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Synthesis and Characterisation of Selected Group 4 Metallocene Complexes with 1,2-Bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)acetylene

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The reactions of the metallocene generators $\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ [**1a**-Ti: $\text{Cp}' = \text{Cp} = \eta^5\text{-cyclopentadienyl}$, $\text{M} = \text{Ti}$, $\text{L} = \text{none}$; **1b**-Ti: $\text{Cp}' = \text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$, $\text{M} = \text{Ti}$, $\text{L} = \text{none}$; **1c**-Ti: $\text{Cp}'_2 = \text{rac}(\text{ebthi}) = \text{rac-ethylenebistetrahydroindenyl}$, $\text{M} = \text{Ti}$, $\text{L} = \text{none}$; **1a**-Zr: $\text{Cp}' = \text{Cp}$, $\text{M} = \text{Zr}$, $\text{L} = \text{pyridine}$; **1b**-Zr: $\text{Cp}' = \text{Cp}^*$, $\text{M} = \text{Zr}$, $\text{L} = \text{none}$; **1c**-Zr: $\text{Cp}'_2 = \text{rac}(\text{ebthi})$, $\text{M} = \text{Zr}$, $\text{L} = \text{none}$] with 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)acetylene (**2**) as a di-heteroatom-substituted alkyne were investigated. A slightly special reaction of **1a**-Ti with **2** produced no titanacyclopentadiene or titanacyclopentadiene, but instead complex **3** was produced by the coupling of two alkyne units with one of the Cp ligands to form a six-membered ring annelated to a five-membered one. The titanocene com-

plexes **1b**-Ti and **1c**-Ti reacted with **2** to form the titanacycloprenes **4** and **5**. The complex **1a**-Zr reacts with **2** to the corresponding zirconacyclopentadiene **6** as a byproduct, in which the pyridine ligand remains coordinated. If the pyridine ligand dissociates, a coupling with a second alkyne yields the zirconacyclopentadiene **7** as the main product. The reaction of the sterically more demanding zirconocene precursor **1c**-Zr also yielded the zirconacyclopentadiene **8**, whereas **1b**-Zr did not react with **2**. The complex $\text{rac}(\text{ebthi})\text{-Ti}(\eta^2\text{-bPinBA})$ (**5**) reacts with gaseous dry CO_2 directly to form the titanafuranone **9**. The molecular structures of complexes **5** and **6** were characterised by single-crystal X-ray crystallography.

Introduction

During recent years, we have intensively investigated the synthesis and reactions of group 4 metallocene complexes with bis(trimethylsilyl)acetylene $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ (**btmsa**), in which several complexes such as $\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)$ with different substituted and unsubstituted as well as bridged and unbridged Cp' ligands [$\text{M} = \text{Ti}$, Zr and Hf ; $\text{Cp}' = \text{Cp} = \text{cyclopentadienyl}$; $\text{Cp}^* = \text{pentamethylcyclopentadienyl}$; $\text{Cp}'_2 = \text{rac}(\text{ebthi}) = \text{rac-ethylenebistetrahydroindenyl}$, etc.] were used.^[1–5] To gain deeper insight into the existence and stability of such three-membered, unsaturated metallacycles with different heteroatoms as substituents, the coordination chemistry of a series of neutral-donor-substituted acetylenes such as $\text{R}_2\text{NC}\equiv\text{CNR}_2$,^[6] $\text{R}_2\text{PC}\equiv\text{CPR}_2$,^[7] $\text{ROC}\equiv\text{COR}$ ^[8] and $\text{RSC}\equiv\text{CSR}$ ^[9] with group 4 metallocene complexes was of high interest.

Here, the *cis* and possibly *trans* coordination by additional interaction of the donor atoms N, P, O and S together with the general stability of the alkynyl–heteroatom bond should be investigated. For group 4 metallocene complexes, an alkynyl–heteroatom cleavage was described for $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ ^[10] and $\text{Me}_3\text{SnC}\equiv\text{CSnMe}_3$.^[11] For the donor-substituted alkynes $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ ^[7g] and $\text{BnSC}\equiv\text{CSBn}$,^[8g] similar cleavages also occurred.

Compared to the C-substituted examples $\text{RC}\equiv\text{CR}$, the thermal stability of heteroatom-substituted acetylenes should follow the order:^[12]



As a part of this program, we describe reactivity studies with 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']dioxaborolan-2'-yl)acetylene (**2**, **bPinBA**)^[13] towards group 4 metallocene complexes. The aim of this work is to find out if the combination of alkynes substituted with electron-deficient boron atoms and the electron-poor early transition metal centres features any uncommon reaction behaviour.

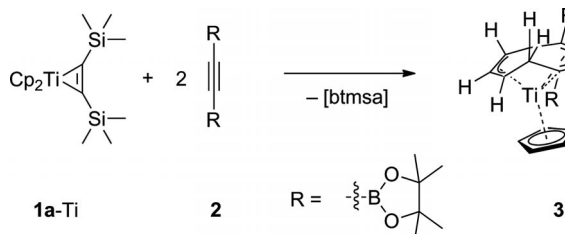
The reactions of the metallocene generators $\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-btmsa})$ [**1a**-Ti: $\text{Cp}' = \text{Cp}$, $\text{M} = \text{Ti}$, $\text{L} = \text{none}$; **1b**-Ti: $\text{Cp}' = \text{Cp}^*$, $\text{M} = \text{Ti}$, $\text{L} = \text{none}$; **1c**-Ti: $\text{Cp}'_2 = \text{rac}(\text{ebthi})$, $\text{M} = \text{Ti}$, $\text{L} = \text{none}$; **1a**-Zr: $\text{Cp}' = \text{Cp}$, $\text{M} = \text{Zr}$, $\text{L} = \text{pyridine}$; **1b**-Zr: $\text{Cp}' = \text{Cp}^*$, $\text{M} = \text{Zr}$, $\text{L} = \text{none}$; **1c**-Zr: $\text{Cp}'_2 = \text{rac}(\text{ebthi})$, $\text{M} = \text{Zr}$, $\text{L} = \text{none}$] with **2** were studied. Ad-

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ditionally, in one case the reactivity of the resulting complex towards CO₂ was investigated.

Results and Discussion

Complex **1a-Ti** reacts with **2** to form **3** by coupling of two alkynes and one of the Cp ligands (Scheme 1). In this special manner, the titanocene generator reacts neither with one alkyne to form the titanacyclopentadiene nor with two alkynes to form the tetrasubstituted titanacyclopentadiene. Instead, the two alkynes are coupled to each other and to one of the cyclopentadienyl ligands, and thus a six-membered ring annelated to a five-membered one originating from the cyclopentadienyl ligand is formed. This moiety will be referred to as dihydroindenyl.



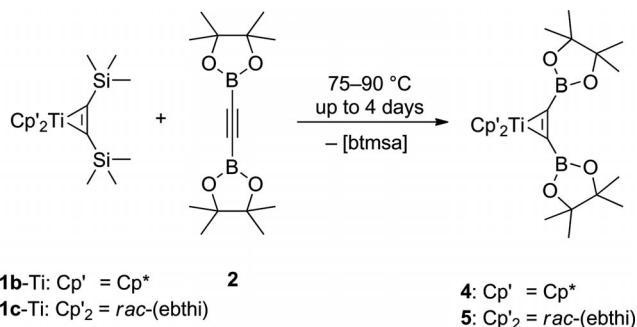
Scheme 1. Unusual Cp ring activation to form **3**.

Unfortunately, crystals suitable for X-ray analysis could not be obtained by recrystallisation of **3** from *n*-hexane, toluene, diethyl ether or tetrahydrofuran (THF). Such a coupling of a Cp ligand with the C₄ unit of a metallacyclopentadiene is very unusual, but not totally new.^[14] It was first found by us in the reaction of **1a-Ti** with two equivalents of Me₃SiC≡Cpy,^[15] in which after elimination of btmsa by alkyne coupling, only two differently tetrasubstituted titanacyclopentadienes were found: the symmetrical product with both Me₃Si groups in α positions and an unsymmetrical one. Although the symmetrically substituted product was stable, the unsymmetrically substituted titanacyclopentadiene gave a similar product as that described here. By these and other reactions, it is evident that titanocene “Cp₂Ti” is not as inert as is usually considered.

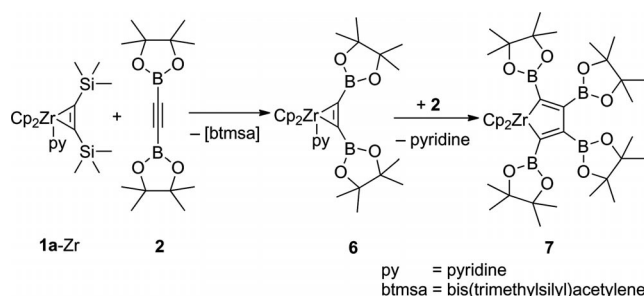
For the reaction of the alkyne **2** with the sterically more demanding titanocene complexes **1b-Ti** and **1c-Ti**, an alkyne exchange and the formation of titanacycloprenes **4** and **5** was observed (Scheme 2).

These reactions with the sterically more demanding metallocene precursors needed high reaction temperatures of 75 and 90 °C, respectively, and longer reaction times of up to four days. The obtained titanacycloprenes represent further examples of such complexes without additional stabilising ligands, which have been very rare to date.

In the reaction of **1a-Zr** with **2**, the btmsa ligand is initially displaced by **2** and Cp₂Zr(py)(η^2 -bPinBA) (**6**) is formed. If the pyridine ligand dissociates, a second alkyne is added, and both alkynes are coupled to form the tetrasubstituted zirconacyclopentadiene **7** (Scheme 3) as shown by NMR experiments.



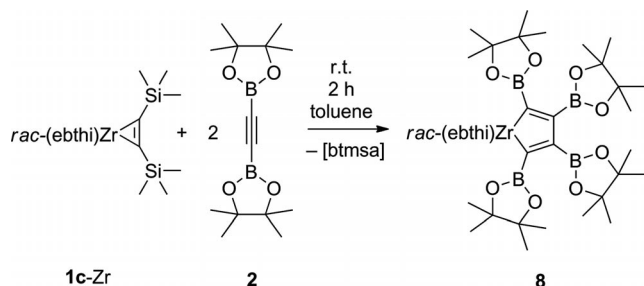
Scheme 2. Alkyne exchange reactions of the sterically more demanding metallocene complexes.



Scheme 3. Synthesis and reactivity of **6**.

This behaviour of the metallacyclopene **6** is the reason why it could be isolated only as a side-product in the reaction with one equivalent of **2**. The zirconacyclopentadiene **7** is the main product. When the stoichiometry of the reaction of **1a-Zr** with **2** was 1:2, only **7** was obtained and no traces of the pyridine-stabilised complex **6** could be detected. To increase the yield of **6**, the second reaction step needs to be suppressed. To achieve this, a mixture of pyridine/toluene/hexane (1:2:2) was used as the reaction medium to discourage the elimination of the pyridine ligand and prevent the reaction with a second alkyne. Furthermore, the zirconocene precursor **1a-Zr** was used in slight excess. These modified reaction conditions yielded 35% of the zirconacyclopene **6** as a red solid [m.p. 131 °C (dec.)].

A change of the Cp ligand to *rac*-(ebthi) in **1c-Zr** yields, in the reaction with **2**, the zirconacyclopentadiene **8** (Scheme 4). The zirconacyclopene was not obtained even by using a 1:1 stoichiometry.



Scheme 4. Coupling of two alkynes and formation of **8**.

The complex **1b**-Zr did not react with **2** even by applying longer reaction times, elevated temperatures and UV irradiation.

The molecular structures of the titanium complex *rac*-(ebthi)Ti(η^2 -bPinBA) (**5**) and the zirconium complex Cp₂Zr(py)(η^2 -bPinBA) (**6**) are depicted in Figures 1 and 2, respectively.

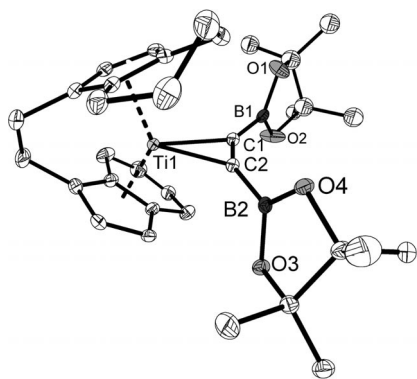


Figure 1. ORTEP drawing of the molecular structure of **5**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

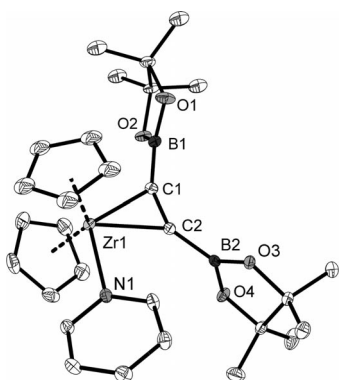


Figure 2. ORTEP drawing of the molecular structure of **6**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

To characterise the alkyne complexation of bPinBA in **5** and **6**, the obtained structural data of these compounds were compared to those of the similar metallacycloprenes of btmsa **1b**-Ti and **1a**-Zr. Selected bond lengths and angles of the complexes are summarised in Table 1. Three parameters are usually used to interpret the strength of the coordination in complexes incorporating the same alkyne: the C1–C2 bond length in the bound alkyne, for which a longer bond indicates stronger coordination; the M–C_{alkyne} distances, for which a greater value implies weaker coordination; and the so-called bend-back angle, which describes the deviation of the C1–C2–X angle from the ideal 180° found in the free alkyne. Here, a larger bend-back angle hints at stronger coordination.^[17] The alkyne bond lengths of 1.289(3) Å for **5** and 1.301(3) Å for **6** are similar to those of the corresponding btmsa complexes **1b**-Ti and **1a**-Zr. These bonds are significantly longer than those of the free alkynes, namely, btmsa [1.208(3) Å]^[16] and bPinBA [1.192(3),

1.199(3) Å].^[13] The M–C_{alkyne} distances of 2.113(2) and 2.106(2) Å for **5** and 2.245(2) and 2.276(2) Å for **6** are also not greatly different from the values found for the corresponding btmsa complexes. This indicates that there is a similar bonding situation in all compounds, which feature a metallacycloprenene with four-electron donation from the alkyne to the metal centre. The coordinated pyridine ligand causes a strong variation of the M–C_{alkyne} distances in **6**; a similar effect was already described for **1a**-Zr.

Table 1. Selected bond lengths and angles of **5** and **6** displayed in comparison with those of **1b**-Ti and **1a**-Zr.^[19]

	5	1b -Ti	6	1a -Zr
C1–C2	1.289(3)	1.309(4)	1.301(3)	1.312(3)
M1–C1	2.113(2)	2.122(3)	2.245(2)	2.216(2)
M1–C2	2.106(2)	2.126(3)	2.276(2)	2.242(2)
C1–C2–B2/Si	149.9(2)	134.8(3)	144.5(2)	138.7(2)
C2–C1–B1/Si	146.8(2)	136.8(3)	153.8(2)	135.5(2)

Probably due to the different substituents of the alkyne and the resulting different steric demand larger C–C–B angles, which correlate with smaller bend-back angles, are obtained for **5** and **6** compared to those in the corresponding btmsa complexes. All in all, it is not possible to evaluate the electronic situation on the basis of these structural data alone. We obtained similar results when we compared the complexation of alkynes by “L₂Ni⁰” and “Cp₂Ti⁰”.^[17]

A better indicator of the electron donation is often given by the shift of the wavenumber of the valence vibration of the alkyne C≡C bond from the free to the coordinated alkyne.^[17] To obtain values for the free alkynes, Raman measurements were needed because the symmetry of the molecule renders the C≡C vibration IR-inactive. Again, a comparison of **5**, **6** and also Cp₂Ti(bPinBA) (**4**) with similar complexes of btmsa is possible (Table 2).

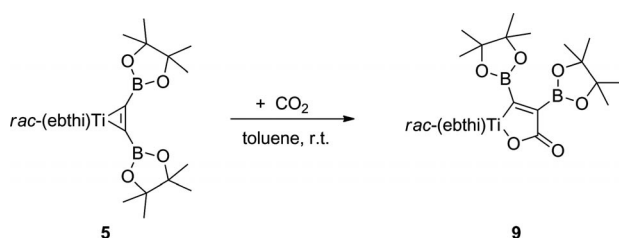
Table 2. C≡C vibration band positions [cm^{−1}] of the btmsa and the bPinBA (**2**) ligand in Ti and Zr complexes and in the free form. The difference to the free alkyne is given in brackets.

Alkyne (L)	Free L	Cp ₂ Zr(py)(L)	<i>rac</i> -(ebthi)Ti(L)	Cp ₂ Ti(L)
bPinBA (2)	2196	1707 (489)	1770 (426)	1719 (477)
btmsa	2107	1579/1599 (528/508)	1594 (513)	1598/1563 (509/544)

The IR bands of the C≡C bond are at 2196 cm^{−1} for free bPinBA and 89 cm^{−1} lower (2107 cm^{−1}) for free btmsa. From this, it is deduced that the free bPinBA ligand has a stronger C≡C bond than free btmsa. Considering the influence of Ti and Zr, the coordination shifts are, as expected, larger for the Zr than for the Ti complexes in both cases. With respect to the different substituents, –SiMe₃ and –BO₂C₂Me₂, the shifts are larger for btmsa than for bPinBA. As a result, it can be deduced that the C1–C2 bond is stronger in the bPinBA complexes than it is in the btmsa complexes. This effect is especially pronounced in *rac*-(ebthi)Ti(η^2 -bPinBA) (**5**), in which this bond is significantly stronger than it is in the Zr complex **6**. Furthermore, the difference in bond strength between free and bound alkyne, represented by the corresponding wavenumbers, is sig-

nificantly smaller in the bPinBA complexes than in the btmsa complexes. This is again especially pronounced in **5**. As electron donation from the alkyne to the metal centre results in a weakened C≡C bond, it could in reverse be surmised that a weaker bond corresponds to stronger donation. Applying this on the above-described results induces the following statements: the bPinBA ligand donates less electron density to the metal centre than the btmsa ligand does. Furthermore, the coordination in the zirconium complex **6** is significantly stronger than that in **5**; a fact that is only pronounced in the bPinBA complexes. The btmsa complexes do not show such a significant difference in their coordination strength. In contrast to the corresponding *rac*-(ebthi) complex **5**, the wavenumber of the vibration of the coordinated C≡C bond for Cp₂Ti(bPinBA) (**4**) is rather low (1719 cm⁻¹) and is very close to that of the above-discussed zirconium complex **6**. This shows that the wavenumber is not influenced by the metal centre and the substituents of the alkyne alone and that the discussion of these values should be done very carefully. Nevertheless, the weaker electron donation from the bPinBA ligand would be in accordance with the smaller deviation from linearity found in the above-described X-ray measurements. An even better indicator for the coordination strength would be the shift of the signals of the alkyne carbon atoms in the ¹³C NMR spectra.^[17] Unfortunately, these signals were strongly broadened by the coupling with the boron atoms and were, therefore, undetectable.

In addition to the structural investigations of the metallacycloprenes, their reactivity towards carbon dioxide was examined (Scheme 5). Therefore, **5** was treated with gaseous dry CO₂. The reaction was immediate and afforded the insertion product **9** as an orange solid [m.p. 129–131 °C (dec.)] in 92% yield.



Scheme 5. Reaction of the titanacycloprenene **5** with carbon dioxide to form the titanafuranone **9**.

In **9**, one molecule of CO₂ was inserted into the M–C bond of the metallacycloprenene to form a titanafuranone directly as a five-membered ring system consisting of the titanium atom, the alkyne and the carbon and one oxygen atom of CO₂. Such ring systems have been reported for a number of complexes, but only from dinuclear complexes and subsequent oxidation with air.^[18]

Conclusions

From the results of this work, it is clear that the existence and reactivity of metallacycloprenes, formed by coordi-

nation of 1,2-bis(4',4',5',5'-tetramethyl[1',3',2']-dioxaborolan-2'-yl)acetylene (bPinBA, **2**), strongly depends on the metal centre and the Cp' and additional ligands. A slightly special reaction of Cp₂Ti(η²-btmsa) (**1a**-Ti) with **2** was observed, which produced no titanacycloprenene and no titanacyclopentadiene, but instead two alkynes coupled with one of the cyclopentadienyl ligands to form a dihydroindenyl ring system in complex **3**. Although this reaction occurs even if a 1:1 stoichiometry is applied, the precursors with more sterically demanding cyclopentadienyl ligands, namely Cp* and *rac*-(ebthi), only react with one equivalent of **2** to yield the titanacycloprenes **5** and **6**, even if an excess of alkyne is applied. Cp₂Zr(py)(btmsa) (**1a**-Zr) reacts with **2** to form the corresponding zirconacycloprenene **6** as a byproduct, in which the pyridine ligand remains coordinated. Elimination of the pyridine ligand leads to coupling with a second molecule of **2** and yields the zirconacyclopentadiene **7** as the main product. In the reaction of the sterically more demanding zirconocene precursor **1c**-Zr with the *rac*-(ebthi) ligand, the zirconacyclopentadiene **8** was obtained, whereas Cp₂Zr(η²-btmsa) (**1b**-Zr) did not react with **2**. The complex *rac*-(ebthi)Ti(η²-bPinBA) (**5**) reacted with carbon dioxide directly to the titanafuranone **9**.

Experimental Section

General: All experiments were conducted with the exclusion of oxygen and moisture. All operations were performed under argon by using standard Schlenk techniques. Prior to use, *n*-hexane and toluene were distilled from sodium tetraethylaluminate and stored under argon. THF and diethyl ether were dried with sodium, distilled from sodium tetraethylaluminate and stored under argon. The metallocene btmsa complexes^[19] and bis(pinacylboryl)acetylene (**2**)^[13] were prepared according to literature procedures. The following instruments were used. Mass spectrometry: MAT 95-XP spectrometer (Thermo Electron). NMR spectroscopy: Bruker AV400 and AV300 spectrometers. ¹H and ¹³C chemical shifts were referenced to the solvent signals: [D₆]benzene (δ_H = 7.16 ppm, δ_C = 128.0 ppm). IR spectroscopy: Nicolet 6700 FT-IR spectrometer with a smart endurance attenuated total reflection (ATR) device and a Bruker Alpha FT-IR spectrometer. Melting points: Mettler Toledo MP70 instrument. Melting points were measured with samples in sealed capillaries. Elemental analyses: Leco Tru Spec elemental analyzer. X-ray analysis: Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F² (SHELXL-97).^[20] The Diamond program was used to produce graphical representations.^[21]

CCDC-924626 (for **5**) and -924625 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CpTiC₉H₅(BO₂C₂Me₂)₄ (3**):** Cp₂Ti(η²-btmsa) (**1a**-Ti, 1 equiv., 0.5 mmol, 178 mg) and **2** (1 equiv., 0.5 mmol, 139 mg) were each dissolved in dry toluene (15 mL). The solution of **2** was added to the stirred solution of **1a**-Ti at room temp., whereupon the colour began to change from yellow-brown to dark green-brown. The solution was stirred vigorously for a short time and then left to

stand at room temp. overnight to yield brown needles. Recrystallisation in toluene afforded pure **3** as brown crystals, yield 88 mg (48%), m.p. 184 °C (dec.). $C_{38}H_{58}B_4O_8Ti$ (734.01): calcd. C 62.18, H 7.96; found C 62.52, H 7.85. 1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 1.17, 1.21, 1.47, 1.48 (s, 12 H, CH_3); 1.93 (t, 3J = 1.6 Hz, 2 H, CH); 3.63 (dt, 3J = 3.2, 1.6 Hz, 2 H, CH); 5.39 (s, 5 H, Cp); 5.46 (t, 3J = 3.3 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 21.9, 24.4, 25.1, 25.5, 25.7, 58.7, 82.4, 83.7 [CO, CH, CH_3]; 101.1 (Cp) ppm. MS (EI, 70 eV): m/z (%) = 733 (11) [M^+], 620 (3), 607 (3), 494 (7), 367 (6), 83 (100). IR (ATR): $\tilde{\nu}$ = 2993 (w), 2974 (w), 2927 (w), 2882 (w), 1384 (m), 1366 (m), 1338 (w), 1303 (m), 1264 (m), 1247 (m), 1214 (m), 1199 (w), 1141 (s), 1111 (m), 1080 (w), 1066 (m), 1009 (w) cm^{-1} .

Cp*₂Ti(η^2 -bPinBA) (4): Cp*₂Ti(η^2 -btmsa) (**1b**-Ti, 1 equiv., 0.5 mmol, 244 mg) and **2** (1 equiv., 0.5 mmol, 139 mg) were each dissolved in dry toluene (15 mL). The solution of **2** was added to the stirred solution of **1b**-Ti at room temp.; no change in colour was observed. The solution was stirred at 75 °C for 3 d, which resulted in a green solution, and an NMR experiment confirmed the completion of the reaction. The solvent was removed in vacuo, and the residue was recrystallised from *n*-hexane/toluene (30:1) to yield **4** as brown-green crystals, yield 195.5 mg (65%), m.p. 132 °C (dec.). $C_{34}H_{54}B_2O_4Ti$ (596.32): calcd. C 68.49, H 9.13; found C 67.49, H 9.25. IR (ATR): $\tilde{\nu}$ = 1719 (C≡C) cm^{-1} . 1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 1.02 (s, 24 H, CM_e_2), 1.88 (s, 30 H, Cp*) ppm. ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 12.1 (Cp*), 24.8 (Me), 81.7 (OCMe₂), 121.6 (Cp*) ppm. MS (EI, 70 eV): m/z (%) = 595 (3) [M^+], 461 (16), 326 (5), 318 (100), 83 (11).

rac-(ebthi)Ti(η^2 -bPinBA) (5): *rac*-(ebthi)Ti(η^2 -btmsa) (**1c**-Ti, 1 equiv., 0.5 mmol, 241 mg) and **2** (1 equiv., 0.5 mmol, 139 mg) were each dissolved in dry toluene (15 mL). The solution of **2** was added to the stirred solution of **1c**-Ti at room temp.; no change in colour was observed. The solution was stirred at 90 °C for 3 d and turned brown-green. The solvent was removed in vacuo, and the residue was dissolved in *n*-hexane and stored at –30 °C for two days. Green crystals of **5** suitable for X-ray measurements were obtained, yield 207 mg (70%), m.p. 210–213 °C (dec.). $C_{34}H_{48}B_2O_4Ti$ (590.27): calcd. C 68.97, H 8.30; found C 69.19, H 8.20. IR (ATR): $\tilde{\nu}$ = 1770 (C≡C) cm^{-1} . 1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 0.54–0.66 (m, 2 H, CH_2); 0.97, 0.98 (s, 24 H, CH_3); 0.80–1.26, 1.43–1.55, 1.64–1.76, 1.83–1.99, 2.02–2.20, 3.38–3.50, 3.61–3.73 (m, 20 H, CH_2); 4.32 (d, J = 3.2 Hz, 2 H, CH); 8.76 (d, J = 3.2 Hz, 2 H, CH) ppm. ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 23.2, 24.0, 24.4 (ebthi); 24.8, 25.0 (Me); 25.1, 26.6 (ebthi); 82.0 (OCMe₂); 114.1, 115.9, 124.5, 126.6, 127.5 (ebthi) ppm. MS (EI, 70 eV): m/z (%) = 590 (1) [M^+], 532 (2), 312 (100).

Cp₂Zr(py)(η^2 -bPinBA) (6): Alkyne **2** (0.9 equiv., 0.5 mmol, 278 mg) was dissolved in toluene (8 mL) and added to a stirred solution of Cp₂Zr(py)(η^2 -btmsa) (**1a**-Zr, 1 equiv., 0.55 mmol, 261.6 mg) in *n*-hexane (8 mL) and pyridine (4 mL). The colour quickly began to change from dark lilac to red-brown. The solution was stirred for 1 min and left at room temp. overnight. Thereupon, all volatiles were removed in vacuo, and the residue was dissolved in *n*-hexane/pyridine (30:1). The solution was stored at –30 °C for 1 d. The bright red precipitate was collected by filtration and dried to yield **6**, yield 100 mg (0.173 mmol, 35%), m.p. 131 °C (dec.). $C_{29}H_{39}B_2NO_4Zr$ (578.47): calcd. C 60.21, H 6.80, N 2.42; found C 55.55, H 6.76, N 1.86. IR (ATR): $\tilde{\nu}$ = 1707 (C≡C) cm^{-1} . 1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 1.15 (s, 12 H, CH_3), 1.29 (s, 12 H, CH_3), 5.65 (s, 10 H, Cp), 6.56 (m, 2 H, *m*-py), 8.53 (m, 1 H, *p*-py), 9.15 (m, 2 H, *o*-py) ppm. ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 25.2, 25.2 (CH_3); 81.8, 82.0 (OCMe₂); 107.1 (Cp); 123.3, 136.6,

155.4 (py) ppm. MS (CI, isobutane): m/z (%) = 557 (7) [M^+], 499 (47), 441 (5), 367 (5), 279 (61).

Cp₂Zr[C₄(BO₂C₂Me₂)₄] (7): Cp₂Zr(py)(η^2 -btmsa) (**1a**-Zr, 1 equiv., 0.5 mmol, 236 mg) and **2** (2 equiv., 1 mmol, 278 mg) were each dissolved in dry toluene (15 mL). The solution of **2** was added to the stirred solution of **1a**-Zr at room temp.; the colour changed immediately from dark violet to yellow-brown. After 2 h, the solution had turned red-brown, and an NMR experiment revealed complete consumption of **1a**-Zr. The solvent was removed in vacuo, and the residue was dissolved in *n*-hexane. The solution was stored at –30 °C overnight to yield **7** as bright orange crystals, yield 323 mg (0.416 mmol, 83%), m.p. 215–216 °C. $C_{38}H_{58}B_4O_8Zr$ (777.33): calcd. C 58.71, H 7.52; found C 57.76, H 7.99. 1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 1.24, 1.26 (s, 48 H, CH_3); 6.16 (s, 10 H, Cp) ppm. ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 25.0, 25.3 (CH_3); 81.9, 83.0 (OCMe₂); 111.3 (Cp) ppm. MS (EI, 70 eV): m/z (%) = 776 (2) [M^+], 499 (14), 220 (16).

Reaction of 6 with 2: Compound **6** (1 equiv., 0.052 mmol, 30 mg) and **2** (1 equiv., 0.052 mmol, 15 mg) were transferred under argon into a Young NMR tube and dissolved in C_6D_6 . Upon mixing, the initial dark red colour disappeared, and the solution turned bright orange. NMR spectroscopy revealed the product to be Cp₂Zr[C₄(BO₂C₂Me₂)₄] (**7**). Free pyridine was also observed.

rac-(ebthi)Zr[C₄(BO₂C₂Me₂)₄] (8): *rac*-(ebthi)Zr(η^2 -btmsa) (**1c**-Zr, 1 equiv., 0.5 mmol, 261 mg) and **2** (1 equiv., 0.5 mmol, 139 mg) were each dissolved in dry toluene (15 mL). The solution of **2** was added to the stirred solution of **1c**-Zr at room temp.; no change in colour was observed. The solution was stirred for two days at 90 °C. The solution turned red-brown and an NMR experiment showed no **2** in the reaction mixture. The solvent was removed in vacuo, and the residue was dissolved in *n*-hexane. The solution was stored at –78 °C for 3 d, and **8** precipitated as a yellow solid. The solution was concentrated and again stored at –78 °C to yield more **8**, yield 57.9 g (25%), m.p. 229–231 °C. $C_{48}H_{72}B_4O_8Zr$ (911.55): calcd. C 63.25, H 7.96; found C 63.03, H 8.10. 1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 1.15–1.51 (m, 52 H, CH_3 , CH_2), 2.06–2.84 (m, 16 H, CH_2), 5.63 (d, J = 3.0 Hz, 2 H, Cp), 6.76 (d, J = 3.0 Hz, 2 H, Cp) ppm. ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 22.4, 23.2, 23.7, 23.7, 24.1, 24.7, 25.7, 26.6, 27.0 (CH_2 , CH_3); 82.1, 83.2 (OCMe₂); 103.4, 115.1, 121.8, 122.5, 124.0 (Cp) ppm. MS (EI, 70 eV): m/z (%) = 910 (2) [M^+], 826 (1), 784 (2), 632 (8), 354 (36).

Titanafuranone 9: *rac*-(ebthi)Ti(η^2 -bPinBA) (**5**, 0.153 mmol, 90 mg) was dissolved in toluene in a three-necked-flask equipped with a pressure release valve. CO₂ (from solid CO₂) was passed through a column filled with P₄O₁₀ and then bubbled through the solution of **5**. The colour immediately changed from green to orange. After 5 min, the inflow of CO₂ was stopped and all volatiles were removed in vacuo. The residue was dissolved in *n*-hexane and the solution stored at –78 °C to yield the insertion product **9** as orange solid, yield 89 mg (92%), m.p. 129–131 °C. $C_{35}H_{48}B_2O_6Ti$ (634.28): calcd. C 66.28, H 7.63; found C 66.52, H 7.751. IR (ATR): $\tilde{\nu}$ = 1626 (C=O) cm^{-1} . 1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 1.08–1.51 (m, 28 H), 1.54–1.87 (m, 6 H), 1.99–2.18 (m, 3 H), 2.33–2.43 (m, 3 H), 2.55–2.81 (m, 2 H), 2.81–3.01 (m, 1 H), 3.14–3.39 (m, 1 H), 4.91 (d, J = 2.9 Hz, 1 H), 5.38 (d, J = 3.2 Hz, 1 H), 6.33 (d, J = 3.2 Hz, 1 H), 7.53 (d, J = 3.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 21.8, 22.0, 22.3, 22.4, 23.9, 24.0, 24.2, 24.8, 25.0, 25.4, 25.6, 27.2, 27.6 (CH_2 , CH_3); 82.7, 83.1 (OCMe₂); 110.8, 111.4, 119.8, 124.6, 126.8, 127.2, 129.0, 129.8, 130.8, 134.0 (Ar); 164.6 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 910 (2) [M^+], 826 (1), 784 (2), 632 (8), 354 (36). MS (70 eV) [EI]: m/z = (3) [M^+] 635, 606 (6), 589 (1), 355 (10), 312 (15), 305 (54).

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- [1] T. S. N. Suzuki, Y. Sakaguchi, Y. Masuyama, *Pure Appl. Chem.* **2011**, *83*, 1781–1788.
- [2] U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2005**, *24*, 456–471.
- [3] U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack, V. V. Burlakov, *Angew. Chem.* **1994**, *106*, 1678–1680; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1605–1607.
- [4] N. Suzuki, M. Nishiura, Y. Wakatsuki, *Science* **2002**, *295*, 660–663.
- [5] T. Beweries, U. Rosenthal, *Science of Synthesis Knowledge Updates 2011/4*, **2011**, Thieme, Stuttgart, Germany, New York, p. 11–71.
- [6] For selected examples, see: a) J. A. Acho, S. J. Lippard, *Organometallics* **1994**, *13*, 1294–1299; b) C. Collazo, D. Rodewald, H. Schmidt, D. Rehder, *Organometallics* **1996**, *15*, 4884–4887; c) P. W. R. Corfield, L. M. Baltusis, S. J. Lippard, *Inorg. Chem.* **1981**, *20*, 922–929; d) J. C. Dewan, C. M. Giandomenico, S. J. Lippard, *Inorg. Chem.* **1981**, *20*, 4069–4074; e) A. C. Filippou, W. Grünleitner, C. Völkl, P. Kiprof, *Angew. Chem.* **1991**, *103*, 1188–1191; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1167–1169; f) A. C. Filippou, C. Völkl, W. Grünleitner, P. Kiprof, *J. Organomet. Chem.* **1992**, *434*, 201–223; g) C. T. Lam, P. W. R. Corfield, S. J. Lippard, *J. Am. Chem. Soc.* **1977**, *99*, 617–618; h) A. R. Petrov, T. Bannenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Dalton Trans.* **2011**, *40*, 10503–10512; i) selected examples for group 4 metallocenes were studied by O. Arias, M. Tamm (unpublished results).
- [7] For selected examples, see: a) F.-E. Hong, Y. Chang, Y. Chang, R.-E. Chang, S.-C. Chen, B.-T. Ko, *Organometallics* **2002**, *21*, 961–967; b) F.-E. Hong, Y.-C. Huang, S.-L. Wang, F.-L. Liao, *Inorg. Chem. Commun.* **1999**, *2*, 450–452; c) A. K. Powell, M. J. Went, *J. Chem. Soc., Dalton Trans.* **1992**, 439–445; d) P. Sevilano, O. Fuhr, D. Fenske, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1783–1786; e) P. Sevilano, S. Koenig, D. Himmel, O. Fuhr, D. Fenske, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2236–2240; f) D. Rodewald, C. Schulzke, D. Rehder, *J. Organomet. Chem.* **1995**, *498*, 29–35; g) for selected examples for group 4 metallocenes, see: M. Haehnel, *PhD Thesis*, University of Rostock, Germany, publication expected in **2013**.
- [8] For selected examples, see: a) A. Bou, M. A. Pericàs, F. Serratos, *Tetrahedron* **1981**, *37*, 1441–1449; b) M. E. García, D. García-Vivó, M. A. Ruiz, *Organometallics* **2008**, *27*, 543–554; c) R. Gleiter, D. B. Werz, F. Rominger, E. Zhutov, N. S. Zefirov, M. V. Proskurnina, *Eur. J. Org. Chem.* **2007**, 5834–5839; d) A. Messeguer, F. Serratos, J. Rivera, *Tetrahedron Lett.* **1973**, *14*, 2895–2898; e) P. A. Bianconi, S. J. Lippard, C. P. Rao, R. N. Vrtis, Massachusetts Institute of Technology, US5026884 (A), **1991**; f) R. N. Vrtis, S. G. Bott, R. L. Rardin, S. J. Lippard, *Organometallics* **1991**, *10*, 1364–1373; g) for selected Examples for group 4 metallocenes: K. Altenburger, *PhD Thesis*, University of Rostock, Germany, publication expected in **2014**.
- [9] For selected examples, see: a) W. W. Seidel, M. Schaffrath, T. Pape, *Angew. Chem.* **2005**, *117*, 7976–7979; *Angew. Chem. Int. Ed.* **2005**, *44*, 7798–7800; b) W. W. Seidel, M. Schaffrath, T. Pape, *Chem. Commun.* **2006**, 3999–4000; c) W. W. Seidel, M. J. Meel, U. Radius, M. Schaffrath, T. Pape, *Inorg. Chem.* **2007**, *46*, 9616–9629; d) W. W. Seidel, M. J. Meel, F. Hupka, J. J. Weigand, *Dalton Trans.* **2010**, *39*, 624–631; e) for selected examples for group 4 metallocenes, see: K. Altenburger, *PhD Thesis*, University of Rostock, Germany, publication expected in **2014**.
- [10] P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, V. V. Burlakov, V. B. Shur, *Angew. Chem.* **2003**, *115*, 1455; *Angew. Chem. Int. Ed.* **2003**, *42*, 1414.
- [11] V. Varga, K. Mach, J. Hiller, U. Thewalt, P. Sedmera, M. Polášek, *Organometallics* **1995**, *14*, 1410–1416.
- [12] F. Serratos, *J. Chem. Educ.* **1973**, *50*, 402–403.
- [13] Y. K. Kang, P. Deria, M. J. Therien, University of Pennsylvania, US2011257356 (A1), **2011**.
- [14] a) A. Tillack, W. Baumann, A. Ohff, C. Lefebvre, A. Spannenberg, R. Kempe, U. Rosenthal, *J. Organomet. Chem.* **1996**, *520*, 187–193; b) D. Thomas, N. Peulecke, V. V. Burlakov, B. Heller, W. Baumann, A. Spannenberg, R. Kempe, U. Rosenthal, R. Beckhaus, *Z. Anorg. Allg. Chem.* **1998**, *624*, 919–924; c) Z. Song, Y.-F. Hsieh, K.-I. Kanno, K. Nakajima, T. Takahashi, *Organometallics* **2011**, *30*, 844–851.
- [15] a) U. Rosenthal, C. Lefebvre, P. Arndt, A. Tillack, W. Baumann, R. Kempe, V. V. Burlakov, *J. Organomet. Chem.* **1995**, *503*, 221–223; b) C. H. Suresh, N. Koga, *Organometallics* **2006**, *25*, 1924–1931.
- [16] J. Bruckmann, C. Krüger, *Acta Crystallogr., Sect. C* **1997**, *53*, 1845–1846.
- [17] a) U. Rosenthal, C. Nauck, P. Arndt, S. Pulst, W. Baumann, V. V. Burlakov, H. Görls, *J. Organomet. Chem.* **1994**, *484*, 81–87; b) U. Rosenthal, H. Görls, *J. Organomet. Chem.* **1988**, *348*, 135–139.
- [18] a) D. Thomas, N. Peulecke, V. V. Burlakov, W. Baumann, A. Spannenberg, R. Kempe, U. Rosenthal, *Eur. J. Inorg. Chem.* **1998**, 1495–1502; b) V. V. Burlakov, A. I. Yanovsky, Y. T. Struchkov, U. Rosenthal, A. Spannenberg, R. Kempe, O. G. Ellert, V. B. Shur, *J. Organomet. Chem.* **1997**, *542*, 105–112.
- [19] For **1a**-Ti, **1b**-Ti, see: V. V. Burlakov, A. V. Polyakov, A. I. Yanovsky, Y. T. Struchkov, V. B. Shur, M. E. Vol'pin, U. Rosenthal, H. Görls, *J. Organomet. Chem.* **1994**, *476*, 197–206; for **1a**-Zr, see: U. Rosenthal, A. Ohff, W. Baumann, A. Tillack, H. Görls, V. V. Burlakov, V. B. Shur, *Z. Anorg. Allg. Chem.* **1995**, *621*, 77–83; for **1b**-Zr, see: J. Hiller, U. Thewalt, M. Polášek, L. Petrusová, V. Varga, P. Sedmera, K. Mach, *Organometallics* **1996**, *15*, 3752–3759; for **1c**-Ti, **1c**-Zr, see: C. Lefebvre, W. Baumann, A. Tillack, R. Kempe, H. Görls, U. Rosenthal, *Organometallics* **1996**, *15*, 3486–3490.
- [20] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
- [21] K. Brandenburg, *DIAMOND*, v. 3.1e, Crystal Impact Gbr, **2007**, Bonn, Germany.

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