Synthesis of (*s-trans*-η^4-Butadiene)tantalocene Cation and Its CC-Coupling Reactions with Ketones, Nitriles, and Alkynes†

Hans Christian Strauch, Gerhard Erker,* and Roland Fröhlich

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

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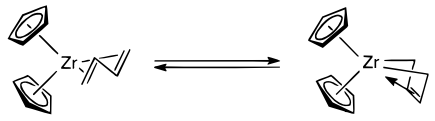
(η^4-Butadiene)(η^5-cyclopentadienyl)tantalum dichloride (**6**), synthesized by treatment of $CpTaCl_4$ (**5**) with (butadiene)magnesium (**7**), was treated with 2 molar equiv of sodium cyclopentadienide to yield Cp_3Ta(butadiene) (**9**). The spectroscopic analysis revealed the $(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})(\eta^2\text{-}C_4H_6)$Ta structure of **9**. Treatment of **9** with 1 molar equiv of the salt $[(Cp_2Zr{-}CH_3)^+(CH_3B(C_6F_5)_3)^-]$ (**11**) resulted in the clean transfer of a cyclopentadienide ligand from tantalum to zirconium with formation of the neutral zirconium compound $Cp_3Zr{-}CH_3$ (**12**) and the cation Cp_2Ta(butadiene)$^+$ (**10**; with $CH_3B(C_6F_5)_3^-$ counteranion). The spectroscopic characterization and an X-ray crystal structure analysis has revealed that **10** is a cationic (*s-trans*-η^4-butadiene)bis(η^5-cyclopentadienyl)tantalum complex. It reacts cleanly with a variety of ketones at 60 °C to form the respective 7,7-disubstituted tetrahydrotantalaoxepines **13**. These cationic seven-membered metallacyclic σ-allyl complexes undergo a rapid topomerization process on the NMR time scale ($\Delta G^{\ddagger}_{top} \approx 12$ kcal/mol^{-1}). Organic nitriles add similarly at 60 °C to the (*s-trans*-η^4-butadiene)tantalocene cation (**10**) to yield the respective 7-substituted 3,4-dihydrotantala-6*H*-azepines (**14**) that exhibit a similar dynamic NMR behavior due to conformational equilibration. Two examples of the seven-membered σ-allyl metallacyclic cation complexes **14** were characterized by X-ray crystal structure analyses (**14a**, R = CH_3, and **14d**, R = CH_2-*p*-$C_6H_4CH_3$). In contrast, 2-butyne adds to the (*s-trans*-η^4-butadiene)tantalocene cation in a 1:1 ratio to yield the corresponding metallacyclic (π-allyl)metallocene cation complex **15a** (characterized by X-ray diffraction). The addition of 1-pentyne gave a 60:40 mixture of the respective regioisomers **15b** and **15c**, exhibiting the *n*-C_3H_7 substituent at the ring position C5 and C6, respectively.

Introduction

(Butadiene)zirconocene was the first system where a η^4-coordination mode of an *s-trans*-conjugated diene was shown to be present in a stable mononuclear organometallic complex.[1] Bonding of all four carbon atoms of the C_4H_6 ligand to a single transition metal center requires some distortion of the butadiene framework from planarity, but interaction of the conjugated diene π-system with the group 4 bent metallocene valence orbitals[2] has provided a more than ample compensation for the strain introduced by constructing the Cp_2M(1,3-diene) framework. Theoretical work has shown that the very special bonding features of the bent metallocenes result in the ability to form stable *s-trans*-η^4-conjugated diene complexes so easily at their frameworks.[3] All three valence orbitals of, for example, the Cp_2Zr unit are oriented in the major plane bisecting the Cp−Zr−Cp angle. The more linearly expanded π-system of the *s-trans*-butadiene ligand binds quite favorably to the central metal center using these orbitals. In fact, the *s-cis*-butadiene ligand also coordinates strongly to Cp_2Zr and gives rise to the formation of the respective (*s-cis*-C_4H_6)$ZrCp_2$ isomer, found in a 1:1 ratio with its (*s-trans*-C_4H_6)$ZrCp_2$ congener under equilibrium conditions at ambient temperature, but *cis*-**1** exhibits a σ^2,π-type metallacyclic structure.[1]



trans-**1** *cis*-**1**

* Corresponding author. E-mail: erker@uni-muenster.de. Tel: +49 251 83 33221. Fax: +49 251 83 36503.

† Dedicated to Professor Carl Krüger on the occasion of his 65th birthday.

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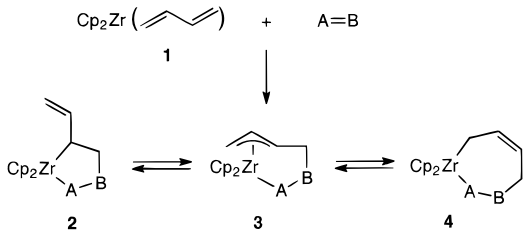
(Butadiene)zirconocene has been used extensively as an organometallic butadiene-dianion equivalent. It undergoes a variety of template reactions in the course of which organic or organometallic reagents are CC-coupled with the terminal atoms of the C_4 chain.[4] Metallacyclic allyl complexes (**2**−**4**) are the primary products of these synthetically useful template couplings. Many specific examples were isolated. In some cases the mutual interconversion of the (allyl)metallocene isomers was followed experimentally when synthetic pathways to the thermodynamically favored final products were mechanistically investigated.[5] Also, the (conjugated diene) group 4 metallocene complexes have successfully been used as precursors for very active single component metallocene Ziegler catalysts.[6]



In the meantime a number of structurally related L_nM(butadiene) complexes have been described. Stable *s-trans*-η^4-diene coordination is observed in a number of cases, although this bonding mode still has to be regarded as not frequently encountered.[7] The best chances of observing such species appear to be with metal complex frameworks that resemble the unique Cp_2M bent metallocene situation electronically. This is mostly achieved by selecting a specific d-block element and then attaching to it ligand systems that in their combination introduce a similar situation as found at the group 4 metallocenes.[8] Nakamura et al. have successfully used the neutral CpM(5)(η^4-butadiene) unit for this purpose to which an additional (*s-trans*-η^4-butadiene) ligand has been coordinated.[9]

We thought of a different way of effecting a close group 4 metallocene analogy, which simply involves substitution of the group 4 metal by a group 5 metal atom in the center of the metallocene. If care is taken that a resulting stable system is cationic, then a $Cp_2M(5)X_2^+$ system is obtained that should be very closely related to the neutral $Cp_2M(4)X_2$ bent metallocene systems. We have developed synthetic pathways to

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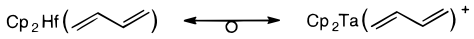
such $Cp_2M(5)(butadiene)^+$ complexes. Here we describe as a first example the corresponding tantalum system,[10,11] which should be isolobal to (butadiene)zirconocene or -hafnocene[12] and should exhibit a related structural chemistry and undergo CC-coupling reactions similar to these systems, except that the typical bent metallocene chemistry would be carried out at a monocation stage.[13]



Results and Discussion

Synthesis of $Cp_2Ta(butadiene)$ Cation. We chose $CpTaCl_2(butadiene)$ (**6**) as the starting material of our synthesis. Complex **6** was prepared by treatment of $CpTaCl_4$ (**5**)[14] with the oligomeric (butadiene)magnesium reagent **7**,[15] as previously described by A. Nakamura et al.[9,16] Complex **6** contains an *s-cis*-η^4-butadiene ligand. We first tried to substitute one of the chloride ligands in **6** selectively by cyclopentadienide. In a NMR experiment this was actually achieved, but in experiments on a preparative scale this reaction was hard to control in our hands to yield $Cp_2TaCl(butadiene)$ (**8**) sufficiently pure. We, therefore, treated $CpTaCl_2$-(butadiene) with two molar equivalents of sodium cyclopentadienide. This resulted in the formation of tris(cyclopentadienyl)Ta(butadiene) (**9**), which was isolated in ca. 45% yield as a red-brown amorphous solid.

A thorough NMR analysis, including TOCSY−NMR of the separated spin systems, has revealed that complex **9** contains a η^2-coordinated butadiene ligand (Figure 1).[17] The C_4H_6 ligand shows four ^{13}C NMR resonances at δ 24.0 (C1), 36.1 (C2), 149.0 (C3), and 104.9 (C4),[18] and it features a ^1H NMR six-spin system with butadiene hydrogen signals at δ 1.11, 1.51 (1-H, 1-H′), 2.31 (2-H), 6.06 (3-H), 4.21 and 4.54 (4-H, 4-H′). In **9** the three cyclopentadienides are not equal. Two of them are η^5-coordinated, and they are diastereotopic (^1H NMR in THF-d_8: δ 5.30 (s, 5H) and 4.51 (s, 5H)). The remaining cyclopentadienide is σ-bonded. It exhibits five separate $^1H/^{13}C$ NMR methine resonances (δ 6.89, 6.67, 6.21, 6.13, 3.74/145.5, 145.4, 121.1, 120.8, 43.3 ppm). Thus, complex **9** is to be characterized as bis(η^5-cyclopentadienyl)(η^1-cyclopentadienyl)(η^2-butadiene)tantalum.[19]

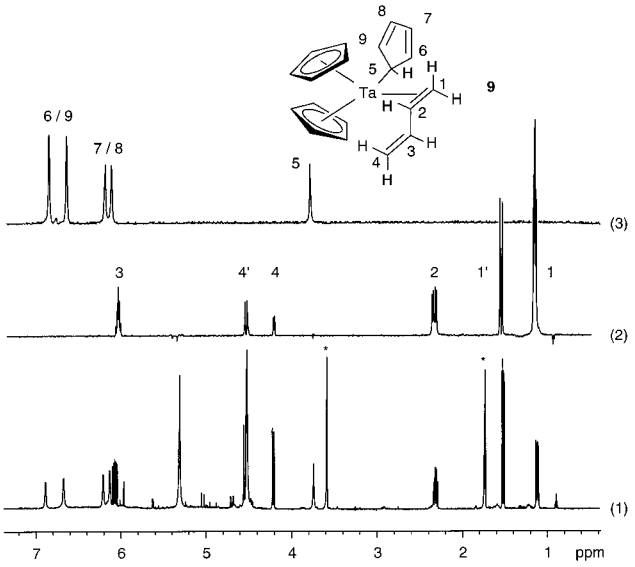


Figure 1. ^1H NMR TOCSY spectra of **9**: (top) η^1-C_5H_5 ligand (signal at δ 3.74 (5-H) was irradiated); (center) η^2-butadiene ligand (signal at δ 1.11 (1-H) was irradiated); (bottom) complete ^1H NMR spectrum (600 MHz, 298 K, THF-d_8).

The presence of a σ-cyclopentadienyl ligand in **9** was fortunate because this should facilitate the Cp-anion abstraction that was necessary to convert **9** to the Cp_2-Ta(butadiene)$^+$ cation (**10**). Actually, treatment of **9** with the strong organometallic Lewis acid $B(C_6F_5)_3$[20,21] eventually resulted in the formation of (η^4-butadiene)-bis(η-cyclopentadienyl)Ta^+, but the reaction was never clean enough to isolate the pure product, and the exact nature of the counteranion remained unclear. We tried a variety of other metallocene cation generating methods[22] on the **9** → **10** conversion, and eventually the following new procedure was successful.

We had recently developed the chemistry of the Cp_3-Zr−CH_3/Cp_3Zr^+ pair of complexes.[23] From this chemistry it was known that Cp_3Zr-CH_3 (**12**) is readily

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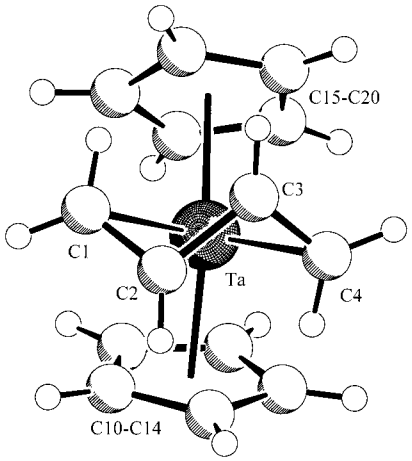


Figure 2. A view of the molecular geometry of the (*s-trans*-η^4-butadiene)TaCp_2^+ complex **10** (cation only). Selected bond lengths (Å) and angles (deg): Ta−C1 2.418(17), Ta−C2 2.306(15), Ta−C3 2.313(12), Ta−C4 2.297(19), C1−C2 1.32(3), C2−C3 1.53(4), C3−C4 1.33(3) (distances C1−C2 and C3−C4 refined with restraints, also C1−C3 and C2−C4), Ta−C_{Cp} 2.387; C1−C2−C3 102(2), C2−C3−C4 102-(2), Ta−C1−C2 69.1(10), Ta−C2−C1 78.5(11), Ta−C2−C3 70.9(8), Ta−C3−C2 70.4(10), Ta−C3−C4 72.5(10), Ta−C4−C3 73.8(11); C1−C2−C3−C4 140(2).

formed by treatment of $Cp_2Zr(Cl)CH_3$ with a Cp-anion equivalent. The formation of Cp_3Zr-CH_3 should be even more favorable if the cationic $Cp_2Zr-CH_3^+$ reagent was employed as a Cp-anion abstracting reagent. Indeed, (η^5-Cp)$_2$(σ-Cp)Ta(η^2-butadiene) (**9**) reacts readily with the salt [$(Cp_2ZrCH_3)^+(CH_3B(C_6F_5)_3)^-$] (**11**),[21] generated in situ by treatment of dimethylzirconocene with tris(pentafluorophenyl)borane in an aromatic solvent, to give a precipitate that turned out to be the Cp_2Ta-(butadiene)$^+$ cation (**10**) (with $CH_3B(C_6F_5)_3^-$ anion).

Complex **10** contains an *s-trans*-η^4-butadiene ligand. This follows from the NMR data (see below) and the results of an X-ray crystal structure analysis. The latter suffers from some disorder problem that is described in the Experimental Section, but is sufficient to characterize the butadiene ligand as *s-trans*-η^4-coordinated (see Figure 2). The butadiene ligand C1−C2/C3−C4 bonds are short (1.32(3)/1.34(3) Å); the C2−C3 linkage is long (1.53(4) Å). The Ta−C(butadiene) distances are in a range between 2.42(2) and 2.30(2) Å. The butadiene framework is, of course, no longer planar (θ C1−C2−C3−C4 140(2)°). In solution, complex **10** gives only a single set of NMR signals that are very characteristic of an (*s-trans*-η^4-butadiene)metallocene system (Figure 3).[1] There is only a single ^{1}H NMR Cp resonance (δ 5.40 in dichloromethane-d_2; ^{13}C NMR at 97.2) due to the C_2-symmetric structure of the cation. The ^{13}C NMR signals of the η^4-butadiene ligand appear at δ 57.8 (C1/C4) and 90.1 (C2/C3). The corresponding ^{1}H NMR

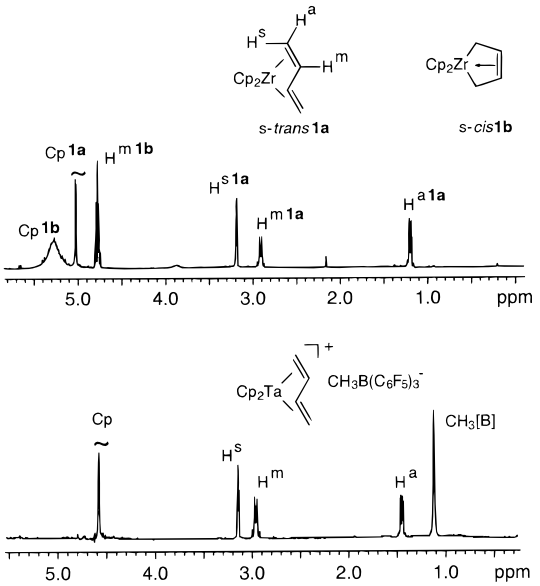
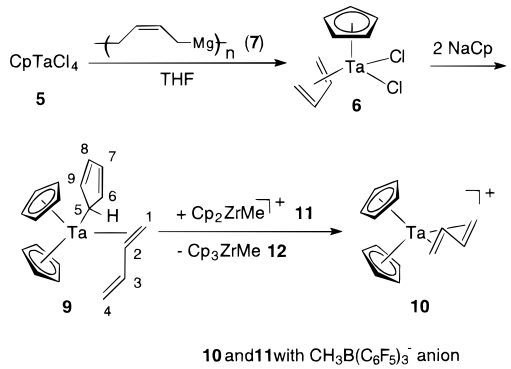


Figure 3. A comparison of the characteristic ^{1}H NMR spectra of (*s-trans*-η^4-butadiene)zirconocene and (*s-trans*-η^4-butadiene)tantalocene cation in bromobenzene-d_5 (600 MHz) at 298 K.

Scheme 1



resonances are found in the typical *s-trans*-η^4-butadiene range [δ 3.81 (1-H_{syn}, 4-H_{syn}), 3.69 (2-H, 3-H), 2.14 (1-H_{anti}, 4-H_{anti})]. This is very different from the typical *s-cis*-η^4-butadiene resonances, as they are, for example, observed in the $CpTaCl_2$(butadiene) starting material **5** (^{13}C NMR δ 127.5 (C2/C3), 58.4 (C1/C4); ^{1}H NMR δ 6.8 (2-H, 3-H), 0.85, 0.10 (1-H, 4-H)).

Reactions of 10 with Ketones, Nitriles, and Alkynes. We have seen that Cp_2Ta(butadiene)$^+$ (**10**) is readily formed by our novel route (see Scheme 1). The complex is thermodynamically stable. It contains an *s-trans*-η^4-butadiene ligand coordinated to the group 5 bent metallocene backbone, and it behaves structurally very similar to the related neutral group 4 metallocene butadiene complex (*s-trans*-η^4-butadiene)zirconocene (*trans*-**1**). The latter reacts readily with a great variety of reagents that contain reactive π-systems.[4,5a,b,24] With equimolar amounts of ketones, nitriles, or alkynes (butadiene)ZrCp_2 reacts cleanly to yield the metallacyclic allyl complexes (structural types **2**−**4**, see above), formed by CC-coupling at a conjugated diene terminus. To characterize the new cationic Cp_2Ta(butadiene)$^+$ complex **10** chemically, we have treated it with a variety of respective organic reagents and determined the structures of the obtained products.

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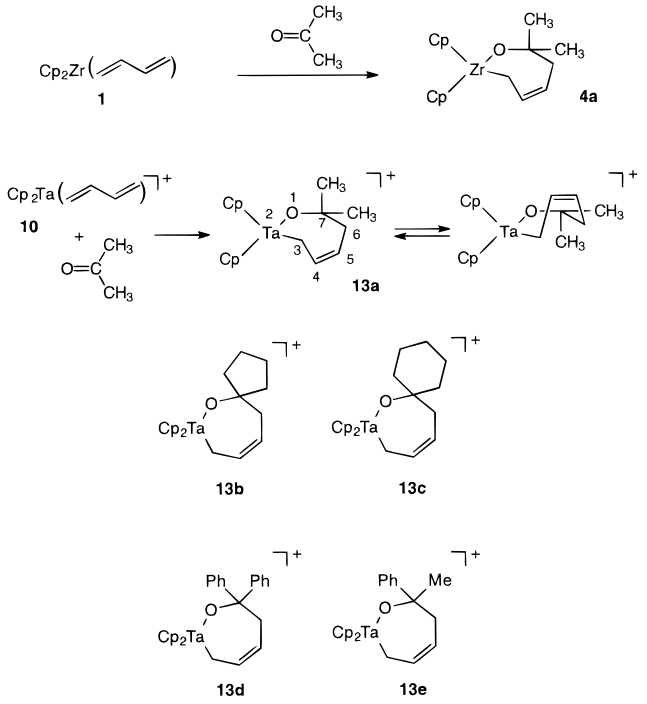
Scheme 2



10 and **13a** - **13e** with $CH_3B(C_6F_5)_3^-$ anion

The salt $[Cp_2Ta(butadiene)^+(CH_3B(C_6F_5)_3)^-]$ (**10**) was dissolved in bromobenzene. A ca. 3-fold excess of acetone was added. The $Cp_2Ta(butadiene)^+$ cation reacts only slowly with the organic carbonyl compound at ambient temperature. However, at 60 °C the reaction proceeds facilely. One molar equivalent of acetone is incorporated and CC-coupled with the butadiene ligand as expected to give the seven-membered metallacyclic (σ-allyl)tantalocene cation complex **13a** (with $CH_3B(C_6F_5)_3^-$ anion).

The structural description of **13a** as a seven-membered metallacycle follows from its typical NMR behavior. Just like its neutral zirconocene analogue [**4a** (A = O, B = CMe_2), see above and Scheme 2], the cation **13a** exhibits temperature-dependent dynamic NMR spectra. In the zirconium compound **4a** it was shown by X-ray diffraction and dynamic NMR spectroscopy that such frameworks are characterized by a pronounced envelope-like ring conformation.[24] It consists of two planar subunits (here: C3, Ta, O, C7, C6, and C3, C4, C5, C6). This typical nonplanar structure renders the Cp groups in **10** at tantalum diastereotopic, and it leads to the generation of diastereotopic hydrogens at the former butadiene carbon atoms C3 and C6 as well as a pair of diastereotopic methyl substituents at the acetone-derived carbon atom C7. This is in fact observed for **10** in dichloromethane-d_2 solution at 198 K. In the ^{1}H NMR spectrum (600 MHz) we observe two Cp singlets (δ 6.26/6.19), two methyl resonances (δ 1.33/0.92), and diastereotopic 6-H, 6-H′ hydrogens (δ 2.03/1.31). Conformational equilibration takes place upon increasing the monitoring NMR temperature, which leads to pairwise coalescence of the respective diastereotopic groups. From the Cp coalescence (T_c = 258 K) we have obtained a Gibbs activation energy of $\Delta G^{\ddagger}_{top}$ = 12.3 ± 0.3 kcal/mol^{-1} for this ring-inverting topomerization process[25] of **13a**. This is in a range similar to that observed previously for the analogous topomerization process of the neutral seven-membered zirconocenacycle **4a**.[24]

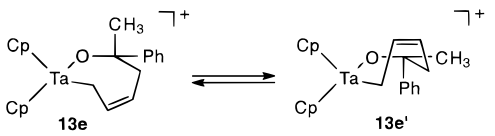
Table 1. Activation Energies $\Delta G^{\ddagger}_{top}$ of the Thermally Induced Ring Topomerization Process of the Cationic Seven-Membered Ring Metallacycles 13 and 14[a]

compd	heteroatom	R at C7	$\Delta G^{\ddagger}_{top}$	T_c (K)
13a	O	CH_3/CH_3	12.3	258
13b	O	$-(CH_2-)_4$	11.9	251
13c	O	$-(CH_2-)_5-$	12.5	260
13d	O	Ph/Ph	11.7	245
13e	O	CH_3/Ph	12.0	255
14a	N	CH_3	11.4	239
14b	N	C_2H_5	11.8	248
14c	N	Ph	11.5	241
14d	N	CH_2-*p*-$C_6H_4CH_3$	11.8	239
14e	N	$CHPh_2$	11.8	251

[a] $\Delta G^{\ddagger}_{top}$ (±0.3 kcal/mol^{-1}) determined from the coalescence of the ^{1}H NMR Cp resonances (600 MHz in dichloromethane-d_2 solution).

(η^4-Butadiene)tantalocene cation (**10**) reacts similarly to the ketones cyclopentanone, cyclohexanone, or benzophenone to give the seven-membered metallacyclic cations **13b**, **13c**, and **13d**, respectively. Again, envelope-shaped metallacyclic conformations must be assumed to prevail for these molecules, as judged from their typical NMR features (for details see the Experimental Section). Conformational equilibration takes place at elevated temperatures by a thermally induced ring topomerization process, analogously to that described above for the acetone coupling product **13a**. The Gibbs activation energies of the ring inversion process of **13b**−**d** are in the same range as observed for **13a** ($\Delta G^{\ddagger}_{top} \approx 12 \pm 0.5$ kcal/mol^{-1}; see Table 1).

Coupling of acetophenone with (butadiene)tantalocene cation gives rise to the formation of a carbon chirality center. In combination with the preferred chiral conformation of the metallacyclic product this should give rise to the presence of two diastereoisomers. These are observed in a 55:45 ratio by NMR under conditions where the topomerization process, which must in this case lead to diastereomeric interconversion, is slow on the NMR time scale. At 213 K in dichloromethane-d_2 we observe thus two pairs of Cp singlets of the **13e/13e′** diastereomeric mixture in the ^{1}H/^{13}C NMR spectrum (600/150 MHz) at δ 6.14, 6.04/112.2, 109.5 and δ 6.38, 6.28/111.9, 109.2 ppm. From the temperature-dependent dynamic NMR spectra a Gibbs activation energy of the topomerization process, i.e., the **13e** ⇌ **13e′** diastereomeric interconversion, of $\Delta G^{\ddagger}_{top}$(255 K) ≈ 12.0 ± 0.3 kcal/mol^{-1} was obtained.



We next treated the (*s-trans*-η^4-butadiene)$TaCp_2$ cation **10** with acetonitrile. At 60 °C in bromobenzene

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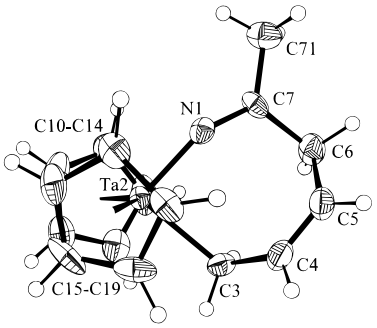


Figure 4. View of the molecular structure of the (butadiene)$TaCp_2^+$/acetonitrile addition product **14a** (cation only).

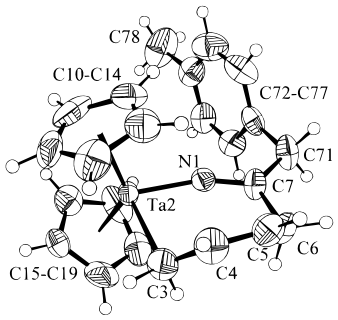
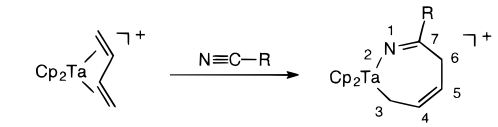


Figure 5. Molecular geometry of **14d** (cation only).

solution the [(η^4-C_4H_6)$TaCp_2^+CH_3B(C_6F_5)_3^-$] salt cleanly adds 1 molar equiv of the organic nitrile. The reaction requires ca. 5 h to go to completion, and the 1:1 addition product **14a** was isolated as a red-colored solid in ca. 75% yield. Gas-phase diffusion of pentane into a solution of **14a** in dichloromethane led to the formation of single crystals of **14a** that were suited for an X-ray crystal structure analysis (see Figure 4).

Complex **14a** exhibits separated anion and cation units in the crystal. The cation shows a seven-membered metallacyclic ring structure. Addition of the acetonitrile to (butadiene)$TaCp_2^+$ has led to the formation of a 2,3-dihydro-7-methyl-2-tantala-6*H*-azepine ring system. The structure shows the presence of the C7−N1 (1.253(7) Å) and C4−C5 (1.338(10) Å) double bonds inside the organometallic seven-membered ring system. There are two σ-bonded ligands at tantalum, namely, Ta2−C3 (2.264(6) Å) and the rather short Ta2−N1 bond (1.918(5) Å). The short Ta2−N1 bond lengths in combination with the very large angle at nitrogen (Ta2−N1−C7: 158.3(5)°) may indicate some metal−nitrogen π-interaction.[26] The pseudo-tetrahedral coordination around tantalum in **14a** is completed by the presence of the two uniformally η^5-bonded cyclopentadienyl ligands. The corresponding Cp(centroid)−Ta2−Cp(centroid) angle is 134.7°; the C3−Ta2−N1 angle amounts to 86.7(2)°. The rigid C3−Ta2−N1−C7−C6 part of the metallacyclic framework shows a coplanar orientation, as does the remaining C6−C5═C4−C3 moiety. The metallacyclic framework of **14a** exhibits a typical envelope-type conformational arrangement. The angle between the planes P1 (C3−Ta2−N1−C7−C6) and P2 (C6−C5−C4−C3) is 60.9(3)°.

In solution, complex **14a** exhibits an analogous structure, as evidenced by NMR. At low temperature (198 K, 600 MHz, CD_2Cl_2) the ^{1}H NMR spectrum of **14a** shows the resonances of two diastereotopic Cp ligands at δ 5.99 and 5.92 ppm and diastereotopic pairs of 6-H/H′ (δ 3.11, 2.09 ppm, ^2J = 13.7 Hz) and 3-H/H′ (δ 2.04, 1.38 ppm, ^2J = 10.0 Hz) methylene hydrogen atoms. The seven-membered metallacycle **14a** shows dynamic NMR spectra due to a ring topomerization process at elevated temperature that results in a pairwise exchange of the diastereotopic Cp ligands, as well as the diastereotopic C^6H_2 and C^3H_2 hydrogens, leading to the observation of the respective averaged signals above the coalescence temperature. From the coalescence of the ^{1}H NMR Cp signals a Gibbs activation energy of $\Delta G^{\ddagger}_{top}$(239 K) = 11.4 ± 0.3 kcal/mol^{-1} was determined for the activation barrier of the topomerization process of **14a** (see Table 1).



cations with $CH_3B(C_6F_5)_3^-$ anion

14 (**a** : R = CH_3)
(**b** : R = C_2H_5)
(**c** : R = Ph)
(**d** : R = -CH_2-p-$C_6H_4CH_3$)
(**e** : R = $CHPh_2$)

The reaction of (*s-trans*-η^4-butadiene)$TaCp_2^+$ cation with propionitrile, benzonitrile, *p*-tolylacetonitrile, or diphenylacetonitrile proceeds analogously. In the course of several hours at 60 °C in the polar bromobenzene solvent, clean addition to yield the respective systems **14b**−**e** is observed. All these systems exhibit structures similar to **14a**. They undergo the intramolecular conformational equilibration processes of their respective envelope-shaped metallacyclic seven-membered ring frameworks with Gibbs activation energies that are very similar to the $\Delta G^{\ddagger}_{top}$ value determined for the parent compound **14a** (see above and Table 1).

Single crystals were also obtained from the complex **14d**, and its structure was determined by an X-ray crystal structure analysis (Figure 5). The molecular structure of the cation **14d** is in its essential parameters very similar to that of the parent compound **14a** (see above). Selected bond lengths and angles of the two structures are listed in Table 2 for a comparison.

Finally, we have treated the (*s-trans*-η^4-butadiene)-$TaCp_2^+$ cation with the alkynes 2-butyne and 1-pentyne in this study, respectively. The alkyne addition reaction is the slowest trapping reaction of (C_4H_6)$TaCp_2^+$ found in this series so far. It has taken ca. 36 h at 60 °C to have the reaction between **10** and 2-butyne go to completion. The metallacyclic 1:1 addition product **15a** was obtained and isolated in ca. 70% yield. It was characterized spectroscopically (for details see the Experimental Section) and by an X-ray crystal structure analysis. Although the structure determination was complicated due to a disorder problem of the C1−C4 moiety of the ring, it has revealed a pronounced structural difference between the complex types **15** and **13/14**. In the acetonitrile coupling product **14a** (see above) only one of the former butadiene carbon atoms

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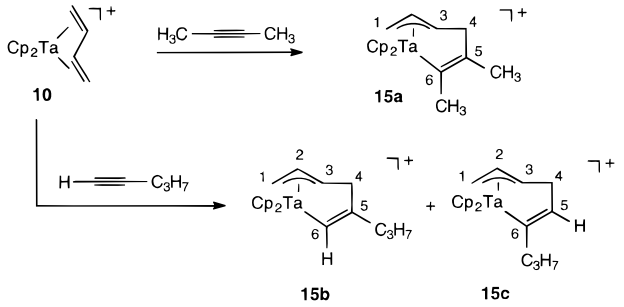
Table 2. Comparison of Selected Structural Parameters of the Cation Systems 14a (R = CH_3) and 14d (R−CH_2-*p*-$C_6H_4CH_3$)

bond lengths (Å)/ angles (deg)	14a	14d
Ta2−N1	1.918(5)	1.903(5)
Ta2−C3	2.264(6)	2.278(7)
N1−Ta2−C3	86.7(2)	85.0(2)
Ta2−N1−C7	158.3(5)	159.9(5)
N1−C7	1.253(7)	1.270(8)
C6−C7	1.536(9)	1.520(10)
N1−C7−C6	116.5(5)	116.7(6)
C3−C4	1.484(9)	1.426(11)
C4−C5	1.338(10)	1.354(11)
C5−C6	1.499(9)	1.472(11)
C3−C4−C5	126.5(6)	128.7(8)
C4−C5−C6	126.2(6)	124.8(7)
C7−C71	1.478(8)	1.497(9)
N1−C7−C71	124.3(6)	123.1(6)
N1−C7−C6	116.5(5)	116.7(6)
Ta2−C3−C4	111.1(4)	112.6(5)
C5−C6−C7	115.1(5)	114.9(6)
N1−Ta2−C3−C4	50.2(5)	49.3(6)
C7−N1−Ta2−C3	8.1(12)	1.7(15)
Ta2−N1−C7−C6	164.9(9)	−3.6(19)
N1−C7−C6−C5	−43.6(9)	−46.6(10)
C3−C4−C5−C6	2.0(12)	2.4(14)

shows a close contact to tantalum—the Ta···C3 to C6 separations in **14a** are 2.264(6), 3.134(8), 3.685(7), and 3.767(7) Å—whereas the analogous Ta···C1 to C4 separations in **15a** are quite different at 2.365(5), 2.421(5), 2.523(10) (averaged value of the disordered C3A and C3B centers), and 3.411(5) Å. Thus, complex **15a** has to be regarded as a distorted metallacyclic π-allyl system[5,27] with only one typical tantalum−carbon σ-bond present (Ta−C6 2.283(4) Å), in contrast to the seven-membered metallacyclic σ-allyl complexes **14**. A view of the structure of **15a** is shown in Figure 6, together with a list of typical bond lengths and angles. A discussion of structural details is omitted because of the disorder problem at the π-allyl structural subunit that has complicated the X-ray crystal structure analysis of the specific example **15a**.



The addition of 1-pentyne to the (butadiene)tantalocene cation was carried out under similar conditions (40 h at 60 °C in bromobenzene, ca. 75% yield of isolated product). We have obtained a 60:40 mixture of the regioisomeric metallacyclic (π-allyl)metallocene complexes **15b** and **15c**. The isomers could clearly be distinguished by selective ^{1}H NMR TOCSY experiments. This has revealed that the hydrogen atom 5-H in **15c** is connected with the coupled 1−4-H spin system, whereas in **15b** it is separated by the quaternary center at C5 and thus does not respond to, for example, TOCSY irradiation at 1-H.

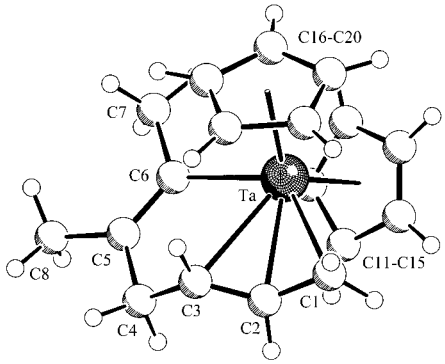


Figure 6. Projection of the metallacyclic π-allyl metallocene framework of **15a** (only the cation is depicted) with selected bond lengths (Å) and angles (deg); the substituted (π-allyl)tantalocene subunit is enantiomerically disordered. Ta−C6 2.283(4), C5−C6 1.351(7), Ta−C6−C5 124.1(3), Ta−C6−C7 118.9(3), C6−C5−C4 119.3(4), C6−C5−C8 125.2-(5), C4−C5−C8 115.5(5), C4−C5 1.489(8), Cp(centroid)−Ta−Cp(centroid) 129.1, C1−C2 1.329(9), C2−C3A 1.295(14), C3A−C4−C5 109.2(5), C3B−C4−C5 106.3(6), C3A−C4 1.449(10), C2−C3B 1.261(15), C3B−C4 1.464(14).

Conclusions

The bent metallocene complexes of the d-block metals exhibit unique stereoelectronic features. Proposed on the grounds of theoretical calculations and verified by means of a variety of experiments, it is now clear that the Cp_2M moieties are distinguished by having their valence orbitals arranged such that additional ligands bind almost exclusively in the Cp−M−Cp bisecting plane at the front of the bent metallocene. This specific arrangement of the available metallocene coordination sites in a singular plane leads to a number of coordinative situations that are very specifically favored at the Cp_2M bent metallocene framework.[28] Binding butadiene (and other conjugated diene ligands, as well) preferably in an *s-trans*-η^4-C_4H_6 bonding mode is one of the consequences of the specific Cp_2M stereoelectronic situation.

(*s-trans*-η^4-Butadiene)zirconocene to our knowledge was the very first example in this series, prepared and described by us and independently by A. Nakamura and H. Yasuda and their co-workers and structurally characterized by C. Krüger et al.[1] The (butadiene)$ZrCp_2$ system still exists as an (*s-cis*/*s-trans*-η^4-C_4H_6)zirconocene equilibrium mixture. Going to the Cp_2Hf system shifts the equilibrium considerably to the side of the σ,π-structured (*s-cis*-η^4-diene)hafnocene. This is quite different upon going to the group 5 system that is isoelectronic to neutral bis(cyclopentadienyl)hafnium, namely, the singly positively charged bis(cyclopentadienyl)tantalum$^+$ cation framework.[2] The Cp_2Ta^+ template binds

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butadiene strongly through all four carbon atoms as expected, and in contrast to $(C_4H_6)HfCp_2$, exclusively (*s-trans*-η^4-butadiene)$TaCp_2^+$ has been found and observed experimentally so far. It appears that the unique *s-trans*-η^4-conjugated diene bonding mode is even more favored, i.e., thermodynamically stabilized, at Cp_2Ta^+ cation than it was previously found for the neutral bis(cyclopentadienyl) group 4 bent metallocene systems.

Our new synthesis has made $Cp_2Ta(butadiene)^+$ cation—and probably substituted derivatives as well—readily available. This has allowed for a first series of addition reactions to be carried out. The addition of organic carbonyl compounds proceeded as expected and gave the corresponding tetrahydrotantalaoxepine cation systems (**13**). They probably draw much of their stabilization from a strong metal oxygen π-back-bonding interaction,[29] similar to that previously observed with their neutral zirconium and hafnium analogues.[24]

Nitrogen to tantalum back-bonding is quite pronounced in the seven-membered metallacyclic cations **14**, as well. Actually, this stabilizing effect seems to be even more pronounced in the dihydro-tantala-6*H*-azepine cations than in the corresponding neutral zirconium or hafnium systems. In the latter series we have only in a singular example seen the seven-membered metallacyclic σ-complex to be present at all; usually their five-membered σ-allyl isomers (and tautomers) were more stable.[4a] In the case of the cationic (butadiene)$TaCp_2^+$/N≡C−R addition products we have exclusively observed the seven-membered σ-allyl metallocene systems. Nevertheless, there is evidence that the Cp_2Ta^+ complexes are able to respond to variations of the electronic features around tantalum. Binding an sp^2 carbon center instead of O or N heteroatoms to the metal center results in an increased local electronic unsaturation at the metal that is consequently compensated by shifting the remaining allyl moiety inside the framework of the corresponding (butadiene)$TaCp_2^+$/alkyne addition (**15**) in the direction of an η^3-coordination mode. Overall, the (butadiene)tantalocene$^+$ cation system appears to behave electronically, structurally, and chemically similar to the well-studied neutral (conjugated diene) bent metallocene systems described in the literature. It may be that the very characteristic features that make (η^4-butadiene)MCp_2 systems so unique are even slightly more pronounced in the (*s-trans*-η^4-butadiene)$TaCp_2^+$ cation complex **10** than they are for the other members of this general complex family. Whether this may lead to the disclosure of novel reaction types and novel applications of such systems in stoichiometric chemistry and in catalysis will be investigated in our laboratory.

Experimental Section

All compounds described are air and moisture sensitive: They were prepared and handled in an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. NMR spectra were recorded on a Varian Unity Plus (^{1}H, 599.8 MHz; ^{13}C, 150.8 MHz) NMR spectrometer, on a Bruker AC 200 P-FT-NMR spectrometer, or on a Bruker ARX 300 spectrometer. IR spectroscopy: Nicolet 5 DXC FT-IR spectrometer (KBr). Elemental analyses: Foss Heraeus CHNO-Rapid. DSC: DuPont 2910 DSC (STA instruments). X-ray crystal structure analyses: Data sets were collected with Enraf Nonius CAD4 and MACH3 diffractometers, equipped with sealed tube or rotating anode generators. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93 and SHELXL-97, graphics DIAMOND or SCHAKAL. $CpTaCl_2$(butadiene) (**6**),[16] (butadiene)magnesium (**7**),[15] and $[(Cp_2ZrCH_3)^+(CH_3\text{-}B(C_6F_5)_3)^-]$ (**11**)[21] were prepared according to the literature procedures. For a compilation of the 1D and 2D NMR experiments used, see ref 30.

Bis(η^5-cyclopentadienyl)(η^1-cyclopentadienyl)(η^2-butadiene)tantalum (9). A 1.00 g (2.70 mmol) sample of **5** and 474 mg (5.39 mmol) of sodium cyclopentadienide were suspended in 40 mL of toluene and stirred for 12 h at room temperature. The reaction mixture was filtered, and the solvent was evaporated. The residue was taken up in 30 mL of pentane and stirred for 12 h. Afterward the product was collected on a Schlenk frit, washed with two 10 mL portions of pentane, and dried in vacuo. Yield: 540 mg (47%), mp 101 °C. Anal. Calcd for $C_{19}H_{21}Ta$ (430.32): C, 53.07; H, 4.92. Found: C, 52.79; H, 5.09. IR (KBr): $\tilde{\nu}$ = 3100, 2961, 1595, 1436, 1383, 1193, 1159, 1010, 833, 774, 721, 668 cm^{-1}. ^{1}H NMR (THF-d_8, 599.8 MHz, 298 K): δ = 6.89/6.67 (each br s, 1H, 6-H, 9-H), 6.21/6.13 (each br s, 1H, 7-H, 8-H), 6.06 (ddd, ^3J = 8.1 Hz, ^3J = 16.9 Hz, ^3J = 10.2 Hz, 1H, 3-H), 5.30/4.51 (each s, 5H, Cp−H), 4.54 (ddd, ^2J = 2.3 Hz, ^3J = 16.9 Hz, ^4J = 1.3 Hz, 1H, 4-H′), 4.21 (ddd, ^2J = 2.3 Hz, ^3J = 10.2 Hz, ^4J = 1.1 Hz, 1H, 4-H), 3.74 (br s, 1H, 5-H), 2.31 (m, 1H, 2-H), 1.51 (dd, ^2J = 6.5 Hz, ^3J = 10.3 Hz, 1H, 1-H′), 1.11 (dd, ^2J = 6.5 Hz, ^3J = 11.7 Hz, 1H, 1-H). TOCSY NMR (THF-d_8, 599.8 MHz, 298 K) experiment 1: Irradiation at δ = 3.74 (5-H) gave resonances at δ = 6.89/6.67 (6-H, 9-H), 6.21/6.13 (7-H, 8-H). Experiment 2: Irradiation at δ = 1.11 (1-H) gave resonances at δ = 6.06 (3-H), 4.54 (4-H′), 4.21 (4-H), 2.31 (2-H), 1.51 (1-H). ^{13}C NMR (THF-d_8, 150.8 MHz, 298 K): δ = 149.0 (C3), 145.5/145.4 (C6/C9), 121.1/120.8 (C7/C8), 104.9 (C4), 102.2/101.6 (C−Cp), 43.3 (C5), 36.1 (C2), 24.0 (C1).

(*s-trans*-η^4-Butadiene)bis(η^5-cyclopentadienyl)tantalum(V) Methyltris(pentafluorophenyl)borate (10). To generate $[(Cp_2ZrCH_3)^+(CH_3B(C_6F_5)_3)^-]$ (**11**) in situ, 2.00 g (3.91 mmol) of $B(C_6F_5)_3$ and 1.08 g (4.29 mmol) of dimethylzirconocene were mixed and then dissolved in 20 mL of toluene. This solution was transferred at room temperature to a stirred solution of 1.90 g (4.41 mmol) of **9** in 20 mL of toluene. An oily product precipitated, and the supernatant solution was decanted. The oily residue was washed with three portions of 20 mL of toluene and dried in vacuo. The crude product was suspended in 20 mL of pentane, filtered, washed with two portions of 20 mL of pentane, and dried in vacuo. Yield: 3.13 g (90%), mp 201 °C. Anal. Calcd for $C_{33}H_{19}F_{15}BTa$ (892.21): C, 44.43; H, 2.15. Found: C, 44.78; H, 2.58. IR (KBr): $\tilde{\nu}$ = 3126, 2944, 2933, 1641, 1511, 1457, 1380, 1265, 1088, 1012−942, 847, 802, 756, 659 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 5.40 (s, 10H, Cp−H), 3.81 (m, 2H, H-syn), 3.69 (m, 2H, H-meso), 2.14 (m, 2H, H-anti), 0.52 (br s, 3H, *Me*−$B(C_6F_5)_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 298 K): Irradiation at δ = 3.31 (H-syn) gave resonances at δ = 3.69 (H-meso), 2.14 (H-anti). GCOSY NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 3.81/3.64, 2.14 (H-syn/H-meso, H-anti), 3.69/3.81, 2.14 (H-meso/H-syn, H-anti), 2.14/

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3.81, 3.69 (H-anti/H-syn, H-meso). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 298 K): δ = 148.3 (pd, $^1J_{CF}$ = 236 Hz, *o*-B(C_6F_5)$_3$), 136.9 (pd, $^1J_{CF}$ = 233 Hz, *p*-B(C_6F_5)$_3$), 136.9 (pd, $^1J_{CF}$ = 236 Hz, *m*-B(C_6F_5)$_3$), 128.8 (br m, *ipso*-B(C_6F_5)$_3$), 97.2 (C−Cp), 90.1 (C2/C3), 57.8 (C1/C4), 10.8 (br s, *Me*−B(C_6F_5)$_3$). GHSQC NMR (dichloromethane-d_2, 150.8/599.8 MHz): δ = 97.2/5.40 (C−Cp /Cp−H), 90.1/3.69 (C2, C3/H-meso), 57.8/3.81 (C1, C4/H-syn), 57.8/2.14 (C1, C4/H-anti), 10.8/0.52 (*Me*−B(C_6F_5)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz): δ = −15.0. ^{19}F NMR (dichloromethane-d_2, 360 MHz): δ = −130 (br s, 6F, *o*-C_6F_5); −136 (br s, 3F, *p*-C_6F_5); −166 (br s, 6F, *m*-C_6F_5).

X-ray crystal structure analysis of **10**: formula $C_{33}H_{19}BF_{15}Ta\cdot CH_2Cl_2$, M = 977.17, yellow crystal, 0.20 × 0.15 × 0.10 mm, a = 12.714(3) Å, b = 14.821(3) Å, c = 17.367(3) Å, V = 3272.5(12) Å^3, ρ_{calc} = 1.983 g cm^{-3}, $F(000)$ = 1888 e, μ = 36.35 cm^{-1}, empirical absorption correction via φ scan data (0.729 ≤ C ≤ 0.998), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.710 73 Å, T = 173 K, $\omega/2\theta$ scans, 3693 reflections collected ($+h$, $+k$, $+l$), [(sin θ)/λ] = 0.62 Å^{-1}, 3693 independent and 3108 observed reflections [$I \geq 2\,\sigma(I)$], 461 refined parameters, R = 0.038, wR2 = 0.092, max. residual electron density 1.07 (−0.96) e Å^{-3}, butadiene unit refined with restraints (SADI 0.01 C1−C2 and C3−C4, SADI 0.01 C1−C3 and C2−C4), hydrogens calculated and refined as riding atoms.

2,2-Bis(η^5-cyclopentadienyl)-7,7-dimethyl-2,3,6,7-tetrahydro-2-tantalaoxepine Methyltris(pentafluorophenyl)borate (13a). A 350 mg (0.39 mmol) sample of **10** was dissolved in 20 mL of bromobenzene; 0.1 mL (1.36 mmol) of acetone was added, and the solution was stirred for 12 h at 60 °C. Then the solvent was evaporated, and the residue was taken up in 20 mL of pentane and stirred for 5 h at −20 °C. The product was collected on a Schlenk frit, washed with three portions of 20 mL of pentane, and dried in vacuo. Yield: 222 mg (70%), mp 135 °C. Anal. Calcd for $C_{36}H_{25}BF_{15}OTa$ (950.19): C, 45.51; H, 2.65. Found: C, 44.71; H, 3.01. IR (KBr): $\tilde{\nu}$ = 3126, 2963, 2934, 1641, 1511, 1458, 1383, 1368, 1265, 1087, 1028−934, 841−802 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz): δ = 6.44 (pq, J = 10.6 Hz, 1H, 4-H), 6.27 (s, 10H, Cp−H), 5.39 (pq, J = 10.3 Hz, 1H, 5-H), 2.56 (pd, J = 8.3 Hz, 2H, 3-H), 1.75 (br s, 2H, 6-H), 1.27−1.20 (br s, 6H, 8-H), 0.52 (br s, 3H, *Me*−B(C_6F_5)$_3$). ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 198 K): δ = 6.38 (pq, J = 9.0 Hz, 1H, 4-H), 6.26/6.19 (each s, 5H, Cp−H), 5.31 (pq, J = 8.9 Hz, 1H, 5-H), 2.45 (m, 2H, 3-H), 2.03 (dd, ^3J = 13.0 Hz, ^2J = 8.2 Hz, 1H, 6-H′), 1.33 (s, 3H, CH_3), 1.31 (m, 1H, 6-H), 0.92 (s, 3H, CH_3), 0.39 (br s, 3H, *Me*−B(C_6F_5)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 198 K) = 43.2 Hz; coalescence temperature T_c = 258 K; activation energy: $\Delta G^{\ddagger}$(258 K) = 12.3 ± 0.3 kcal mol^{-1}; with $\Delta G^{\ddagger} = RT_c\ln((RT_c2^{1/2})/(2\pi N_A h\Delta\nu))$. TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 198 K): Irradiation at δ = 2.45 (3-H) gave resonances at δ = 6.38 (4-H), 5.31 (5-H), 2.03 (6-H′), 1.31 (6-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 198 K): δ = 147.3 (pd, $^1J_{CF}$ = 235 Hz, *o*-B(C_6F_5)$_3$), 136.8 (pd, $^1J_{CF}$ = 235 Hz, *p*-B(C_6F_5)$_3$), 136.0 (C4), 135.6 (pd, $^1J_{CF}$ = 235 Hz, *m*-B(C_6F_5)$_3$), 127.5 (br m, *ipso*-B(C_6F_5)$_3$), 124.5 (C5), 111.9 (C−Cp), 109.0 (C−Cp), 99.3 (C7), 38.8 (C3), 38.4 (C6), 28.3 (CH_3), 24.4 (CH_3), 9.19 (br m, *Me*−B(C_6F_5)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): δ = −131 (br s, 6F, *o*-C_6F_5); −163 (br s, 3F, *p*-C_6F_5); −166 (br s, 6F, *m*-C_6F_5).

2,2-Bis(η^5-cyclopentadienyl)-7,7-tetramethylene-2,3,6,7-tetrahydro-2-tantalaoxepine Methyltris(pentafluorophenyl)borate (13b). In a procedure similar to that for **13a** the cationic compound **13b** was obtained starting from 300 mg (0.336 mmol) of **10** and 0.1 mL (1.13 mmol) of cyclopentanone. Yield: 221 mg (67%), mp 130 °C (dec). Anal. Calcd for $C_{38}H_{27}BF_{15}OTa$ (976.33): C, 46.75; H, 2.79. Found: C, 46.19; H, 2.97. IR (KBr): $\tilde{\nu}$ = 3125, 2958, 1641, 1511, 1458, 1381, 1265, 1087, 1028−950, 847−802 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 6.43 (pq, J = 8.2 Hz, 1H, 4-H), 6.26 (s, 10H, Cp−H), 5.39 (pq, J = 8.5 Hz, 1H, 5-H), 2.58 (pd, J = 8.3 Hz, 2H, 3-H), 1.85 (br s, 2H, 6-H), 1.75−1.56 (m, 8H, 8-H, 9-H, 10-H, 11-H), 0.51 (br s, 3H, *Me*−B(C_6F_5)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 213 K) = 51.4 Hz; coalescence temperature T_c = 251 K; activation energy: $\Delta G^{\ddagger}$(251 K) = 11.9 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 198 K): δ = 6.36 (pq, J = 8.7 Hz, 1H, 4-H), 6.27/6.18 (each s, 5H, Cp−H), 5.34 (m, 1H, 5-H), 2.49 (m, 2H, 3-H), 2.01 (m, 1H, 6-H′), 1.55 (m, 1H, 6-H), 1.76−1.21 (m, 8H, 8-H, 9-H, 10-H, 11-H), 0.40 (br s, 3H, *Me*−B(C_6F_5)$_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 198 K): Irradiation at δ = 2.49 (3-H) gave resonances at δ = 6.36 (4-H), 5.34 (5-H), 2.01 (6-H′), 1.55 (6-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 198 K): δ = 147.6 (d, $^1J_{CF}$ = 234.8 Hz, *o*-B(C_6F_5)$_3$), 136.9 (d, $^1J_{CF}$ = 244.1 Hz, *p*-B(C_6F_5)$_3$), 135.6 (C4), 135.4 (d, $^1J_{CF}$= 247.8 Hz, *m*-B(C_6F_5)$_3$), 127.7 (br m, *ipso*-B(C_6F_5)$_3$), 124.7 (C5), 112.0 (C−Cp), 109.1 (C−Cp), 110.3 (C7), 39.3 (C3), 36.1 (C6), 38.5, 35.0, 23.2, 22.4 (C8, C9, C10, C11), 9.35 (br m, *Me*−B(C_6F_5)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH_3)B(C_6F_5)$_3$), −163 (m, 6F, *p*-(CH_3)B(C_6F_5)$_3$), −166 (m, 6F, *m*-(CH_3)B(C_6F_5)$_3$).

2,2-Bis(η^5-cyclopentadienyl)-7,7-pentamethylene-2,3,6,7-tetrahydro-2-tantalaoxepine Methyltris(pentafluorophenyl)borate (13c). The reaction of 350 mg (0.392 mmol) of **10** with 0.1 mL (0.965 mmol) of cyclohexanone according to the procedure of **13a** gives **13c**. Yield: 264 mg (69%), mp 139 °C (dec). Anal. Calcd for $C_{38}H_{27}BF_{15}OTa$ (976.33): C, 47.30; H, 2.95. Found: C, 46.57; H, 3.14. IR (KBr): $\tilde{\nu}$ = 3126, 2940, 2858, 1642, 1511, 1459, 1287, 1264, 1088, 997−936, 848, 840, 801 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 6.44 (pq, J = 7.5 Hz, 1H, 4-H), 6.25 (s, 10H, Cp−H), 5.33 (pq, J = 8.5 Hz, 1H, 5-H), 2.56 (pd, J = 8.3 Hz, 2H, 3-H), 1.85−1.20 (m, 12H, 6-H, 8-H, 9-H, 10-H, 11-H, 12-H), 0.50 (br s, 3H, *Me*−B(C_6F_5)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 213 K) = 37.5 Hz; coalescence temperature T_c = 260 K; activation energy $\Delta G^{\ddagger}$(260 K) = 12.5 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 213 K): δ = 6.38 (pq, J = 9.0 Hz, 1H, 4-H), 6.26/6.20 (each s, 5H, Cp−H), 5.30 (m, 1H, 5-H), 2.48 (m, 2H, 3-H), 1.98 (m, 1H, 6-H′), 1.24 (m, 1H, 6-H), 1.81−1.10 (m, 10H, 8-H, 9-H, 10-H, 11-H, 12-H), 0.41 (br s, 3H, *Me*−B(C_6F_5)$_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 198 K): Irradiation at δ = 2.48 (3-H) gave resonances at δ = 6.38 (4-H), 5.30 (5-H), 1.98 (6-H′), 1.24 (6-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 198 K): δ = 147.5 (pd, $^1J_{CF}$ = 235.8 Hz, *o*-B(C_6F_5)$_3$); 136.9 (pd, $^1J_{CF}$ = 244.2 Hz, *p*-B(C_6F_5)$_3$), 135.8 (C4), 135.7 (pd, $^1J_{CF}$ = 244.8 Hz, *m*-B(C_6F_5)$_3$); 127.6 (br m, *ipso*-B(C_6F_5)$_3$), 124.3 (C5), 112.2 (C−Cp), 109.6 (C−Cp), 102.5 (C7), 39.5 (C3), 39.3 (C6), 36.6, 33.8, 24.6, 22.2, 21.5 (C8, C9, C10, C11, C12), 9.36 (br m, *Me*−B(C_6F_5)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15 ppm. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): δ = −131 (m, 6F, *o*-(CH_3)B(C_6F_5)$_3$), −163 (m, 6F, *p*-(CH_3)B(C_6F_5)$_3$), −166 (m, 6F, *m*-(CH_3)B(C_6F_5)$_3$).

2,2-Bis(η^5-cyclopentadienyl)-7,7-diphenyl-2,3,6,7-tetrahydro-2-tantalaoxepine Methyltris(pentafluorophenyl)borate (13d). A 400 mg (0.448 mmol) sample of **10** and 163 mg (0.897 mmol) of benzophenone were dissolved in 20 mL of bromobenzene and stirred for 48 h at 60 °C. Afterward the solvent was removed, and the residue was taken up in 5 mL of dichloromethane. Addition of 10 mL of pentane led to the precipitation of an oily product. The solvent was decanted and the crude product stirred for 8 h at −20 °C in 20 mL of pentane. Subsequently the product was collected on a Schlenk frit, washed with two portions of 20 mL of pentane (cooled to −20 °C), and dried in vacuo. Yield: 373 mg (77%), mp 136 °C (dec). Anal. Calcd for $C_{46}H_{29}BF_{15}OTa$ (1074.33): C, 51.43; H,

2.72. Found: C, 49.71; H, 3.06. IR (KBr): $\tilde{\nu}$ = 3123, 2960, 1645, 1510, 1458, 1382, 1267, 1087, 1032−945, 842−786 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 7.40−7.38 (m, 4H, *m*-Ph), 7.35−7.33 (m, 2H, *p*-Ph), 7.16−7.14 (m, 4H, *o*-Ph), 6.52 (pq, J = 8.5 Hz, 1H, 4-H), 6.21 (s, 10H, Cp−H), 5.31 (pq, J = 8.3 Hz, 1H, 5-H), 2.71 (br pd, 6-H, 3-H), 0.54 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 213 K) = 42.9 Hz; coalescence temperature T_c = 245 K; activation energy $\Delta G^{\ddagger}$(245 K) = 11.7 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 213 K): δ = 7.37−7.25 (m, 6-H, *m*-Ph, *p*-Ph), 7.15−7.03 (each pd, 7.49 and 7.65 Hz, 2H, *o*-Ph), 6.47 (pq, J = 9.2 Hz, 1H, 4-H), 6.20/6.13 (each s, 5H, Cp−H), 5.18 (pq, J = 9.1 Hz 1H, 5-H), 3.11 (pq, J = 7.5 Hz, 1H, 6-H′), 2.76 (pt, J = 10.3 Hz, 1H, 3-H′), 2.49 (pq, J = 8.1 Hz, 1H, 3-H), 2.07 (pt, J = 10.7 Hz, 1H, 6-H), 0.43 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 213 K): Irradiation at δ = 5.18 (5-H) gave resonances at δ = 6.47 (4-H), 3.11 (6-H′), 2.76 (3-H′), 2.49 (3-H), 2.07 (6-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 213 K): δ = 147.3 (pd, $^1J_{CF}$ = 237.6 Hz, *o*-B(C$_6$F$_5$)$_3$), 143.8, 142.3 (*ipso*-Ph), 136.9 (C4), 136.7 (pd, $^1J_{CF}$ = 243.6 Hz, *p*-B(C$_6$F$_5$)$_3$), 135.7 (pd, $^1J_{CF}$ = 246.3 Hz, *m*-B(C$_6$F$_5$)$_3$), 128.5, 128.2 (*m*-Ph), 128.2, 127.4 (*p*-Ph), 127.7 (br m, *ipso*-B(C$_6$F$_5$)$_3$), 125.7, 125.4 (*o*-Ph), 124.4 (C5), 112.0 (C−Cp), 109.9 (C−Cp), 104.8 (C7), 40.9 (C3), 37.4 (C6), 9.2 (br m, *Me*−B(C$_6$F$_5$)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): δ = −131 (m, 6F, *o*-(CH$_3$)B(C$_6$F$_5$)$_3$), −163 (m, 6F, *p*-(CH$_3$)B(C$_6$F$_5$)$_3$), −166 (m, 6F, *m*-(CH$_3$)B(C$_6$F$_5$)$_3$).

2,2-Bis(η^5-cyclopentadienyl)-7-methyl-7-phenyl-2,3,6,7-tetrahydro-2-tantalaoxepine Methyltris(pentafluorophenyl)borate (13e). According to the procedure of **13d** reaction of 500 mg of **10** and 0.2 mL (1.71 mmol) of acetophenone resulted in the formation of the adduct **13e**. Yield: 361 mg (64%), mp 141 °C (dec). Anal. Calcd for C$_{41}$H$_{27}$BF$_{15}$OTa (1012.26): C, 48.65; H, 2.68. Found: C, 46.36; H, 2.85. IR (KBr): $\tilde{\nu}$ = 3122, 2930, 1646, 1510, 1458, 1274, 1095, 992−951, 850, 776, 767 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 7.43−7.41 (m, 2H, *m*-Ph), 7.37−7.35 (m, 1H, *p*-Ph), 7.25−7.24 (m, 2H, *o*-Ph), 6.49 (pq, J = 8.5 Hz, 1H, 4-H), 6.36, 6.09 (each s, 5 H, Cp−H), 5.48 (pq, J = 8.7 Hz, 1H, 5-H), 2.63 (m, 4H, 3-H, 6-H), 1.51 (br s, 3H, 14-H), 0.53 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 213 K) = 58.8 Hz; coalescence temperature T_c = 255 K; activation energy $\Delta G^{\ddagger}$(255 K) = 12.0 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 198 K): The ^{1}H NMR spectrum showed two isomers in a ratio of 55:45. δ = 7.40−7.24 and 7.10−7.08 (m, 10H, Ph−H isomers **A** and **B**). Isomer **A**: δ = 6.26 (m, 1H, 4-H), 6.14/6.04 (each s, 5H, Cp−H), 5.29 (m, 1H, 5-H), 2.93 (m, 1H, 6-H′), 2.64 (m, 2H, 3-H′), 2.45 (m, 1H, 3-H), 1.55 (m, 1H, 6-H), 1.60 (s, 3H, 14-H). Isomer **B:** δ = 6.54 (m, 1H, 4-H), 6.38/6.28 (each s, 5H, Cp−H), 5.47 (m, 1H, 5-H), 2.59 (m, 1H, 6-H′), 2.52 (m, 2H, 3-H), 1.75 (m, 1H, 6-H), 1.25 (s, 3H, 14-H) 0.42 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$, isomers **A** und **B**). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 198 K) isomer **A**: Irradiation at δ = 5.29 (5-H) gave resonances at δ = 6.26 (4-H), 2.93 (6-H′), 2.64 (3-H′), 2.45 (3-H), 1.55 (6-H). Isomer **B**: Irradiation at δ = 5.47 (5-H) gave resonances at δ = 6.54 (4-H), 2.59 (6-H′), 2.52 (3-H), 1.75 (6-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 213 K): The resonances of the methyltris(pentafluorophenyl)borate anions were identical for both isomers **A** and **B**: δ = 147.4 (pd, $^1J_{CF}$ = 234.0 Hz, *o*-B(C$_6$F$_5$)$_3$), 136.7 (pd, $^1J_{CF}$ = 243.2 Hz, *p*-B(C$_6$F$_5$)$_3$), 135.7 (pd, $^1J_{CF}$= 243.3 Hz, *m*-B(C$_6$F$_5$)$_3$), 127.7 (br m, *ipso*-B(C$_6$F$_5$)$_3$), 9.2 (br m, *Me*−B(C$_6$F$_5$)$_3$); isomer **A**: δ = 141.8 (*ipso*-Ph), 135.9 (C4), 128.3 (*m*-Ph), 127.5 (*p*-Ph), 124.6 (C5), 124.2 (*o*-Ph), 112.2 (C−Cp), 109.5 (C−Cp), 102.8 (C7), 39.8 (C3), 36.1 (C6), 31.2 (C14), isomer **B**: δ = 143.5 (*ipso*-Ph), 136.8 (C4), 128.2 (*m*-Ph), 127.9 (*p*-Ph), 124.3 (C5), 124.5 (*o*-Ph), 111.9 (C−Cp), 109.2 (C−Cp), 101.1 (C7), 39.4 (C3), 34.6 (C6), 25.8 (C14). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH$_3$)B(C$_6$F$_5$)$_3$), −163 (m, 6F, *p*-(CH$_3$)B(C$_6$F$_5$)$_3$), −166 (m, 6F, *m*-(CH$_3$)B(C$_6$F$_5$)$_3$).

2,2-Bis(η^5-cyclopentadienyl)-2,3-dihydro-7-methyl-2-tantala-6*H*-azepine Methyltris(pentafluorophenyl)borate (14a). A 300 mg (0.34 mmol) sample of **10** was dissolved in 15 mL of bromobenzene, and 0.1 mL (1.90 mmol) of acetonitrile was added. Then the solution was stirred for 5 h at 60 °C. Afterward the reaction mixture was filtered, and the solvent was removed in vacuo. The crude product was taken up in 20 mL of pentane and stirred for 5 h at − 20 °C. Subsequently the product was collected on a Schlenk frit, washed with two portions of 20 mL of pentane, and dried in vacuo. Yield: 235 mg (75%). Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **14a** at room temperature; mp 205 °C (dec). Anal. Calcd for C$_{35}$H$_{22}$BF$_{15}$NTa (933.16): C, 45.05; H, 2.39; N, 1.51. Found: C, 44.19; H, 2.89; N, 1.62. IR (KBr): $\tilde{\nu}$ = 3125, 2958, 2917, 1699, 1640, 1510, 1457, 1381, 1368, 1266, 1087, 965, 951, 845, 841, 757, 725, 659 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 6.28 (pq, 1H, 4-H), 6.00 (s, 10 H, Cp−H), 4.91 (pq, 1H, 5-H), 2.72 (br s, 2H, 6-H), 2.18 (s, 3H, 8-H), 1.83 (br s, 2H, 3-H), 0.50 (br s, *Me*−B(C$_6$F$_5$)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 198 K) = 42.7 Hz; coalescence temperature T_c = 239 K; activation energy $\Delta G^{\ddagger}$(239 K) = 11.4 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 198 K): δ = 6.20 (pq, 1H, 4-H), 5.99/5.92 (each s, 5H, Cp−H), 4.80 (pq, 1H, 5-H), 3.11 (dd, ^2J = 13.7 Hz, ^3J = 8.3 Hz, 1H, 6-H′), 2.09 (m, 1H, 6-H), 2.11 (s, 3H, 8-H), 2.04 (dd, ^2J = 10.0 Hz, ^3J = 8.1 Hz, 1H, 3-H′), 1.38 (pt, J = 10.0 Hz, 1H, 3-H). 0.37 (br s, *Me*−B(C$_6$F$_5$)$_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 198 K): Irradiation at δ = 4.76 (5-H) gave resonances at δ = 6.20 (4-H), 3.08 (6-H′), 2.09 (6-H), 2.01 (3-H′), 1.36 (3-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 198 K): δ = 181.1 (C7), 147.3 (pd, $^1J_{CF}$ = 253 Hz, *o*-B(C$_6$F$_5$)$_3$), 138.0 (C4), 136.7 (pd, $^1J_{CF}$ = 240 Hz, *p*-B(C$_6$F$_5$)$_3$), 135.6 (pd, $^1J_{CF}$ = 243 Hz, *m*-B(C$_6$F$_5$)$_3$), 127.3 (br m, *ipso*-B(C$_6$F$_5$)$_3$), 112.7 (C5), 107.3 (C−Cp), 104.7 (C−Cp), 35.2 (C6), 29.6 (C3), 26.3 (C8), 9.3 (br m, *Me*−B(C$_6$F$_5$)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH$_3$)B(C$_6$F$_5$)$_3$), −163 (m, 6F, *p*-(CH$_3$)B(C$_6$F$_5$)$_3$), −166 (m, 6F, *m*-(CH$_3$)B(C$_6$F$_5$)$_3$).

X-ray crystal structure analysis of **14a**: formula C$_{35}$H$_{22}$BF$_{15}$NTa, M = 933.30, yellow crystal, 0.30 × 0.30 × 0.20 mm, a = 10.020(1) Å, b = 10.813(1) Å, c = 15.027(1) Å, α = 80.38(1)°, β = 84.55(1)°, γ = 81.00(1)°, V = 1581.5(2) Å^3, ρ_{calc} = 1.960 g cm^{-3}, F(000) = 904 e, μ = 35.93 cm^{-1}, empirical absorption correction via φ scan data (0.831 ≤ C ≤ 0.999), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 173 K, $\omega/2\theta$ scans, 6680 reflections collected (±h, ±k, +l), [(sin θ)/λ] = 0.62 Å^{-1}, 6425 independent and 6036 observed reflections [$I \geq 2\,\sigma(I)$], 480 refined parameters, R = 0.036, wR2 = 0.103, max. residual electron density 1.46 (−3.31) e Å^{-3}, hydrogens calculated and refined as riding atoms.

2,2-Bis(η^5-cyclopentadienyl)-2,3-dihydro-7-ethyl-2-tantala-6*H*-azepine Methyltris(pentafluorophenyl)borate (14b). According to the procedure of **14a** the reaction of 300 mg (0.34 mmol) of **10** with 0.1 mL (1.40 mmol) of propionitrile resulted in the formation of **14b**. Yield: 181 mg (57%), mp 201 °C (dec). Anal. Calcd for C$_{36}$H$_{24}$BF$_{15}$NTa (947.19): C, 45.56; H, 2.56; N, 1.48. Found: C, 44.77; H, 2.93; N, 1.51. IR (KBr): $\tilde{\nu}$ = 3127, 2963, 2949, 1694, 1641, 1511, 1458, 1381, 1273, 1087, 968, 951, 846, 803, 756 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 6.27 (pq, 1H, 4-H), 5.96 (s, 10H, Cp−H), 4.87 (pq, 1H, 5-H), 2.66 (br s, 2H, 6-H), 2.43 (q, ^3J = 7.2 Hz, 2H, 8-H), 1.82 (br s, 2H, 3-H), 1.10 (t, ^3J = 7.2 Hz, 3H, 9-H), 0.50 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). Result of the

dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 213 K) = 44.4 Hz; coalescence temperature T_c = 248 K; activation energy: $\Delta G^{\ddagger}$(248 K) = 11.8 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 213 K): δ = 6.18 (pq, 1H, 4-H), 5.96/5.88 (each s, 5H, Cp−H), 4.79 (pq, 1H, 5-H), 3.05 (dd, ^2J = 13.6 Hz, ^3J = 8.3 Hz, 1H, 6-H′), 2.47 (m, 1H, 8-H′), 2.26 (m, 1H, 8-H), 2.07 (m, 1H, 6-H), 2.05 (m, 1H, 3-H′), 1.38 (pt, J = 9.4 Hz, 1H, 3-H), 1.00 (pt, J = 7.1 Hz, 3H, 9-H), 0.40 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 213 K): δ = 184.64 (C7), 147.5 (pd, $^1J_{CF}$ = 237.6 Hz, *o*-B(C$_6$F$_5$)$_3$), 138.1 (C4), 136.8 (pd, $^1J_{CF}$ = 243.6 Hz, *p*-B(C$_6$F$_5$)$_3$), 135.7 (pd, $^1J_{CF}$ = 246.3 Hz, *m*-B(C$_6$F$_5$)$_3$), 127.5 (br m, *ipso*-B(C$_6$F$_5$)$_3$), 112.5 (C5), 107.4, 104.8 (C−Cp), 35.0 (C6), 33.0 (C8), 29.7 (C3), 9.4 (br m, *Me*−B(C$_6$F$_5$)$_3$), 9.1 (C9). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH$_3$)B(C$_6$F$_5$)$_3$), −163 (m, 6F, *p*-(CH$_3$)B(C$_6$F$_5$)$_3$), −166 (m, 6F, *m*-(CH$_3$)B(C$_6$F$_5$)$_3$).

2,2-Bis(η^5-cyclopentadienyl)-2,3-dihydro-7-phenyl-2-tantala-6*H*-azepine Methyltris(pentafluorophenyl)borate (14c). A 300 mg (0.34 mmol) sample of **10** and 0.1 mL (0.98 mmol) of benzonitrile were dissolved in 15 mL of bromobenzene and stirred for 10 h at 60 °C. The reaction mixture was filtered, and the solvent was removed. The residue was taken up in 5 mL of dichloromethane. After addition of 15 mL of pentane the crude product precipitated. The solvent was decanted, and the crude product was stirred for 5 h at − 20 °C in 20 mL of pentane. Subsequently the product was collected on a Schlenk frit, washed with three portions of 15 mL of pentane (cooled at −20 °C), and dried in vacuo. Yield: 231 mg (69%), mp 198 °C (dec). Anal. Calcd for $C_{40}H_{24}BF_{15}NTa$ (995.23): C, 48.27; H, 2.43; N, 1.41. Found: C, 46.77; H, 2.68; N, 1.41. IR (KBr): $\tilde{\nu}$ = 3125, 2959, 1652, 1512, 1457, 1266, 1087, 995−935, 849 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 7.79 (m, 2H, 9-H), 7.63 (m, 1H, 11-H), 7.55 (m, 2H, 10-H), 6.43 (pq, 1H, 4-H), 6.08 (s, 10H, Cp−H), 5.63 (pq, 1H, 5-H), 3.20 (v br, 2H, 6-H), 1.99 (br, 2H, 3-H), 0.52 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 198 K) = 40.9 Hz; coalescence temperature T_c = 241 K; activation energy $\Delta G^{\ddagger}$(241 K) = 11.5 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 213 K): δ = 7.78 (pd, 2H, 9-H), 7.57 (pt, 1H, 11-H), 7.48 (pt, 2H, 10-H), 6.34 (pq, 1H, 4-H), 6.08/6.01 (each s, 5H, Cp−H), 4.93 (pq, 2H, 5-H), 3.99 (dd, ^2J = 13.5 Hz, ^3J = 8.4 Hz, 1H, 6-H′), 2.22 (dd, ^2J = 13.5 Hz, ^3J = 5.8 Hz, 1H, 6-H), 2.15 (dd, ^2J = 11.2 Hz, ^3J = 8.5 Hz, 1H, 3-H′), 1.62 (pt, ^3J = 8.5 Hz, 1H, 3-H), 0.41 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 213 K): Irradiation at δ = 2.22 (6-H) gave resonances at δ = 6.34 (4-H), 4.93 (5-H), 3.99 (6-H′), 2.15 (3-H′), 1.62 (3-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 213 K): δ = 175.5 (C7), 147.3 (pd, $^1J_{CF}$ = 241 Hz, *o*-B(C$_6$F$_5$)$_3$), 138.9 (C4), 136.72 (pd, $^1J_{CF}$ = 244 Hz, *p*-B(C$_6$F$_5$)$_3$), 135.7(pd, $^1J_{CF}$ = 249 Hz, *m*-B(C$_6$F$_5$)$_3$), 133.0 (C8), 130.7 (C11), 129.0 (C9), 128.5 (C10), 127 (br m, *ipso*-B(C$_6$F$_5$)$_3$), 113.4 (C5), 107.4/104.9 (each Cp−H), 30.2 (C6), 29.1 (C3), 9.2 (*Me*−B(C$_6$F$_5$)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH$_3$)B(C$_6$F$_5$)$_3$), −163 (m, 6F, *p*-(CH$_3$)B(C$_6$F$_5$)$_3$), −166 (m, 6F, *m*-(CH$_3$)B(C$_6$F$_5$)$_3$).

2,2-Bis(η^5-cyclopentadienyl)-2,3-dihydro-7-(p-tolylmethyl)-2-tantala-6*H*-azepine Methyltris(pentafluorophenyl)borate (14d). According to the procedure of **14c** the reaction of 500 mg (0.56 mmol) of **10** with 0.2 mL (1.52 mmol) of *p*-tolylacetonitrile led to the formation of **14d**. Yield: 369 mg (65%). Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **14d** at room temperature; mp 188 °C (dec). Anal. Calcd for $C_{42}H_{38}BF_{15}NTa$ (1023.3): C, 49.30; H, 2.76; N, 1.37. Found: C, 48.03; H, 2.90; N, 1.46. IR (KBr): $\tilde{\nu}$ = 3123, 2952, 1696, 1642, 1510, 1453, 1383, 1266, 1087, 1005−939, 850 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 298 K): δ = 7.21 (d, ^3J = 7.7 Hz, 10-H), 7.00 (d, ^3J = 7.7 Hz, 2H, 11-H), 6.26 (pq, 1H, 4-H), 5.83 (s, 5H, Cp−H), 4.84 (m, 1H, 5-H), 3.65 (s, 2H, 8-H), 2.72 (br s, 2H, 6-H), 2.36 (s, 3H, 13-H), 1.79 (br s, 2H, 3-H), 0.53 (br s, *Me*−B(C$_6$F$_5$)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 198 K) = 10.4 Hz; coalescence temperature T_c = 233 K; activation energy $\Delta G^{\ddagger}$(233 K) = 11.8 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 198 K): δ = 7.15 (d, ^3J = 7.8 Hz, 2H, 11-H), 6.96 (d, ^3J = 7,8 Hz, 2H, 10-H), 6.19 (pq, ^3J = 8.3 Hz, ^2J = 16.8 Hz, 1H, 4-H), 5.77/5.75 (each s, 5H, Cp−H), 4.77 (pdd, ^3J = 7.4 Hz, ^2J = 16.9 Hz, 1H, 5-H), 3.72/3.56 (each d, ^2J = 17.6 Hz, 1H, 8-H′, 8-H), 3.18 (pdd, ^3J = 8.2 Hz, ^2J = 13.7 Hz, 1H, 6-H′), 2.24 (s, 3H, 13-H), 2.20 (pdd, ^3J = 5.5 Hz, ^2J = 13.7 Hz,1H, 6-H), 1.98 (pdd, ^3J = 8.1 Hz, ^2J = 10.0 Hz, 1H, 3-H′), 1.38 (pt, J = 10.0, 1H, 3-H), 0.41 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 198 K): Irradiation at δ = 4.77 (5-H) gave resonances at δ = 6.19 (4-H), 3.18 (6-H′), 2.20 (6-H), 1.98 (3-H′), 1.38 (3-H). ^{13}C NMR (dichloromethane-d_2, 150.8 MHz, 198 K): δ = 181.6 (C7), 147.3 (pd, $^1J_{CF}$ = 244 Hz, *o*-B(C$_6$F$_5$)$_3$), 138.3 (C4), 136.9 (C9), 136.7 (pd, $^1J_{CF}$ = 244 Hz, *p*-B(C$_6$F$_5$)$_3$), 135.7 (pd, $^1J_{CF}$ = 244 Hz, *m*-B(C$_6$F$_5$)$_3$), 130.7 (C12), 128.9 (C11), 128.5 (C10), 127.3 (br m, *ipso*-B(C$_6$F$_5$)$_3$), 112.6 (C5), 107.2/104.7 (C−Cp), 45.1 (C8), 34.2 (C6), 29.7 (C3), 20.6 (C13), 9.35 (br m, *Me*−B(C$_6$F$_5$)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH$_3$)B(C$_6$F$_5$)$_3$), −163 (m, 6F, *p*-(CH$_3$)B(C$_6$F$_5$)$_3$), −166 (m, 6F, *m*-(CH$_3$)B(C$_6$F$_5$)$_3$).

X-ray crystal structure analysis of **14d**: formula $C_{42}H_{28}BF_{15}NTa$, M = 1023.41, yellow-orange crystal, 0.30 × 0.20 × 0.20 mm, a = 14.464(3) Å, b = 12.282(2) Å, c = 21.057(3) Å, β = 90.39(2)°, V = 3771.4(11) Å^3, ρ_{calc} = 1.802 g cm^{-3}, F(000) = 2000 e, μ = 30.23 cm^{-1}, empirical absorption correction via φ scan data (0.899 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 7858 reflections collected (±h, +k, +l), [(sin θ)/λ] = 0.62 Å^{-1}, 7648 independent and 6242 observed reflections [$I \geq 2\,\sigma(I)$], 543 refined parameters, R = 0.039, wR2 = 0.105, max. residual electron density 0.84 (−0.99) e Å^{-3}, hydrogens calculated and refined as riding atoms.

2,2-Bis(η^5-cyclopentadienyl)-2,3-dihydro-7-(diphenylmethyl)-2-tantala-6*H*-azepine Methyltris(pentafluorophenyl)borate (14e). According to the procedure of **14c** the reaction of 400 mg (0.45 mmol) of **10** with 0.2 mL (0.897 mmol) of diphenylacetonitrile led to the formation of **14e**. Yield: 321 mg (66%), mp 207 °C (dec). Anal. Calcd for $C_{47}H_{30}BF_{15}NTa$ (1085.36): C, 52.01; H, 2.79; N, 1.29. Found: C, 51.10; H, 3.14; N, 1.39. IR (KBr): $\tilde{\nu}$ = 3110, 1695, 1640, 1510, 1457, 1264, 1087, 994−934, 841, 702 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz): δ = 7.42 (m, 4-H, *m*-Ph), 7.37 (m, 2H, *p*-Ph), 7.08 (m, 4-H, *o*-Ph), 6.32 (pq, 1H, 4-H), 5.83 (s, 10, Cp−H), 5.05 (s, 1H, 8-H), 4.86 (pq, 1H, 5-H), 2.76 (br s, 2H, 6-H), 1.84 (br s, 2H, 3-H), 0.53 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). Result of the dynamic ^{1}H NMR spectroscopy (dichloromethane-d_2, 599.8 MHz): $\Delta\nu$ of the Cp resonances without exchange (T = 198 K) = 67.3 Hz; coalescence temperature T_c = 251 K; activation energy $\Delta G^{\ddagger}$(251 K) = 11.8 ± 0.3 kcal mol^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.8 MHz, 198 K): δ = 7.36 (m, 4H, *m*-Ph), 7.30 (m, 2H, *p*-Ph), 7.06/6.93 (each d, ^3J = 7.5 Hz, ^3J = 7.3 Hz, 2H, *o*-Ph), 6.25 (pq, 1H, 4-H), 5.81/5.70 (each s, 5H, Cp−H), 5.12 (s, 1H, 8-H), 4.77 (pq, 1H, 5-H), 3.10 (dd, ^2J = 13.6 Hz, ^3J = 8.3 Hz, 1H, 6-H′), 2.24 (dd, ^2J = 13.6 Hz, ^3J = 5.1 Hz, 1H, 6-H), 2.00 (pt, J = 10.3 Hz, 1H, 3-H′), 1.45 (pt, J = 10.3 Hz, 1H, 3-H), 0.41 (br s, 3H, *Me*−B(C$_6$F$_5$)$_3$). TOCSY NMR (dichloromethane-d_2, 599.8 MHz, 198 K): Irradiation at δ = 2.24 (6-H′) gave resonances at δ = 6.25 (4-H), 4.77 (5-H), 3.10 (6-H′), 2.00 (3-H′), 1.45 (3-H). ^{13}C NMR (dichloromethane-

d_2, 150.8 MHz, 198 K): δ = 182.4 (C7), 147.4 (pd, $^1J_{CF}$ = 234 Hz, *o*-B(C_6F_5)$_3$), 138.5 (C4), 138.0, 136.7 (C9, C13), 136.7 (pd, $^1J_{CF}$ = 243 Hz, *p*-B(C_6F_5)$_3$), 135.7 (pd, $^1J_{CF}$ = 246 Hz, *m*-B(C_6F_5)$_3$), 128.8, 128.5, 128.2, 128.1 (C10, C11, C14, C15), 127.6, 127.5 (C12, C16), 127.4 (br m, *ipso*-B(C_6F_5)$_3$), 113.2 (C5), 107.2/104.7 (C−Cp), 59.7 (C8), 34.4 (C6), 30.2 (C3), 9.4 (br m, *Me*−B(C_6F_5)$_3$). ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15 ppm. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH_3)B(C_6F_5)$_3$), −163 (m, 6F, *p*-(CH_3)B(C_6F_5)$_3$), −166 (m, 6F, *m*-(CH_3)B(C_6F_5)$_3$).

(1−3:6-η)-5,6-Dimethylhexa-2,5-dien-1,6-ylenebis(η⁵-cyclopentadienyl)tantalum Methyltris(pentafluorophenyl)borate (15a). A 500 mg (0.56 mmol) sample of **10** and 0.2 mL of butyne were dissolved in 25 mL of bromobenzene and stirred for 48 h at 60 °C. Subsequently the solvent was removed and the residue was stirred in 20 mL of pentane. After collecting the product on a Schlenk frit the product was washed with two portions of 20 mL of pentane and dried in vacuo. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **15a** at room temperature. Yield: 381 mg (72%), mp 158 °C. Anal. Calcd for $C_{37}H_{25}BF_{15}Ta$ (946.20): C, 46.97; H, 2.66. Found: C, 46.61; H, 2.92. IR (KBr): $\tilde{\nu}$ = 3128, 2961, 2910, 2852, 1639, 1511, 1457, 1272, 1088, 1017−934, 861, 839 cm^{-1}. ^{1}H NMR (bromobenzene-d_5, 599.8 MHz, 298 K): δ = 5.00/4.88 (each s, 5H, Cp−H), 4.87−4.82 (m, 1H, 3-H), 4.77−4.71 (m, 1H, 2-H), 2.91 (pdd, ^2J = 16.1 Hz, ^3J = 4.6 Hz, 1H, 4-H′), 2.44−2.40 (m, 1H, 4-H), 2.11 (pdd, ^2J = 5.4 Hz, ^3J = 7.7 Hz, 1H, 1-H′), 1.44 (m, 3H, 7-H), 1.37 (s, 3H, 8-H), 1.10 (br s, 3H, *Me*−B(C_6F_5)$_3$), 1.03 (pdd, ^2J = 5.43 Hz, ^3J = 13.2 Hz, 1H, 1-H): TOCSY NMR (bromobenzene-d_5, 599.8 MHz, 298 K): Irradiation at δ = 4.87 (3-H) gave resonances at δ = 4.75 (2-H), 2.91 (4-H′), 2.42 (4-H), 2.11 (1-H′), 1.03 (1-H). ^{13}C NMR (bromobenzene-d_5, 599.8 MHz, 298 K): δ = 163.8 (C6), 148.6 (d, $^1J_{CF}$ = 237 Hz, *o*-B(C_6F_5)$_3$), 143.5 (C5), 137.6 (d, $^1J_{CF}$ = 244 Hz, *p*-B(C_6F_5)$_3$), 136.7 (d, $^1J_{CF}$ = 244 Hz, *m*-B(C_6F_5)$_3$), 112.2 (C2), 105.2 (C3), 102.8/101.8 (C−Cp), 43.3 (C4), 36.3 (C1), 28.3 (C7), 20.8 (C8), 11.2 (br m, *Me*−B(C_6F_5)$_3$). The resonance signal of the *ipso*-carbon atom of the tris(pentafluorophenyl)borane fragment was not observed. ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH_3)B(C_6F_5)$_3$), −163 (m, 6F, *p*-(CH_3)B(C_6F_5)$_3$), −166 (m, 6F, *m*-(CH_3)B(C_6F_5)$_3$).

X-ray crystal structure analysis of **15a**: formula $C_{37}H_{25}BF_{15}Ta$, M = 946.33, yellow crystal, 0.50 × 0.50 × 0.25 mm, a = 12.722(1) Å, b = 14.150(1) Å, c = 19.317(1) Å, β = 107.50(1)°, V = 3316.4(4) Å^3, ρ_{calc} = 1.895 g cm^{-3}, F(000) = 1840 e, μ = 34.28 cm^{-1}, empirical absorption correction via φ scan data (0.945 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 6941 reflections collected (±h, +k, +l), [(sin θ)/λ] = 0.62 Å^{-1}, 6739 independent and 5610 observed reflections [$I \geq 2\,\sigma(I)$], 500 refined parameters, R = 0.032, wR^2 = 0.089, max. residual electron density 1.33 (−1.78) e Å^{-3}, atom C3 disordered with ratio 054(2):046(2), thermal parameters of C11, C12, C15, and C16 indicate disorder, refinement with split positions leads to no improvement, hydrogens calculated and refined as riding atoms.

(1−3:6-η)-5-Propylhexa-2,5-dien-1,6-ylenebis(η⁵-cyclopentadienyl)tantalum Methyltris(pentafluorophenyl)borate (15b) and (1−3:6-η)-6-Propylhexa-2,5-dien-1,6-ylenebis(cyclopentadienyl)tantalum Methyltris(pentafluorophenyl)borate (15c). According to the procedure of **15a** the reaction of 500 mg (0.56 mmol) of **10** and 0.2 mL of pentyne led to the formation of a mixture of **15b** and **15c**. Yield: 412 mg (77%), mp 173 °C. Anal. Calcd for $C_{38}H_{27}BF_{15}Ta$ (960.23): C, 47.53; H, 2.83. Found: C, 47.54; H, 3.25. IR (KBr): $\tilde{\nu}$ = 3130, 2959, 2933, 2871, 1640, 1510, 1458, 1273, 1089, 1017−934, 854 cm^{-1}. ^{1}H NMR (bromobenzene-d_5, 599.8 MHz, 298 K): The ^{1}H NMR spectrum showed two regioisomers **15b**:**15c** in a ratio of 60:40. Isomer **15b**: δ = 6.64−6.61 (m, 1H, 6-H), 5.12−5.07 (m, 1H, 3-H), 5.03/4.89 (each s, 5H, Cp−H), 4.84−4.79 (m, 1H, 2-H), 2.86−2.82 (m, 1H, 4-H′), 2.30−2.24 (m, 1H, 4-H), 2.10−2.08 (m, 1H, 1-H′), 1.72−1.68 (m, 1H, 7-H′), 1.58−1.54 (m, 1H, 7-H), 1.27−1.21 (m, 1H, 8-H′), 1.17−1.15 (m, 1H, 8-H), 1.05−1.02 (m, 1H, 1-H), 0.87 (t, ^3J = 4.8 Hz, 9-H). Isomer **15c**: δ = 5.81−5.80 (m, 1H, 5-H), 5.04−4.89 (m, 1H, 3-H), 5.00−4.87 (each s, 5H, Cp−H), 4.61−4.55 (m, 1H, 2-H), 2.81−2.77 (m, 1H, 4-H′), 2.36−2.31 (m, 1H, 4-H), 2.07−2.04 (m, 1H, 1-H′), 1.83−1.78 (m, 1H, 7-H′), 1.75−1.72 (m, 1H, 7-H), 1.27−1.21 (m, 2H, 8-H), 1.01−0.97 (m, 1H, 1-H), 0.78 (t, ^3J = 7.8 Hz, 9-H). The resonance of the methyltris(pentafluorophenyl)borate anion was identical for both regioisomers at δ = 1.11. TOCSY NMR (bromobenzene-d_5, 599.8 MHz, 298 K) **15b**: Irradiation at δ = 2.09 (1-H′) gave resonances at δ = 5.10 (3-H), 4.82 (2-H), 2.84 (4-H′), 2.27 (4-H), 1.03 (1-H). **15c**: Irradiation at δ = 2.06 (1-H′) gave resonances at δ = 5.81 (5-H), 5.00 (3-H), 4.57 (2-H), 2.79 (4-H′), 2.33 (4-H), 0.99 (1-H). ^{13}C NMR (bromobenzene-d_5, 150.8 MHz, 298 K) **15b**: δ = 154.8 (C6), 147.9 (C5), 112.9 (C3), 111.5 (C2), 102.5/101.8 (C−Cp), 47.2 (C7), 37.9 (C4), 35.0 (C1), 23.7 (C8), 14.2 (C9). **15c**: δ = 157.9 (C6), 140.1 (C5), 114.2 (C3), 109.3 (C2), 103.0/102.9 (C−Cp), 43.6 (C7), 39.1 (C4), 33.6 (C1), 21.3 (C8), 13.9 (C9). The resonance signals of the methyltris(pentafluorophenyl)borate anion were identical for both regioisomers: 148.6 (pd, $^1J_{CF}$ = 237 Hz, *o*-B(C_6F_5)$_3$), 137.6 (pd, $^1J_{CF}$ = 246 Hz, *p*-B(C_6F_5)$_3$), 136.5 (pd, $^1J_{CF}$ = 246 Hz, *m*-B(C_6F_5)$_3$), 11.2 (br m, *Me*−B(C_6F_5)$_3$). The resonance signal of the *ipso*-carbon atom of the tris(pentafluorophenyl)borane fragment was not observed. ^{11}B NMR (dichloromethane-d_2, 200 MHz, 298 K): δ = −15. ^{19}F NMR (dichloromethane-d_2, 360 MHz, 298 K): −131 (m, 6F, *o*-(CH_3)B(C_6F_5)$_3$), −163 (m, 6F, *p*-(CH_3)B(C_6F_5)$_3$), −166 (m, 6F, *m*-(CH_3)B(C_6F_5)$_3$).

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Supporting Information Available: Details of the X-ray crystal structure analyses of complexes **10**, **14a**, **14d**, and **15a**, including complete listings of bond lengths and angles, thermal parameters, and atomic positional parameters and listings of additional NMR data (GCOSY and GHSQC) (43 pages). Ordering information is given on any current masthead page.

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