Reactions of permethylmetallocene alkyne complexes of titanium and zirconium with tris(perfluorophenyl)borane

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Functionalization of the pentamethylcyclopentadienyl ligands by an electrophilic substitution of hydrogen atoms by [$B(C_6F_5)_3$] is observed at the Cp* ligands of the alkyne complexes [$Cp^*_2M(\eta^2\text{-}PhC_2SiMe_3$], connnected with (M = Ti, formation of 1) or without (M = Zr, formation of 2) loss of the alkyne and molecular hydrogen.

Recently we have published the reaction of the bis(trimethylsilyl)acetylene complex of titanocene [$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$][1] with [$HNMe_3$][$BPh_4$] giving cationic complexes of the type [Cp_2TiL_2][BPh_4] with L = THF and pyridine.[2] More recently we have found that in the interaction of [$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] with [$B(C_6F_5)_3$] an electrophilic substitution of a hydrogen atom in one of the $\eta^5\text{-}C_5H_5$ rings takes place, and the paramagnetic zwitterionic titanium complex [$(\eta^5\text{-}C_5H_5)Ti\{\eta^5\text{-}C_5H_4B(C_6F_5)_3\}$] is formed together with liberation of dihydrogen.[3] In this complex the *ortho*-fluorine atoms of two perfluorphenyl groups coordinate at the titanium centre.

Such an interaction but with only one perfluorphenyl group was described previously in the reaction product of the zirconacyclopentadiene [$Cp_2Zr(C_4Me_4)$] with [$B(C_6F_5)_3$] giving [$(\eta^5\text{-}C_5H_5)Zr\{\sigma\text{-}C(Me){=}C(Me){-}C(Me){=}CHMe\}\{\eta^5\text{-}C_5H_4B(C_6F_5)_3\}$].[4] Starting from the alkyne complex [$Cp_2Zr(PMe_3)(\eta^2\text{-}EtC_2Et)$] and [$HB(C_6F_5)_2$] the alkenyl complex [$(\eta^5\text{-}C_5H_5)Zr\{\sigma\text{-}C(Et){=}CHEt\}\{\eta^5\text{-}C_5H_4BH(C_6F_5)_2\}$] was obtained in which the hydrogen of the B–H groups coordinate at the Zr centre.[5]

Also, the so-called 'tuck in' permethylmetallocene complexes[5] were obtained with [$B(C_6F_5)_3$] and [$HB(C_6F_5)_2$]. Some aspects of these compounds were reviewed by Piers in 1998.[5]

Here, we report the different reactions of the permethylmetallocene alkyne complexes [$Cp^*_2M(\eta^2\text{-}PhC_2SiMe_3)$] (M = Ti[6] and Zr[7]) with [$B(C_6F_5)_3$], leading to functionalization of the pentamethylcyclopentadienyl ligand.

The compound [$(\eta^5\text{-}C_5Me_5)Ti\{\eta^5\text{-}C_5Me_4CH_2B(C_6F_5)_3\}$] **1** is formed by dissociation of the alkyne and an electrophilic substitution of a hydrogen atom in one methyl group of the Cp* ligand together with liberation of dihydrogen (Scheme 1).†

The composition of the Ti(III) complex **1** was verified by elemental analysis‡ and crystallography.

The X-ray crystal structure analysis of **1**§ (Fig. 1) revealed a bent permethyltitanocene which consists of one unsubstituted and one substituted pentamethylcyclopentadienyl ligand. In this complex the *ortho*-fluorine atom of only one of the perfluorphenyl groups coordinates at the titanium centre [Ti–F152.406(3) Å]. This is longer than found in [$(\eta^5\text{-}C_5H_5)Ti\{\eta^5\text{-}C_5H_4B(C_6F_5)_3\}$][3] (2.248, 2.223 Å).

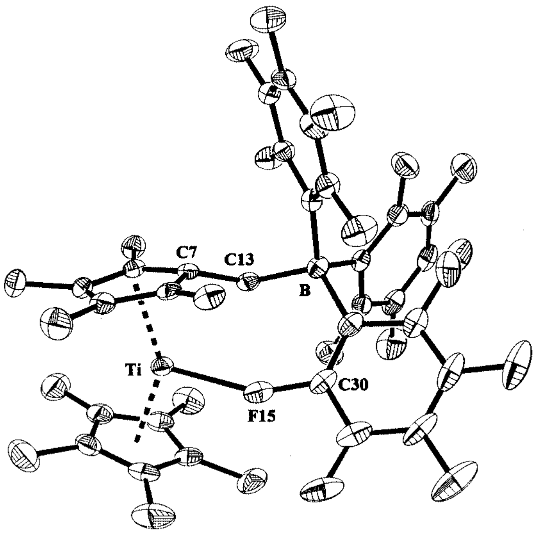
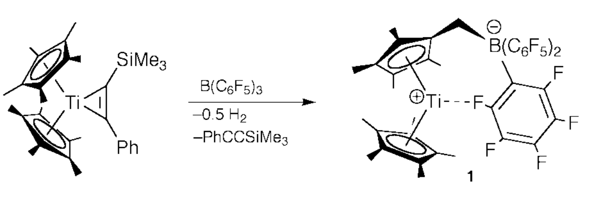


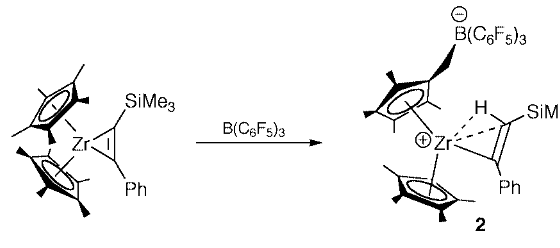
Fig. 1 Crystal structure of **1** at the 30% probability level for thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–F15 2.406(3), C30–F15 1.391(5), C7–C13 1.514(5), C13–B 1.649(6); B–C13–C7 124.8(3).

The alkenyl compound [$(\eta^5\text{-}C_5Me_5)Zr\{C(Ph){=}CH(SiMe_3)\}\{\eta^5\text{-}C_5Me_4CH_2B(C_6F_5)_3\}$] **2** is formed also by an electrophilic substitution of a hydrogen atom in one methyl group of the Cp* ligand but without dissociation of the alkyne and liberation of dihydrogen (Scheme 2).¶

The composition of the diamagnetic complex **2** was verified by elemental analysis and crystallography. For solubility reasons, NMR investigations had to be carried out in THF-d_8, but some undefined changes prevented a full analysis of the spectra.‖ However, the borane attack at one methyl group is evident from a strong line broadening of both the ^1H and ^{13}C methylene signals (diastereotopic protons at 2.65 and 2.81 ppm). The chemical shifts for the vinyl group, a strong deshielding for the α carbon atom (228.9 ppm) and an upfield



Scheme 1



Scheme 2

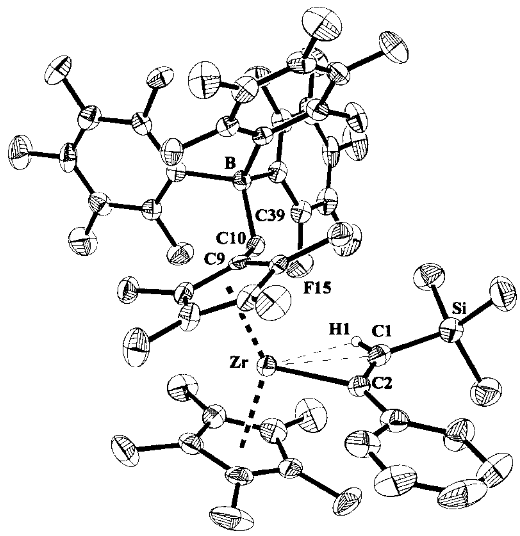


Fig. 2 Crystal structure of **2** at the 30% probability level for thermal ellipsoids. Hydrogen atoms except H1 are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr–C1 2.518(6), Zr–C2 2.238(5), C9–C10 1.487(6), C10–B 1.694(6), Zr–H1 2.250, Zr–F15 4.744, C39–F15 1.369(5); C1–C2–Zr 86.5(4), B–C10–C9 121.6(4).

shift with a small coupling constant $^1J_{\mathrm{CH}}$ (104.9 ppm, 111 Hz) for the β position, are characteristic for a 'β-CH agostic' structure[8] although the deshielding of the proton is not as pronounced for complex **2** as was found for other zirconium cyclopentadienyl compounds with this structural feature.[8,10b,12]

The X-ray crystal structure analysis of **2**§ (Fig. 2) revealed, similarly as found also for complex **1**, a bent permethylmetallocene which consists also of one unsubstituted and one substituted pentamethylcyclopentadienyl ligand, but no fluorine atom coordinates at the zirconium centre [shortest distance Zr–F15 4.744 Å]. Additionally an alkenyl group is σ-bonded with an agostic interaction[8] to the zirconium atom presenting the typical small angle Zr–C2–C1 of 86.5° for such a type of bonding. In complexes **1** and **2** an identically functionalized Cp* ligand [η^5-$C_5Me_4CH_2B(C_6F_5)_3$] is shown. Owing to the additional interaction in **1** the angle B–C13–C7 of 124.8(3)° is larger compared to the corresponding angle B–C10–C9 of 121.6(4)° in **2**.

The reactions of the corresponding complexes of bis(trimethylsilyl) acetylene [$Cp^*_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (M = Ti[6] and Zr[9]) gave with [$B(C_6F_5)_3$] only oils or such solids which could not be purified by crystallisation.

The novelty of the reactions in this work is, in contrast to former observed *inter*molecular reactions for titanium[7b,10] and zirconium[7b,11] an *intra*molecular course *via* C–H activation for the formation of **1** and **2**. In the *inter*- and the *intra*molecular reactions the higher stability of the Ti(III) oxidation state as well as the larger zirconium atom can give an explanation for the different types of reaction: elimination or addition of the reacting substrate or group.

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Notes and references

† *General procedure* for the preparation of complex **1**: 0.507 g (0.990 mmol) of [$B(C_6F_5)_3$] was dissolved in 10 mL of toluene and added to 0.474 g (0.962 mmol) of [$Cp^*_2Ti(\eta^2\text{-}PhC_2SiMe_3)$].[6] The yellow–brown solution was filtered. After standing for 2 days at room temperature 0.123 g (15.4%) of yellow–brown crystals of **1** were formed which were separated from the mother-liquor, washed with cooled toluene and dried *in vacuo*; mp 141–143 °C (decomp.).

‡ *Data* for **1**: elemental analysis for $C_{38}H_{29}TiBF_{15}$ (*M* = 829.31). Calc.: C, 55.04; H, 3.52. Found: C, 55.02; H, 3.59%. NMR: As expected for Ti(III),[3] no NMR signals (^{1}H and ^{13}C) could be obtained from solutions of **1** in THF.

§ *X-Ray structure analysis* of **1** and **2**: STOE-IPDS diffractometer, graphite monochromated Mo-Kα radiation, solution of structures by direct methods (SHELXS-86: G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467), refinement with full matrix least square techniques against F^2 (SHELXL-93: G. M. Sheldrick, University of Göttingen, Germany, 1993).

1: monoclinic, space group *C*2/*c*, a = 37.705(8), b = 10.990(2), c = 18.178(4) Å; β = 106.48(3)°; V = 7223(3) Å^3, Z = 8, D_c = 1.525 g cm^{-3}; 10465 reflections measured, 5758 were symmetry independent and 2868 were observed [$I > 2\sigma(I)$], R = 0.052, wR^2 (all data) = 0.116, 496 parameters.

2: monoclinic, space group $P2_1/c$; a = 12.827(3), b = 18.862(4), c = 19.499(4) Å, β = 94.26(3)°; V = 4704.6(18) Å^3, Z = 4, D_c = 1.480 g cm^{-3}; 13886 reflections measured, 7099 were symmetry independent and 3131 were observed [$I > 2\sigma(I)$], R = 0.045, wR^2 (all data) = 0.074, 608 parameters. CCDC 182/1520. See http://www.rsc.org/suppdata/cc/a9/a908591b/ for crystallographic files in .cif format.

¶ *General procedure* for the preparation of complex **2**: 0.368 g (0.719 mmol) of [$B(C_6F_5)_3$] was dissolved in 15 mL of toluene and added to 0.370 g (0.690 mmol) of [$Cp^*_2Zr(\eta^2\text{-}PhC_2SiMe_3)$].[7] The green solution was filtered. After standing for one day at room temperature red crystals deposited which were separated from the mother liquor, washed with cooled toluene and dried *in vacuo* to give 0.684 g (94.6%) of **2**;. mp 176–178 °C (decomp.).

‖ *Data* for **2**: elemental analysis for $C_{49}H_{44}SiBZrF_{15}$ (*M* = 1047.98). Calc.: C, 56.16; H, 4.23. Found : C, 55.99; H, 4.24%. ^{1}H NMR (THF-d_8, 297 K): δ 0.07 (s, 9H, SiMe$_3$); 1.30, 1.51, 1.64, 1.80 (4 s, 3H each, Cp-Me); 1.95 (s, 15H, Cp*); 2.65, 2.81 (br, 1H each, BCH$_2$); 4.49 (s, 1H, CH); 7.14 (2H, *o*-Ph); 7.19 (1H, *p*-Ph); 7.34 (2H, *m*-Ph). ^{13}C NMR (THF-d_8, 297 K, not all signals unambiguously identified): δ 1.2 (SiMe$_3$); 12.2, 12.4, 12.6, 12.7 (Cp-Me); 12.7 (Cp*); 22.9 (br, BCH$_2$); 104.9 (CH); 123.7 (Cp*); 126.6 (*o*-Ph); 126.8 (*p*-Ph); 128.7 (*m*-Ph); 228.9 (Zr–C).

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