The reaction of (butadiene)tantalocene cation with bulky carbonyl derivatives

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Abstract

The (*s-trans*-η^4-butadiene)tantalocene cation (**1**, with $CH_3B(C_6F_5)_3^-$ anion) adds one molar equivalent of adamantanone to yield the metallacyclic seven-membered ring product **2a**. The X-ray crystal structure analysis of the tetrahydrotantalaoxepine cation **2a** reveals a non-planar envelope shaped structure of the metallacyclic framework. In solution a conformational equilibration of this framework is observed to take place on the NMR time scale with a Gibbs-activation energy of $\Delta G^{\neq}$ (260 K) = 12.5 ± 0.3 kcal mol^{-1}. Treatment of (η^4-C_4H_6)TaCp$_2^+$ (**1**) with 1-cyano-adamantane at 60°C in bromobenzene gave the analogously structured 2,2-bis(η^5-cyclopentadienyl)-3,6-dihydro-7-(1-adamantyl)-2-tantala-2*H*-azepine cation complex (**3a**) (topomerization barrier in solution: $\Delta G^{\neq}$ (256 K) = 12.1 ± 0.3 kcal mol^{-1}). © 1999 Published by Elsevier Science S.A. All rights reserved.

1. Introduction

We have recently described the synthesis, structure and several reactions of the bis(η^5-cyclopentadienyl)(*s-trans*-η^4-butadiene)tantalum cation [1]. It was prepared by Cp-anion ligand abstraction from (η^5-Cp)$_2$(η^1-Cp)(η^2-butadiene)Ta with [Cp$_2$ZrCH$_3^+$][CH$_3$B(C$_6$F$_5$)$_3^-$] [3]. (η^5-Cp)$_2$(η^1-Cp)(η^2-butadiene)Ta was prepared by treatment of CpTa(butadiene)Cl$_2$ [2] with two equivalents of sodium cyclopentadienide. The resulting salt [Cp$_2$Ta(η^4-C$_4$H$_6$)$^+$][CH$_3$B(C$_6$F$_5$)$_3^-$] (**1**) was characterized by X-ray diffraction. The Cp$_2$Ta(*s-trans*-η^4-butadiene)$^+$ cation is structurally analogous to the neutral Group 4 (*s-trans*-η^4-C$_4$H$_6$)MCp$_2$ complexes (M = Zr, Hf) [4], and it undergoes similar addition reactions [5]. Ketones as well as nitriles add readily to **1** to yield the seven-membered metallacyclic cation systems **2** and **3**, respectively (see Scheme 1). Several examples of the dihydrotantalaazepines **3** were characterized by X-ray

diffraction, but until recently we were not able to describe an example of the tetrahydrotantalaoxepine cations **2** by means of an X-ray crystal structure analysis. We have now obtained single crystals of a prime example of this class of compounds. The structural and spectroscopic features of this system (**2a**) are described in this article.

2. Results and discussion

The (butadiene)TaCp$_2^+$ cation (**1**, with CH$_3$B(C$_6$F$_5$)$_3^-$ anion) was treated with an equimolar quantity of adamantanone in bromobenzene. The reaction required heating to 60°C for 6 h reaction time to go to completion. The 1:1 addition product **2a** was isolated in > 70% yield as a gray–green solid. At 298 K the ^{1}H-NMR spectrum of **2a** (in dichloromethane-d_2) is rather simple. It features a single Cp resonance (10H) at δ 6.25 ppm and broad signals of the 2-tantala-tetrahydrooxepine CH$_2$ groups. The corresponding C^{4}H=C^{5}H double bond ^{1}H-NMR signals are observed at δ 6.45 and 5.32 ppm. However, complex **2a** shows a dynamic

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[1] X-ray crystal structure analyses by Roland Fröhlich and Birgit Wibbeling.
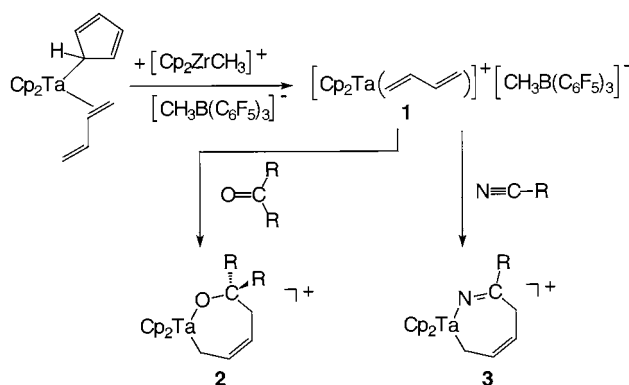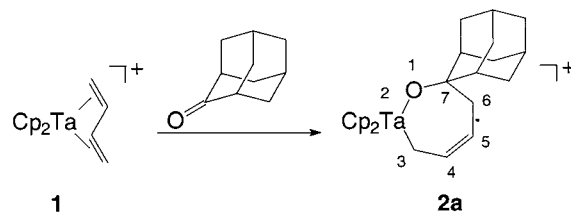
Scheme 1.

NMR behavior, and the CH_2 and Cp signals listed above are averaged resonances at high temperature. Lowering the temperature rapidly results in broadening of the respective signals and eventually to monitoring a pair of diastereotopic ^{1}H-NMR Cp singlets at (213 K) δ 6.26 and 6.20 ppm. The metallacyclic methylene groups feature ^{1}H-NMR resonances that are pairwise diastereotopic at δ 2.78 and 0.91 ppm (6-H, H′, see Scheme 2) and δ 2.58 and 2.49 ppm (3-H, H′). From the Cp coalescence of the ^{1}H-NMR Cp resonances a Gibbs activation energy of $\Delta G^{\neq}$ (260 K) = 12.5 ± 0.3 kcal mol^{-1} was obtained for the ring topomerization process [6] of the non-planar 2-tantala-tetrahydrooxepine framework of complex 2a.

The non-planar framework structure of complex 2a was also established by X-ray diffraction. Diffusion of pentane vapor into a solution of 2a in dichloromethane gave single crystals of the metallacycle that were suited for an X-ray crystal structure analysis. In the crystal, complex 2a exhibits an envelope-shaped core of atoms as it is typical for many early transition metal seven-membered ring systems [5]. To a first approximation, the atoms C6, Ta, O1, C2, C3 (atom numbering as in Fig. 1) are almost coplanarly arranged. A second plane is comprised of the atoms C3–C6, which originate from the butadiene building block. These two planes are arranged relative to each other at an angle of ca. 64°.

Carbon atom C2 has the adamantane framework spiro-connected with the seven-membered metallacycle. The corresponding O1–C2–C3 angle is 103.1(2)°. The most prominent feature of the structure of complex 2a is the very large Ta–O1–C2 angle (160.76(17)°). This indicates a pronounced metal–oxygen in-plane π-bonding component of the Cp_2Ta^+–O-linkage [5,7]. Consequently, the Ta–O1 bond is very short at 1.846(2) Å. The adjacent Ta–C6 bond is much longer at 2.247(3) Å and the in-plane bond angle at the Cp_2Ta bent metallocene unit is 90.15(11)° (O1–Ta–C6). The remaining bond lengths and angles inside the metallacyclic framework of the cationic complex 2a are in the normal expected range (for details see the legend of Fig. 1).

For the purpose of a structural comparison we have added 1-cyano-adamantane to (*s-trans*-η^4-butadiene)tantalocene cation (1). The reaction takes place smoothly at 60°C. The 1:1 addition product is formed during 6 h at that temperature in bromobenzene solution, and it was also isolated in > 70% yield. Again the ^{1}H- and ^{13}C-NMR spectra indicate the presence of a non-planar conformation of the heterocyclic ring system. At 223 K (at 150.8/599.8 MHz in dichloromethane-d_2) the features of a pair of diastereotopic Cp ligands at tantalum appear at δ 107.4, 105.0 (^{13}C) and δ 5.96, 5.87 ppm (^{1}H), respectively. The C^6H_2 methylene hydrogens are diastereotopic (δ 3.90, 1.72 ppm) as are the C^3H_2 hydrogen atoms (δ 2.10, 1.38 ppm). Increasing the monitoring temperature rapidly leads to a broadening and eventually pairwise coalescence of the NMR signals listed above (see Fig. 2). From the ^{1}H-NMR Cp coalescence a Gibbs activation energy of $\Delta G^{\neq}$ (256 K) = 12.1 ± 0.3 kcal mol^{-1} was deduced for the ring-inversion process of the dihydrotantala-2*H*-azepine cation complex (3a) (see Scheme 3).

Single crystals of 3a were obtained from CH_2Cl_2:pentane by means of the diffusion method. In
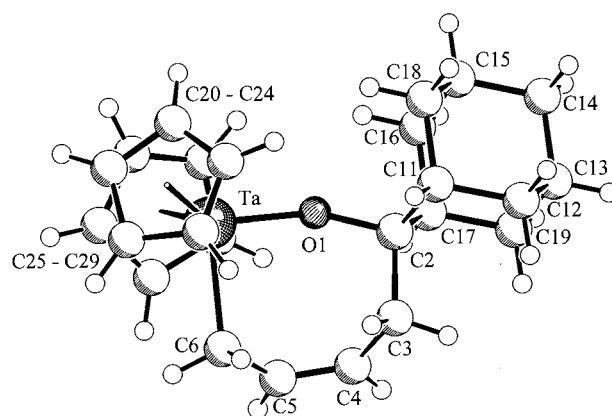

Scheme 2.

Fig. 1. A view of the molecular structure of complex 2a (cation only, with unsystematical atom numbering scheme). Selected bond lengths (Å) and angles (°): Ta–O1 1.846(2), O1–C2 1.443(3), C2–C11 1.542(4), C2–C17 1.532(4), C2–C3 1.556(4), C3–C4 1.501(5), C4–C5 1.328(5), C5–C6 1.483(5), Ta–C6 2.247(3); O1–Ta–C6 90.15(11), Ta–O1–C2 160.76(17), O1–C2–C3 103.1(2), O1–C2–C17 109.6(2), O1–C2–C11 108.7(2), C2–C3–C4 114.0(2), C3–C4–C5 125.4(3), C4–C5–C6 126.1(3), C5–C6–Ta 108.5(2).
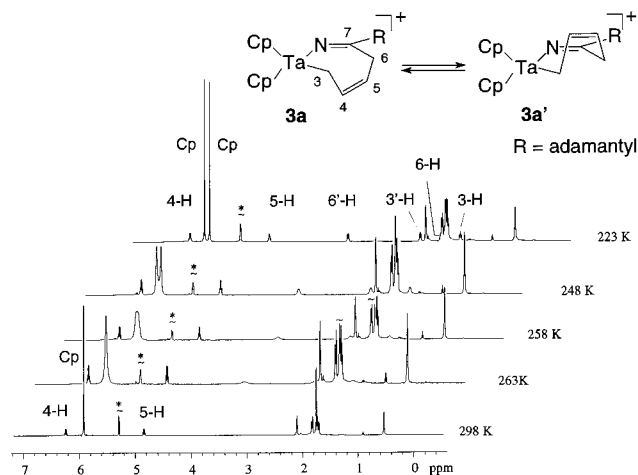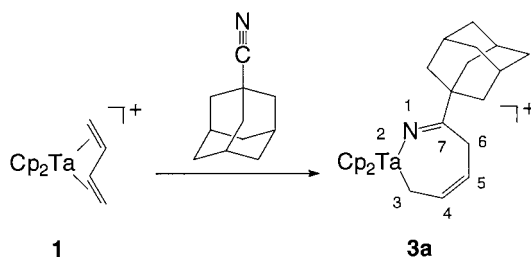
Fig. 2. Temperature-dependent dynamic ^{1}H-NMR spectra of complex **3a** (in CD_2Cl_2).

Fig. 3. Molecular structure of **3a** (cation only). Selected bond lengths (Å) and angles (°): Ta2–N1 1.897(4), Ta2–C3 2.294(5), C3–C4 1.462(7), C4–C5 1.331(7), C5–C6 1.477(7), C6–C7 1.555(7), C7–C8 1.520(7), N1–C7 1.266(6); Ta2–N1–C7 161.4(4), N1–Ta2–C3 85.70(19), Ta2–C3–C4 111.9(4), C3–C4–C5 127.8(6), C4–C5–C6 126.6(6), C5–C6–C7 113.4(4), C6–C7–C8 121.8(4), N1–C7–C8 123.5(5), N1–C7–C6 114.6(5).

the crystal complex **3a** exhibits a non-planar envelope-shaped seven-membered metallacyclic ring system. The idealized C3–C6 and C3, Ta2, N1, C7, C6 planes of atoms are arranged in an angle of ca. 60°. The bond angle at nitrogen (Ta2–N1–C7) is very large at 161.4(4)°. Again this probably indicates a substantial nitrogen lone-pair interaction with the available and spatially very favorably oriented acceptor orbital at tantalum in the σ-ligand ring plane [7,8]. The corresponding Ta2–N1 bond consequently is very short at 1.897(4) Å. The Ta2–C3 bond length is 2.294(5) Å, and the σ-ligand bond angle at the bent metallocene unit is 85.70(19)° (C3–Ta2–N1) [9]. The remaining bond lengths and angles of the seven-membered metallacycle are unexceptional and as expected (see Fig. 3).

This study shows that the (*s-trans*-η^4-butadiene)tantalocene cation (**1**) exhibits a reaction pattern that is typical for many (diene)metallocene complexes of the d-block elements at the left side of the periodic table. The structural properties of the metallacyclic insertion products of **1** with organic carbonyl compounds and derivatives fall within the typical range expected for such early metal heterometallacycles. The pronounced acceptor properties of the coordinatively unsaturated bent metallocene unit in the complexes **2** and **3** strongly determine the structural features of the obtained metallacycles. It appears that the cationic
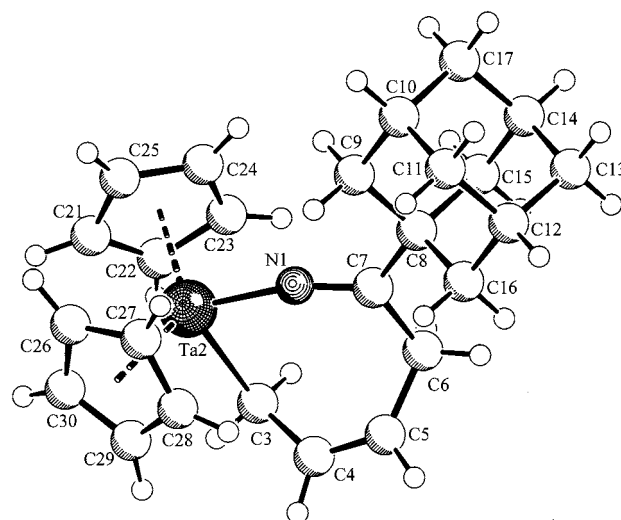
Cp_2Ta^+ unit in these complexes behaves quite analogously as the neutral Cp_2M moiety in the respective zirconocene and hafnocene systems [7]. Experimental studies are currently carried out in order to reveal the close structural and chemical similarities of the neutral $[Cp_2M^{IV}]$ and cationic $[Cp_2M^V]^+$ derived systems, but also to characterize their differences.

3. Experimental

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glove-box. For the preparation of the $[Cp_2Ta(butadiene)^+]$-$[CH_3B(C_6F_5)_3^-]$ starting material (**1**) and general information, including a list of the instruments used for spectroscopic and physical characterization of the compounds, see Ref. [1]. X-ray crystal structure analyses: data sets were collected with Enraf–Nonius KappaCCD (**2a**) and MACH3 (**3a**) diffractometers, equipped with a rotating anode generator. Programs used: DENZO-SMN/MOLEN (data reduction), SHELXS-86 (structure solution), SHELXL-97 (structure refinement), and SCHAKAL (graphics). For a compilation of the 1D and 2D NMR experiments used, see Ref. [10].

3.1. Reaction of (s-trans-η^4-butadiene)tantalocene cation (1·CH$_3$B(C$_6$F$_5$)$_3^-$) with adamantanone, preparation of 2a

$[(C_4H_6)TaCp_2^+][CH_3B(C_6F_5)_3^-]$ (**1**, 300 mg, 340 mmol) was mixed with 55.6 mg (370 mmol) of adaman-

Scheme 3.

tanone. Bromobenzene (10 ml) was added and the mixture stirred for 6 h at 60°C. After cooling to room temperature 10 ml of pentane was added. The supernatant solvent was decanted from the resulting precipitate, which was then dissolved in 5 ml of dichloromethane. The product was again precipitated by addition of 10 ml of pentane and collected by filtration; yield of **2a** 253 mg (72%), m.p. (dec.) 178°C. ^{1}H-NMR (dichloromethane-d_2, 599.8 MHz, 213 K): $\delta = 6.40$ (m, 1H, 4-H), 6.26, 6.20 (each s, 5H, Cp-H), 5.30 (m, 1H, 5-H), 2.78 (dd, $^3J_{HH} = 7.9$, $^2J_{HH} = 12.9$ Hz, 1H, 6-H′), 2.58 (dd, $^3J_{HH} = 8.4$, $^2J_{HH} = 12.1$ Hz, 1H, 3-H′), 2.49 (dd, $^3J_{HH} = 7.9$, $^2J_{HH} = 12.1$ Hz, 1H, 3-H), 1.94–1.38 (m, 14H, adamantane-moiety), 0.91 (pt, $J_{HH} = 12.9$ Hz, 1H, 6-H), 0.40 (br s, 3H, $\underline{Me}$–B(C_6F_5)$_3$) ppm; dynamic ^{1}H-NMR spectra: Δv of the Cp-resonances at 213 K: 35.3 Hz, coalescence temperature $T_c = 260$ K, $\Delta G^{\neq}$ (260 K) $= 12.5 \pm 0.3$ kcal mol^{-1} with $\Delta G^{\neq} = RT_c \ln((RT_c2^{1/2})/(2\pi N_A h\Delta v))$. 1D-TOCSY-NMR (dichloromethane-d_2, 599.8 MHz, 213 K): irradiation at $\delta = 5.25$ (5-H) ppm: response at $\delta = 6.40$ (4-H), 2.78 (6-H′), 2.58 (3-H′), 2.49 (3-H), 0.91 (6-H) ppm. GCOSY-NMR (dichloromethane-d_2, 599.8 MHz, 213 K): $\delta = 6.40/5.25$, 2.58, 2.49 (4-H/5-H, 3-H′, 3-H), 5.25/6.40, 2.78, 0.91 (5-H/4-H, 6-H′, 6-H), 2.78/5.25, 0.91 (6-H′/5-H, 6-H), 2.58/6.40, 2.49 (3-H′/4-H, 3-H), 2.49/6.40, 2.58 (3-H/4-H, 3-H′), 0.91/5.25, 2.78 (6-H/5-H, 6-H′) ppm. ^{13}C-NMR (dichloromethane-d_2, 599.8 MHz, 213 K): $\delta = 147.5$ (d, $^1J_{CF} = 235$ Hz, o-B(C_6F_5)$_3$), 136.9 (d, $^1J_{CF} = 234$ Hz, p-B(C_6F_5)$_3$), 135.8 (d, $^1J_{CF} = 234$ Hz, m-B(C_6F_5)$_3$), 135.7 (C4), 127.8 (br m, $ipso$-B(C_6F_5)$_3$), 124.1 (C5), 112.4, 109.9 (each C–Cp), 108.3 (C7), 39.3 (C3), 33.8 (C6), 37.5, 36.8, 34.2, 34.1, 34.0, 33.2, 32.3, 26.5, 26.3 (adamantane), 9.4 (br m, $\underline{Me}$–B(C_6F_5)$_3$) ppm. GHSQC-NMR (dichloro-methane-d_2, 150.8/599.8 MHz, 213 K): $\delta = 135.7/6.40$ (C4/4-H), 124.1/5.25 (C5/5-H), 112.4/6.20, 109.6/6.26 (C–Cp/Cp-H), 39.3/2.58 (C3/3-H′), 39.3/2.49 (C3/3-H), 33.8/2.78 (C6/6-H′), 33.8/0.91 (C6/6-H), 9.4/0.40 ($\underline{Me}$–B(C_6F_5)$_3$) ppm. ESI MS (dichloromethane): cation: $m/z = 516$ (100%), 462 (3%), 328 (95%). IR (KBr): $\tilde{v} = 3123$ (w), 2925 (m), 2904 (m), 2894 (s), 1641 (m), 1510 (vs), 1459 (vs), 1265 (s), 1101 (s), 1085 (vs), 993 (s), 963–937 (br m), 848 (vs), 841 (vs), 802 (m) cm^{-1}. Anal. Calc. for $C_{43}H_{33}BOF_{15}Ta$ (1042.4): C, 49.54; H, 3.19. Found: C, 48.52; H, 3.73%.

X-ray crystal structure analysis of **2a**: diffusion of pentane vapor into a dichloromethane solution (1.5 ml) containing 30 mg of **2a** gave single crystals suited for X-ray diffraction. Formula $C_{43}H_{33}BOF_{15}Ta$, $M_r = 1042.45$, yellow–orange crystal, $0.45 \times 0.25 \times 0.25$ mm, $a = 24.678(1)$, $b = 11.961(1)$, $c = 27.183(1)$ Å, $\beta = 110.03(1)°$, $V = 7538.4(8)$ Å^3, $D_{calc} = 1.837$ g cm^{-3}, $F(000) = 4096$ e, $\mu = 30.27$ cm^{-1}, absorption correction via SORTAV ($0.343 \leq T \leq 0.518$), $Z = 8$, monoclinic, space group $C2/c$ (no. 15), $\lambda = 0.71073$ Å, $T = 198$ K, φ

and ω scans, 20595 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin $\theta)/\lambda] = 0.72$ Å^{-1}, 8881 independent and 8130 observed reflections [$I \geq 2\sigma(I)$], 551 refined parameters, $R = 0.028$, $wR^2 = 0.070$, max. residual electron density 1.91 (-1.29) e Å^{-3} close to Ta, hydrogens calculated and refined as riding atoms.

3.2. Synthesis of 2,2-bis(η^5-cyclopentadienyl)-3,6-dihydro-7-(1-adamantyl)-2-tantala-2H-azepine methyltris(pentafluorophenyl)borate (3a)

A solution containing 350 mg (390 µmol) of **1** and 70.0 mg (430 µmol) of 1-cyanoadamantane in bromobenzene (10 ml) was kept at 60°C for 6 h. The product was precipitated by adding pentane (10 ml) at ambient temperature. It was dissolved in dichloromethane (5 ml) and precipitated again with pentane (10 ml) to give 303 mg (73%) of **3a**, m.p. (dec.) 180°C. ^{1}H-NMR (dichloromethane-d_2, 599.8 MHz, 223 K): $\delta = 6.22$ (m, 1H, 4-H), 5.96, 5.87 (each s, 5H, Cp-H), 4.80 (m, 1H, 5-H), 3.90 (dd, $^3J_{HH} = 8.5$, $^2J_{HH} = 13.1$ Hz, 1H, 6-H′), 2.10 (dd, $^3J_{HH} = 8.2$, $^2J_{HH} = 10.8$ Hz, 1H, 3-H′), 1.72 (dd, $^3J_{HH} = 6.9$, $^2J_{HH} = 13.1$ Hz, 1H, 6-H), 2.04–1.95, 1.71–1.57 (m, 15H, adamantyl), 1.38 (pt, $J_{HH} = 8.2$ Hz, 1H, 3-H), 0.40 (br s, 3H, $\underline{Me}$–B(C_6F_5)$_3$) ppm; dynamic ^{1}H-NMR spectra: Δv of the Cp-resonances at 223 K: 54.2 Hz, coalescence temperature $T_c = 256$ K, $\Delta G^{\neq}$ (256 K) $= 12.1 \pm 0.3$ kcal mol^{-1}. 1D-TOCSY-NMR (dichloromethane-d_2, 599.8 MHz, 223 K): irradiation at $\delta = 4.80$ (5-H) ppm: response at $\delta = 6.22$ (4-H), 3.90 (6-H′), 2.10 (3-H′), 1.72 (6-H), 1.38 (3-H) ppm. GCOSY-NMR (dichloromethane-d_2, 599.8 MHz, 223 K): $\delta = 6.22/4.80$, 2.10, 1.38 (4-H/5-H, 3-H′, 3-H), 4.80/6.22, 3.90, 1.72 (5-H/4-H, 6-H′, 6-H), 3.90/4.80, 1.72 (6-H′/5-H, 6-H), 2.10/6.22, 1.38 (3-H′/5-H, 3-H), 1.72/4.80, 3.90 (6-H/5-H, 6-H′), 1.38/6.22, 2.10 (3-H/5-H, 3-H′). ^{13}C-NMR (dichloromethane-d_2, 150.8 MHz, 223 K): $\delta = 188.3$ (C7), 147.6 (d, $^1J_{CF} = 233$ Hz, o-B(C_6F_5)$_3$), 138.4 (C4), 137.3 (d, $^1J_{CF} = 235$ Hz, p-B(C_6F_5)$_3$), 135.9 (d, $^1J_{CF} = 236$ Hz, m-B(C_6F_5)$_3$), 127.9 (br m, $ipso$-B(C_6F_5)$_3$), 113.3 (C5), 107.4, 105.0 (each C–Cp), 41.5 (C$_{quart}$–adamantyl), 37.6, 35.6, 27.3 (adamantyl), 29.5 (C3), 28.9 (C6), 9.4 (br m, $\underline{Me}$–B(C_6F_5)$_3$) ppm. GHSQC-NMR (dichloromethane-d_2, 150.8/599.8 MHz, 223 K): $\delta = 138.4/6.22$ (C4/4-H), 113.3/4.80 (C5/5-H), 107.4/5.87, 105.0/5.96 (C–Cp/Cp-H), 29.5/2.10 (C3/3-H′), 29.5/1.38 (C3/3-H), 28.9/3.90 (C6/6-H′), 28.9/1.72 (C6/6-H), 9.4/0.40 ($\underline{Me}$–B(C_6F_5)$_3$) ppm. ESI MS (dichloromethane): cation: $m/z = 526$ (100%), 472 (22%), 365 (10%), 311 (1%). IR (KBr): $v = 3127$ (w), 3118 (w), 2914 (s), 2850 (m), 1677 (w), 1641 (m), 1604 (m), 1510 (vs), 1458 (vs), 1265 (m), 1086 (vs), 944–933 (br m), 844 (s), 802 (w) cm^{-1} Anal. Calc. for $C_{44}H_{34}BNF_{15}Ta$ (1053.5): C, 50.16; H, 3.25; N, 1.33. Found: C, 49.17; H, 3.46; N, 1.41%.

X-ray crystal structure analysis of **3a**: single crystals were obtained from dichloromethane:pentane by the diffusion method. Formula $C_{44}H_{34}BNF_{15}Ta$, $M_r = 1053.48$, red–orange crystal, $0.25 \times 0.20 \times 0.10$ mm, $a = 13.707(3)$, $b = 12.329(2)$, $c = 23.714(5)$ Å, $\beta = 103.30(2)°$, $V = 3900.0(13)$ Å^3, $D_{calc} = 1.794$ g cm^{-3}, $F(000) = 2072$ e, $\mu = 29.26$ cm^{-1}, absorption correction via ψ scan data $(0.528 \leq T \leq 0.759)$, $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 15812 reflections collected $(\pm h, -k, \pm l)$, $[(\sin \theta)/\lambda] = 0.62$ Å^{-1}, 7913 independent and 4459 observed reflections $[I \geq 2\sigma(I)]$, 560 refined parameters, $R = 0.031$, $wR^2 = 0.058$, max. residual electron density 1.15 (-0.53) e Å^{-3} close to Ta, hydrogens calculated and refined as riding atoms.

4. Supplementary material

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 114300 and 114301. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: int. code + 44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc. cam.ac.uk).

Acknowledgements

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