Reaction of phenylacetylene with (butadiene)tantalocene cation

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

Treatment of the (s-*trans*-η^4-butadiene)tantalocene cation complex **3** (with [$CH_3B(C_6F_5)_3^-$] anion) with phenylacetylene results in the formation of the regioisomeric alkyne–butadiene coupling products **4a** (featuring the phenyl substituent in the β-position) and **4b** (Ph at the α-carbon) in a 70:30 ratio. The minor insertion product **4b** was characterized by an X-ray crystal structure analysis. © 2000 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

We have recently shown that (s-*trans*-η^4-butadiene)tantalocene cation (**3**) is readily available by treatment of (s-*cis*-η^4-C_4H_6)CpTaCl$_2$ (**1**) with two molar equivalents of sodium cyclopentadienide, to give (η^2-butadiene)(η^5-Cp)$_2$(η^1-Cp)Ta (**2**), followed by selective Cp-anion abstraction, e.g. employing [Cp$_2$ZrCH$_3^+$]. The co-product Cp$_3$ZrCH$_3$ is easily removed and the [Cp$_2$Ta(s-*trans*-η^4-C_4H_6)$^+$] product (**3**) isolated in good yield (with [$CH_3B(C_6F_5)_3^-$] anion, see Scheme 1) [1].

[(Butadiene)TaCp$_2^+$] (**3**) shows a chemical behavior similar to its neutral Group 4 analogue [(C_4H_6)ZrCp$_2$] [2]. Treatment with excess methylalumoxane results in the generation of a Ziegler catalyst system of medium activity for ethene polymerization [3]. The [(C_4H_6)TaCp$_2^+$] cation reacts cleanly with a variety of ketones or nitriles to yield seven-membered metallacycles. 2-Butyne is similarly inserted, but in this case a metallacyclic (η^3-allyl)metallocene cation complex is formed that was characterized by X-ray diffraction. Reaction of **3** with the terminal alkyne 1-pentyne gave a 60:40 mixture of two regioisomeric products (75%

overall yield) [1]. We have now treated (butadiene)tantalocene cation with phenylacetylene and investigated the regiochemical outcome of this alkyne-insertion reaction to differentiate between dominating steric or electronic control of the outcome of this general alkyne insertion reaction. Predominant formation of a regioisomeric insertion product that features the phenyl substituent in the α-position to the metal could be taken as an indication of dominating electronic control in the actual carbon–carbon coupling step [4], whereas substantial deviation from such a regiochemical behavior might be expected if steric factors predominantly influence the course of the reaction sequence.
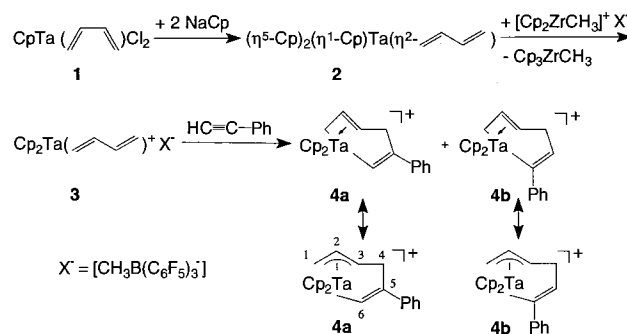
Scheme 1.

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[1] X-ray crystal structure analysis.

2. Results and discussion

(Butadiene)tantalocene cation (**3**, with [CH$_3$B(C$_6$F$_5$)$_3^-$] counteranion) was treated with an excess of phenylacetylene in bromobenzene solution. It required ca. 24 h at 60°C for the reaction to go to completion. Work-up furnished the 1:1 addition product in ca. 75% yield. Single crystals suitable for an X-ray crystal structure analysis were obtained by the diffusion method, i.e. by letting pentane vapor diffuse into a solution of the product in dichloromethane. The X-ray analysis revealed the presence of a single regioisomeric phenylacetylene addition product (**4b**) in the obtained solid.

In the crystal, the cations and anions of the product **4b** are well separated, but there is a ca. 1:1 positional disorder in the hexadienylene group. Averaged bonding features are given of the disordered parts. The addition of phenylacetylene to [(butadiene)TaCp$_2^+$] cation **3** has resulted in a clean carbon–carbon coupling reaction between the primary acetylene carbon atom and the terminal butadiene carbon atom. A metallacyclic (1–3:6-η-hexadienylene)tantalocene cation moiety has resulted, that bears the phenyl substituent regioselectively at the sp^2-carbon atom C6, which is also bonded to the tantalum center (see Fig. 1 and Scheme 1). The Ta–C6 bond length is 2.321(7) Å. In addition, the carbon atoms C1–C3 are bonded to tantalum. The resulting substituted (η^3-allyl)Ta unit is slightly unsymmetrical (Ta–C1 2.38(3) Å, Ta–C2 2.45(2) Å, Ta–C3 2.56(2) Å). The corresponding C1–C2 (1.40(3) Å) and C2–C3 (1.35(3) Å) bond length difference suggests some participation of a σ(C1), π(C2, C3) resonance structure of the η^3-allyl unit in complex **4b**, which seems to be a characteristic feature of such metallacyclic (π-allyl)metallocene complexes of the early transition metals [5].

In contrast, two isomeric phenylacetylene addition products, **4a** and **4b**, are found in a ca. 70:30 ratio in solution. Both contain very similar η^3-allyl units bonded to tantalum, as is evident from the corresponding ^{1}H- and ^{13}C-NMR features (see Table 1). The two compounds are regioisomers featuring the phenyl substituent either at carbon atom C5 (major isomer **4a**) or at carbon atom C6 of the σ-ligand chain (minor isomer **4b**, see Scheme 1). This is evident from the typical alterations of the HC≡CPh derived NMR signals [C(5)H in **4b**: δ 143.4 (^{13}C), 6.78 (^{1}H); C(5)Ph in **4a**: δ 153.7 (^{13}C); C(6)H in **4a**: δ 159.3 (^{13}C), 6.55 (^{1}H); C(6)Ph in **4b**: δ 168.1 (^{13}C)].

Thus we conclude that the minor regioisomer (**4b**) was characterized by X-ray diffraction. The reaction of [(butadiene)tantalocene$^+$] cation with phenylacetylene proceeds rather unselectively. The slightly preferred regioisomeric carbon–carbon coupling product (**4a**) bears the phenyl substituent in the β- rather than in the α-position to the metal. It appears that the regiochemical outcome of this carbon–carbon coupling process at
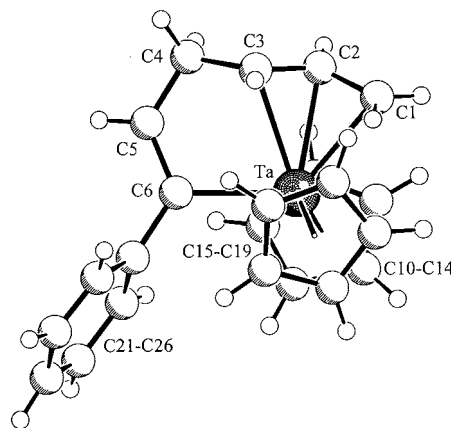

Fig. 1. Molecular structure of complex **4b** (cation only; one of the equivalent independent molecules is depicted). Selected bond lengths (Å) and angles (°) (averaged values of the two disordered parts): Ta–C1 2.38(3), Ta–C2 2.45(2), Ta–C3 2.56(2), Ta–C6 2.321(7), C1–C2 1.40(3), C2–C3 1.35(3), C3–C4 1.50(3), C4–C5 1.49(3), C5–C6 1.37(3), C6–C21 1.50(1); Ta–C1–C2 76.0(14), Ta–C2–C1 70.6(14), Ta–C2–C3 79.0(12), Ta–C3–C2 70.1(12), Ta–C3–C4 114.2(14), C1–C2–C3 123(3), C2–C3–C4 126(3), C3–C4–C5 108(2), C4–C5–C6 120(2).

Table 1
Selected ^{1}H- and ^{13}C-NMR data of the regioisomers **4a** (major) and **4b** (minor) [a]

	4a	**4b**
^{1}H		
Cp	5.10/4.93	5.07/4.89
1-H/H′	1.21/2.24	1.09/2.17
2-H	5.01	4.74
3-H	5.15	4.98
4-H/H′	2.44/2.99	2.82/3.46
5-H	–	6.78
6-H	6.55	–
^{13}C		
Cp	103.6/101.5	103.1/102.9
C1	36.4	34.4
C2	113.9	110.4
C3	110.7	110.1
C4	38.2	38.1
C5	153.7	143.4
C6	159.3	168.1

[a] In [D$_5$] bromobenzene at 298 K, atom numbering as depicted in Scheme 1.

the Group 5 metallocene template is dominated by steric rather than electronic factors, which would probably have resulted in a preferred formation of the α-isomer [4,6].

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$_2$Ta(butadiene)$^+$] [CH$_3$B(C$_6$F$_5$)$_3^-$] starting material (**3**) and additional general information, including a list of the instruments used for spectroscopic and physical characterization of the compounds, see Ref. [1].

3.1. Reaction of (butadiene)tantalocene cation with phenylacetylene, preparation of **4a** and **4b**

A 400 mg (450 μg) sample of **3** and 0.2 ml of phenylacetylene were dissolved in 10 ml of bromobenzene and stirred for 24 h at 60°C. The product was precipitated by adding 10 ml of pentane at ambient temperature. The supernatant solvent was decanted and the resulting precipitate was dissolved in 5 ml of dichloromethane and precipitated again with 10 ml of pentane. After removing the supernatant solvent, the residue was dried in vacuo to give a brown solid as a mixture of **4a** and **4b**; yield of **4**, 332 mg (75%), m.p. 173°C. ^{1}H-NMR (bromobenzene-d_5, 599.8 MHz, 298 K): The ^{1}H-NMR spectrum showed two regioisomers **4a**:**4b** in a ratio of 70:30. Isomer **A**: $\delta = 6.57$–5.54 (m, 1H, 6-H), 5.18–5.13 (m, 1H, 3-H), 5.10 (s, 5H, Cp–H), 5.03–5.00 (m, 1H, 2-H), 4.93 (s, 5H, Cp–H), 2.97 (dd, $^2J_{HH} = 16.8$ Hz, $^3J_{HH} = 4.2$ Hz, 1H, 4–H′), 2.39 (dd, $^2J_{HH} = 16.8$ Hz, $^3J_{HH} = 8.7$ Hz, 1H, 4–H), 2.24 (dd, $^2J_{HH} = 5.4$ Hz, $^3J_{HH} = 7.8$ Hz, 1H, 1-H′), 1.21 (dd, $^2J_{HH} = 5.4$ Hz, $^3J_{HH} = 13.2$ Hz, 1H, 1-H); Isomer **B**: $\delta = 6.78$ (m, 1H, 5-H), 5.07 (s, 5H, Cp–H), 5.01–4.97 (m, 1H, 3-H), 4.89 (s, 5H, Cp–H), 4.77–4.71 (m, 1H, 2-H), 3.46 (dd, $^2J_{HH} = 15.4$ Hz, $^3J_{HH} = 4.7$ Hz, 1H, 4-H′), 2.82 (ddd, $^2J_{HH} = 15.4$ Hz, $^3J_{HH} = 9.0$ Hz, $^4J_{HH} = 2.4$ Hz, 1H, 4-H), 2.17 (dd, $^2J_{HH} = 5.8$ Hz, $^3J_{HH} = 7.2$ Hz, 1H, 1-H′), 1.09 (dd, $^2J_{HH} = 5.8$ Hz, $^3J_{HH} = 13.1$ Hz, 1H, 1-H). The resonances of the methyltris(pentafluorophenyl)borate anion and of the phenyl substituents were not distinguished for the two regioisomers: $\delta = 7.27$–7.23 (m, 4H), 7.18–7.14 (m, 2H), 6.79–6.77 (m, 4H, Ph), 1.11 (Me–B(C$_6$F$_5$)$_3$). TOCSY-NMR (bromobenzene-d_5, 599.8 MHz, 298 K): Isomer **A**: Irradiation at $\delta = 2.24$ (1-H′) response at $\delta = 6.55$ (6-H), 5.15 (3-H), 5.01 (2-H), 2.97 (4-H′), 2.82 (4-H), 1.21 (1-H); Isomer **B**: Irradiation at $\delta = 3.46$ (4-H′) response at $\delta = 6.78$ (5-H), 4.98 (3-H), 4.74 (2-H), 2.82 (4-H), 2.17 (1-H′), 1.09 (1-H). GCOSY-NMR (brombenzene-d_5, 599.8 MHz, 298 K): Isomer **A**: $\delta = 6.55/2.97$, 2.39 (6-H/4-H′, 4-H), 5.15/5.01, 2.97, 2.39 (3-H/2-H, 4-H′, 4-H), 5.01/5.15, 2.24, 1.21 (2-H/3-H, 1-H′, 1-H), 2.97/6.55, 5.15, 2.39 (4-H′/6-H, 3-H, 4-H), 2.39/6.55, 5.15, 2.97 (4-H/6-H, 3-H, 4-H′), 2.24/5.01, 1.21 (1-H′/2-H, 1-H), 1.21/5.01, 2.24 (1-H/2-H, 1-H′); Isomer **B**: $\delta = 6.78/3.46$, 2.82 (5-H/4-H′, 4-H), 4.98/4.74, 3.46, 2.82 (3-H/2-H, 4-H′, 4-H), 4.74/4.98, 2.17, 1.09 (2-H/3-H, 1-H′, 1-H), 3.46/6.78, 4.98, 2.82 (4-H′/5-H, 3-H, 4-H), 2.82/6.78, 4.98, 3.46 (4-H/3-H, 4-H′), 2.17/4.74, 1.09 (1-H′/2-H, 1-H), 1.09/4.74, 2.17

(1-H/2-H, 1-H′). ^{13}C-NMR (bromobenzene-d_5: 150.8 MHz, 298 K): Isomer **A**: $\delta = 159.3$ (C6), 158.4 (*ipso*-C of Ph), 153.7 (C5), 128.5, 126.8, 124.8 (Ph), 113.9 (C2), 110.7 (C3), 103.6/101.5 (Cp), 38.2 (C4), 36.4 (C1); Isomer **B**: $\delta = 168.1$ (C6), 143.4 (C5), 141.3 (*ipso*-C of Ph), 128.4, 127.3, 126.8 (Ph), 110.4 (C2), 110.1 (C3), 103.1/102.9 (Cp), 38.1 (C4), 34.4 (C1); methyltris(pentafluorophenyl)borate anion: $\delta = 148.6$ (d, $^1J_{CF} = 235$ Hz, *o*-B(C$_6$F$_5$)$_3$), 137.6 (d, $^1J_{CF} = 235$ Hz, *p*-B(C$_6$F$_5$)$_3$), 136.6 (d, $^1J_{CF} = 246$ Hz, *m*-B(C$_6$F$_5$)$_3$), 11.2 (br m, Me–B(C$_6$F$_5$)$_3$) ppm (*ipso*-C of C$_6$F$_5$ not found). GH-SQC-NMR (bromobenzene-d_5, 150.8/599.8 MHz, 298 K): Isomer **A**: $\delta = 159.3/6.55$ (C6/6-H), 128.5/7.25, 126.8/6.78, 124.8/7.16 (arom.-C/-H), 113.9/5.01 (C2/2-H), 110.7/5.15 (C3/3-H), 103.6/5.10, 101.5/4.93 (C–Cp/Cp–H), 38.2/2.97 (C4/4-H′), 38.2/2.82 (C4/4-H), 36.4/2.24 (C1/1-H′), 36.4/1.21 (C1/1-H); Isomer **B**: $\delta = 143.4/6.78$ (C5/5-H), 128.4/7.25, 127.3/7.16, 126.8/6.78 (arom.-C/–H), 110.4/4.74 (C2/2-H), 110.1/4.98 (C3/3-H), 103.1/5.07, 102.9/4.89 (C–Cp/Cp–H), 38.1/3.46 (C4/4-H′), 38.1/2.82 (C4/4-H), 34.4/2.17 (C1/1-H′), 34.4/1.09 (C1/1-H); methyltris(pentafluorophenyl)-borate anion: $\delta = 11.2/1.12$ (Me–B(C$_6$F$_5$)$_3$) ppm. ^{11}B-NMR (bromobenzene-d_5, 64.2 MHz, 298 K): $\delta = -15$. ^{19}F-NMR (bromobenzene-d_5, 282.4 MHz, 298 K): $\delta = -131$ (m, 6F, *o*-CH$_3$B(C$_6$F$_5$)$_3$), -163 (m, 3F, *p*-CH$_3$B(C$_6$F$_5$)$_3$), -166 (m, 6F, *m*-CH$_3$B(C$_6$F$_5$)$_3$). IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3124 (w), 3051 (vw), 2959 (w), 2934 (w), 2844 (w), 1640 (m), 1595 (w), 1540 (w), 1511 (vs), 1456 (vs), 1379 (w), 1339 (w), 1265 (s), 1084 (vs), 1016/934 (br s), 847 (s), 803 (m), 756 (m), 700 (m), 658 (w), 641 (w), 546 (m). Anal. Calc. for C$_{41}$H$_{25}$BF$_{15}$Ta (994.4): C, 49.52; H, 2.53; found: C, 49.76; H, 2.70%.

X-ray crystal structure analysis of **4b**: diffusion of pentane vapor into a dichloromethane solution (1.5 ml) containing 30 mg of the **4a**–**4b** mixture gave single crystals of **4b** suited for X-ray diffraction. formula C$_{41}$H$_{25}$BF$_{15}$Ta, $M = 994.37$, $0.25 \times 0.25 \times 0.15$ mm, $a = 12.255(1)$, $b = 14.866(1)$, $c = 19.201(1)$ Å, $V = 3498.1(4)$ Å^3, $\rho_{calc.} = 1.888$ g cm^{-3}, $\mu = 32.55$ cm^{-1}, empirical absorption correction $(0.497 \leq T \leq 0.641)$, $Z = 4$, orthorhombic, space group $P2_12_12_1$ (no. 19), $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 30413 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin \theta)/\lambda$] = 0.67 Å^{-1}, 8565 independent ($R_{int} = 0.078$) and 7982 observed reflections [$I \geq 2\sigma(I)$], 570 refined parameters, $R = 0.042$, $wR^2 = 0.087$, max. residual electron density 1.78 (-1.68) e Å^{-3}, Flack parameter 0.06(1), positional disorder in the hexadienylene group (0.48(3): 0.52(3)), hydrogens calculated and refined as riding atoms.

Data set was collected with a Nonius KappaCCD diffractometer, using a rotating anode generator FR591. Programs used: data acquisition COLLECT, data reduction DENZO-SMN, absorption correction SORTAV, structure solution SHELXS-97, structure refinement SHELXL-97, graphics SCHAKAL-92 [7].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132962. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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