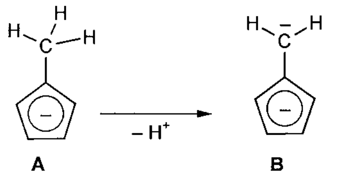
A Novel Route to Fulvene Complexes of Titanium—Diastereoselective Complexation of Pentafulvenes to Cyclopentadienyltitanium Fragments**

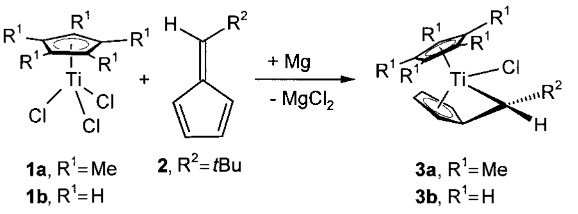
Rüdiger Beckhaus,* Arne Lützen, Detlev Haase, Wolfgang Saak, Jörg Stroot, Sigurd Becke, and Jürgen Heinrichs

Metallocene compounds dominate broad fields in organometallic chemistry.[1] Particularly, the bent dicyclopentadienyl derivates of titanium group metals have gained great importance as catalysts in olefin polymerization.[2] It was already observed at an early stage that alkyl-substituted ligands such as $C_5Me_xH_{5-x}$ ($x = 1-5$) undergo spontaneous C–H activation under thermolytic conditions leading to fulvene complexes.[3] Recently these so-called "tuck-in" complexes have attracted more and more interest not only with regard to their coordination chemistry[3d, 4, 5] but also with regard to their catalytic properties.[6] The conversion **A** → **B** can be discussed formally as deprotonation of an alkyl cyclopentadienyl ligand under formation of a fulvene dianion [Eq. (1)].[7]



(1)

Herein we report on the first direct complexation of fulvenes to titanium(II) fragments.[8] Treatment of a solution of the cyclopentadienyltitanium trihalides [Cp*TiCl$_3$] (**1a**) (Cp* = C_5Me_5) or [CpTiCl$_3$] (**1b**) (Cp = C_5H_5) in THF with magnesium in the presence of 6-*tert*-butylfulvene (**2**) (molar ratio 1:1:1) led to a color change from red (**1a**) and yellow (**1b**), respectively, to dark green in only one hour [Eq. (2)]. After removal of the solvent, addition of *n*-pentane to the residue, and separation from insoluble $MgCl_2$ by filtration, **3a** and **3b** can be isolated as dark green, needle-shaped crystals. The complex formation proceeds in a highly diastereoselective manner (*de* > 98 %).



(2)

The structures of **3a** and **3b** have been confirmed by X-ray structre analysis,[9] and Figure 1 shows the structure of **3a** as an example.[10] Comparable structural data have been found for **3b**, consequently both compounds are discussed together.

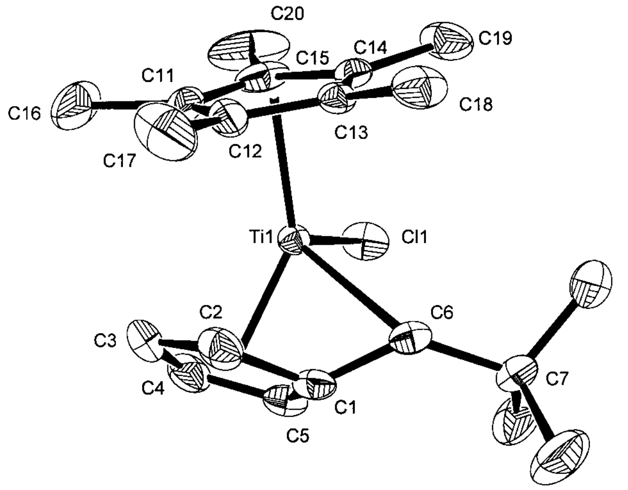
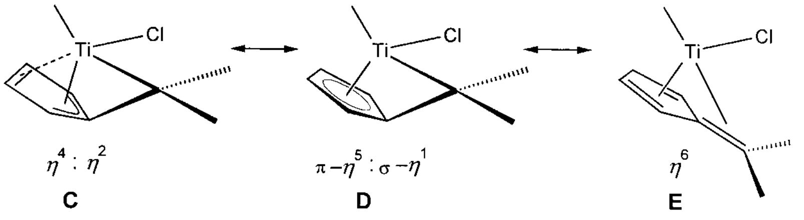


Figure 1. Structure of **3a** in the crystal (50 % probability, without H-atoms). Selected bond lengths [Å] and angles [°] (values for **3b** in parentheses): Ti-C1 2.151(2) (2.155(2)), Ti-C6 2.355(2) (2.367(2)), Ti-C2 2.279(2) (2.286(2)), Ti-C5 2.293(2) (2.291(2)), Ti-C3 2.446(3) (2.443(2)), Ti-C4 2.452(2) (2.446(2)), Ti-Cl 2.355(1) (2.354(1)), Ti-Ct2 1.993(2) (1.991(2)), Ti-Ct1 2.062(2) (2.045(2)), C1-C6 1.432(3) (1.434(3)), C1-C2 1.431(4) (1.443(3)), C1-C5 1.440(3) (1.440(3)), C2-C3 1.401(4) (1.395(3)), C4-C5 1.394(4) (1.400(3)), C3-C4 1.395(4) (1.405(3)); Ct1-Ti-Ct2 136.8 (138.3)) (Ct1 = ring centroid of C11 – C15, Ct2 = ring centroid of C1 – C5).

Generally, the coordinated fulvene can be considered as a neutral olefinic (**E**, Ti^{II} complex) or as a dianionic ligand (**C**, **D**, Ti^{IV} complex; Scheme 1).

Compared to classical [(η^5-Cp)$_2$Ti] derivatives, in **3a** and **3b** the normal from the metal center to the C1–C5 plane is shifted by 0.32 and 0.31 Å, respectively, from the ring centroid



Scheme 1. Coordination modes of fulvene ligands.

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[*] Prof. Dr. R. Beckhaus, Dr. A. Lützen, D. Haase, W. Saak, J. Stroot
Fachbereich Chemie
Universität Oldenburg
Postfach 2503, 26111 Oldenburg (Germany)
Fax: (+49) 441-798-3581
E-mail: ruediger.beckhaus@uni-oldenburg.de

Dr. S. Becke
Bayer AG
ZSB Zentrale Forschung
Materialforschung
Gebäude Q 18, 51368 Leverkusen (Germany)

Dr. J. Heinrichs
Condea Chemie GmbH
Römerstrasse 733, 47443 Moers (Germany)

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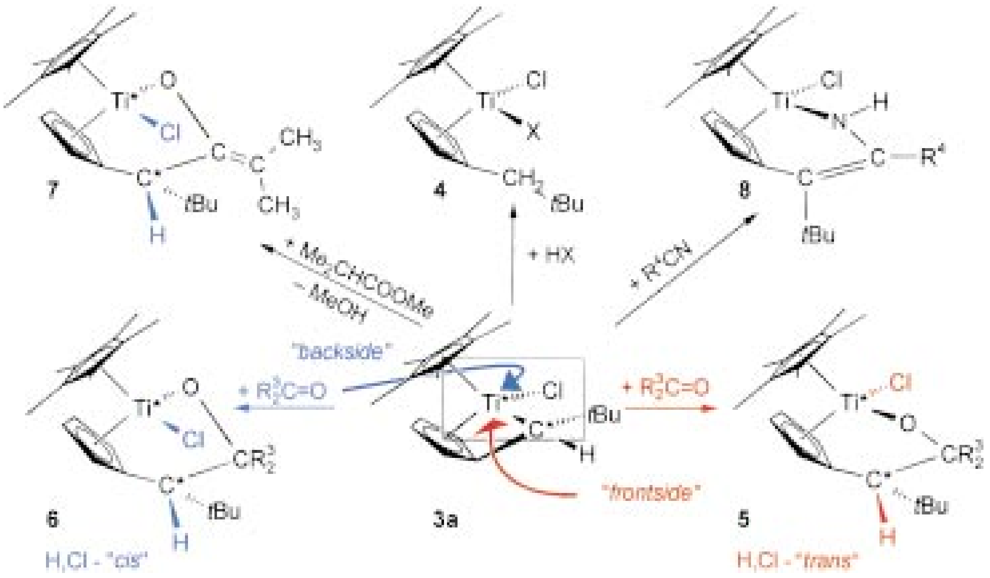
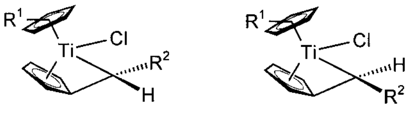
in the direction of C1. Hence, the Ti–C3 and Ti–C4 distances are considerably longer than the other Ti–C distances. The concurrent shortening of the C3–C4 bond (1.395(4) (**3a**), 1.405(3) Å (**3b**)) compared to that in free fulvenes (1.476,[11a] 1.462(9) Å[11b]) is an indication for a trimethylenemethane-like η^4:η^2-coordination (**C**) as described for fulvene complexes with ansa-structure.[4b, 12] The angle Θ formed between the C1–C6 bond and the plane C1–C5 in **3a** and **3b** (35.6°) is in the expected range for this class of compounds (35(1)°[5]). The distance Ti–C6 (2.355(2) Å **3a**, 2.367(2) Å **3b**) is longer than that in exocyclic unsubstituted fulvene complexes (2.281(14) Å[5]). NMR data confirm the structural integrity of compounds **3a** and **3b** in solution. The proton signals in **3a** and **3b** are shifted upfield compared with those for **2**, with large differences for the signal positions of the fulvene protons.[10] Owing to the change of hybridization from C_{sp^2} to C_{sp^3} expected for **C** and **D**, the H6 resonance signal experiences the strongest shift to high field ($\delta = 6.18$ (**2**), 1.68 (**3a**), 2.04 (**3b**)). Contributions of mesomer **E** can be concluded, however, from the value of the C–H coupling constant for the exocyclic carbon atom C6 (^1J(C,H) = 149.8 (**2**), 148.6 (**3a**), 144.0 (**3b**) Hz), which is in the olefinic region, and from the UV/Vis spectral data. Therefore, the green color of **3a** and **3b** results from a weak absorption ($\lambda_{max}(\varepsilon) = 670(150)$ (**3a**), 665 nm(150) (**3b**)) probably caused by d–d transitions. Thus, electron density remains at the titanium center and this corresponds with a lower oxidation state.



Scheme 3. Selected subsequent reactions of **3a**.

The high diastereoselectivity of the formation of **3a** and **3b** is caused by the comparatively high difference in energy between the diastereomeric pairs **I** and **II** (Scheme 2).[16] Density functional theory (DFT) calculations with the B3LYP functional show for **3a** ($R^1 = Me$, $R^2 = t$Bu) preference for the diastereomer **I** over **II** by 29.1 kcal mol^{-1}. This difference in energy decreases on lowering the steric demands of the fulvene substituents. For $R^1 = R^2 = Me$ the difference is lowered to 4.5 kcal mol^{-1}. This behavior corresponds with the experimental results for the synthesis of $[(C_5R^1_5)(C_5H_4{=}CR^2H)TiCl]$ complexes with different substituents: *de* = 98 % ($R^1 = Me$, $R^2 = i$Pr), 49 % ($R^1 = Me$, $R^2 = Ph$), 81 % ($R^1 = H$, $R^2 = i$Pr).[17a]



I II

Scheme 2. Diastereomeric pairs **I** and **II**.

Compared with the described dianionic character of the fulvene ligands, a change of reactivity is observed. Whereas free fulvenes undergo reactions with nucleophiles, due to the electrophilic character of the exococylic carbon, the C6 position in the titanium–fulvene complexes becomes strongly nucleophilic. First examples of the reactivity are given in Scheme 3.[17] Mixed substituted titanocene complexes **4** are formed with simple electrophiles (HX, X = OH, Cl, RO). Insertion reactions with ketones confirm the side differentiation during the primary attack according to the substrate ("frontside" and "backside" attack, respectively). Thus, the diastereomers **5** and **6** are formed in a reaction of **3a** with benzophenone derivatives $R^3_2C{=}O$ ($R^3 = p$-XC_6H_4; X = H, F, Cl, Br, Me, MeO, Me_2N). These differ in the arrangement of the fulvene proton (H6) to the chlorine atom related to a plane formed by the diastereogenic centers and the O atom. The separation of the diastereomers can be achieved for the used benzophenones by selective crystallization, owing to the low solubility of **6** in *n*-hexane. The ratio of **5** to **6** is controlled by electronic and steric properties of the used ketones. With $R^3 = p$-$NMe_2C_6H_4$ the formation of **5** dominates, whereas with $R^3 = p$-FC_6H_4 the *cis* isomer **6** is preferred. Unlike the used benzophenones, camphor (bulky carbonyl compound) reacts exclusively to give **6**. With isomethyl butyrate (less electrophilic carbonyl carbon atom) exclusively isomer **7** is isolated as a result of a primary "backside" attack, followed by thermal elimination of methanol. Insertion reactions with nitriles take place in a similar manner, but the stereochemical information is lost because of an imine–enamine rearrangement to give **8** ($R^4 = C_6H_5$-*p*-Cl).

The described fulvene complexes of titanium, easily available through the reported diastereoselective procedure, and their subsequent reactions have substantially enriched the access to substituted metallocene derivatives of early transition metals especially those with stereochemically, well-defined σ,π ligands.

Experimental Section

General remarks: The compounds **3a** and **3b** were prepared and handled in a nitrogen atmosphere with rigorous exclusion of oxygen (Schlenk technique). Solvents were thoroughly dried and saturated with nitrogen prior to use.

3a: A solution of **2** (1.356 g, 10.1 mmol) [13] in THF (20 mL) was added dropwise to a reaction mixture of **1a** (2.895 g, 10 mmol)[14] and Mg (0.255 g, 10.5 mmol) in THF (40 mL). After about 1 h the color of the solution turned from red to green. The reaction mixture was stirred at room temperature until the magnesium was consumed (8 h). After the THF had been removed, the residue was dissolved in *n*-pentane (60 mL), and separated from the insoluble $MgCl_2$ by filtration. The filtrate was evaporated to 10 mL and cooled to $-20\,^{\circ}C$. Compound **3a** was isolated as dark green, needle-shaped crystals (2.388 g, 68%). M.p. 118 °C; ^1H NMR (500 MHz, C_6D_6, 300 K): $\delta = 1.15$ (s, 9H; *t*Bu), 1.68 (s, 1H; H6), 1.71 (s, 15H; Cp*), 3.17 (m, 1H; H2), 4.76 (m, 1H; H3), 5.96 (m, 1H; H4), 6.60 (m, 1H; H5); ^{13}C NMR (125 MHz, C_6D_6, 300 K): $\delta = 13.1$ ($C_5(CH_3)_5$), 33.6 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 115.7 (C3), 119.2 (^1J(C,H) = 148,6 Hz, C6), 119.7 (C4), 120.2 (C2), 121.8 ($C_5(CH_3)_5$), 126.1 (C5), 129.6 (C1);[15] MS (70 eV): *m*/*z* (%): 352 (6) [M^+], 316 (100) [$M^+ - HCl$], 218 (32) [$M^+ - C_{10}H_{14}$]; IR (KBr): $\tilde{\nu} = 2947$, 2903, 2863, 1481, 1452, 1377, 1360, 1248, 1217, 1049, 1024 cm^{-1}; UV/Vis (*n*-pentane): $\lambda_{max}(\varepsilon) = 670$ nm (150); C,H analysis calcd (%) for $C_{20}H_{29}TiCl$: C 68.09, H 8.29; found: C 68.57, H 8.03.

3b: Procedure analogous to that for **3a**, [$CpTiCl_3$] (2.194 g, 10 mmol),[13] Mg (0.255 g, 10.5 mmol), **2** (1.356 g, 10.5 mmol)[14] gave **3b** (1.362 g, 48%). M.p. 92 °C; ^1H NMR (500 MHz, C_6D_6, 300 K): $\delta = 1.05$ (s, 9H; *t*Bu), 2.04 (s, 1H; H6), 3.25 (m, 1H; H2), 4.80 (m, 1H; H3), 6.17 (m, 1H; H4), 6.61 (m, 1H; H5), 5.84 (s, 5H; C_5H_5); ^{13}C NMR (125 MHz, C_6D_6, 300 K): $\delta = 32.7$ ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 111.0 (C_5H_5), 111.4 (C3), 116.5 (^1J(C,H) = 144,0 Hz, C6), 117.2 (C2), 121.5 (C4), 127.3 (C1), 127.5 (C5);[15] MS (70 eV): *m*/*z* (%): 282 (2) [M^+], 246 (95) [$M^+ - HCl$]; 148 (100) [$M^+ - C_{10}H_{14}$); IR (KBr): $\tilde{\nu} = 3102$, 2959, 2905, 2866, 1466, 1454, 1387, 1362, 1252, 1215, 1194, 1159, 1055, 1022 cm^{-1}; UV/Vis (*n*-pentane): $\lambda_{max}(\varepsilon) = 665$ (150); C,H analysis calcd (%) for $C_{15}H_{19}TiCl$: C 63.74, H 6.78; found: C 63.70, H 7.00.

Subsequent products **4**–**8** were characterized spectroscopically and structurally, as well as by correct elemental analyses. Preparation of **5** and **6**: A solution of benzophenone (0.911 g,(5.0 mmol) (**a**) in *n*-hexane (10 mL) was added to a stirred solution of **3a** (1.764 g, 5.0 mmol) in *n*-hexane (20 mL) at room temperature. After 8 h, **5a** began to precipitate as a yellow nacreous deposit. After a total reaction time of 60 h, **5a** was isolated by filtration and drying (82%). After evaporation to 10 mL and cooling to $-20\,^{\circ}C$, **6a** (12%) was isolated from the filtrate as yellow-orange, cube-shaped crystals. (An analogous procedure was used for other benzophenone derivatives; reaction conditions for the reaction with camphor; 8 d 60 °C).

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[8] Fulvene complexes derived from titanium(0) arenes (J. A. Bandy, V. S. B. Mtetwa, K. Prout, J. C. Green, C. E. Davies, M. L. H. Green, N. J. Hazel, A. Izquierdo, J. J. Martin-Polo, *J. Chem. Soc. Dalton Trans.* **1985**, 2037–2049); for reductive dimerization of fulvenes to ansa-metallocenes see ref. [4e].

[9] Crystallographic data for **3a**: STOE-IPDS diffractometer ($Mo_{K\alpha}$ radiation); **3a**: 175 measurements, Θ/measurements = 1.2°, $T = 193$ K. Crystal dimensions $0.77 \times 0.18 \times 0.07\ mm^3$, $C_{20}H_{29}ClTi$; $M_r = 352.78$, monoclinic, space group $C2/c$, $a = 15.9880(14)$, $b = 8.2220$ (4), $c = 28.952(2)$ Å, $V = 3736.8(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.254\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.596\ mm^{-1}$, $F(000) = 1504$, $\Theta_{max} = 25.97°$; 14604 measured reflections, 3394 independent reflections ($R_{int} = 0.0438$). All non-hydrogen atoms were anisotropically refined and the H atoms were inserted in the calculated positions. H6 was refined free; 2539 reflections $I > 2\Theta(I)$ and 203 refined parameters, GOF(F^2) = 0.991, final *R* indices: $R_1 = 0.0358$, $wR_2 = 0.0858$, max./min. residual electron density 0.498 and -0.299 e Å^{-3}. Crystallographic data for **3b**: STOE-IPDS diffractometer ($Mo_{K\alpha}$ radiation); 136 measurements, Θ/measurement = 1.4°, $T = 193$ K. Crystal dimensions $0.31 \times 0.25 \times 0.14\ mm^3$, $C_{15}H_{19}ClTi$; $M_r = 282.65$, monoclinic, space group $I2/c$, $a = 14.0197(10)$, $b = 11.8928$ (6), $c = 16.7877(13)$ Å, $V = 2792.5(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.345\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.780\ mm^{-1}$, $F(000) = 1184$, $\Theta_{max} = 25.94°$; 10130 measured reflections, 2704 independent reflections ($R_{int} = 0.0462$). All non-hydrogen atoms were anisotropically refined and the H atoms were inserted in the calculated positions; 1915 reflections $I > 2\Theta(I)$ and 154 refined parameters, GOF(F^2) = 0.892, final *R* indices: $R_1 = 0.0291$, $wR_2 = 0.0582$, max./min. residual electron density 0.236 and -0.268 e Å^{-3}. The structures were solved by direct phase determination (SHELXS-97[18]) and refined on F^2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-149627 (**3a**) and CCDC-149628 (**3b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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