Reduction of 1,4-dichlorobut-2-yn-1,3-butatriene. Formation of a 1-titanacyclopent-3-yne and a 2,5-ditinatanobicyclo[2.2.0]hex-1(4)-ene

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The 2,5-ditinatanobicyclo[2.2.0]hex-1(4)-ene (bis-titanocene-µ-(Z)-1,2,3-butatriene complex) (3) is formed starting from [Cp₂Ti(η²-Me₂SiC₅SiMe₃)] by in situ generated titanocene and 1,4-dichlorobut-2-yne via the 1-titanacyclopent-3-yne (2).

The complexation of titanocene with butatriene was described by Maeker, but the suggested structures resulting from Me₂C–C–C–Me₂ and “Cp₂Ti” further reactions with CH-activation to yield more stable complexes. Suzuki and coworkers recently reported 1-zirconacyclopent-3-yne was realized. Despite that, the structure of the complex was not a σ-propargyl or a π-allyl complex and is also different from the “bridged allylic” structures found in μ-butatriene-bis(tricarbonyliron) complexes or substituted butatriene diionium diildinium, μ-butene-1,4-diyl and units as well as μ-butadiyne complexes with μ-[η₅-C₅(PhC–C–C–Ph)] units.

The X-ray crystal structure analysis of 3 revealed two bent titanocenes which are bridged symmetrically by a “zig-zag” C₄-ligand. The four carbon and two titanium atoms are in a plane with a mean deviation of 0.0017 Å. The central bond of the C₄-ligand is coordinated to both titanium centers, unsymmetrically for each titanium atom with C₃–C(1A) 1.325(5); C1–Ti 2.152(3); C(1A)–Ti 2.286(3) Å, whereas each of the methylene groups is coordinated to only one Ti atom with C2–Ti 2.167(3); C1–C(2A) 1.443(4) Å. By this coordination a bonding mode is formed with a C(1)–C(1A)–C(2) angle of 135.1(3)°.

The molecular structure of 3 is represented by the resonance structures of a butynediyl-bridged σ-propargylic complex (A) and a butatriene-bridged π-complex (B), but in contrast to complex 2 here in a bridging mode (Scheme 2). The structure of complex 3 as a μ-trans-butatriene complex is best described as a zitanobicycle (C) in analogy with μ-trans-butadiyne complexes (D), formed by analogous titanocene complexation of 1-titanacyclopenta-2,3,4-trienes (five-membered titanacycloheptulenes) (Scheme 3).

![Scheme 1 Preparation of complexes.](image1)

![Scheme 2 Resonance structures of complex 3.](image2)
The calculated geometric parameters are in close agreement with the experimental structure. The bonding in 3 is best described by treating the bridging ligand as formally \( [\text{H}_2\text{CCCCH}_2]^{2-} \) species, making Ti(4+) the TiCl\(_6\) plane does not interact substantially with the metals. The remaining eight valence electrons of the \( [\text{H}_2\text{CCCCH}_2]^{2-} \) ligand occupy four in-plane delocalized orbitals resulting from the interaction with the Cp-Ti fragment orbitals. The bonding here is very similar to that in the \( \mu\text{-trans-butadiyne complex} [\text{Cp}_2\text{Ti}(\text{HCCCH})\text{TiCl}_3] \) (type D) except that 3 has an ethylene \( \pi \) bond in place of the \( \mu\text{-trans-butadiene of the butadiyne complex}. \)

A \( \text{C}_2\text{v} \) isomer of 3 derived directly from the complexation of the middle \( \text{C}1-(\text{A}) \) bond of 2 is calculated to be higher in energy by 9.00 kcal mol\(^{-1}\). Experimental and theoretical studies on the details of this species, its conversion to 3, and further transformations of 3 are currently in progress.

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Notes and references

\( ^{\dagger} \) General procedure for the preparation of complex 2: complex 1 (2.040 g, 5.85 mmol) was dissolved in \( n\)-hexane (20 mL) under Ar. The resulting yellow-brown solution was filtered, and CHCl\(_3\)=CCH\(_2\)Cl (0.286 mL, 2.93 mmol) was added to the resulting solution under stirring. The solution rapidly became brown and a dark red precipitate of \( [\text{Cp}_2\text{Ti}] \) formed. The mixture was allowed to stand in an argon atmosphere at 20 °C for 9 days, brown crystals were formed, which were separated from the mother liquor by decanting, and washed with a small amount of cold \( n\)-hexane and dried under vacuum. Yield of 2 was 0.454 g (65%), mp 211–212 °C (dec. at slow heating (3 °C per min); at fast heating (20 °C per min) blows up at ca. 145–150 °C) under Ar.

\( ^{\ddagger} \) Data for 2: elemental analysis calcd for \( \text{Cp}_2\text{Ti} \): C, 72.43; H, 6.13. Found: C, 72.43; H 6.19%. \text{H NMR} (CD\(_2\)\(_2\), 297 K): \( \delta \) 3.03 (s, 4H, \( \text{CH}_2 \)); 6.83 (s, 10H, Cp). \text{C}[\text{H}] \text{NMR} (CD\(_2\)\(_2\), 297 K): \( \delta \) 51.2 (CH\(_2\)); 102.4 (CH); 106.9 (C\(_{\text{Ti}}\)). IR (Nujol, cm\(^{-1}\)): 2029 (weak, \( v\text{C}-\text{C} \)). MS (70 eV, m/z): 230 [M\(^+\)], 178 [Cp-Ti\(^+\)], 113 [Cp-Ti\(^{2+}\)].

\( ^{\S} \) General procedure for the preparation of complex 3: Complex 1 (0.486 g, 1.38 mmol) was dissolved in toluene (7–8 mL) under Ar. The obtained solution was filtered and added gradually to a filtered brown solution of 2 (0.298 g, 1.29 mmol) in 7–8 mL of toluene. The resulting solution rapidly turned green and crystals of 3 appeared on the bottom and walls of the vessel. After 24 h the solution was decanted. Subsequent washing of the dark green crystals with cold toluene and drying in vacuum gave 0.485 g (92%) of 3, mp 220–222 °C (dec.) under Ar.

\( ^{*} \) Data for 3: elemental analysis calcd for \( \text{Cp}_2\text{H}_2\text{Ti} \): C, 70.62; H, 5.93. Found: C, 70.14; H 5.88%. \text{H NMR} (CD\(_2\)\(_2\), 297 K): \( \delta \) 3.97 (br. 4H, \( \text{CH}_2 \)); 5.18 (s, 2H, Cp). \text{C}[\text{H}] \text{NMR} (CD\(_2\)\(_2\), 297 K): \( \delta \) 85.5 (CH\(_2\)); 108.5 (Cp); 153.4 (C-C). MS (70 eV, m/z): 408 [M\(^+\)], 406 [M–2H\(^+\)], 352 [M–C\(_2\text{H}_4\)], 178 [Cp-Ti\(^+\)].

\( ^{\|} \) X-Ray crystal structure analysis of 3: STOE-IPDS diffractometer, graphite monochromated MoK\(_\alpha\) radiation, solution of the structure by direct methods (SHELXS-86\(^{[15]} \)), refinement with full-matrix least-squares techniques against \( F^2 \) (SHELXL-93\(^{[16]} \)). Crystal data: monoclinic, space group \( \text{P}2_1/\text{c} \), \( a = 8.878(2), b = 7.887(2), c = 13.353(3) \text{ Å} \). \( \beta = 90.17(3) \). \( V = 914.9(4) \text{ Å}^3 \). \( Z = 2 \). \( D_x = 1.482 \text{ g cm}^{-3} \). 2621 reflections measured, 1429 were independent of symmetry and 1221 were observed \( (I > 2\sigma(I)) \). \( R1 = 0.036, wR^2(\text{all data}) = 0.096, 126 \) parameters. CCDC 239591. See http://www.rsc.org/suppdata/cc/b4/b406494a for crystallographic data in cif or other electronic format.