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

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The 2,5-dititanabicyclo[2.2.0]hex-1(4)-ene (bis-titanocene-μ-(*Z*)-1,2,3-butatriene complex) (3) is formed starting from [$Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)$] by *in situ* generated titanocene and 1,4-dichlorobut-2-yne *via* the 1-titanacyclobut-3-yne (2).

The complexation of titanocene with butatriene was described by Maercker, but the suggested structures resulting from $Me_2C{=}C{=}C{=}CMe_2$ and "Cp_2Ti" gave further reactions with CH-activation to yield more stable complexes.[1] Suzuki and coworkers recently reported 1-zirconacyclopent-3-ynes, formed from a divalent zirconocene-equivalent "Cp_2Zr" (generated by the Negishi reagent, [Cp_2ZrCl_2] and 2 equivalents of *n*-BuLi) with 1,4-disubstituted (*Z*)-butatrienes RHC=C=C=CHR (R = Me_3Si, *t*-Bu).[2] In the reaction mixture of [Cp_2ZrCl_2], 1,4-dichlorobut-2-yne and 2 equivalents of magnesium, even the coordination of an unsubstituted butatriene $H_2C{=}C{=}C{=}CH_2$ with the "Cp_2Zr" formed, to give 1-zirconacyclopent-3-yne was realized.[3] Closely related 1-metallacyclopenta-2,3,4-trienes (five-membered metallacyclocumulenes)[4] were obtained in reactions of 1,3-butadiynes RC≡C–C≡CR by using the excellent metallocene sources [$Cp_2M(\eta^2-Me_3SiC_2SiMe_3)$].[5] Both types of rather exotic metallacycles were discussed and compared by calculations[6] and prompted us to report here on the first results of reactions of [$Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)$] with $ClCH_2C{\equiv}CCH_2Cl$.

Compound **2** is formed by the reaction of two equivalents of [$Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)$] (**1**) with $ClCH_2C{\equiv}CCH_2Cl$ together with the liberation of $Me_3SiC_2SiMe_3$ and [Cp_2TiCl_2] (Scheme 1).†‡

The composition of the diamagnetic complex **2** was verified by analytical and spectral data and by reaction with a second "Cp_2Ti". The ^1H NMR (δ (CH_2) 3.03) and $^{13}C\{^1H\}$ NMR signals (δ (CH_2): 51.2; (C≡C) 106.9 ppm and the IR data (ν (C≡C) 2029 cm^{-1}) of complex **2** correspond very well to those of the analogous zirconium complex (^1H NMR: δ (CH_2) 2.73; $^{13}C\{^1H\}$ NMR: δ (CH_2): 38.64; (C≡C) 102.45 ppm and IR (ν (C≡C) 2018 cm^{-1}).[3]

The molecular structure of **2** represents a resonance structure between a 1-titanacyclopent-3-yne [$Cp_2Ti(\eta^2-1,2,3,4-CH_2C{\equiv}CCH_2)$] and a titanocene-$\eta^4$-(*E*)-butatriene complex [$Cp_2Ti(\eta^4-(E)-H_2C{=}C{=}C{=}CH_2)$] as discussed before for the analogous zirconium complex,[3,6] containing chelating σ-propargyl or π-allenyl structural elements.[7]

Complex **2** reacts with [$Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)$][5] to form complex **3** which can also be obtained by a 3 : 1 reaction of [$Cp_2Ti(\eta^2-Me_3SiC_2SiMe_3)$] with $ClCH_2C{\equiv}CCH_2Cl$ (Scheme 1).§¶

The X-ray crystal structure analysis of **3**¶ (Fig. 1) 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 C_4-ligand is coordinated to both titanium centers, unsymmetrically for each titanium atom [C1–C(1A) 1.325(5); C1–Ti1 2.152(3); C(1A)–Ti1 2.268(3) Å], whereas each of the methylene groups is coordinated to only one Ti atom [C2–Ti1 2.167(3); C1–C(2A) 1.443(4) Å]. By this coordination a bonding mode is formed with a C1–C(1A)–C2 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).[6] Despite that, the structure of **3** as a μ-*trans*-butatriene complex is best described as a dititanabicycle (**C**) in analogy with μ-*trans*-butadiyne complexes (**D**), formed by analogous titanocene complexation of 1-titanacyclopenta-2,3,4-trienes (five-membered titanacyclocumulenes)[4] (Scheme 3).[5] **3** is not a σ-propargyl or a π-allenyl complex[6,7] and is also different from the "bridged allylic" structures found in μ-butatriene-bis(tricarbonyliron) complexes[8a] or substituted butatriene dianion dilithium,[8b] μ-butyne-1,4-diyl[8b] structures as well as μ-butadiyne complexes with μ-(η^2,η^2)-(PhC=C=C=CPh) units.[8c]

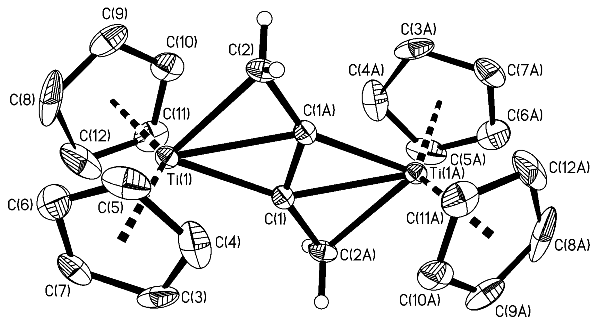
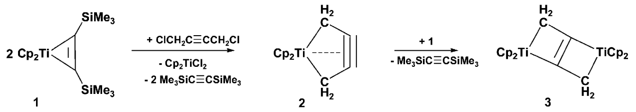
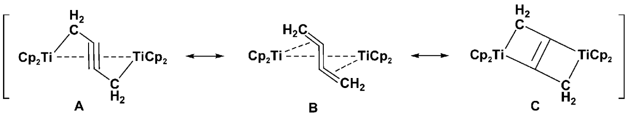


Fig. 1 Molecular structure of complex **3**. Hydrogen atoms except the H-atoms of the C_4-ligand are omitted for clarity. The thermal ellipsoids correspond to 30% probability.



Scheme 1 Preparation of complexes.



Scheme 2 Resonance structures of complex **3**.

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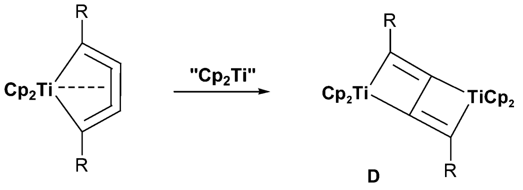

Scheme 3 Formation of μ-butadiyne complexes (**D**).

We have studied the structure and bonding of these molecules using Density Functional Theory calculations (B3LYP/LANL2DZ).[9] The calculated geometrical parameters are in close agreement with the experimental structure. The bonding in **3** is best described by treating the bridging ligand as formally $[H_2CCCCH_2]^{(-4)}$ species, making Ti(+4). The C1–C(1A) π bond perpendicular to the TiC_4Ti plane does not interact substantially with the metals. The remaining eight valence electrons of the $[H_2CCCCH_2]^{(-4)}$ ligand occupy four in-plane delocalized orbitals resulting from the interaction with the Cp_2Ti fragment orbitals. The bonding here is very similar to that in the μ-*trans*-butadiyne complex $[Cp_2Ti(HCCCCH)TiCp_2]$ (type **D**) except that **3** has an ethylenic π bond in place of the *trans*-butadiene of the butadiyne complex.[10] A C_{2v} isomer of **3** derived directly from the complexation of the middle C1–C(1A) 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

† *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 $ClCH_2C{\equiv}CCH_2Cl$ (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 $[Cp_2TiCl_2]$ was formed. The mixture was allowed to stand in an argon atmosphere at 20 °C. After 24 h the solution was filtered and evaporated to 10 ml under vacuum. Upon cooling to −78 °C for 1 day, 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.

‡ *Data* for **2**: elemental analysis calcd for $C_{14}H_{14}Ti$: C, 73.07; H, 6.13. Found: C, 72.43; H 6.19%. ^1H NMR (C_6D_6, 297 K): δ 3.03 (s, 4H, CH_2); 4.68 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 51.2 (CH_2); 102.4 (Cp); 106.9 (C≡C). IR (Nujol mull, cm^{-1}): 2029 (weak, νC≡C). MS (70 eV, *m/z*): 230 $[M]^+$, 178 $[Cp_2Ti]^+$, 113 $[CpTi]^+$.

§ *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 filtrated 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 $C_{24}H_{24}Ti_2$: C, 70.62; H, 5.93. Found: C, 70.14; H 5.88%. ^1H NMR (C_6D_6, 297 K): δ 3.97 (br., 4H, CH_2); 5.18 (s, 20H, Cp). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K): δ 85.5 (CH_2); 108.5 (Cp); 153.4 (C=C). MS (70 eV, *m/z*): 408 $[M]^+$, 406 $[M - 2H]^+$, 352 $[M - C_4H_8]^+$, 178 $[Cp_2Ti]^+$.

‖ *X-Ray crystal structure analysis* of **3**: STOE-IPDS diffractometer, graphite monochromated MoKα radiation, solution of the structure by direct methods (SHELXS-86[11]), refinement with full-matrix least-squares techniques against F^2 (SHELXL-93[12]). Crystal data: monoclinic, space group $P2_1/n$, $a = 8.687(2)$, $b = 7.887(2)$, $c = 13.353(3)$ Å; $\beta = 90.17(3)°$; $V = 914.9(4)$ Å^3, $Z = 2$, $D_c = 1.482$ g cm^{-3}; 2621 reflections measured, 1429 were independent of symmetry and 1221 were observed $[I > 2\sigma(I)]$, $R1 = 0.036$, wR^2(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.

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