University of Groningen

Structure and reactivity of the beta-agostic [ansa-Cp-arene]Ta(Pr-n) cation

Otten, Edwin; Meetsma, Auke; Hessen, Bart

Published in:
Journal of the American Chemical Society

DOI:
[10.1021/ja073956j](https://doi.org/10.1021/ja073956j)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2007

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Otten, E., Meetsma, A., & Hessen, B. (2007). Structure and reactivity of the beta-agostic [ansa-Cp-arene]Ta(Pr-n) cation: Ambivalent behavior induced by intramolecular arene coordination. *Journal of the American Chemical Society*, 129(33), 10100-+. <https://doi.org/10.1021/ja073956j>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Structure and Reactivity of the β -Agostic [*ansa*-Cp-arene]Ta(η 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-CMe₂- η^5 -C₅H₄][Ta(R)]⁺ (R = η Pr, H; Ar = 3,5-dimethylphenyl), bearing an arene-substituted cyclopentadienyl ligand involving *ansa*-(η^5 -C₅H₄, 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-CMe₂- η^5 -C₅H₄][TaMe₃Cl] (1) was prepared by treatment of TaMe₃Cl₂ with [Ar-CMe₂-C₅H₄]-Li in toluene and obtained as yellow-orange crystals in 67% isolated yield. Addition of 2 equiv of η PrMgCl to 1 at –50 °C in Et₂O 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-Me₂C₆H₂-CMe₂- η^5 -C₅H₄][Ta(η Pr)-(C₃H₆)] (2) in moderate yield (33%) (Scheme 1).⁵ ¹H NMR spectroscopy shows that 2 is present in C₆D₆ 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 tantalacyclop propane 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 [PhNMe₂H][B(C₆F₅)₄] in C₆D₅Br results in liberation of propene and quantitative formation of {[η^6 -Ar-CMe₂- η^5 -C₅H₄][Ta(η Pr)][B(C₆F₅)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 η Pr group. The C–C distances within the C₆ fragment manifest

Scheme 1

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 (C₆Me₆)Ta(OAr)₂Cl).⁴ Nevertheless, the structural parameters of 3 clearly indicate significant resonance contribution from the Ta(V)/dienediyl structure (B, Scheme 1). The ¹H NMR resonances of the pendant arene in 3 are shifted upfield

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.

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 ¹H NMR spectrum of **3** at -30°C also shows features characteristic for a β -agostic alkyl group. The α -CH₂ protons are diastereotopic (δ 0.61 and -0.54 ppm), and the β -CH₂ 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 -CH₂ groups are coalesced) shows exchange between all propyl ¹H resonances, suggesting the dynamics occur through a thermally accessible olefin-hydride intermediate.⁷

The reaction of **3** with H₂ 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 C₁ symmetric structure (possibly indicating solvation by bromobenzene)⁸ and an η^6 -coordinated arene. The Ta-H ¹H NMR resonance at δ -4.65 ppm corresponds to 1H intensity, revealing a contrast to neutral metallocene analogues, which form trihydrides (Cp₂MH₃).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 ¹H 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 $\nu(\text{CO})$ IR band at 2033 cm^{-1} lies at considerably higher frequency than in Cp₂TaR(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 $11.4(4)^\circ$. The CO bond is only modestly elongated at $1.107(8)$ versus $1.148(7)\text{ \AA}$ in Cp₂TaR(CO) (R = CH₂SiH(*i*Bu)₂).^{10b} Whereas CO adducts of d⁰ 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 ($C_{\text{alkyl}}\text{--Ta--}C_{\text{carbonyl}} = 84.9(2)^\circ$).^{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 ¹H 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

- (a) Van Leeuwen, P. W. N. M. *Homogeneous Catalysis: Understanding the Art*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2004; pp 36–41. (b) De Meijere, A.; Diederich, F., Eds. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, Germany, 2004; pp 1–40.
- (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.
- (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) Töbisch, S.; Ziegler, T. *Organometallics* **2003**, *22*, 5392.
- (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.
- 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.
- (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.
- (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.
- (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.
- Antinolo, A.; Carrillo-Hermosilla, F.; Fajardo, M.; Fernandez-Baeza, J.; Garcia-Yuste, S.; Otero, A. *Coord. Chem. Rev.* **1999**, *193*–195, 43.
- (a) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *165*, 31. (b) Berry, D.; Koloski, T.; Carroll, P. *Organometallics* **1990**, *9*, 2952.
- (a) Marsella, J.; Curtis, C.; Bercaw, J.; Caulton, K. J. *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