Group 5 Metal Complexes with Cyclooctatetraene: Formation and Characterization of (Butadiene)(cyclooctatetraene)(cyclopentadienyl)tantalum Systems

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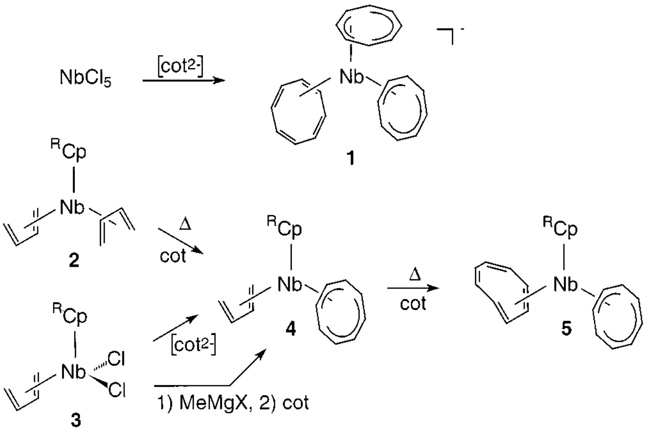
The [(η^4-diene)(η^5-^{R}Cp)$TaCl_2$] complexes **6a-e** (diene = butadiene, isoprene or 2,3-dimethylbutadiene; ^{R}Cp = pentamethylcyclopentadienyl, methylcyclopentadienyl or cyclopentadienyl) react with cyclooctatetraene dianion (employed as [(cot)Li_2]) to yield the (η^4-diene)(η^3-cyclooctatetraene)(η^5-^{R}Cp)tantalum complexes **7**. The η^3-cot coordination was confirmed by an X-ray crystal structure analysis of the compound [(*supine-s-cis*-η^4-C_4H_6)(η^3-cot)(η^5-Cp*)Ta] **7a**. In solution, the cot ligand of all the complexes **7** is fluxional. Two isomers [*supine* and *prone* orientation of the (diene)CpTa subunit] were found for the (η^4-butadiene)(η^3-cot)CpTa system (**7e**/**7e**′ = 95:5). Complex **7e** cleanly adds the organometallic Lewis acid $B(C_6F_5)_3$ to yield the betaine system [(η^4-C_4H_6){$C_8H_8B(C_6F_5)_3$}Cp*Ta] **8**, which contains a substituted bicyclo[5.1.0]octadienyl ligand.

Introduction

Cyclooctatetraene binds to the electropositive d-block metals of the left side of the periodic table (and to the f-elements) in a variety of coordination modes.[1] η^8-Coordination, η^4-conjugated diene-like and also η^2-bonding of the cot ligand can be found[2–4] and, most interestingly, η^3-coordination is not uncommon.[5] In these cases a π^5-section of the C_8H_8 ligand remains uncoordinated, which formally leads to an unsymmetrical, potentially dipolar electronic distribution at the M(η^3-C_8H_8) subunit. Such complexes were first reported by Schrock et al. The [(η^4-cot)(η^3-cot)$_2$Nb]$^-$ anion (**1**) is a typical example.[5] Recent examples include the [(*supine*-η^4-*s-cis*-butadiene)CpNb(η^3-cot)] system (**4**)[6] and its Cp*Nb analogue.[7] We have now prepared a series of related tantalum complexes. This work supplements the Nb-series, reported recently, but also has revealed a variety of subtle, but important, differences and variations.



Scheme 1. Previous syntheses of (cot)Nb complexes

Results and Discussion

Most examples of Cp- and Cp*Nb(η^4-butadiene)(η^3-cyclooctatetraene) complexes known so far have been prepared either by butadiene ligand displacement starting from [Cp(η^4-butadiene)$_2$Nb] **2** or by trapping of the bent metallocene analogue Cp*(η^4-butadiene)Nb, generated in situ, with cyclooctatetraene.[5–7] For this study we have exclusively used the [^{R}Cp(η^4-diene)$TaCl_2$] complexes **6** as precursors[8] and treated them with the cyclooctatetraene dianion[9] to form the corresponding [^{R}Cp(η^4-diene)(η^3-cyclooctatetraene)Ta] complexes **7** [^{R}Cp = η^5-C_5H_5, η^5-$C_5H_4(CH_3)$ or η^5-$C_5(CH_3)_5$; diene = butadiene, isoprene or 2,3-dimethylbutadiene].

A typical example is the reaction of [(η^4-butadiene)(η^5-pentamethylcyclopentadienyl)$TaCl_2$] **(6a)** with the cyclooctatetraene dianion (employed as the corresponding dilithium salt). The reaction is carried out in toluene solution and takes about 15 h at 50°C to go to completion. Workup gives the product **7a** as a very dark-colored solid in approximately 50% yield. Dark red single crystals suitable for an X-ray crystal structure analysis were obtained from a toluene/pentane solution.

Complex **7a** has a central tantalum atom that is surrounded by a trigonal array of three π ligands. The pentamethylcyclopentadienyl ligand is η^5-coordinated [average Ta–C(Cp*) distance = 2.439(6) Å]. The η^4-*s-cis*-butadiene

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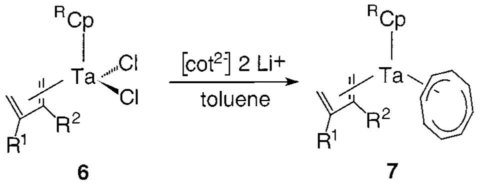
[+] NMR spectroscopy.

[++] X-ray crystal structure analysis.



	^{R}Cp	R^1	R^2
a	η^5-$C_5(CH_3)_5$	H	H
b	η^5-$C_5(CH_3)_5$	CH_3	H
c	η^5-$C_5(CH_3)_5$	CH_3	CH_3
d	η^5-$C_5H_4(CH_3)$	H	H
e	η^5-C_5H_5	H	H

Scheme 2. Preparation of the (η^4-diene)(η^3-cot)^{R}CpTa complexes **7**

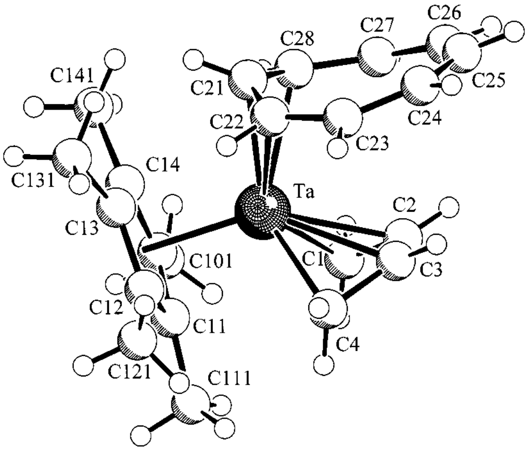


Figure 1. Molecular structure of **7a** with unsystematical atom numbering scheme

ligand opens toward the Cp* ligand (i.e. *supine*[8] oriented) and the Ta−C_4H_6 subunit exhibits some metallacyclopentene structural properties. It can probably best be described as approaching a metallacyclic σ^2,π-type structure as is often observed for early transition metal conjugated diene complexes.[10−12] This description is supported by the observed long-short-long bond alternation of the carbon framework of the butadiene ligand in complex **7a** (see Table 1). Also, the bonds between tantalum and the terminal diene ligand carbon atoms are markedly shorter [Ta−C1 = 2.252(6), Ta−C4 = 2.240(6) Å] than the bonds to the internal butadiene carbon centers [Ta−C2 = 2.433(5), Ta−C3 = 2.424(5) Å]. Similar conjugated diene C−C lengths were observed for both the [Cp*(η^4-butadiene)(η^3-cot)Nb] complex **4a**[7] and the related [(MeCp)(η^4-cot)(η^3-cot)Nb] complex **5a**.[6] These three systems, however, differ markedly in their relative M−C(diene) lengths (see Table 1). From these data a trend becomes apparent and it is possible to assign to the new tantalum complex **7a** the most pronounced σ-complex character of the M(diene) subunit in this series of compounds.

The cot ligand in **7a** is only η^3-coordinated. The central Ta−C21 bond length is 2.239(5) Å. It is the shortest metal to carbon bond of this group. The adjacent (η^3-cot)Ta linkages are slightly longer at 2.426(5) Å (Ta−C28) and 2.455(5) Å (Ta−C22). The next pair of distances (Ta···C27: 3.228(5) Å and Ta···C23: 3.333(5) Å) lie outside the range of a significant bonding interaction. The η^3-cot ligand in **7a** is coordinated in a *prone* orientation[8] and the ligand is slightly folded away from tantalum (see Table 1). There is no significant bond alternation visible in the η^3-C_8H_8 framework, so it appears that the cot ligand in **7a** has substantially retained its aromatic character with regard to its structural properties. It is structurally apart from the examples of "semiaromatic" cot character, that have recently been reported in the literature.[8b,13]

Table 1. A comparison of selected structural parameters of the complexes **7a, 4a** and **5a**[a]

	7a (Ta)	**4a** (Nb)	**5a** (Nb)
M−C1	2.252(6)	2.307(4)	2.453(5)
M−C2	2.433(5)	2.424(4)	2.363(4)
M−C3	2.424(5)	2.393(4)	2.375(3)
M−C4	2.240(6)	2.270(4)	2.456(3)
C1−C2	1.414(8)	1.415(6)	1.418(6)
C2−C3	1.392(8)	1.382(6)	1.394(8)
C3−C4	1.448(9)	1.423(6)	1.401(7)
α (C1, C4)[b]	104.5	101.9	[c]
M−C21	2.239(5)	2.255(4)	2.259(4)
M−C22	2.455(5)	2.452(4)	2.421(3)
M−C28	2.426(5)	2.424(4)	2.463(4)
M···C23	3.333(5)	[c]	3.192(4)
M···C27	3.228(5)	[c]	3.287(4)
α (C22, C28)[b]	25.3	[c]	23.6
α (C23, C27)[b]	12.7	[c]	11.8
α (C24, C26)[b]	4.9	[c]	4.2
C21−C28	1.423(7)	1.415(6)	1.408(6)
C21−C22	1.438(7)	1.415(6)	1.423(5)
C22−C23	1.411(7)	1.411(6)	1.401(5)
C23−C24	1.387(8)	1.411(6)	1.365(5)
C24−C25	1.412(9)	1.385(7)	1.384(7)
C25−C26	1.382(9)	1.384(7)	1.375(6)
C26−C27	1.396(8)	1.376(7)	1.382(6)
C27−C28	1.394(8)	1.392(6)	1.413(6)

[a] **7a**: [Cp*(*supine-s-cis*-η^4-C_4H_6)(*prone*-η^3-cot)Ta], this work; **4a**: [Cp*(*supine-s-cis*-η^4-C_4H_6)(*prone*-η^3-cot)Nb], from ref.[7]; **5a**: [(MeCp)(*supine*-η^4-cot)(*prone*-η^3-cot)Nb], from ref.[6] bond lengths in Å, angles in deg. − [b] Angles of fold along the indicated vectors. − [c] Values not given.

In solution, complex **7a** shows a singlet for the methyl groups of the Cp* ligand in the ^{1}H NMR spectrum at δ = 1.46 ([D$_8$]toluene, ^{13}C NMR: δ = 109.7 and 10.6). There is only a single resonance for the cot ligand in the ^{1}H NMR spectrum which remains sharp even down to 143 K (δ = 5.18 in $CDCl_2F/CDClF_2$).[14] The resonance in the ^{13}C NMR spectrum for the cot ligand of **7a** is observed at δ = 102.5 ([D$_8$]toluene), which is between the corresponding resonances of free cyclooctatetraene (δ = 131) and Li_2(cot) (δ = 90). We assume that a rapid interchange is responsible for this symmetrized appearance of the cot ligand in the ^{1}H/^{13}C NMR spectra.[15] We regard it unlikely that **7a** exhibits a fundamentally different structure in solution and in the solid state. An η^8-cot bonding situation would mean that **7a** would have more than 18 valence electrons as the other ligands have retained their coordination character as η^5-Cp* and (σ^2,π)η^4-C_4H_6 (see below). We therefore regard it very likely that a rapid equilibration on the NMR times-

Table 2. A comparison of selected ^{1}H NMR and ^{13}C NMR spectroscopic data of the complexes **7**[a] and **4a**[b]

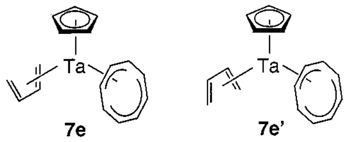
^{1}H NMR	Compd.				^{13}C NMR		
	1-/4-H$_{anti}$	1-/4-H$_{syn}$	2-/3-H	cot-H	C-1/-4	C-2/-3	C-cot
7a	−0.92	3.05	4.45	5.08	47.4	127.5	102.5
7b	−0.97	2.82	−	5.10	49.8	135.8	102.4
	−0.93	2.57	3.50		46.1	114.6	
7c	−0.83	2.70	−	5.02	51.8	120.2	102.2
7d	−0.98	3.48	4.25	5.20	46.6	126.0	101.0
7e	−1.05	3.56	4.20	5.22	45.3	125.4	100.7
7e′	1.50	2.45	4.79	5.22	45.4	122.8	100.4
4a	−0.36	3.05	4.51	5.16	53.6	126.4	103.6

[a] Complexes **7** in [D$_8$]toluene at 298 K, this work. − [b] **4a** in [D$_6$]benzene at 303 K, from ref.[7]

cale of the (η^3-cot)Ta subunit causes the simple spectroscopic features that were observed.

In solution a single set of signals in the NMR spectrum is observed, i.e. only a single stereoisomer is present in solution. This is likely to contain the η^4-butadiene ligand in the *supine* orientation, with its "open" side pointing toward the Cp* ligand as was observed in the X-ray crystal structure of **7a**. The complex shows the typical signals in the ^{1}H NMR spectrum of a σ^2,π-structured η^4-butadiene ligand at the metal center[10−12] [δ = −0.92 (1-/4-H$_{anti}$), 3.05 (1-/4-H$_{syn}$), 4.45 (2-/3-H)]. The corresponding signals in the ^{13}C NMR spectrum of the butadiene ligand of **7a** are observed at δ = 47.4 (C1/4) and δ = 127.5 (C2/3).

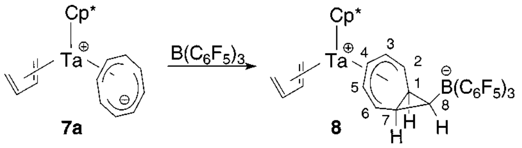
The complexes **7b** and **7c** show very similar NMR spectra (see Table 2). In each case a single isomer of the [Cp*(η^4-diene)(cot)Ta] system is observed. This is also the case for the [(MeCp)(butadiene)(cot)Ta] complex **7d**, but a different situation is encountered with the [Cp(η^4-butadiene)(cot)Ta] system. In this case, a mixture of two stereoisomers **7e** and **7e′** in a ratio of 95:5 is observed in solution by NMR spectroscopy. Each shows the typical single resonance for the cot ligand in the ^{1}H and ^{13}C NMR spectra (δ = 100.7, major isomer **7e**; δ = 100.4, minor isomer **7e′**). Both complexes also exhibit sets of resonances in their ^{1}H- and ^{13}C NMR spectra which are typical for σ^2,π-type *s-cis*-η^4-butadiene ligands at the group 5 metal center,[8][12] but the two are quite different from each other. We therefore assume that this is the first case in this series of complexes where we observe both a *supine* and a *prone* [Cp(butadiene)(cot)Ta] isomer. In view of the spectroscopic similarity with the other members of the series of complexes **7** (and **4a**, see Table 2) we assign to the major isomer (**7e**) the "conventional" *supine*-type structure, and to the minor isomer (**7e′**) the *prone* orientation of the C$_4$H$_6$ and Cp ligands at the tantalum center.



7e **7e′**

Scheme 3. The (*supine* and *prone*-η^4-diene)(η^3-cot)CpTa isomers **76e** and **7e′**

We have recently shown that (butadiene)zirconocene and related group 4 metal complexes add the organometallic Lewis acid B(C$_6$F$_5$)$_3$[16] to a terminal carbon atom of the butadiene ligand to form a (π-allyl)metalloceneborate betaine complex that is of interest as an active, single-component Ziegler-type catalyst.[17] Complex **7a** was, therefore, also treated with B(C$_6$F$_5$)$_3$ but reacted differently. A single compound (**8**) that still contained the intact η^4-butadiene ligand was formed. This is evident from the typical features of the ^{1}H and ^{13}C NMR spectra of the C$_4$H$_6$ moiety [δ = 0.18, 2.86 (1-/4-H), 5.48 (2-H); δ = 54.2 (C1) and 118.6 (C2)]. The B(C$_6$F$_5$)$_3$ reagent was found to add to the cot ligand. In contrast to compounds **7**, complex **8** exhibits signals in the ^{1}H and ^{13}C NMR spectra of a static cot-derived subunit. By a combination of pertinent 1D and 2D NMR experiments the structure of the C$_8$H$_8$B(C$_6$F$_5$)$_3$ ligand was established as being of the bicyclo[5.1.0]octadienyl type. The ^{1}H/^{13}C NMR spectroscopic assignments (including their very characteristic $^1J_{CH}$ coupling constants) are as follows (see Scheme 4 for the atom numbering scheme): δ = 1.23/39.4 ($^1J_{CH}$ = 165 Hz, C1/7−H), 6.66/158.7 (157 Hz, C2/6−H), 3.30/91.8 (155 Hz, C3/5−H), 3.86/71.4 (167 Hz, C4−H), 3.33/(^{13}C signal not observed, C8−H). The newly formed ligand is probably η^5-coordinated to tantalum. Addition of the B(C$_6$F$_5$)$_3$ Lewis acid has apparently occurred at the central carbon atom of the open, noncoordinated π^5-pentadienyl anion section of the cot ligand in **7a**, which resulted in a rapid subsequent disrotatory ring closure to give the bicyclic cot-B(C$_6$F$_5$)$_3$-derived ligand in **8**. In principle four different diastereoisomers of **8** could have been formed in this reaction, depending on whether B(C$_6$F$_5$)$_3$ had attacked from "inside" or from "outside" the complex framework of **7a**, each attack being followed by two possible modes of disrotatorial ring closure. Apparently, one of these electrophilic addition/ring closure combinations has prevailed here, leading to a single observed diastereoisomer **8** of the [Cp*(η^4-C$_4$H$_6$){8-B(C$_6$F$_5$)$_3$-η^5-bicyclo[5.1.0]-octadienyl}Ta] system. We assume that the structure depicted in Scheme 4 is favored, with the B(C$_6$F$_5$)$_3$ substituent *endo* to the bicyclic framework (the observed ^3J(1-H/8-H) coupling constant of ca. 8 Hz would be in accord with the *cis* substitution pattern at the three-membered ring), and the Cp*(η^4-C$_4$H$_6$)Ta "metallocene" η^5-coordinated from the *exo*-face, as was observed for a remotely related example in the early (cot)Nb chemistry described by Schrock et al.[5b]



Scheme 4. Reaction of **7a** with $B(C_6F_5)_3$ and atom numbering scheme for **8**

Conclusion

Our study has shown that [^{R}Cp(η^4-butadiene)TaCl$_2$] complexes react cleanly with the cot dianion to yield the [^{R}Cp(η^4-butadiene)(η^3-cot)Ta] complexes **7**. These complexes exhibit a slightly greater σ^2,π-character of the (η^4-butadiene) ligand than their niobium analogues. Most of the complexes **7** exhibit a *supine*-oriented butadiene ligand, but for the [Cp(η^4-butadiene)(η^3-cot)Ta] system we have for the first time observed the *prone* isomer as a minor equilibrium component in solution. This probably indicates that steric factors dominate this equilibrium situation. In the complexes **7** the ^{R}Cp(η^4-diene)Ta subunit seems to function structurally and chemically in a similar manner to the Cp$_2$M bent metallocene unit in group 4 metal chemistry:[19] treatment of **7a** with $B(C_6F_5)_3$ leaves the bent metallocene surrogate intact; the attack occurs exclusively at the adjacent cot ligand. This ligand system seems to be chemically active in these complexes. It serves as a carbon nucleophile at the center of its uncomplexed pentadienyl moiety to yield the addition product **8**. Further chemical reactions and the catalytic potential of the complexes **7** will be investigated in our laboratory

Experimental Section

All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information including a list of instruments used for the spectroscopic and physical characterization of the compounds see ref.[20] The [^{R}Cp(η^4-diene)TaCl$_2$] complexes **6** were prepared analogously as described by Yasuda et al.[8][21] The [(cot)Li$_2$] reagent was prepared according to a literature procedure.[9]

Synthesis of (η^4-Butadiene)(η^3-cyclooctatetraene)(η^5-pentamethylcyclopentadienyl)tantalum (7a): A solution of **6a** (1.00 g, 2.70 mmol) in toluene (20 mL) was added to a suspension of [(cot)Li$_2$] (330 mg, 2.80 mmol) in 20 mL of toluene. The mixture was stirred for 15 h at 50°C, then filtered and the solvent removed from the filtrate in vacuo. The crude reaction product was stirred for 10 h in 10 mL of pentane, then the product was collected by filtration to give 653 mg (54%) of **7a** as a black solid. Single crystals of **7a** suitable for an X-ray crystal structure analysis were obtained from a solution containing 100 mg of **7a** in 3 mL of toluene and 8 mL of pentane. − M.p. 185°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3050, 2984, 2904, 1547, 1496, 1422, 1375, 1229, 1159, 1147, 1054, 1041, 1023, 902, 840, 805, 797, 686, 614 cm^{-1}. − ^{1}H NMR ([D$_8$]toluene, 599.8 MHz, 298 K): δ = 5.16 (s, 8 H, cot-H), 4.40 (m, 2 H, 2-H), 3.04 (m, 2 H, 1-H′), 1.46 [s, 15 H, C$_5$(C*H*$_3$)$_5$], −0.93 (m, 2 H, 1-H). − ^{1}H NMR [CDClF$_2$/CDCl$_2$F (2:1), 599.8 MHz, 143 K]: δ = 5.18 (s, 8 H, cot-H), 3.97 (m, 2 H, 2-H), 3.08 (m, 2 H, 1-H′), 1.86 [s, 15 H, C$_5$(C*H*$_3$)$_5$], −0.97 (m, 2 H, 1-H). − 1D TOCSY ([D$_8$]toluene, 599.8 MHz, 298 K): irradiation at δ = 4.45 (2-H): response at 3.05 (1-H′) and −0.92 (1-H). − GCOSY ([D$_8$]toluene, 599.8 MHz, 298 K): δ = 4.45/3.05, −0.92 (2-H/1-H′, 1-H), −0.92/4.45, 3.05 (1-H/2-H, 1-H′). − ^{13}C NMR ([D$_8$]toluene, 599.8 MHz, 298 K): δ = 127.0 (C2), 109.7 [*C*$_5$(CH$_3$)$_5$], 102.5 (C-cot), 46.9 (C1), 10.6 [C$_5$(*C*H$_3$)$_5$]. − GHSQC ([D$_8$]toluene, 150.8/599.8 MHz, 298 K): δ = 127.0/4.45 (C2, 2-H), 102.5/5.16 (C-cot/cot-H), 46.9/3.05 (C1/1-H′), 46.9/−0.92 (C1/1-H), 10.6/1.93 C$_5$(*C*H$_3$)$_5$/C$_5$(C*H*$_3$)$_5$. − C$_{22}$H$_{29}$Ta (474.4): calcd. C 55.70, H 6.16; found C 56.06, H 6.60.

X-ray Crystal Structure Analysis of 7a: Formula C$_{22}$H$_{29}$Ta, M = 474.40, dark red crystal, 0.45 × 0.35 × 0.15 mm, a = 12.134(1), b = 11.086(1), c = 14.376(1) Å, β = 112.31(1)°, V = 1789.1(3) Å^3, ρ_{calc} = 1.761 g cm^{-3}, F(000) = 936 e, μ = 61.42 cm^{-1}, absorption correction by SORTAV (0.169 ≤ T ≤ 0.459), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 8258 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 4056 independent and 3555 observed reflections [$I \geq 2\,\sigma(I)$], 213 refined parameters, R = 0.054, wR^2 = 0.141, max. residual electron density 5.893 (−4.069) eÅ^{-3} less than 1 Å from Ta, hydrogen atoms calculated and refined as riding atoms. The data set was collected with a Nonius Kappa CCD diffractometer, placed on a rotating anode generator FR591. Programs used: data collection COLLECT, data reduction DENZO-SMN, absorption correction SORTAV, structure solution SHELXS-86, structure refinement SHELXL-97, graphics SCHAKAL-92. 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-118700. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Preparation of (η^3-Cyclooctatetraene)(η^4-isoprene)(η^5-pentamethylcyclopentadienyl)tantalum (7b): The reaction between **6b** (1.00 g, 2.20 mmol) and [(cot)Li$_2$] (285 mg, 2.41 mmol) in 50 mL of toluene was performed as described above. The product (**7b**) was suspended in pentane for purification, collected by filtration, washed with pentane (2 × 5 mL) and dried in vacuo to yield 666 mg (62%) of **7b** as a black solid. − m.p. 178°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3049, 2981, 2953, 2856, 1556, 1519, 1488, 1446, 1433, 1376, 1367, 1260, 1091, 1026, 868, 807, 800, 686, 615, 584 cm^{-1}. − ^{1}H NMR ([D$_8$]toluene, 599.8 MHz, 298 K): δ = 5.10 (s, 8 H, cot-H), 3.50 (m, 1 H, 2-H), 2.82 (pt, J_{HH} = 8.9 Hz, 1 H, 1-H′), 2.57 (dd, $^2J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1 H, 4-H′), 2.31 (s, 3 H, 2-CH$_3$), 1.47 [s, 15 H, C$_5$(C*H*$_3$)$_5$], −0.93 (dd, $^2J_{HH}$ = 10.0 Hz, $^4J_{HH}$ = 2.1 Hz, 1 H, 4-H), −0.97 (m, 1 H, 1-H). − GCOSY ([D$_8$]toluene, 599.8 MHz, 298 K): δ = 3.49/2.82, −0.97 (2-H/1-H′, 1-H), 2.82/3.49, −0.97 (1-H′/2-H, 1-H), 2.57/3.49, −0.93 (4-H′/2-H, 4-H), −0.93/3.49, 2.57 (4-H/2-H, 4-H′), −0.97/3.49, 2.82 (1-H/2-H, 1-H′). − ^{13}C NMR ([D$_8$]toluene, 150.8 MHz, 298 K): δ = 135.8 (C3), 114.6 (C2), 109.9 [*C*$_5$(CH$_3$)$_5$], 102.4 (C-cot), 49.8 (C4), 46.1 (C1), 30.2 (2-CH$_3$), 10.6 [C$_5$(*C*H$_3$)$_5$]. − GHSQC ([D$_8$]toluene, 150.8/599.8 MHz, 298 K): δ = 114.6/3.49 (C2, 2-H), 102.4/5.10 (C-cot/cot-H), 49.8/2.57 (C4/4-H′), 49.8/−0.93 (C4/4-H), 46.1/2.82 (C1/1-H′), 46.1/−0.97 (C1/1-H), 30.2/2.31 (2-*C*H$_3$/2-C*H*$_3$), 10.6/1.47 C$_5$(*C*H$_3$)$_5$/C$_5$(C*H*$_3$)$_5$. − C$_{23}$H$_{31}$Ta (488.44): calcd. C 56.55, H 6.40; found C 56.47, H 6.80.

Preparation of (η^3-Cyclooctatetraene)(η^4-2,3-dimethylbutadiene)(η^5-pentamethylcyclopentadienyl)tantalum (7c): The reaction between

6c (1.00 g, 2.13 mmol) and [(cot)Li_2] (277 mg, 2.34 mmol) was performed as described above to yield 482 mg (45%) of **7c**. − m.p. 155 °C (decomp.). − IR (KBr): ṽ = 3104, 3093, 3074, 2993, 2953, 2920, 2866, 1546, 1494, 1438, 1306, 1235, 1078, 1054, 1029, 856, 826, 688, 611 cm^{-1}. − ^{1}H NMR ([D_8]toluene, 599.8 MHz, 298 K): δ = 5.02 (s, 8 H, cot-H), 2.70 (d, $^{2}J_{HH}$ = 10.1 Hz, 2 H, 1-H′), 1.79 (pd, $^{4}J_{HH}$ = 1.0 Hz, 6 H, 2-CH_3), 1.46 [s, 15 H, $C_5(CH_3)_5$], −0.83 (dd, J_{HH} = 10.5 Hz, 2 H, 1-H). − GCOSY ([D_8]toluene, 599.8 MHz, 298 K): δ = 2.70/−0.83 (1-H′/1-H), 1.79/−0.83 (2-CH_3, 1-H), −0.83/2.70, 1.79 (1-H/1-H′, 2-CH_3). − ^{13}C NMR ([D_8]toluene, 150.8 MHz, 298 K): δ = 120.0 (C2), 110.0 [$C_5(CH_3)_5$], 102.2 (C-cot), 51.8 (C1), 25.5 (2-CH_3), 10.4 [$C_5(CH_3)_5$]. − GHSQC ([D_8]toluene, 150.8/599.8 MHz, 298 K): δ = 102.2/5.02 (C-cot/cot-H), 51.8/2.70 (C1/1-H′), 51.8/−0.83 (C1/1-H), 25.5/1.79 (2-CH_3/2-CH_3), 10.4/1.46 $C_5(CH_3)_5$/$C_5(CH_3)_5$. − $C_{24}H_{33}Ta$ (502.47): calcd. C 57.37, H 6.62; found C 57.13, H 6.83.

Preparation of (η^4-Butadiene)(η^3-cyclooctatetraene)(η^5-methylcyclopentadienyl)tantalum (7d): The reaction between **6d** (1.00 g, 2.60 mmol) and [(cot)Li_2] (337 mg, 2.85 mmol) was performed as described above to yield 720 mg (66%) of **7d** as a dark-brown solid. − m.p. 148 °C (decomp.). − IR (KBr): ṽ = 3097, 3074, 2990, 2956, 2942, 1547, 1493, 1456, 1438, 1429, 1305, 1230, 1054, 1029, 857, 825, 807, 689, 613 cm^{-1}. − ^{1}H NMR ([D_8]toluene, 599.8 MHz, 298 K): δ = 5.24 (s, 8 H, cot-H), 4.83 (d, J_{HH} = 2.5 Hz, 2 H), 4.35 (pt, J_{HH} = 2.5 Hz, 6 H, C_5H_4), 4.24 (m, 2 H, 2-H), 3.48 (m, 2 H, 1-H′), 1.74 (s, 3 H, CH_3), −0.98 (m, 2 H, 1-H). − ^{13}C NMR ([D_8]toluene, 150.8 MHz, 298 K): δ = 126.0 (C2), 113.4, 103.0, 99.7 (C_5H_4), 101.0 (C-cot), 46.6 (C1), 14.3 (CH_3). − GHSQC ([D_8]toluene, 150.8/599.8 MHz, 298 K): δ = 126.0/4.24 (C2/2-H), 113.5/4.83 (C_5H_4/C_5H_4), 101.0/5.24 (C-cot/cot-H), 99.7/4.35 (C_5H_4/C_5H_4), 46.6/3.48 (C1/1-H′), 46.6/−0.98 (C1/1-H). − $C_{18}H_{21}Ta$ (418.31): calcd. C 51.68, H 5.06; found C 52.16, H 5.32.

Preparation of the (η^4-Butadiene)(η^3-cyclooctatetraene)(η^5-cyclopentadienyl)tantalum Isomers 7e and 7e′: The reaction between **6e** (1.50 g, 4.04 mmol) and [(cot)Li_2] (525 mg, 4.45 mmol) was performed as described above to yield 902 mg (55%) of a 95:5 mixture of **7e** and **7e′**. − m.p. 147 °C (decomp.). − IR (KBr): ṽ = 3098, 3085, 2998, 2947, 1437, 1429, 1367, 1236, 1070, 1020, 1011, 817, 844, 822, 690, 612, 430 cm^{-1}. − ^{1}H NMR ([D_8]toluene, 599.8 MHz, 298 K): **7e** (major isomer): δ = 5.22 (s, 8 H, cot-H), 4.79 (d, 5 H, Cp-H), 4.20 (m, 2 H, 2-H), 3.56 (m, 2 H, 1-H′), −1.04 (m, 2 H, 1 H). **7e′** (minor isomer): δ = 5.22 (s, 8 H, cot-H, under signal of the major isomer), 4.81 (d, 5 H, Cp-H), 4.78 (m, 2 H, 2-H, under **7e** resonance), 2.45 (m, 2 H, 1-H′), 1.50 (m, 2 H, 1-H). − 1D TOCSY ([D_8]toluene, 599.8 MHz, 298 K): **7e**: irradiation at δ = 3.56 (1-H′): response at δ = 4.20 (2-H) and −1.05 (1-H). **7e′**: irradiation at δ = 1.50 (1-H): response at δ = 4.79 (2 H) and 2.45 (1-H′). − GCOSY ([D_8]toluene, 599.8 MHz, 298 K): **7e**: δ = 4.20/3.56, −1.05 (2-H/1-H′, 1-H), 3.56/4.20, −1.05 (1-H′/2-H, 1-H), −1.05/4.20, 3.56 (1-H/2-H, 1-H′). **7e′**: δ = 4.79/2.45, 1.50 (2-H/1-H′, 1-H), 2.45/4.79, 1.50 (1-H′/2-H, 1-H), 1.50/4.79, 2.45 (1-H/2-H,1-H′). − ^{13}C NMR ([D_8]toluene, 150.8 MHz, 298 K): **7e**: δ = 125.4 (C2), 100.7 (C-cot), 100.6 (C−Cp), 45.3 (C1). **7e′**: δ = 122.8 (C2), 100.4 (C-cot), 99.6 (C−Cp), 45.4 (C1). − GHSQC ([D_8]toluene, 150.8/599.8 MHz, 298 K): **7e**: δ = 125.4/4.20 (C2/2-H), 100.5/5.22 (C-cot/cot-H), 100.6/4.74 (C−Cp/Cp-H). 45.3/3.56 (C1/1-H′), 45.3/−1.05 (C1/1-H). **7e′**: δ = 122.8/4.79 (C2/2-H), 100.4/5.22 (C-cot/cot-H), 99.6/4.81 (C-Cp/Cp-H), 45.4/2.45 (C1/1-H′), 45.4/−1.50 (C1/1-H). − $C_{17}H_{19}Ta$ (404.29): calcd. C 50.51, H 4.74; found C 50.12, H 4.73.

Reaction of Complex 7a with B(C_6F_5)$_3$. − Generation of 8: (The reaction was carried out in deuterated solvent and the product was not isolated. At room temperature complex **8** starts to decompose after about 2 h; therefore some NMR experiments had to be carried out at low temperature.) An NMR tube was charged with a sample of **7a** (50 mg, 54.1 μmol) and a solution of B(C_6F_5)$_3$ (81.0 mg, 158 μmol) in 0.8 mL of [D_2]dichloromethane was added at −78 °C. The sample was warmed to +10 °C inside the NMR spectrometer. After ca. 1 h, the addition reaction to give **8** was complete and the sample was cooled to −30 °C to collect the NMR spectroscopic data. − ^{1}H NMR ([D_2]dichloromethane, 599.8 MHz, 223 K, bco = bicyclo[5.1.0]octadienyl): δ = 6.66 (m, 2 H, bco-2/6-H), 5.42 (m, 2 H, butadiene-2-H), 3.86 (m, 1 H, bco-4-H), 3.33 (m, 1 H, bco-8-H), 3.30 (m, 2 H, bco-3/5-H), 2.86 (m, 2 H, butadiene-1-H′), 1.94 [s, 15 H, $C_5(CH_3)_5$], 1.23 (m, 2 H, bco-1/7-H), 0.17 (m, 2 H, butadiene-1-H). − 1D TOCSY ([D_2]dichloromethane, 599.8 MHz, 223 K): (i) irradiation at δ = 5.42 (butadiene-2-H): response at δ = 2.86 (1-H′), 0.17 (1-H). (ii) irradiation at δ = 6.66 (bco-2/6-H): response at δ = 3.86 (4-H), 3.33 (8-H), 3.30 (3/5-H), 1.23 (1/7-H). − GCOSY ([D_2]dichloromethane, 599.8 MHz, 223 K): δ = 6.66/3.30, 1.23 (bco-2/6-H//3/5-H, 1/7-H), 5.42/2.86, 0.17 (butadiene-2-H/1-H, 1-H′), 3.86/3.30 (bco-4-H//3/5-H), 3.33/1.23 (bco-8-H//1/7-H), 3.30/3.86, 6.66 (bco-3/5-H//4-H, 2/6-H), 2.86/5.42, 0.17 (butadiene-1-H′//2-H, 1-H), 1.23/3.33 (bco-1/7-H//8-H), 0.17/5.42, 2.86 (butadiene-1-H//2-H, 1−1H′). − ^{13}C NMR ([D_2]dichloromethane, 150.8 MHz, 223 K): δ = 158.7 ($^{1}J_{CH}$ = 157 Hz, bco-C2/6), 148.2 [$^{1}J_{CF}$ = 249 Hz, *o*-B(C_6F_5)$_3$], 144.7 [$^{1}J_{CF}$ = 260 Hz, *p*-B(C_6F_5)$_3$], 137.1 [$^{1}J_{CF}$ = 251 Hz, *m*-B(C_6F_5)$_3$], 113.2 (butadiene-C2), 110.1 [$C_5(CH_3)_5$], 91.8 ($^{1}J_{CH}$ = 155 Hz, bco-C3/5), 71.4 ($^{1}J_{CH}$ = 167 Hz, bco-C4), 39.4 ($^{1}J_{CH}$ = 165 Hz, bco-C1/7), 10.6 [$C_5(CH_3)_5$], *ipso*-C of B(C_6F_5)$_3$ and bco-C8 not observed, butadiene-C1 hidden by solvent. − GHSQC ([D_2]dichloromethane, 150.8 MHz, 223 K): δ = 158.7/6.66 (bco-C2/6//2/6-H), 113.3/5.42 (butadiene-C2/2-H), 91.8/3.30 (bco-C3/5//3/5-H), 71.4/3.86 (bco-C4//4-H), 65.1/3.33 (bco-C8//8-H), 54.1/2.86, 0.17 (butadiene-C1//1-H/H′), 39.4/1.23 (bco-C1/7//1/7-H), 10.6/1.94 (Cp*). − ^{11}B NMR ([D_2]dichloromethane, 64.2 MHz, 243 K): δ = −14.0. − ^{19}F NMR ([D_2]dichloromethane, 564.3 MHz, 243 K): δ = −130.4 [m, 6 F, *o*-B(C_6F_5)$_3$], −161.7 [m, 3 F, *p*-B(C_6F_5)$_3$], −165.6 [m, 6 F, *m*-B(C_6F_5)$_3$].

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