-1}). For reasons similar to those discussed for **1**, the chemical shifts of C4 and C6 are at higher and lower fields, respectively, than expected. The crystal structure of **2**[11,13] exhibits an unsymmetric complexation of the hexatriyne to form a five-membered zirconacyclocumulene substituted with one alkynyl group. The structural data provide no evidence of a bonding of this alkynyl group to the Zr in the solid state.

To investigate the possibility that the free triple bonds of **1** and **2** may interact with the metal in solution, variable-temperature NMR measurements were performed in toluene-d_8. Cooling

solutions of complex **1** to 191 K does not lead to significant changes in the NMR line shapes. In contrast, the NMR spectra of complex **2**, which exhibit an unsymmetric species at ambient temperature, are temperature-dependent and show a slight line broadening at 340 K, although no coalescence is achieved. The underlying dynamic process, as revealed by 2D ^{13}C NMR exchange spectroscopy,[12] is depicted in Scheme 1. The spectrum shows cross-peaks arising from an exchange between positions C1 and C6, C2 and C5, C3 and C4, and between the *tert*-butyl groups.

Scheme 1
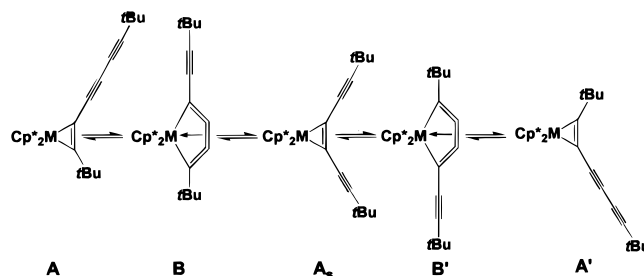
This result suggests the existence of an equilibrium between the η^2-zirconacyclopropene structures (**A**) and the η^4-coordinated zirconacyclocumulene structure (**B**) in solution. Which one is preferred is most likely governed by steric factors.

In complex **1** the combination of the smaller titanium with the bulky pentamethylcyclopentadienyl and tBu groups disfavors the formation of type **B** (as already demonstrated for Cp*$_2$Ti(η^2-Me$_3$-SiC$_2$—C≡CSiMe$_3$)).[4a] Therefore, complex **1** is found in the form **A$_s$**, the only one avoiding a close approximation of the Cp* ligands and bulky tBu groups.

The reverse is found for complex **2**, having the larger zirconium as its central atom: **B** is no longer disfavored for steric reasons.[14] Alternatively, the larger radial extension of the 4d orbitals of Zr compared to the 3d orbitals of Ti should enhance the ability of the former to interact with more than one alkyne fragment, thereby promoting η^4-interactions that lower the barrier for alkyne migration in **2**. Nevertheless, η^2-structures (**A**) cannot be excluded, making **A$_s$** the most probable intermediate in the dynamic process described above.[15] In the sequence **A$_s$**, **B/B′**, and **A/A′** increased steric crowding must be assumed.

On the basis of the observed degenerate rearrangement between **B** and **B′** for complex **2**, we conclude that the zirconocene unit is migrating back and forth along the hexatriyne backbone. This is illustratively described as "sliding" along the polyyne chain. The migration of an electrophilic metal center along a hydrocarbon backbone is an important fundamental process because of its relevance to transition metal-mediated isomerization reactions and can explain the lack of selectivity in some reactions of di- and polyynes.[3d]

Supporting Information Available: Tables of crystallographic data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **2** (PDF). X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Yellow crystals, mp 171–172 °C. Anal. Calcd for C$_{34}$H$_{48}$Zr (547.98): C, 74.52; H, 8.83. Found: C, 74.33; H, 9.03. MS (70 eV): m/z 546 (M$^+$). ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 297 K): δ 1.36 (s, 9H, 6-tBu), 1.56 (9H, 1-tBu), 1.76 (s, 30H, 2 Cp*). ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 297 K): δ 11.8 (C$_5$*Me$_5$*), 29.6 (C7), 31.2 (7-Me), 34.7 (21-Me), 38.8 (C21), 77.8 (C5), 113.4 (*C$_5$*Me$_5$), 114.4 (C2), 115.8 (C3), 118.7 (C6), 160.0 (C4), 193.8 (C1).

(11) Crystal data for **2**: monoclinic, P2$_1$/c, a = 9.093(2), b = 30.743(6), and c = 11.625(2) Å, β = 106.23(3)°, V = 3120.2(11) Å^3, Z = 4, ρ = 1.166 g cm^{-3}, 6266 measured reflections, 3340 were independent of symmetry, 2499 were observed ($I > 2\sigma(I)$), 316 refined parameters, $R1$ = 0.037, $wR2$ (all data) = 0.086.

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(13) STOE-IPDS diffractometer, graphite monochromated Mo Kα radiation, structures were solved by direct methods (SHELXS-86. Sheldrick, G. M. *Acta Crytallogr., Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares method against F^2 (SHELXL-93); structure representation by XP (Siemens). Atoms of disordered groups (in **1**) are refined isotropically. All other non-hydrogen atoms are refined anisotropically. Hydrogen atoms are included at calculated positions and refined riding with the corresponding atom.

(14) Ab initio and DFT calculations on sterically unstressed systems revealed that type **B** is an energetic minimum in the system L$_2$M/HC≡CC≡CH, M = Ti, Zr: Jemmis, E. D.; Giju, K. T. *J. Am. Chem. Soc.* **1998**, *120*, 6952.

(15) A rough estimation from proton NMR (81 Hz distance for the lines of exchanging tBu groups at 340 K, *below coalescence temperature*) reveals that the activation barrier for the interconversion **B** → **B′** and vice versa must be higher than 69 kJ mol^{-1}.