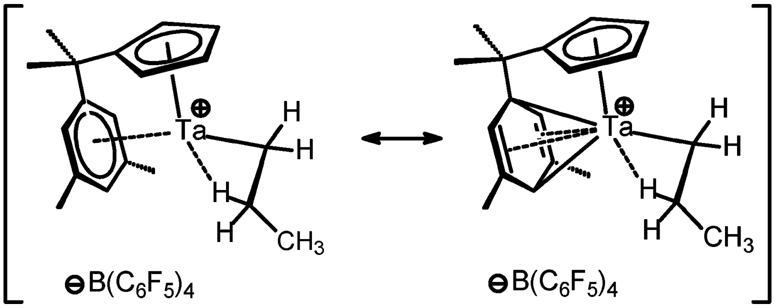
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Structure and Reactivity of the β-Agostic [*ansa*-Cp-arene]Ta(Pr) Cation: Ambivalent Behavior Induced by Intramolecular Arene Coordination

Edwin Otten, Auke Meetsma, and Bart Hessen

J. Am. Chem. Soc., **2007**, 129 (33), 10100-10101• DOI: 10.1021/ja073956j • Publication Date (Web): 27 July 2007



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Structure and Reactivity of the β-Agostic [*ansa*-Cp-arene]Ta(^{n}Pr) Cation: Ambivalent Behavior Induced by Intramolecular Arene Coordination

Edwin Otten, Auke Meetsma, and Bart Hessen*

Centre for Catalytic Olefin Polymerization, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Received June 1, 2007; E-mail: b.hessen@rug.nl

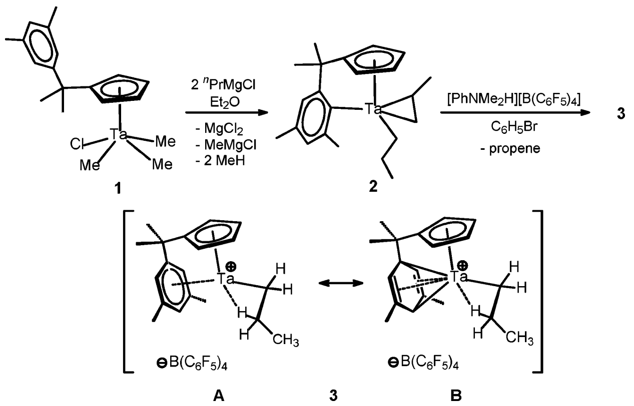
Early transition metal catalysis largely involves complexes with the metal center in its highest (d^0) oxidation state. Oxidative addition−reductive elimination sequences, which are of prime importance to many processes catalyzed by noble metal complexes,[1] are therefore very rare for these metals. To extend the possibilities for useful catalytic conversions with non-noble metals, it would be desirable to facilitate two-electron redox reaction steps for these metals. Recently, we reported cationic monocyclopentadienyl titanium catalysts that selectively trimerize ethylene to 1-hexene, by virtue of a pendant arene moiety on the Cp ligand.[2] Computational studies on the catalytic cycle have shown the process to involve the Ti(II)/Ti(IV) couple, in which the low-valent state in particular is stabilized by interaction with the pendant arene.[3] Thus, a pendant arene group may be more generally useful to stabilize low-valent states for non-noble metals.

For the group 5 metal Ta, examples of “low-valent” complexes with η^6-arene ligands have been reported, but these are more appropriately described as 7-metallanorbornadienes, through resonance contribution of a Ta(V) species, with a doubly reduced arene (cyclohexa-2,5-diene-1,4-diyl).[4] Here we report the cationic tantalum complexes [η^6-Ar-CMe$_2$-η^5-C$_5$H$_4$]Ta(R)$^+$ (R = ^{n}Pr, H; Ar = 3,5-dimethylphenyl), bearing an arene-substituted cyclopentadienyl ligand involving *ansa*-(η^5-C$_5$H$_4$,η^6-arene) coordination. These species show migratory insertion reactions as well as ambivalent [Ta(III)↔Ta(V)] character.

As starting material, the complex [Ar-CMe$_2$-η^5-C$_5$H$_4$]TaMe$_3$Cl (**1**) was prepared by treatment of TaMe$_3$Cl$_2$ with [Ar-CMe$_2$-C$_5$H$_4$]-Li in toluene and obtained as yellow-orange crystals in 67% isolated yield. Addition of 2 equiv of ^{n}PrMgCl to **1** at −50 °C in Et$_2$O afforded, after gradual warming to room temperature and extraction with and crystallization from pentane, dark red crystals of the cyclometalated species [η^1-3,5-Me$_2$C$_6$H$_2$-CMe$_2$-η^5-C$_5$H$_4$]Ta(^{n}Pr)-(C$_3$H$_6$) (**2**) in moderate yield (33%) (Scheme 1).[5] ^{1}H NMR spectroscopy shows that **2** is present in C$_6$D$_6$ solution as a 80:20 mixture of two isomers, presumably corresponding to two orientations of the methyl substituent on the coordinated propene moiety. In the solid state, **2** is found to be present as a single isomer (Figure 1), although redissolution of these crystals again produced the above mixture of isomers, suggesting an equilibrium. The coordinated propene shows predominant tantalacyclopropane character, as seen from its Ta−C bond lengths (that with 2.174(4) and 2.150(4) Å lie within the range observed for tantalum alkyls) and the elongated C−C bond of 1.472(6) Å.[6]

Treatment of **2** with 1 equiv of the Brønsted acid [PhNMe$_2$H]-[B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br results in liberation of propene and quantitative formation of {[η^6-Ar-CMe$_2$-η^5-C$_5$H$_4$]Ta(^{n}Pr)}[B(C$_6$F$_5$)$_4$] (**3**, Scheme 1). On a preparative scale, **3** was isolated in 88% yield as dark greenish-brown crystals from bromobenzene/hexane. An X-ray structure determination (Figure 1) shows the presence of a β-agostic ^{n}Pr group. The C−C distances within the C$_6$ fragment manifest considerable π-localization, with contracted C(110)−C(111) and C(113)−C(114) bond lengths and elongation of the remaining C−C bonds (Table S1). The ring is folded by 8.6(5)° along the C(19)−C(112) axis. It should be noted that the distortions of the arene moiety are much smaller than in Ta(III) arene complexes where the arene is not linked to a Cp ligand and the overlap between metal d- and arene π*-orbitals is optimal (ring folding up to 34.4° has been observed for (C$_6$Me$_6$)Ta(OAr)$_2$Cl).[4] Nevertheless, the structural parameters of **3** clearly indicate significant resonance contribution from the Ta(V)/dienediyl structure (**B**, Scheme 1). The ^{1}H NMR resonances of the pendant arene in **3** are shifted upfield

Scheme 1



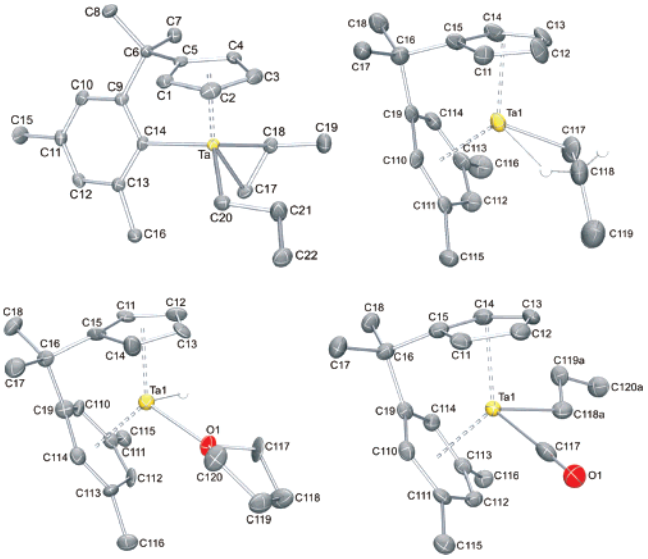
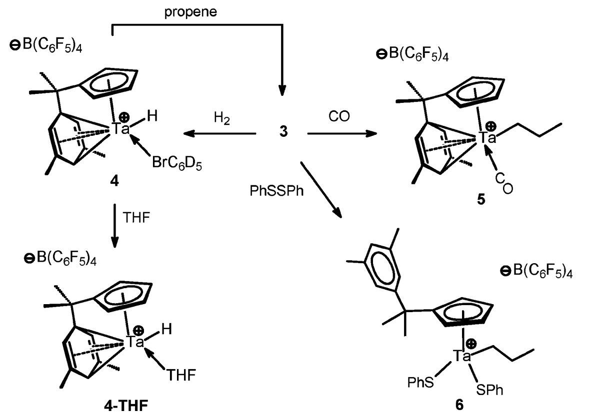


Figure 1. Molecular structures of (from left to right and top to bottom) **2**, **3**, **4-THF**, and **5** with 50% probability ellipsoids. The anion (for **3**, **4-THF**, and **5**) and hydrogens (except those on C(118) in **3** and Ta−H in **4-THF**) are omitted for clarity.

10.1021/ja073956j CCC: $37.00

Scheme 2



(*o*-ArH: δ 4.55/4.23; *p*-ArH: 2.22 ppm), consistent with formation of an η^6-adduct and partial disruption of the aromaticity. The ^{1}H NMR spectrum of **3** at −30 °C also shows features characteristic for a β-agostic alkyl group. The α-CH$_2$ protons are diastereotopic (δ 0.61 and −0.54 ppm), and the β-CH$_2$ resonances are broad and shifted significantly upfield (δ −1.9 and −5.9 ppm). The β-agostic Ta-^{n}Pr structure of **3** stands in marked contrast to the isoelectronic neutral group 5 metal (*ansa*-)metallocene analogues, which have olefin−hydride ground states.[6a,7] Two-Dimensional EXSY NMR spectroscopy at 70 °C (at which temperature the diastereotopic α- and β-CH$_2$ groups are coalesced) shows exchange between all propyl ^{1}H resonances, suggesting the dynamics occur through a thermally accessible olefin−hydride intermediate.[7]

The reaction of **3** with H$_2$ in bromobenzene results in immediate formation of the corresponding cationic hydride **4** (Scheme 2). As is the case for **3**, the NMR spectra of **4** indicate a C_1 symmetric structure (possibly indicating solvation by bromobenzene)[8] and an η^6-coordinated arene. The Ta−H ^{1}H NMR resonance at δ −4.65 ppm corresponds to 1H intensity, revealing a contrast to neutral metallocene analogues, which form trihydrides (Cp$_2$MH$_3$).[9] Upon addition of 1 bar of propene to a solution of **4**, quantitative regeneration of **3** is observed within 1 h. In agreement with this, **4** can catalyze the hydrogenation of 1-hexene at ambient temperature (15 t.o. in 16 h). Although **4** is stable for at least 24 h in cold (−25 °C) bromobenzene solution, attempted isolation by removal of the volatiles led to decomposition. Addition of THF to solutions of **4** gave the THF adduct **4-THF**, which was isolated in crystalline form. Its ^{1}H NMR spectrum shows a singlet at −3.98 ppm, and in the IR spectrum, a broad band at 1760 cm^{-1} is observed, both consistent with the presence of a Ta−H moiety. An X-ray structure (Figure 1) confirmed the overall geometry of the complex.

Treatment of **3** with 1 bar of CO at room temperature results in the formation of the CO adduct **5** (Scheme 2). The ν(CO) IR band at 2033 cm^{-1} lies at considerably higher frequency than in Cp$_2$TaR(CO) (R = H, alkyl; 1880−1895 cm^{-1}).[10] The reduced ability of the metal center in **5** for π-backdonation to CO reflects the acceptor properties of the η^6-arene and is in agreement with substantial Ta(V) character. The X-ray structure of **5** (Figure 1) shows again that the arene moiety is slightly folded by 11.4(4)°. The CO bond is only modestly elongated at 1.107(8) versus 1.148(7) Å in Cp$_2$TaR(CO) (R = CH$_2$SiH(^{t}Bu)$_2$).[10b] Whereas CO adducts of d^0 early transition metal centers are in general weak and often stabilized by electron donation of a M−L σ-bond into the CO π^* orbital,[11] **5** is a stable compound in spite of the apparent high-valent character of the metal center and absence of Ta−alkyl $\sigma \rightarrow \pi^*$ backdonation (C$_{\text{alkyl}}$−Ta−C$_{\text{carbonyl}}$ = 84.9(2)°).[11c] Reaction of **3** with PhSSPh at room temperature immediately gives the cationic dithiolate alkyl complex **6**. Liberation of the pendant arene moiety from the metal center in **6** is seen from the shift of its ^{1}H NMR signals back into the aromatic region (δ 7.3−6.9 ppm). This oxidative addition reaction shows that, despite the considerable Ta(V)/dienediyl (**B**) character of **3**, it can readily display reactivity corresponding to a Ta(III) compound.

Thus, in cationic *ansa*-Cp-arene complexes of tantalum, the coordination of the pendant arene allows resonance stabilization of low-valent species, resulting in ambivalent character. It causes considerable differences in chemistry relative to the isoelectronic neutral tantalocene analogues. The cationic *ansa*-Cp-arene tantalum complexes can display both migratory insertion and oxidative addition reactions. Use of these intramolecular interactions thus could provide a fruitful strategy to give early transition metals a more “noble” character.

Acknowledgment. Financial support was provided by NRSC-Catalysis.

Supporting Information Available: Text giving full experimental and characterization data, and crystallographic data for compounds **2**, **3**, **4-THF**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Van Leeuwen, P. W. N. M. *Homogeneous Catalysis: Understanding the Art*; Kluwer Academic Publishers: Dordrecht, The Netherland, 2004; pp 36−41. (b) De Meijere, A., Diederich, F., Eds. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, Germany, 2004; pp 1−40.
(2) (a) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2516. (b) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 5122.
(3) (a) Blok, A. N. J.; Budzelaar, P. H. M.; Gal, A. W. *Organometallics* **2003**, *22*, 2564. (b) De Bruin, T. J. M.; Magna, L.; Raybaud, P.; Toulhoat, H. *Organometallics* **2003**, *22*, 3404. (c) Tobisch, S.; Ziegler, T. *Organometallics* **2003**, *22*, 5392.
(4) (a) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (b) Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282.
(5) The presence of MeMgCl as the only NMR active component in the white residue suggests that trans-alkylation is a key step in this transformation.
(6) (a) Chirik, P. J.; Zubris, D. L.; Ackerman, L. J.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *Organometallics* **2003**, *22*, 172. (b) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 1602. (c) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Kooijman, H.; Spek, A. L.; Van Koten, G. *Angew. Chem., Int. Ed.* **1991**, *30*, 996.
(7) (a) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134. (b) Green, M. L. H.; Sella, A.; Wong, L. L. *Organometallics* **1992**, *11*, 2650. (c) Shin, J. H.; Parkin, G. *Chem. Commun.* **1999**, 887. (d) Ackerman, L. J.; Green, M. L. H.; Green, J. C.; Bercaw, J. E. *Organometallics* **2003**, *22*, 188.
(8) (a) Wu, F.; Dash, A. K.; Jordan, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 15360. (b) Bouwkamp, M. W.; Budzelaar, P. H. M.; Gercama, J.; Del Hierro Morales, I.; De Wolf, J.; Meetsma, A.; Troyanov, S. I.; Teuben, J. H.; Hessen, B. *J. Am. Chem. Soc.* **2005**, *127*, 14310.
(9) Antinolo, A.; Carrillo-Hermosilla, F.; Fajardo, M.; Fernandez-Baeza, J.; Garcia-Yuste, S.; Otero, A. *Coord. Chem. Rev.* **1999**, *193−195*, 43.
(10) (a) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *165*, 31. (b) Berry, D.; Koloski, T.; Carroll, P. *Organometallics* **1990**, *9*, 2952.
(11) (a) Marsella, J.; Curtis, C.; Bercaw, J.; Caulton, K. *J. Am. Chem. Soc.* **1980**, *102*, 7244. (b) Guo, Z.; Swenson, D.; Guram, A.; Jordan, R. *Organometallics* **1994**, *13*, 766. (c) Burckhardt, U.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 6328.

JA073956J