Formation of the [(*s-trans*-η⁴-Butadiene)TaCp*Cp]⁺ Cation and Its Reaction with Organic Carbonyl Derivatives

Hans Christian Strauch,[a] Gerhard Erker,*[a] Roland Fröhlich,[a][+] and Maija Nissinen[a][+]

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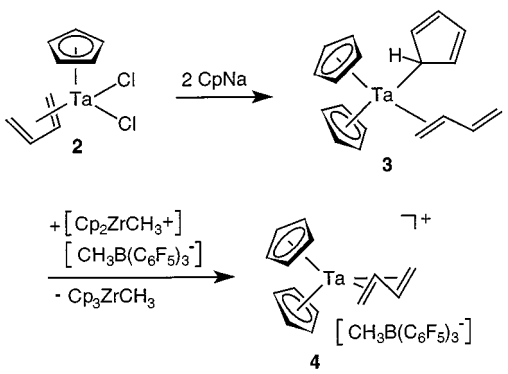
(Butadiene)TaCp*Cl_2 (**6**) was treated with CpNa to yield (η²-butadiene)TaCp*CpCl (**7**). Subsequent reaction with $[Cp_2ZrCH_3^+][CH_3B(C_6F_5)_3^-]$ resulted in transfer of the chloride ligand from tantalum to zirconium with formation of the [(*s-trans*-η⁴-butadiene)TaCp*Cp]⁺ cation [**8**, with $CH_3B(C_6F_5)_3^-$ anion]. Complex **8** was characterized spectroscopically and by an X-ray crystal structure analysis. The group-5 [(*s-trans*-η⁴-C_4H_6)TaCp*Cp]⁺ bent metallocene cation complex **8** reacts with ketones (acetone, adamantanone) to yield the corresponding seven-membered 2-tantalatetrahydrooxepine cation complexes (**9**, **10**). 1-Cyanoadamantane reacts with **8** to yield the 2-tantala-3,6-dihydro-2*H*-azepine cation system **11**. Activation of **8** with methylalumoxane gives an active ethene polymerization catalyst.

Introduction

(Butadiene)zirconocene (**1**) was the first organometallic example exhibiting a stable *s-trans*-η⁴-conjugated diene coordination to a single transition metal center.[1] Since then a variety of additional examples have been found and described,[2] but mononuclear (*s-trans*-η⁴-butadiene)metal complexes are still not too frequently encountered. The (butadiene)zirconocene system has turned out to be a very useful reagent in organic and organometallic synthesis, serving as a mildly nucleophilic C_4-building block,[3] and it has successfully been applied as a suitable catalyst precursor in homogeneous metallocene Ziegler catalysis.[4] Therefore, we considered it desirable to expand the scope of such (butadiene) bent metallocene chemistry and search for additional examples of (η⁴-butadiene)metallocenes that are structurally and chemically related to the parent system **1** and its congeners.

We have recently synthesized the group-5 metal analogue of (butadiene)hafnocene. Our synthesis started from the readily available complex (η-cyclopentadienyl)(*s-cis*-η⁴-butadiene)$TaCl_2$ (**2**)[5] that was treated with two molar equivalents of CpNa to yield $(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})(\eta^2\text{-butadiene})$tantalum (**3**). Subsequent treatment with $[Cp_2ZrCH_3^+][CH_3B(C_6F_5)_3^-]$[6] led to a clean transfer of a Cp-anion ligand to give the neutral Cp_3ZrCH_3[7] and the [(*s-trans*-η⁴-butadiene)$TaCp_2$]⁺ cation complex **4** (isolated with $CH_3B(C_6F_5)_3^-$ anion).[8] Spectroscopically and structurally complex **4** behaves as an isoelectronic analogue of the neutral (*s-trans*-η⁴-butadiene)hafnocene. The system **4** appears to be the first simple cationic group-5 equivalent of the well-established group-4 (η⁴-conjugated diene)metallocene complexes.[9] First scouting experiments have revealed that **4** also adds a variety of unsaturated reagents, similarly as **1**, to yield heterometallacyclic ring systems,[10] although the reactivity of the cationic group-5 metal complex system **4** seemed to be lower than that of the group-4 analogue **1**.

We have now developed a synthetic pathway to a second example of a group-5 (*s-trans*-η⁴-butadiene)metallocene cation system. The system contains a pentamethylcyclopentadienyl ligand that allows for a different synthetic entry and results in increased activities of the group-5 bent metallocene systems. Moreover, the presence of two differently substituted cyclopentadienide moieties at tantalum introduces an additional stereochemical marker into the system that has been useful in controlling the dynamic features of a variety of derived organometallic ring systems. The preparation of [(*s-trans*-η⁴-butadiene)TaCp*Cp]⁺ (**8**), its structural and spectroscopic characterization and the preliminary results of a few representative addition reactions are described in this article.



Scheme 1

[a] Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, D-48149 Münster, Germany
Fax: (internat.) + 49(0)251/8336503
E-mail: erker@uni-muenster.de
[+] X-ray crystal structure analysis.

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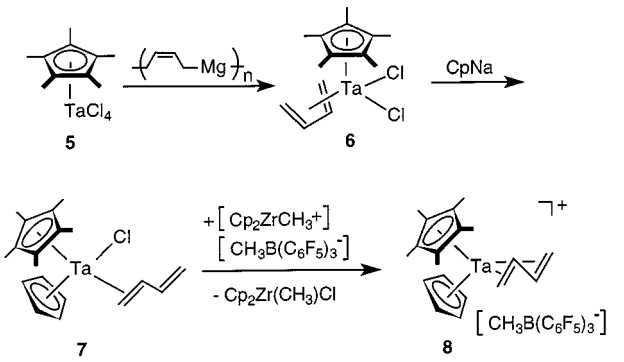
Results and Discussion

Our synthesis of the new group-5 (butadiene) bent metallocene cation system **8** starts from Cp^*TaCl_4 (**5**) which is readily available by treatment of $TaCl_5$ with (trimethylsilyl)-pentamethylcyclopentadiene, as described by W. A. Herrmann et al.[11] This was then treated with ca. one molar equivalent of the oligomeric (butadiene)magnesium reagent,[12] according to the procedure developed by H. Yasuda et al.,[13] to yield (*s-cis*-η^4-butadiene)$TaCp^*Cl_2$ (**6**). We have then treated **6** with ca. one molar equivalent of sodium cyclopentadienide in tetrahydrofuran at 0 °C. This resulted in the formation of the (η^2-butadiene)TaCp*CpCl complex **7**, isolated in 45% yield as a pale brown solid.

The η^2-coordination of the butadiene ligand to the tantalum center in **7** was deduced from its NMR spectra.[14] The ^{13}C-NMR spectrum shows two pairs of butadiene resonances at δ = 111.2 and 157.4 (noncoordinated $H_2C^4{=}C^3H$ moiety) and δ = 42.4 and 60.4 (η^2-coordinated $H_2C^1{=}C^2H$ unit). The η^2-butadiene ligand features ^{1}H-NMR resonances at δ = 0.88, 1.37 (1-H, 1-H′), 0.71 (2-H) of the coordinated vinyl group and δ = 6.33 (3-H), 4.27, and 4.00 (4-H,H′) of the free butadiene vinyl moiety.



Scheme 2

Complex **7** was then treated with $[Cp_2ZrCH_3^+]$-$[CH_3B(C_6F_5)_3^-]$[6] at room temperature in toluene solution. The tantalum-containing product precipitated as an oil, and it was shown by NMR spectroscopy that the supernatant toluene phase contained the neutral zirconium product $Cp_2Zr(CH_3)Cl$.[15] The oil was recovered and solidified by treatment with pentane and shown to consist of [CpCp* Ta(butadiene)$^+$][$CH_3B(C_6F_5)_3^-$] (**8**, isolated in > 80% yield). Thus, treatment of Cp*Cp(η^2-butadiene)TaCl (**7**) with the $Cp_2ZrCH_3^+$ cation has selectively resulted in transfer of the chloride ligand from tantalum to zirconium. The resulting tantalum complex contains an *s-trans*-η^4-butadiene ligand. This is evident from the NMR spectra which are to be compared with the characteristic NMR features of the *s-trans*-η^4-C_4H_6 ligand system in (*s-trans*-η^4-butadiene)zirconocene[1][9] [^{1}H NMR: δ = 1.2 (1-,4-H_{anti}), 3.2 (1-,4-H_{syn}), 2.9 (2-,3-H)] or in [(*s-trans*-η^4-C_4H_6)$TaCp_2$]$^+$ cation (**4**)[8] [^{1}H NMR: δ = 1.45 (1-,4-H_{anti}), 3.15 (1-,4-H_{syn}), 2.95 (2-,3-H) in [D_5]bromobenzene; ^{13}C NMR: δ = 57.8 (C-1, -4), 90.1 (C-2, -3) in [D_2]dichloromethane]. Due to the lower symmetry (**4**: C_2; **8**: C_1) the [(*s-trans*-η^4-butadiene)TaCp*Cp]$^+$ cation exhibits four ^{13}C-NMR signals of the η^4-coordinated *s-trans*-C_4H_6 ligand at δ = 59.8 (C-1), 64.3 (C-4), 91.2 (C-2), and 93.6 (C-3). As expected, all six butadiene hydrogen atoms are different due to the unsymmetric structure of **8** in solution. The corresponding ^{1}H-NMR signals appear in the very characteristical range as expected for the (*s-trans*-η^4-butadiene)Ta$^+$ moiety at δ = 0.88 (1-H_{anti}), 2.91 (1-H_{syn}), 1.61 (4-H_{anti}), 2.53 (4-H_{syn}), 3.04 (2-H), 1.61 (3-H).

Pentane vapor was allowed to diffuse into a solution containing 30 mg of **8** in 2 mL of dichloromethane to give single crystals suited for the X-ray crystal structure analysis (see Figure 1). This analysis confirmed the formation of the [(*s-trans*-η^4-butadiene)TaCp*Cp]$^+$ cation complex. The Ta−C(butadiene) distances are between 2.35 and 2.28 Å. Unfortunately, the structure suffers from considerable disorder problems (for details see the Experimental Section) so that structural details will not be discussed (Cp-ring and the butadiene ligand were refined with restraints).

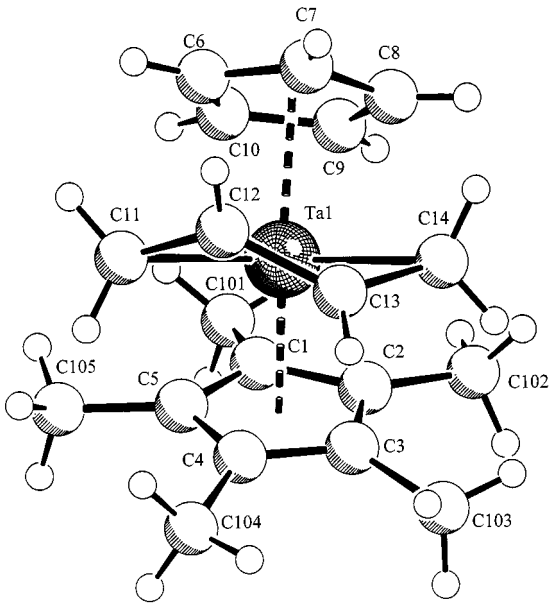


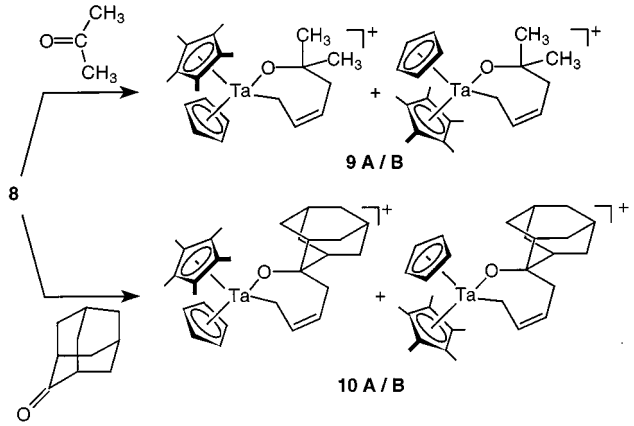
Figure 1. Molecular geometry of **8** in the crystal (cation only)

Both (butadiene)zirconocene and (butadiene)tantalocene cation react with a variety of organic carbonyl compounds and derivatives to yield the corresponding seven-membered 2-metalla-tetrahydrooxepine systems.[8−10] In order to characterize the chemical behavior of **8** we have consequently treated the [(*s-trans*-η^4-butadiene)TaCp*Cp]$^+$ cation complex with a few selected ketones and with a nitrile.

Complex **8** reacts with excess acetone at 50 °C (3 h) resulting in the incorporation of one equivalent of the carbonyl compound. The tantalatetrahydrooxepine cation **9** was isolated in ca. 70% yield. The NMR spectra show that two isomers were formed in a 1:1 ratio. These exhibit the same atom connectivity. They constitute two conformational isomers (isotopomers).[16] It is well-known that such metallatetrahydrooxepines contain nonplanar seven-

membered ring frameworks.[10] To a first approximation these contain two nearly planar subunits (in **9** the planes are defined by the atoms C3,Ta,O,C7,C6 and C3−C6) with an angle between these two planes of ca. 40−50°. Thus, in the case of **9** the two diastereoisomers are characterized by having the $C^4{=}C^5$ double bond oriented *syn* or *anti* to the Cp* ligand. Often such isotopomers rapidly equilibrate on the NMR time scale,[8][10] but in the case of **9** the thermally induced ring-inversion process seems to be kinetically hindered, potentially by an unfavorable transannular Cp*/CH_3 1,3-interaction in the transition state, so that the isomers **9A** and **9B** are distinguished by their separate NMR signals at 150/600 MHz at ambient temperature.

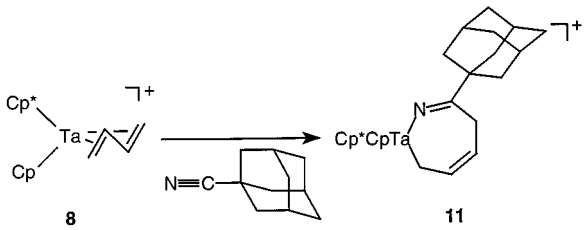
We observe a ^{1}H NMR Cp singlet for **9A** at δ = 5.78, for **9B** at δ = 6.04. Complex **9A** exhibits two methyl singlets at δ = 1.40 and 1.22; the corresponding 7-CH_3 signals of **9B** are at δ = 1.49 and 1.09, and each of the complexes exhibits distinctly different AB-type multiplets of their C^6H_2 and C^3H_2 groups (for details see the Experimental Section).



Scheme 3

Even the bulky ketone 2-adamantanone reacts analogously with the [(*s-trans*-η⁴-butadiene)TaCp*Cp]⁺ cation (**8**). The seven-membered metallacyclic cation complex **10** [with $CH_3B(C_6F_5)_3^-$ anion] was isolated from the reaction mixture in close to 60% yield. Again, a mixture of two isotopomers was observed by NMR spectroscopy at ambient temperature in a 70:30 ratio. The major isomer **10A** exhibits a ^{1}H-NMR Cp singlet at δ = 5.77, whereas the minor **10B** shows the corresponding Cp signal at δ = 6.01 (for additional spectroscopic data see the Experimental Section).

1-Cyanoadamantane reacts cleanly with **8** to yield the 3,6-dihydro-2-tantala-2*H*-azepine cation **11** (> 70% isolated). In this case only a single set of NMR resonances was observed (^{1}H-NMR Cp signal at δ = 5.67, 6-H/H′ multiplet at δ = 3.32 and 1.77, 3-H/H′ multiplet at δ = 1.55 and 0.85). From these data it is not clear whether only a single isotopomer of **11** is present or if the two possible diastereomers **11A/B** are rapidly interconverting by thermally induced ring inversion which is rapid on the NMR time scale under the conditions of the measurement.[8]



Scheme 4

Both the complexes [(*s-trans*-η⁴-butadiene)TaCp$_2$]⁺ cation (**4**) and [(*s-trans*-η⁴-butadiene)TaCp*Cp]⁺ (**8**) may serve as organometallic precursors for the generation of active homogeneous metallocene Ziegler catalyst systems. In a few scouting experiments we have treated **4** or **8** with a large excess of methylalumoxane in toluene. Subsequent introduction of ethene led to the formation of polyethylene (for details see Table 1 and the Experimental Section).

Table 1. Ethene polymerization with the homogeneous **4**/MAO and **8**/MAO Ziegler catalysts[a]

Precursor	μmol of cat.	Al/Ta	*T* [°C]	g of PE	m.p.	act[b]
4	22.4	1470	40	2.4	127	107
4	22.4	1470	50	2.8	128	125
4	22.4	1470	70	4.4	129	196
8	20.8	1580	40	4.1	127	198
8	20.8	1580	50	4.8	128	231
8	20.8	1580	70	7.3	129	351

[a] Reactions in 220 mL of toluene, Büchi glass autoclave at 2 bar ethene pressure. − [b] kg [PE]/mol(cat)·bar·h.

Our study has shown that [Cp*CpTa(*s-trans*-η⁴-butadiene)]⁺ cation as a second example of a stable (*s-trans*-η⁴-conjugated diene)tantalocene cation complex is readily available. The *s-trans*-η⁴-diene coordination mode appears to be even more favored at the group-5 than at the group-4 bent metallocene − the corresponding isoelectronic hafnocene complexes feature a thermodynamically favored *s-cis*-η⁴-diene coordination[17] [the (*s-trans*-η⁴-diene)HfCp$_2$ isomers can be generated photochemically at low temperature].[9] The (butadiene)tantalocene cation examples known so far seem to react cleanly with a variety of unsaturated organic substrates by selective carbon−carbon coupling. These new readily available reagents are potentially useful as stoichiometric C_4-delivering building blocks in organic synthesis and as catalyst precursors.

Experimental Section

Reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for the spectroscopic characterization) were dried and distilled under argon prior to use {dichloromethane, bromobenzene: P_4O_{10} (Sicapent); ether, pentane: $LiAlH_4$; THF: potassium/benzophenone; toluene: sodium/benzophenone; CD_2Cl_2, $CDCl_3$: P_4O_{10}

(Sicapent); [D_6]benzene, [D_8]THF: sodium/potassium alloy; [D_5]bromobenzene: CaH_2; [D_8]toluene: potassium}. For more general information including a list of spectrometers and instrumentation used for physical characterization see ref.[8] The complexes Cp^*TaCl_4 (**5**),[11] (butadiene)$TaCp^*Cl_2$ (**6**),[13] and the reagents "butadiene-magnesium"[12] and $[Cp_2ZrCH_3^+][CH_3B(C_6F_5)_3^-]$[6] were prepared according to literature procedures. For a compilation of 1D- and 2D-NMR experiments used for spectroscopic characterization see ref.[18]

Preparation of (η^2-Butadiene)(η^5-cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)tantalum Chloride (7): A solution of sodium cyclopentadienide (479 mg, 5.44 mmol) in 10 mL of tetrahydrofuran was added at 0 °C to a solution of 2.00 g (4.53 mmol) of (butadiene)$TaCp^*Cl_2$ (**6**) in 50 mL of THF. The reaction mixture was stirred for 15 h at room temperature. The solvent was removed in vacuo. The residue was taken up in 30 mL of toluene and filtered. The filtrate was concentrated to dryness in vacuo and the remaining solid stirred with 30 mL of pentane. The product was collected by filtration, washed twice with pentane (2 × 20 mL), and dried to yield 962 mg (45%) of **7** as a pale brownish solid, m.p. 150 °C (decomp.). − ^{1}H NMR ([D_8]THF, 599.8 MHz, 298 K): δ = 6.33 (ddd, $^3J_{HH}$ = 16.9 Hz, $^3J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 5.7 Hz, 1 H, 3-H), 5.08 (s, 5 H, Cp-H), 4.27 (ptd, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 1.2 Hz, 1 H, 4-H′), 4.00 (ddd, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, 4-H), 1.74 [s, 15 H, $C_5(CH_3)_5$], 1.37 (dd, $^3J_{HH}$ = 12.6 Hz, $^2J_{HH}$ = 6.7 Hz, 1 H, 1-H′), 0.88 (dd, $^3J_{HH}$ = 9.7 Hz, $^2J_{HH}$ = 6.7 Hz, 1 H, 1-H), 0.71 (m, 1 H, 2-H). − 1D-TOCSY NMR ([D_8]THF, 599.8 MHz, 298 K): Isomer **A**: irradiation at δ = 1.37 (1-H′), response at δ = 6.33 (3-H), 4.27 (4-H′), 4.00 (4-H), 0.88 (1-H), 0.70 (2-H). − GCOSY NMR ([D_8]THF, 599.8 MHz, 298 K): δ = 6.33/4.27, 4.00, 0.73 (3-H/4-H′, 4-H, 2-H), 4.27/6.33, 4.00 (4-H′/3-H, 4-H), 4.00/6.33, 4.27 (4-H/3-H, 4-H′),1.37/0.88, 0.73 (1-H′/1-H, 2-H), 0.88/1.37, 0.73 (1-H/1-H′, 2-H), 0.73/6.33, 1.37, 0.88 (2-H/3-H, 1-H′). − ^{13}C NMR ([D_8]THF, 150.8 MHz, 298 K): δ = 157.4 (C-3), 119.6 [$C_5(CH_3)_5$], 114.9 (C-Cp), 111.2 (C-4), 60.4 (C-2), 42.4 (C-1), 20.6 [$C_5(CH_3)_5$]. − GHSQC ([D_8]THF, 150.8 MHz/599.8 MHz, 298 K): δ = 157.4/6.33 (C-3/3-H), 114.9/5.08 (C-Cp/Cp-H), 111.2/4.27 (C-4/4-H′), 111.2/4.00 (C-4/4-H), 60.4/0.70 (C-2/2-H), 42.4/1.37 (C-1/1-H′), 42.4/0.88 (C-1/1-H), 20.6/1.74 [$C_5(CH_3)_5$]. − IR (KBr): $\tilde{\nu}$ = 3108 (vw), 3085 (vw), 2906 (m), 2857 (m), 1593 (w), 1485 (vw), 1434 (m), 1377 (s), 1260 (w), 1100 (s), 1081 (s), 1028 (s), 1011 (s), 831 (vs), 808 (s), 715 (vs), 663 (w) cm^{-1}. − $C_{19}H_{26}ClTa$ (470.8): calcd. C 48.47, H 5.57; found C 48.44, H 5.65.

Preparation of (*s-trans*-η^4-Butadiene)(η^5-cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)tantalum Methyltris(pentafluorophenyl)-borate (8): The reagent $[Cp_2ZrCH_3^+][CH_3B(C_6F_5)_3^-]$ was generated in situ by treatment of 1.50 g (2.93 mmol) of $B(C_6F_5)_3$ with 753 mg (3.00 mmol) of $Cp_2Zr(CH_3)_2$ in 20 mL of toluene. The resulting orange-colored solution was added with stirring at ambient temperature to a solution of 1.55 g (3.30 mmol) of **7** in 20 mL of toluene. The reaction mixture was stirred for 10 min. Then the oily product was allowed to separate from the solution. The supernatant liquid was removed. The remaining oil was washed with toluene (3 × 15 mL) and dried in vacuo. The dark grey solid was suspended in 20 mL of pentane and then collected by filtration, washed with pentane (2 × 20 mL) and then dried in vacuo to yield 2.29 g (81%) of **8**, m.p. 191 °C (decomp.). − ^{1}H NMR ([D_2]dichloromethane, 599.8 MHz, 298 K): δ = 5.13 (s, 5 H, Cp-H), 3.75−3.68 (m, 1 H, 2-H), 3.46 (dd, $^2J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 7.7 Hz, 1 H, 1-H′), 3.09−3.07 (m, 1 H, 4-H′), 2.20−2.17 (m, 2 H, 3-H, 4-H), 1.88 [s, 15 H, $C_5(CH_3)_5$], 1.42 (ddd, $^2J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 16.2 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, 1-H), 0.48 [br. s, 3 H, *Me*-$B(C_6F_5)_3$]. − ^{1}H NMR ([D_5]bromobenzene, 599.8 MHz, 298 K): δ = 4.44 (s, 5 H, Cp-H), 3.07−3.01 (m, 1 H, 2-H), 2.91 (m, 1 H, 1-H′), 2.53 (m, 1 H, 4-H′), 1.61 (m, 2 H, 3-H, 4-H), 1.32 [s, 15 H, $C_5(CH_3)_5$], 0.88 (dd, $^2J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 16.0 Hz, 1 H, 1-H), 1.12 [br. s, 3 H, *Me*-$B(C_6F_5)_3$]. − 1D-TOCSY NMR ([D_2]dichloromethane, 599.8 MHz, 298 K): irradiation at δ = 3.71 (2-H): response at δ = 3.46 (1-H′), 3.08 (4-H′), 2.18 (3-H, 4-H), 1.42 (1-H). − GCOSY NMR ([D_2]dichloromethane, 599.8 MHz, 298 K): δ = 3.71/3.46, 2.18, 1.42 (2-H/1-H′, 3-H, 1-H), 3.46/3.71, 1.42 (1-H′/2-H, 1-H), 3.08/2.18 (4-H′/3-H, 4-H), 2.18/3.71, 3.08 (3-H, 4-H/2-H, 4-H′), 1.42/3.71, 3.46 (1-H/2-H, 1-H′). − ^{13}C NMR ([D_2]dichloromethane, 150.8 MHz, 298 K): δ = 148.7 [d, $^1J_{CF}$ = 232 Hz, *o*-$B(C_6F_5)_3$], 137.8 [d, $^1J_{CF}$ = 234 Hz, *p*-$B(C_6F_5)_3$], 136.8 [d, $^1J_{CF}$ = 235 Hz, *m*-$B(C_6F_5)_3$], 129.1 [br. m, *ipso*-$B(C_6F_5)_3$], 109.5 [$C_5(CH_3)_5$], 98.6 (C-Cp), 93.6 (C-3), 91.2 (C-2), 64.3 (C-4), 59.8 (C-1), 12.2 [$C_5(CH_3)_5$], 10.4 [br. s, *Me*-$B(C_6F_5)_3$]. − ^{13}C NMR ([D_5]bromobenzene, 150.8 MHz, 298 K): δ = 148.7 [d, $^1J_{CF}$ = 230 Hz, *o*-$B(C_6F_5)_3$], 137.6 [d, $^1J_{CF}$ = 232 Hz, *p*-$B(C_6F_5)_3$], 136.5 [d, $^1J_{CF}$ = 234 Hz, *m*-$B(C_6F_5)_3$], 108.3 [$C_5(CH_3)_5$], 97.4 (C-Cp), 92.9 (C-3), 90.6 (C-2), 63.8 (C-4), 59.2 (C-1), 11.2 [$C_5(CH_3)_5$], 11.0 [br. s, *Me*-$B(C_6F_5)_3$] (*ipso*-C of C_6F_5 not found). − GHSQC ([D_2]dichloromethane, 150.8/599.8 MHz, 298 K): δ = 98.6/5.13 (C-Cp/Cp-H), 93.6/2.18 (C-3/3-H), 91.2/3.71 (C-2/2-H), 64.3/3.08 (C-4/4-H′), 64.3/2.18 (C-4/4-H), 59.2/3.46 (C-1/1-H′), 59.2/1.42 (C-1/1-H), 12.2/1.88 ($C_5(CH_3)_5$/$C_5(CH_3)_5$), 11.0/0.48 (*Me*-$B(C_6F_5)_3$). − ^{11}B NMR ([D_2]dichloromethane, 64.2 MHz): δ = 15.0. − ^{19}F NMR ([D_2]dichloromethane, 282.4 MHz, 298 K): δ = −130 [m, 6 F, *o*-$CH_3B(C_6F_5)_3$], −163 [m, 3 F, *p*-$CH_3B(C_6F_5)_3$], −166 [m, 6 F, *m*-$CH_3B(C_6F_5)_3$]. − IR (KBr): $\tilde{\nu}$ = 3132 (vw), 2963 (w), 2921 (w), 1642 (m), 1512 (vs), 1456 (vs), 1383 (w), 1265 (m), 1087 (vs), 979−934 (br. m), 842 (m), 804 (w) cm^{-1}. − $C_{38}H_{29}BF_{15}Ta$ (962.4): calcd. C 47.43, H 3.04; found C 46.87, H 3.62.

X-ray Crystal Structure Analysis of 8: Formula $C_{19}H_{26}Ta \cdot B(C_6F_5)_3CH_3 \cdot CH_2Cl_2$, M = 1047.30, red crystal, 0.40 × 0.30 × 0.15 mm, a = 9.369(1), b = 12.479(1), c = 17.647(1) Å, α = 102.13(1), β = 102.11(1), γ = 102.59(1)°, V = 1896.7(3) Å^3, $\rho_{calcd.}$ = 1.834 g cm^{-3}, F(000) = 1024 e, μ = 31.43 cm^{-1}, absorption correction by SORTAV (0.366 ≤ T ≤ 0.650), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, φ and ω scans, 16502 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 9284 independent and 8161 observed reflections [$I \geq 2\,\sigma(I)$], 470 refined parameters, R = 0.056, wR^2 = 0.145, max. residual electron density 2.07 (−1.75) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. The butadiene unit is severely disordered, carbon atoms C11−C14 are refined isotropically and with restraints [DFIX 1.38(1) for C11−C12 and C13−C14, DFIX 1.47(1) for C12−C13, SADI (0.1) for C11−C13 and C12−C14]. This disorder affects also the neighboring Cp ring, especially the closest carbon atoms C6, C7, and C8 show large displacement parameters. Therefore the Cp ring is refined isotropically as rigid group. All other non-hydrogen atoms including the solvent molecule CH_2Cl_2 are refined anisotropically. The data set was collected with a Nonius Kappa CCD diffractometer, equipped with a rotating anode generator FR591. Programs used: data collection COLLECT, data reduction DENZO-SMN, absorption correction SORTAV, structure solution SHELXS-97, structure refinement SHELXL-97, graphics SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115170. Copies of the data can be obtained free of charge on application to CCDC, 12 Union

Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.].

Preparation of 2-(η⁵-Cyclopentadienyl)-7,7-dimethyl-2-(η⁵-pentamethylcyclopentadienyl)-2,3,6,7-tetrahydro-2-tantalaoxepine Methyltris(pentafluorophenyl)borate (9): Acetone (36.2 mg, 620 μmol) was added to a solution of 300 mg (310 μmol) of **8** in 5 mL of bromobenzene at ambient temperature. The mixture was stirred for 3 h at 50 °C. The product was then precipitated at room temperature by the addition of 10 mL of pentane. The solvent was decanted off. The residue was dissolved in 5 mL of dichloromethane and the product again precipitated by adding 10 mL of pentane. The solvents were removed and the product dried in vacuo, then suspended in 10 mL of pentane and collected by filtration. Yield of **9**: 230 mg (72%), m.p. 74°C (decomp.). − ^{1}H NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): The ^{1}H-NMR spectrum shows the presence of two isomers, **9A** and **9B** in a 50:50 ratio. Isomer **A**: δ = 6.43 (m, 1 H, 4-H), 5.78 (s, 5 H, Cp-H), 4.48 (m, 1 H, 5-H), 1.99 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.57 (pt, J_{HH} = 6.6 Hz, 1 H, 6-H), 1.40 (s, 3 H, 7-CH$_3$), 1.38 (pt, J_{HH} = 11.2 Hz, 1 H, 3-H), 1.22 (s, 3 H, 7-CH$_3$′); 6-H′ and 3-H′ resonances under C$_5$(C*H*$_3$)$_5$ signal. Isomer **B**: δ = 6.48 (m, 1 H, 4-H), 6.04 (s, 5 H, Cp-H), 5.35 (m, 1 H, 5-H), 2.13 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.96 (dd, $^2J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 13.5 Hz, 6-H′), 1.91 (m, 1 H, 3-H′), 1.82 (m, 1 H, 3-H), 1.65 (dd, $^2J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 14.7 Hz, 1 H, 6-H), 1.49 (s, 3 H, 7-CH$_3$), 1.09 (s, 3 H, 7-CH$_3$′); the C*H*$_3$[B] resonance is at δ = 0.49. − 1D TOCSY NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): Isomer **A**: 1. irradiation at δ = 4.48 (5-H): response at δ = 6.43 (4-H), 2.18 (6-H′), 2.12 (3-H′), 1.57 (6-H), 1.38 (3-H); 2. irradiation at δ = 1.40 (8-H): response at δ = 6.43 (4 H), 4.48 (5-H), 2.12 (3-H′), 1.38 (3-H). Isomer **B**: 1. irradiation at δ = 5.35 (5-H): response at δ = 6.48 (4-H), 1.96 (6-H′), 1.91 (3-H′), 1.83 (3-H), 1.65 (6-H); 2. irradiation at δ = 1.09 (9-H): response at δ = 6.48 (4-H), 5.35 (5-H), 1.96 (6-H′), 1.65 (6-H), 1.49 (8-H). − GCOSY NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): Isomer **A**: δ = 6.43/4.48, 2.12, 1.38 (4-H/5-H, 3-H′, 3-H), 4.48/6.43, 2.18, 1.57 (5-H/4-H, 6-H′, 6-H), 2.18/4.48, 1.57 (6-H′/5-H, 6-H), 1.57/4.48, 2.18 (6-H/5-H, 6-H′), 2.12/6.43, 1.38 (3-H′/6-H, 3-H), 1.38/6.43, 2.12 (3-H/6-H, 3-H′). Isomer **B**: δ = 6.48/5.35, 1.91, 1.83 (4-H/5-H, 3-H′, 3-H), 5.35/6.48, 1.96, 1.65 (5-H/4-H, 6-H′, 6-H), 1.96/5.35, 1.65 (6-H′/5-H, 6-H), 1.91/6.48, 1.83 (3-H′/4-H, 3-H), 1.83/6.48, 1.91 (3-H/4-H, 3-H′), 1.65/5.35, 1.96 (6-H/5-H, 6-H′). − ^{13}C NMR ([D$_2$]dichloromethane, 150.8 MHz, 298 K): Isomer **A**: δ = 146.6 (C-4), 119.2 [*C*(CH$_3$)$_5$], 110.3 (C-5), 107.2 (C-Cp), 99.1 (C-7), 48.8 (C-3), 42.6 (C-6), 37.1 (C-8), 30.1 (C-9), 11.9 (C(CH$_3$)$_5$). Isomer **B**: δ = 137.6 (C-4), 124.0 (C-5), 123.0 [C(CH$_3$)$_5$], 115.4 (C-7), 110.4 (C-Cp), 44.8 (C-3), 37.3 (C-6), 33.4 (C-8), 25.7 (C-9), 12.3 [C(CH$_3$)$_5$]. CH$_3$B(C$_6$F$_5$)$_3$$^-$: δ = 148.5 [d, $^1J_{CF}$ = 235 Hz, *o*-B(C$_6$F$_5$)$_3$], 137.8 [d, $^1J_{CF}$ = 236 Hz, *p*-B(C$_6$F$_5$)$_3$], 136.7 [d, $^1J_{CF}$ = 238 Hz, *m*-B(C$_6$F$_5$)$_3$], 129.3 [br. m, *ipso*-B(C$_6$F$_5$)$_3$], 10.5 [br. s, *Me*-B(C$_6$F$_5$)$_3$]. − GHSQC NMR ([D$_2$]dichloromethane, 150.8/599.8 MHz): Isomer **A**: δ = 146.6/6.43 (C-4/4-H), 110.3/4.48 (C-5/5-H), 107.2/5.78 (C-Cp/Cp-H), 48.8/2.12 (C-3/3-H′), 48.8/1.38 (C-3/3-H), 42.6/2.18 (C-6/6-H′), 42.6/1.57 (C-6/6-H), 37.1/1.40 (C-8/8-H), 30.1/1.22 (C-9/9-H), 11.9/1.99 (C(*C*H$_3$)$_5$/C(C*H*$_3$)$_5$). Isomer **B**: δ = 137.6/6.48 (C-4/4-H), 124.0/5.35 (C-5/5-H), 110.4/6.04 (C-Cp/Cp-H), 44.8/1.91 (C-3/3-H′), 37.3/1.96 (C-6/6-H′), 37.3/1.65 (C-6/6-H), 33.4/1.49 (C-8/8-H), 25.7/1.09 (C-9/9-H), 12.3/2.13 [C(*C*H$_3$)$_5$/C(C*H*$_3$)$_5$]. [*Me*-B(C$_6$F$_5$)$_3$]: δ = 10.5/0.49. − ^{11}B NMR ([D$_2$]dichloromethane, 64.2 MHz): δ = −15.0. − ^{19}F NMR ([D$_2$]dichloromethane, 282.4 MHz, 298 K): δ = −130 [m, 6 F, *o*-CH$_3$B(C$_6$F$_5$)$_3$], −163 [m, 3 F, *p*-CH$_3$B(C$_6$F$_5$)$_3$], −166 [m, 6 F, *m*-CH$_3$B(C$_6$F$_5$)$_3$]. − IR (KBr): $\tilde{\nu}$ = 3124 (w), 2925 (m), 1641 (w), 1511 (vs), 1458 (vs), 1378 (vw), 1362 (vw), 1265 (m), 1084 (vs), 993−953 (br. s), 847 (s), 803 (w) cm^{-1}. − C$_{41}$H$_{35}$BF$_{15}$OTa (1020.5): calcd. C 48.26, H 3.46; found C 48.03, H 3.28.

Reaction of 8 with Adamantanone, Preparation of 10: Adamantanone (51.5 mg, 340 μmol) was added to a solution of 300 mg (310 μmol) of **8** in 5 mL of bromobenzene. The mixture was stirred for 3 h at 50 °C. The product was precipitated by adding 10 mL of pentane. The supernatant liquid was decanted from the oil. The oily product was dissolved in 5 mL of dichloromethane and again precipitated with 10 mL of pentane. The solvent was decanted and the product dried in vacuo. Yield of **10**: 199 mg (57%), m.p. 176 °C (decomp.). − ^{1}H NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): The ^{1}H-NMR spectrum shows the presence of two isomers, **10A** and **10B**, in a 70:30 ratio. Isomer **A**: δ = 6.43 (m, 1 H, 4-H), 5.77 (s, 5 H, Cp-H), 4.64 (m, 1 H, 5-H), 3.01 (dd, $^3J_{HH}$ = 5.0 Hz, $^2J_{HH}$ = 11.8 Hz, 1 H, 3-H′), 2.11 [s, 16 H, 6-H′, C$_5$(C*H*$_3$)$_5$], 1.55 (pt, J_{HH} = 6.5 Hz, 1 H, 6-H), 1.08 (pt, J_{HH} = 11.8 Hz, 1 H, 3-H). Isomer **B**: δ = 6.53 (m, 1 H, 4-H), 6.01 (s, 5 H, Cp-H), 5.31 (m, 1 H, 5-H), 2.85 (br. m, 1 H, 6-H′), 2.01 [s, 15 H, C$_5$(C*H*$_3$)$_5$], 1.11 (br. m, 1 H, 6-H), 3-H/H′ signals under adamantyl signals at δ = 2.10−1.58 (br. m, 30 H, both isomers), C*H*$_3$[B] signal at δ = 0.47. − 1D-TOCSY NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): Isomer **A**: irradiation at δ = 4.64 (5-H): response at δ = 6.42 (4-H), 3.01 (3-H′), 2.11 (6-H′), 1.55 (6-H), 1.08 (3-H). Isomer **B**: irradiation at δ = 5.32 (5-H): response at δ = 6.52 (4-H), 2.80 (6-H′),1.90 (3-H′), 1.83 (3-H), 1.10 (6-H). − GCOSY NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): Isomer **A**: 6.42/4.64, 3.01, 1.08 (4-H/5-H, 3-H′, 3-H), 4.64/6.42, 2.11, 1.55 (5-H/4-H, 6-H′, 6-H), 3.01/6.42, 1.08 (3-H′/4-H, 3-H), 2.11/4.64, 1.55 (6-H′/5-H, 6-H), 1.55/4.64, 2.11 (6-H/5-H, 6-H′), 1.08/6.42, 3.01 (3-H/4-H, 3-H′). Isomer **B**: 6.52/5.32, 1.90, 1.83 (4-H/5-H, 3-H′, 3-H), 5.32/6.52, 2.80, 1.10 (5-H/4-H, 6-H′, 6-H), 2.80/5.32, 1.10 (6-H′/5-H, 6-H), 1.90/6.52, 1.83 (3-H′/4-H, 3-H), 1.83/6.52, 1.90 (3-H/4-H, 3-H′), 1.10/5.32, 2.80 (6-H/5-H, 6-H′). − ^{13}C NMR ([D$_2$]dichloromethane, 150.8 MHz, 298 K): Isomer **A**: δ = 140.9 (C-4), 118.8 [*C*(CH$_3$)$_5$], 115.6 (C-7), 111.4 (C-5), 110.4 (C-Cp), 43.2 (C-3), 42.3 (C-6), 47.4, 37.5, 36.4, 36.3, 35.7, 34.8, 33.7, 27.5, 26.8 (C-adamantyl fragment), 11.8 [C(C*H*$_3$)$_5$]. Isomer **B**: δ = 137.2 (C-4), 123.8 [*C*(CH$_3$)$_5$], 122.3 (C-5), 110.4 (C-Cp), 109.3 (C-7), 45.2 (C-3), 45.0 (C-6), 46.4, 39.2, 38.9, 38.3, 36.1, 36.0, 33.2, 27.0, 26.6, 11.8 [C$_5$(C*H*$_3$)$_5$]. CH$_3$B(C$_6$F$_5$)$_3$$^-$: δ = 148.6 (d, $^1J_{CF}$ = 233 Hz, *o*-B(C$_6$F$_5$)$_3$], 137.9 [d, $^1J_{CF}$ = 235 Hz, *p*-B(C$_6$F$_5$)$_3$], 136.5 [d, $^1J_{CF}$ = 237 Hz, *m*-B(C$_6$F$_5$)$_3$], 129.1 [br. m, *ipso*-B(C$_6$F$_5$)$_3$], 10.5 [br. s, *Me*-B(C$_6$F$_5$)$_3$]. − GHSQC NMR ([D$_2$]dichloromethane, 150.8/599.8 MHz, 298 K): Isomer **A**: δ = 140.9/6.42 (C-4/4-H), 111.4/4.64 (C-5/5-H), 110.4/5.77 (C-Cp/Cp-H), 43.2/3.01 (C-3/3-H′), 43.2/1.08 (C-3/3-H), 42.3/2.11 (C-6/6-H′), 42.3/1.55 (C-6/6-H), 11.8/2.11 [C(*C*H$_3$)$_5$/C(C*H*$_3$)$_5$]. Isomer **B**: δ = 137.2/6.52 (C-4/4-H), 122.3/5.32 (C-5/5-H), 110.4/6.01 (C-Cp/Cp-H), 45.2/1.90 (C-3/3-H′), 45.2/1.83 (C-3/3-H), 42.3/2.80 (C-6/6-H), 42.3/1.10 (C-6/6-H′), 11.8/2.01 [C$_5$(*C*H$_3$)$_5$/C$_5$(C*H*$_3$)$_5$]; δ = 10.5/0.47 [*Me*-B(C$_6$F$_5$)$_3$]. − IR (KBr): $\tilde{\nu}$ = 3120 (vw), 2915 (w), 2858 (w), 1640 (w), 1510 (s), 1457 (vs), 1381 (w), 1266 (w), 1085 (s), 995−933 (br. m), 842 (w), 804 (w) cm^{-1}. − C$_{48}$H$_{43}$BF$_{15}$OTa (1112.6): calcd. C 51.82, H 3.89; found C 52.12, H 4.26.

Preparation of 7-(1-Adamantyl)-2-(η⁵-cyclopentadienyl)-3,6-dihydro-2-(η⁵-pentamethylcyclopentadienyl)-2-tantala-2*H*-azepine Methyltris(pentafluorophenyl)borate (11): 1-Cyanoadamantane (55.3 mg, 340 μmol) was added to a solution of 300 mg (310 μmol) of **8** in 10 mL of bromobenzene. The mixture was kept for 2 h at 50 °C. Pentane (15 mL) was added to precipitate the product. The supernatant liquid was decanted. The residue was dissolved in 5 mL of

dichloromethane and the product again precipitated by adding 10 mL of pentane. The solvent was decanted off and the product dried in vacuo, suspended in 10 mL of pentane and then collected by filtration to yield 252 mg (72%) of **11**, m.p. 205 °C (decomp.). – ^{1}H NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): δ = 6.34 (m, 1 H, 4-H), 5.67 (s, 5 H, Cp-H), 4.82 (m, 1 H, 5-H), 3.32 (dd, $^2J_{HH}$ = 12.7 Hz, $^3J_{HH}$ = 8.4 Hz, 1 H, 6-H′), 2.01 [s, 15 H, C$_5$(CH_3)$_5$], 2.10–2.07, 1.86–1.79, 1.75–1.65 (m, 15 H, adamantyl), 1.77 (ddd, $^2J_{HH}$ = 12.7 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 2.0 Hz, 1 H, 6-H), 1.55 (dd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 7.9 Hz, 1 H, 3-H′), 0.85 (ddd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, 3-H), 0.47 [br. s, 3 H, *Me*-B(C$_6$F$_5$)$_3$]. – 1D-TOCSY NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): irradiation at δ = 4.82 (5-H): response at δ = 6.35 (4-H), 3.32 (6-H′), 1.77 (6-H), 1.55 (3-H′), 0.85 (3-H). – GCOSY NMR ([D$_2$]dichloromethane, 599.8 MHz, 298 K): δ = 6.35/4.82, 1.55, 0.85 (4-H/5-H, 3-H′, 3-H), 4.82/6.35, 3.32, 1.77 (5-H/4-H, 6-H′, 6-H), 3.32/4.82, 1.77 (6-H′/5-H, 6-H), 1.77/4.82, 3.32 (6-H/5-H, 6-H′), 1.55/6.35, 0.85 (3-H′/4-H, 3-H), 0.85/6.35, 1.55 (3-H/4-H, 3-H′). – ^{13}C NMR ([D$_2$]dichloromethane, 150.8 MHz, 298 K): δ = 190.1 (C-7), 148.6 [d, $^1J_{CF}$ = 231 Hz, *p*-B(C$_6$F$_5$)$_3$], 139.6 (C-4), 137.8 [d, $^1J_{CF}$ = 233 Hz, *p*-B(C$_6$F$_5$)$_3$], 136.4 [d, $^1J_{CF}$ = 232 Hz, *m*-B(C$_6$F$_5$)$_3$], 118.1 [C_5(CH$_3$)$_5$], 112.5 (C-5), 107.5 (C-Cp), 35.2 (C-3), 27.6 (C-6), 43.3, 38.7, 36.5, 28.2 (C-adamantyl), 11.9 [C$_5$(*C*H$_3$)$_5$], 10.4 [br. s, *Me*-B(C$_6$F$_5$)$_3$]. – GHSQC ([D$_2$]dichloromethane, 150.8/599.8 MHz, 298 K): δ = 139.6/6.35 (C-4/4-H), 112.5/4.82 (C-5/5-H), 107.5/5.67 (C-Cp/Cp-H), 35.2/1.55 (C-3/3-H′), 35.2/0.85 (C-3/3-H), 27.6/3.32 (C-6/6-H′), 27.6/1.77 (C-6/6-H), 11.9/2.01 [C$_5$(*C*H$_3$)$_5$/C$_5$(CH_3)$_5$], 10.4/0.48 [*Me*-B(C$_6$F$_5$)$_3$]. – ^{11}B NMR ([D$_2$]dichloromethane, 64.2 MHz): δ = –15.0. – ^{19}F NMR ([D$_2$]dichloromethane, 282.4 MHz): δ = -130 [m, 6 F, *o*-CH$_3$B(C$_6$F$_5$)$_3$], –163 [m, 3 F, *p*-CH$_3$B(C$_6$F$_5$)$_3$], –166 [m, 6 F, *m*-CH$_3$B(C$_6$F$_5$)$_3$]. – IR (KBr): $\tilde{\nu}$ = 3120 (vw), 2959 (w), 2915 (m), 2852 (w), 1665 (w), 1640 (w), 1510 (s), 1457 (vs), 1381 (w), 1264 (m), 1085 (vs), 1016–951 (br. m), 838 (m), 803 (m) cm^{-1}. – C$_{49}$H$_{44}$BNF$_{15}$Ta (1123.6): calcd. C 52.38, H 3.95, N 1.25; found C 52.79, H 4.24, N 1.14.

Ethene Polymerization Reactions: The ethene polymerization reactions were carried out in a Büchi glass autoclave. The reaction vessel was charged with 200 mL of toluene and 20 mL (0.033 mol) of a 10.5% solution of methylalumoxane in toluene. The mixture was brought to the preset reaction temperature and saturated with ethene at 2 bar for 1 h with stirring (700 min^{-1}). Then the polymerization reaction was started by the injection of 2 mL of a toluene solution of the catalyst precursors **4** or **8** (see Table 1). The polymerization was stopped after 30 min by quenching with CH$_3$OH/2 N aqueous HCl (1:1) and the polyethylene isolated (m.p. by DSC). For further details see Table 1.

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[1] [1a] G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, C. Krüger, *J. Am. Chem. Soc*. **1980**, *102*, 6344; G. Erker, J. Wicher, K. Engel, C. Krüger, *Chem. Ber*. **1982**, *115*, 3300; G. Erker, K. Engel, C. Krüger, A.-P. Chiang, *Chem. Ber*. **1982**, *115*, 3311. – [1b] H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, K. Lee, A. Nakamura, *Organometallics* **1982**, *1*, 388; Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda, A. Nakamura, *J. Chem. Soc., Chem. Commun*. **1982**, 191.

[2] For recent examples see e.g.: S. A. Benyunes, J. P. Day, M. Green, A. W. Al-Saadoon, T. L. Waring, *Angew. Chem.* **1990**, *102*, 1505; *Angew. Chem. Int. Ed. Engl*. **1990**, *29*, 1416; G. Herberich, U. Englert, K. Linn, P. Roos, J. Runsink, *Chem. Ber*. **1991**, *124*, 975; R. D. Ernst, E. Melendez, L. Stahl, M. L. Ziegler, *Organometallics* **1991**, *10*, 3635; J. D. Debad, P. Legzdins, M. A. Young, R. J. Batchelor, F. W. B. Einstein, *J. Am. Chem. Soc.* **1993**, *115*, 2051; U. Böhme, K.-H. Thiele, A. Rufinska, *Z. Anorg. Allg. Chem*. **1994**, *620*, 1455; C. Gemel, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1997**, *16*, 2623; L.-S. Wang, J. C. Fettinger, R. Poli, *J. Am. Chem. Soc.* **1997**, *119*, 4453; K. Mashima, H. Fukumoto, K. Tani, M. Haga, A. Nakamura, *Organometallics* **1998**, *17*, 410, and references cited therein.

[3] For selected examples see: H. Yasuda, T. Okamoto, Y. Matsuoka, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *Organometallics* **1989**, *8*, 1139; G. Erker, F. Sosna, P. Betz, S. Werner, C. Krüger, *J. Am. Chem. Soc.* **1991**, *113*, 564; G. Erker, R. Pfaff, D. Kowalski, E.-U. Würthwein, C. Krüger, R. Goddard, *J. Org. Chem.* **1993**, *58*, 6771; M. Berlekamp, G. Erker, B. Schönecker, R. Krieg, A. L. Rheingold, *Chem. Ber*. **1993**, *126*, 2119; L. López, M. Berlekamp, D. Kowalski, G. Erker, *Angew. Chem*. **1994**, *106*, 1168; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1114; G. Erker, M. Berlekamp, L. López, M. Grehl, B. Schönecker, R. Krieg, *Synthesis* **1994**, 212. Review: G. Erker, *Angew. Chem*. **1989**, *101*, 411; *Angew. Chem. Int. Ed. Engl*. **1989**, *28*, 397.

[4] K. Mashima, S. Fujikawa, A. Nakamura, *J. Am. Chem. Soc.* **1993**, *115*, 10990; B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich, S. Kotila, *Angew. Chem*. **1995**, *107*, 1867; *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 1755; D. D. Devore, F. J. Timmers, D. L. Hasha, R. K. Rosen, T. J. Marks, P. A. Deck, C. L. Stern, C. L. *Organometallics* **1995**, *14*, 3132; K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka, A. Nakamura, *Organometallics* **1995**, *14*, 2633; B. Temme, J. Karl, G Erker, *Chem. Eur. J.* **1996**, *2*, 919; J. Karl, G. Erker, R. Fröhlich, *J. Am. Chem. Soc*. **1997**, *119*, 11165; G. J. Pindado, M. Thornton-Pett, M. Bowkamp, A. Meetsma, B. Hessen, M. Bochmann, *Angew. Chem.* **1997**, *109*, 2457; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2358; J. Karl, M. Dahlmann, G. Erker, K. Bergander, *J. Am. Chem. Soc.* **1998**, *120*, 5643.

[5] H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *J. Am. Chem. Soc.* **1985**, *107*, 2410.

[6] X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015.

[7] T. Brackemeyer, G. Erker, R. Fröhlich, *Organometallics* **1997**, *16*, 531.

[8] H. C. Strauch, G. Erker, R. Fröhlich, *Organometallics* **1998**, *17*, 5746.

[9] [9a] Reviews: H. Yasuda, K. Tatsumi, A. Nakamura, *Acc. Chem. Res.* **1985**, *18*, 120; G. Erker, C. Krüger, G. Müller, *Adv. Organomet. Chem.* **1985**, *24*, 1. – [9b] For a description of the special bonding features of (*s-trans*-η^4-conjugated diene) bent metallocene complex see: K. Tatsumi, H. Yasuda, A. Nakamura, A. *Isr. J. Chem*. **1983**, *23*, 145; G. Erker, K. Engel, U. Korek, P. Czisch, H. Berke, P. Caubère, P. Vanderesse, *Organometallics* **1985**, *4*, 1531.

[10] H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, A Nakamura, *Chem. Lett*. **1981**, 671; Y. Kai, N. Kanehisa, K. Miki, N. Nasai, M. Akita, H. Yasuda, A. Nakamura, *Bull. Chem. Soc. Jpn*. **1983**, *56*, 3735; G. Erker, K. Engel, J. L. Atwood, W. E. Hunter, *Angew. Chem*. **1983**, *95*, 506; *Angew. Chem. Int. Ed. Engl*. **1983**, *22*, 494, *Angew. Chem. Suppl.* **1983**, 675; H. Yasuda, A. Nakamura, *Angew. Chem.* **1987**, *99*, 745; *Angew. Chem. Int. Ed. Engl*. **1987**, *26*, 723; T. Okamoto, H. Yasuda, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, *Organometallics* **1988**, *7*, 2266; H. Yasuda, T. Okamoto, K. Mashima, A. Nakamura, *J. Organomet. Chem*. **1989**, *363*, 61.

[11] W. A. Herrmann, W. W. Kalcher, H. Biersack, I. Bernal, *Chem. Ber*. **1981**, *114*, 3558.

[12] Y. Nakano, K. Natsukawa, H. Yasuda, H. Tani, *Tetrahedron Lett*. **1972**, 2833; K. Fujita, Y. Ohuma, H. Yasuda, H. Tani, *J. Organomet. Chem.* **1976**, *113*, 201; H. Yasuda, Y. Nakano, K. Natsukawa, H. Tani, *Macromolecules* **1978**, *11*, 586; Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, H. Yasuda, A. Nakamura, *Chem. Lett*. **1982**, 1277.

[13] H. Yasuda, T. Okamoto, A. Nakamura, *Organometallic Syn-*

thesis (Ed.: R. B. King, J. J. Eisch), **1988**, vol. 4; see also ref.[5]
[14] See for a comparison: J. L. Thomas, *Inorg. Chem*. **1978**, *17*, 1507; A. Sen, J. Halpern, *Inorg. Chem*. **1980**, *19*, 1073; W. Beck, K. Raab, U. Nagel, W. Sacher, *Angew. Chem.* **1985**, *97*, 498; *Angew. Chem. Int. Ed. Engl*. **1985**, *24*, 505.
[15] J. R. Surtees, *J. Chem. Soc., Chem. Commun*. **1965**, 567.
[16] G. Binsch, E. L. Eliel, H. Kessler, *Angew. Chem.* **1971**, *83*, 618; *Angew. Chem. Int. Ed. Engl*. **1971**, *10*, 570.
[17] C. Krüger, G. Müller, G. Erker, U. Dorf, K. Engel, *Organometallics* **1985**, *4*, 215, and references cited therein.
[18] S. Braun, H. Kalinowski, S. Berger, *100 and More Basic NMR Experiments*, VCH, Weinheim **1996**, and references cited therein.

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