ORGANOMETALLICS

ansa-Cyclopentadienyl-Arene Tantalum Complexes: Structure and Reactivity of Neutral, Cationic, and Dicationic Derivatives

Edwin Otten,* Auke Meetsma, and Bart Hessen

Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Supporting Information

ABSTRACT: The cationic tantalum complex {[η^6 -Ar-CMe₂- η^5 -C₅H₄]TaPr}[B(C₆F₅)₄] (1; Ar = 3,5-Me₂C₆H₃) serves as a starting material for a series of neutral, monocationic, and dicationic derivatives. The cationic hydride {[η^6 -Ar-CMe₂- η^5 -C₅H₄]TaH}[B(C₆F₅)₄] (2) that results from hydrogenolysis of 1 inserts the di- and trisubstituted olefins cyclopentene and 2-



methyl-2-pentene; it reacts with styrene to give the 2,1-insertion product, for which the Ta–CH(Me)Ph group is bound in a σ^3 allylic fashion. A neutral complex is obtained from 1 by reaction with Br⁻, and a dicationic derivative is available by hydride abstraction from 2 using the Lewis acidic trityl cation. All compounds described here retain the unusual ansa-(η^5 cyclopentadienyl, η^6 -arene) coordination mode of the ligand that stabilizes the formally Ta(III) center. X-ray structures and DFT calculations show that the metal–arene interaction contains a significant π back-donation component (arene \leftarrow Ta(III)) that differs only slightly in the series, despite the variation of charge at the metal center.

INTRODUCTION

A wide range of industrially important transition-metalcatalyzed transformations involve oxidative addition and reductive elimination as key steps in the catalytic cycle (e.g., cross-coupling¹ and cycloaddition² reactions). A prerequisite for productive catalysis is the presence of two metal oxidation states (n and n + 2) that are relatively similar in energy so that these oxidation states can be reversibly addressed. An example of such a redox couple is Pd(0)/Pd(II), which is widely applied to catalytic C-C bond forming reactions. While the prominence of (catalytic) oxidative addition-reductive elimination sequences holds true for a variety of late transition metals, the high thermodynamic stability of the d⁰ high-valent state in the case of the early transition metals has hampered development of processes involving these elementary reaction steps using these metals. Complexes that are able to stabilize early-transition-metal centers in their low-valent state by (partially) delocalizing metal d electron density into the ligand framework have gained increased attention in this context. Indeed, metal complexes with such "redox-active" ligands³ can facilitate (catalytic) redox reactions that are otherwise not accessible, as shown elegantly for example in the work of Heyduk and co-workers.⁴

Previously, we have shown that cationic titanium complexes with cyclopentadienyl-arene (Cp-arene) ligands are highly active catalysts for the selective trimerization of ethylene to 1-hexene.⁵ This unusual reaction most likely occurs by a Ti(IV)/Ti(II) redox mechanism with the involvement of metallacyclic intermediates.⁶ The unique contribution of the aromatic substituent from the *ansa*-Cp-arene ligand in stabilizing various intermediates in the catalytic cycle has been validated for a series of model compounds.⁷ Also, Cp-arene ligated complexes of the group 5 metal tantalum with low

formal oxidation states are stabilized by delocalization of the metal d electrons into the π system of the coordinated arene ring.⁸ X-ray crystallography shows puckering in the arene that indicates resonance contribution of a reduced "dienediyl" ring bound to an oxidized metal center (Scheme 1, structure 1B). Thus, it appears that the ansa-cyclopentadienyl-arene ligand framework provides opportunities to access low-valent oxidation states in cationic early-transition-metal chemistry, without the need for (strongly bound) classical π acids such as CO and isocyanides. The nature of the metal-arene interaction and the stability that it provides in these low-valent compounds is expected to depend on the other ligands present and on the electrophilicity of the metal center. Kochi and co-workers reviewed the effects of charge-transfer bonding in metal arene complexes from the viewpoint of structural changes in the arene fragment and showed that several effects (including π bond localization and loss of planarity) may occur, depending on the nature of the charge transfer interaction and arene hapticity.9

Herein we explore in more detail the reactivity of cationic tantalum(III) complexes bearing the *ansa*-cyclopentadienylarene ligand. Insertion of olefins into the Ta—H bond results in new cationic alkyl and benzyl derivatives, and conversion to neutral and dicationic derivatives is described. All compounds retain the *ansa*-cyclopentadienyl-arene coordination motif, which allows us to explore the influence of charge on the nature of the metal—arene interaction by crystallographic and computational methods. Substantial arene folding is observed, regardless of the charge at the metal center, indicating arene \leftarrow

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Scheme 1. Synthesis of Compounds 3-5 by Olefin Insertion into the Ta-H Bond of 2



metal back-donation from Ta(III) is important in stabilizing these species across the series.

RESULTS AND DISCUSSION

Monocationic Derivatives via Insertion into the Ta-H Bond. Convenient access to new tantalum complexes with the ansa-cyclopentadienyl-arene ligand is provided by the isolable base-free monocationic derivative $\{[\eta^6-\text{Ar-CMe}_{\gamma}-\eta^5-\text{C}_{\varsigma}\text{H}_4]$ -TaPr} $[B(C_6F_5)_4]$ (1; Ar = 3,5-Me₂C₆H₃). As shown in a preliminary communication, compound 1 can be cleanly converted to the monocationic monohydride {[η^6 -Ar-CMe₂- η^{5} -C₅H₄]TaH}[B(C₆F₅)₄] (2).⁸ Although compound 2 is relatively stable in solution, it decomposes upon attempted isolation but may be isolated in crystalline form as its THF adduct. Early-transition-metal and rare-earth-metal hydrides are known to be highly reactive species, and compound 2 is no exception; it readily reacts with aliphatic α -olefins (propene, 1hexene) to give the corresponding Ta-alkyl cations.⁸ While most neutral hydrides of the early transition metals tend to aggregate into higher nuclearity polyhydride compounds,¹⁰ the solubility of cationic 2 in bromobenzene suggests it to be monomeric with a terminal hydride ligand. This is not unexpected: cationic early-transition-metal and rare-earthmetal hydride derivatives, although still quite rare,¹¹ tend to have lower aggregation states due to unfavorable electrostatic interactions. For example, Piers and co-workers were able to prepare the monomeric cationic titanium hydride $[Cp^{*}(^{t}Bu_{3} =$ N)TiH][B(C_6F_5)₄] and structurally characterize its THF adduct.¹² The previously observed facile insertion of terminal olefins (propene, 1-hexene) into the Ta-H bond in 2,⁸ which stands in contrast to the isoelectronic neutral group 5 metallocene hydrides that have olefin-hydride ground states,¹³ and its relevance to olefin polymerization by cationic earlytransition-metal catalysts prompted us to explore the reactivity of 2 toward the di- and trisubstituted olefins cyclohexene and 2methyl-2-pentene.

Treatment of **2** with cyclopentene (1.1 equiv) on an NMR tube scale in C_6D_5Br solution resulted in full conversion of the starting materials in the course of ca. 5 h and clean formation of the tantalum cyclopentyl species {[η^6 -Ar-CMe₂- η^5 -C₅H₄]Ta-

 $(C_{5}H_{9})$ [B($C_{6}F_{5}$)₄] (3; Scheme 1). Similar to the case for the *n*-propyl derivative 1,⁸ the ¹H NMR spectrum of 3 at -30 °C indicates a C_{1} -symmetric complex with diagnostic resonances at δ -0.69 and -7.04 ppm for the diastereotopic cyclopentyl- β -CH₂ group. A small amount of crystals suitable for X-ray diffraction was isolated after slow diffusion of cyclohexane into the $C_{6}D_{5}Br$ solution. Although the diffraction data are of poor quality and only serve to establish connectivity (Figure S1, Supporting Information), the presence of a tantalum-cyclopentyl group (instead of cyclopentene-hydride) is evidenced by a normal Ta-C(alkyl) distance of 2.204(15) Å for Ta-C_{ao} with the other Ta-C bonds being significantly longer (>2.47 Å).

In a similar fashion, the trisubstituted olefin 2-methyl-2pentene (ca. 10 equiv) was reacted with 2 in C₆D₅Br solution to result in formation of the new tantalum alkyl species 4 (Scheme 1). In the ¹H NMR spectrum at -30 °C, three different diastereotopic CH₂ groups are observed for the Taalkyl moiety, one of which has broadened resonances at δ -1.3 and -6.6 ppm that indicate a β -agostic interaction. These data are consistent with 4 being the 4-methylpentyl compound {[η^6 -Ar-CMe₂- η^5 -C₅H₄]Ta(CH₂CH₂CH₂CHMe₂)}[B(C₆F₅)₄]. Complex 4 likely results from isomerization of the initial insertion product by a series of β -hydrogen elimination– reinsertion ("chain walking")¹⁴ events; the observed linear alkyl group is the thermodynamic product for steric reasons.

The formation of tantalum alkyl complexes is in contrast with the observations made by Bercaw and co-workers for the isoelectronic neutral metallocene complexes of niobium and tantalum, which were found to have olefin-hydride ground states.¹⁵ Competitive binding studies for niobocene complexes allowed the determination of relative ground-state energies, which revealed a significantly larger ground-state stabilization for styrene-hydride complexes relative to derivatives with aliphatic olefins.^{15b} The electronic difference between aliphatic and aromatic olefins that is responsible for this stabilization prompted us to investigate whether formation of an olefinhydride species with our system was possible using styrene. Treatment of **2** with styrene resulted in clean 2,1-insertion of styrene into the Ta–H bond. Precipitation with pentane afforded brownish {[η^6 -Ar-CMe₂- η^5 -C₅H₄]TaCH(Me)Ph}[B- $(C_6F_5)_4$ (5) as an analytically pure material in 67% yield (Scheme 1). The electronic preference for the observed 2,1insertion of styrene has been reported for many early- and latetransition-metal compounds,¹⁶ although sometimes 1,2-insertion is competitive and mixtures of terminal and internal insertion products are observed.¹⁷ In this case, the product arising from 2,1-insertion is the only observable species, as is clear from the characteristic mutually coupled ¹H NMR signals at δ 1.51 (doublet, 3H) and -0.22 ppm (quartet, 1H) for the CH₃ and CH groups of the Ta-CH(CH₃)Ph moiety, respectively. One of the o-H resonances of the benzyl group is shifted upfield to δ 2.39 ppm, whereas the other is located at δ 6.62 ppm, which suggests the benzyl ligand is η^3 -bound.^{16c} For the d² tantalum center in Cp*₂Ta(η^3 -C₃H₅), π backdonation into the allyl ligand leads to metallabicyclobutane character (σ^3 -allyl), evidenced by high-field resonances and low CH coupling constants (147–149 Hz) for the C₃H₅ moiety.¹⁸ A similar bonding description may apply for 5, with the "allylic" ortho carbon at δ 73.7 ppm in the ¹³C NMR spectrum (J_{CH} = 145 Hz). In the absence of π back-donation, η^3 -benzyl groups generally show resonances for the coordinated CH moiety at δ >105 ppm.^{16c,19}

Dynamic exchange was observed in the 2D EXSY spectrum of 5, with positive intensity cross peaks correlating the two benzyl o-H signals. Analysis of EXSY spectra at five temperatures in the range of 20-65 °C gave the activation parameters of the process as $\Delta H^{\ddagger} = 71(3)$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -28(5)$ J mol⁻¹ K⁻¹. No exchange correlations are observed for the Cparene ligand, indicating that inversion at the metal center does not occur at an appreciable rate and that the arene moiety is strongly bound. Exchange processes in early-transition-metal d⁰ metal allyl compounds have been investigated, and $\eta^3 \rightarrow \eta^1$ interconversions were shown to occur with lower enthalpies and more negative entropies of activation (e.g., $\Delta H^{\ddagger} = 41(5)$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -63(17) \text{ J mol}^{-1} \text{ K}^{-1}$ for $Cp^*{}_2Sc(\eta^3 - C_3H_5)$ in Et_2O-d_{10}).²⁰ The negative entropy of activation found for 5 (and related allyl species)²⁰ is most consistent with solventassisted loss of the η^3 coordination in the transition state, followed by rotation around the C-C bond, as depicted in Scheme 2.

Scheme 2. Representation of the Process Leading to Exchange of the *o*-Ph Environments of the Benzyl Ligand in 5



Neutral Tantalum Compound with ansa-Cp–arene Ligation. The monocationic Ta-propyl compound 1 reacts in bromobenzene with Bu_4NBr to give the salt $[Bu_4N][B(C_6F_5)_4]$ and the neutral tantalum bromide complex $[\eta^6$ -Ar-CMe₂- η^5 - $C_5H_4]Ta("Pr)Br$ (6; Scheme 3), which could be isolated in 83% yield as dark brown blocks. The number of resonances in the ¹H NMR spectrum of 6 is consistent with a C_1 -symmetric compound, and no evidence is found for agostic interactions for the Ta-propyl moiety. The ¹H NMR signals for the C_6 ring are observed at δ 4.33 and 3.36/3.27 ppm for the para and ortho hydrogens, respectively. The significant upfield shift from the

aromatic region indicates retention of the η^6 -arene coordination and partial disruption of aromaticity (Ta(V)/dienediyl resonance structure), similar to the case for the monocationic Ta-alkyl derivatives described above.

Dark-brown cubic crystals of 6 are obtained by crystallization from toluene. The X-ray crystal structure determination (Figure 1; pertinent interatomic distances and bond angles are given in Table 1) confirms the ansa-cyclopentadienyl-arene coordination in the neutral compound 6. A closer inspection of the metric parameters of the coordinated C₆ ring reveals a similar extent of π localization, whereas the deviation from planarity in 6 is slightly larger than that in 1 (Table 2). The fold angle $(14.7(4)^{\circ})$, however, is not as large as those found for related neutral early-transition-metal arene complexes in which the arene is not linked to the ligand system. For example, arene folding of up to 34.4° has been observed for the Ta(III) complex $(C_6Me_6)Ta(OAr)_2Cl_2^{21}$ whereas corresponding Ti(II) ² This arene complexes have fold angles between 20 and 30°. suggests that the strained ansa-cyclopentadienyl-arene coordination that is enforced by the short C1 bridge between the cyclopentadienyl and arene moieties prevents optimal overlap between the metal d and arene π^* orbitals. A comparison with structurally characterized high-valent, d⁰ metal-arene complexes shows that in these systems the arene ring retains its delocalized π system and planarity.^{23,24} The loss of planarity in the Ta(III) compounds described here underscores the importance of arene \leftarrow metal back-bonding interactions to approach a Ta(V)/ dienediyl resonance structure.

In agreement with its 18-valence-electron count, compound 6 is relatively robust and fails to react with H_2 , CO, or PhSSPh at room temperature. Monitoring solutions of 6 at 80 °C in the presence of CO or PhSSPh shows gradual disappearance of the tantalum starting material, but the products of these reactions are paramagnetic (on the basis of ¹H NMR integration) and have not been identified.

Dicationic Tantalum Compound with *ansa*-**Cp**-**Arene Ligation.** Treatment of the hydride cation 2 with the strong Lewis acid $[Ph_3C][B(C_6F_5)_4]$ results in hydride abstraction to give the dicationic tantalum compound $\{[\eta^6-\text{Ar-CMe}_2-\eta^5-C_5H_4]\text{Ta}(\text{solvent})\}^{2+}[B(C_6F_5)_4]^{-}_2$ (7) and concomitant formation of Ph_3CH (Scheme 3). Although the low solubility of 7 in C_6D_5B r hampers full NMR spectroscopic characterization, its ¹H NMR spectrum is indicative of a C_s -symmetric complex. Singlet resonances are observed at δ 5.26 (1H) and 4.86 (2H) ppm, which can be attributed to the para and ortho H atoms of the coordinated arene ring.

Addition of THF- d_8 to an NMR sample of 7 in C₆D₅Br results in a clear solution of the C_s -symmetric THF adduct {[η^6 -Ar-CMe₂- η^{5} -C₅H₄]Ta(THF- d_{8})₂}²⁺[B(C₆F₅)₄]⁻₂ (7-THF) in near-quantitative yield. The coordinated arene moiety of 7-THF gives rise to resonances at δ 5.32 (1H, p-H) and 4.92 (2H, o-H) ppm in the ¹H NMR spectrum, consistent with Ta(V)/dienediyl resonance contributions. These signals are shifted downfield in comparison to those in the monocationic and neutral derivatives 1 and 6, respectively, suggesting that reduction of the arene ring is somewhat less pronounced in 7-THF. Compound 7-THF could be isolated as dark blue crystals from THF/pentane, and a crystal structure determination confirms the proposed formulation (Figure 2; pertinent interatomic distances and bond angles are given in Table 1). The X-ray data are indicative of some disorder in the orientation of one of the coordinated THF molecules, but the salient structural features are not affected by this disorder.

Scheme 3. Synthesis of Neutral $[\eta^6$ -Ar-CMe₂- η^5 -C₅H₄]Ta(Pr)Br (6) and Dicationic { $[\eta^6$ -Ar-CMe₂- η^5 -C₅H₄]Ta(THF)₂}²⁺[B(C₆F₅)₄]⁻₂ (7-THF)





Figure 1. Molecular structure of **6** showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1, 6 and 7-THF

	1 (x = 1)	6 (x = none)	7-THF $(x = 1)$	
Ta(x)-Cg(Cp)	2.016(3)	2.044(2)	2.033(2)	
Ta(x)-Cg(Ar)	1.917(3)	1.961(2)	1.9628(17)	
Ta(x)-C(x17)	2.234(9)	2.294(5)		
Ta(x)-C(x9)	2.300(6)	2.275(5)	2.283(5)	
Ta(x)-C(x10)	2.361(6)	2.400(5)	2.428(5)	
Ta(x)-C(x11)	2.474(6)	2.473(5)	2.500(4)	
Ta(x)-C(x12)	2.352(6)	2.366(5)	2.372(4)	
Ta(x)-C(x13)	2.425(7)	2.526(6)	2.527(4)	
Ta(x)-C(x14)	2.391(6)	2.460(5)	2.407(5)	
Ta(x) - C(x17) - C(x18)	80.7(5)	121.6(3)		
C(x5) - C(x6) - C(x9)	95.0(5)	93.7(3)	92.0(3)	
Cg(Cp)-Ta- $Cg(Ar)$	128.79(13)	127.79(9)	126.81(8)	
α^{a}	57.7(4)	59.0(3)	61.3(3)	
$a^{a}\alpha$ is the interplanar ang	le between th	e least-square:	s planes of the	

 α is the interplanar angle between the least-squares planes of the cyclopentadienyl and arene rings.

The fold angle of the coordinated C_6 ring and the bond length alternation (Table 2) shows that back-donation from the metal d orbitals into the arene π system occurs despite the high electrophilicity of the dicationic tantalum center in 7-THF.

While dicationic rare-earth-metal alkyl species have been implicated as active species in olefin polymerization,²⁵ well-characterized examples of dicationic early transition metals are rare.²⁶ Green and Saßmannshausen have reported a dicationic zirconocene complex in which the cyclopentadienyl ligands have a pendant arene moiety which is believed to coordinate to the metal center, but no structural confirmation of this binding mode is available.²⁷ In contrast to the case for 7-**THF**, the metal–arene interaction in this zirconocene(IV) system is mainly electrostatic in nature, as there are no d electrons available for arene \leftarrow metal back-donation.

The dicationic tantalum complex 7 is isostructural and isoelectronic with the proposed active species for ethylene trimerization catalyzed by cationic cyclopentadienyl-arene titanium complexes.^{5b,6,28} It was therefore of interest to investigate the reactivity of 7 toward ethylene. Treatment of 7 (generated in situ in C_6D_5Br) with 1 bar of ethylene and monitoring by NMR spectroscopy, however, shows no indication of ethylene consumption. Also, reaction of 7-THF with ethylene gives no observable changes in the ¹H NMR spectrum after 5 h at room temperature. Heating this mixture to 80 °C for several hours results in gradual disappearance of resonances due to 7-THF, but no conversion of ethylene is observed. The poor solubility of 7 in nonpolar solvents limits further reactivity studies. For the 18-electron complex 7-THF it is likely that any reactivity requires dissociation of either the coordinated arene ring or a THF molecule. The observation that 7-THF is unreactive even toward CO suggests that dissociative displacement of ligands in 7-THF is unfavorable under the conditions applied.

Computational Studies. Density functional theory (DFT) calculations were performed to evaluate the nature of the metal-arene interaction in these neutral, monocationic, and dicationic *ansa*-cyclopentadienyl-arene tantalum compounds. The optimized geometries of **1**, **6**, and 7-THF are in good agreement with the crystallographically determined structures. The largest difference between calculated and experimental structures is observed for 7-THF, for which the calculated Ta-O(THF) bonds are somewhat elongated (by ca. 0.05 Å) in comparison to the X-ray structure. Importantly, the metrical parameters for the *ansa*-cyclopentadienyl-arene ligand are similar to the crystallographic values, with arene fold angles that are somewhat larger (Table 2). Nevertheless, the

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Table 2. C–C Bond Lengths (Å) within the Coordinated C₆ Fragment and Fold Angle along the C(x9)–C(x12) Vector in 1, 6, and 7-THF

C(x9



^{*a*}Folding along the C(x9)-C(x12) vector.



Figure 2. Molecular structure of 7-**THF** showing 50% probability ellipsoids. The $B(C_6F_5)_4$ anions, THF solvate molecule, and hydrogen atoms are omitted for clarity.

experimentally observed trends are correctly reproduced in the calculations. Charge decomposition analysis $(CDA)^{29}$ was used to estimate the relative importance of donation (arene \rightarrow metal) and back-donation (arene \leftarrow metal) contributions to the overall metal–arene interaction (see the Supporting Information for details). This fragment-based analysis gives values for the amount of electron transfer (number of electrons) for each molecular orbital upon complex formation. The positive total values (summation over all MOs) for donation (d) and backdonation (b) and negligible residual term (Δ) obtained by CDA analysis (Table 3) indicate that the metal–arene

interaction in these compounds is best characterized as a donor-acceptor interaction in terms of the Chatt-Dewar-Duncanson model.^{29b} As expected for early-transition-metal centers with a formal d² electron count, there is a substantial arene \leftarrow metal back-donation component (b) in all complexes studied (Figure 3 and Table 3). This back-bonding interaction is primarily located in the HOMO of the complex that arises from interaction of the arene LUMO with the HOMO of the metal-containing fragment. Surprisingly, there is little variation in the amount of back-donation in the series of compounds; even the highly electrophilic dicationic Ta center in 7-THF_{calcd} is able to accommodate a substantial back-bonding interaction with the coordinated arene ring. For comparison, CDA analysis was performed for the corresponding "naked" dication in two different geometries: 7_{calcd} corresponds to simple removal of the two THF molecules from 7-THF_{calcd} without further geometry optimization, and 7_{calcd,opt} is the geometry after relaxation to its minimum energy conformation. To complete the bonding picture, we computed the atomic charges from natural population analysis (NPA) for the central Ta atom and the coordinated arene ring (summation over the 6 C atoms, Table 3). The coordinated THF molecules in 7-THF_{calcd} result in a decrease in charge at the Ta center (+0.88) in comparison to the "naked" dication 7_{calcd} (+1.27), which gives rise to a lower total binding energy ($E_{b} = 54.1$ and 93.6 kcal mol⁻¹ for 7- $\text{THF}_{\text{calcd}}$ and 7_{calcd} respectively). For the optimized structure $7_{calcd,opt}$ the metal-C(arene) distances are somewhat contracted, concomitant with a decrease in the donation term (d)and a larger amount of back-donation (b). In all the complexes studied, the arene←metal back-bonding interaction in the HOMO of the complex contributes at least 10% to the total

Table 3. Charge Decomposition Analysis of the Ta-Arene Interaction and NPA Charges^a

					E_{b}		NPA charge	
	d	ь	Δ	d/b	total	НОМО	Та	$\sum(Ar)$
1 _{calcd}	0.716	0.236	0.026	3.0	63.0	6.9	0.50	-0.66
6 _{calcd}	0.801	0.232	0.063	3.5	25.3	3.5	0.47	-0.83
7-THF _{calcd}	0.767	0.248	-0.020	3.1	54.1	6.8	0.88	-0.66
7 _{calcd}	0.713	0.234	-0.022	3.0	93.6	12.4	1.27	-0.68
7 _{calcd,opt}	0.613	0.287	-0.027	2.1	99.5	15.5	1.26	-0.71

^{*a*}Donation (*d*), back-donation (*b*), residual term (Δ) values (in numbers of electrons) and binding energies (E_{br} in kcal/mol) upon complex formation, as obtained from CDA analysis.



Figure 3. Fragment molecular orbitals that give rise to arene \leftarrow metal back-donation upon complexation (top) and HOMOs of 1_{calcd} , 6_{calcd} , and 7-THF_{calcd} (bottom left to right) showing the metal–arene back-bonding interaction. The values given are the total amount of back-donation, with the contribution from the HOMO being given in parentheses.

binding energy. Taken together, these data indicate that while electrostatic contributions are important, delocalization of Ta d electron density into the arene π^* orbitals (back-donation) is a key component in stabilizing these complexes.

SUMMARY AND CONCLUSIONS

The insertion chemistry of olefins into the Ta-H bond of the cation $[\eta^6$ -Ar-CMe₂- η^5 -C₅H₄]TaH⁺ has been examined, and its high reactivity is exemplified by the facile insertion of the trisubsituted olefin 2-methyl-2-pentene. Insertion of styrene exclusively proceeds in a 2,1-fashion to give a Ta-CH(Me)Ph group that shows σ^3 -benzylic character. Neutral and dicationic tantalum complexes with an ansa-cyclopentadienyl-arene ligand are readily available from monocationic precursors by addition of Br⁻ and removal of H⁻, respectively, and their X-ray crystal structures are described. All of the complexes show backdonation from the d² Ta(III) center into the arene π^* system, as judged from the puckering of the C6 ring to result in dienediyl character. The structural and computational data show that enhanced electrostatic interactions on going to more positively charged metal centers increase the binding energy. The charge at the metal center (electrophilicity) does not alter the fundamental nature of the metal-arene interaction, which in all cases may be described by a donor-acceptor type interaction in accordance with the Chatt-Dewar-Duncanson model that includes significant arene←metal back-donation. This suggests that ansa-cyclopentadienyl-arene ligation in earlytransition-metal compounds is a more generally applicable motif for stabilization of complexes in low formal oxidation states.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under a nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al_2O_3 (Fluka). Cyclohexane (Labscan) was distilled from Na/K alloy and bromobenzene (Merck) from CaH₂. All solvents were degassed prior to use and stored under nitrogen. Deuterated solvents were vacuum-transferred from Na/K alloy (THF- d_8 , C₆D₆, Aldrich) or from CaH₂ (C₆D₅Br, Aldrich) and stored under nitrogen. H₂ (AGA, 99.9%) was passed over a column of LiAlH₄ prior to use; cyclopentene (Aldrich) and styrene (Aldrich) were vacuum-transferred from LiAlH₄. [Ph₃C][B(C₆F₅)₄] (Strem) and Bu₄NBr (Fluka) were used as received. The compounds {[η^6 -Ar-CMe₂- η^5 -C₅H₄]Ta(Pr)}[B(C₆F₅)₄] (1; Ar = 3,5-Me₂C₆H₃) and {[η^6 -Ar-CMe₂- η^5 -C₅H₄]TaH}[B(C₆F₅)₄] (2) were synthesized according to published procedures.⁸ NMR spectra were recorded on Varian VXR 300 or Varian Inova 500 spectrometers. The ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm); *J* values are reported in Hz. Assignment of NMR resonances was aided by gradient-selected COSY, NOESY, HSQC, and/or HMBC experiments using standard pulse sequences. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany).

Ionic compounds contain the anion $[B(C_6F_5)_4]^-$, the NMR data for which are identical for all compounds and are as follows. ¹³C NMR (125.7 MHz, C_6D_5Br): δ 148.7 (d, J_{CF} = 242, o-CF), 138.6 (d, J_{CF} = 238, p-CF), 136.6 (d, J_{CF} = 241, m-CF), 124.7 (br, *ipso*-C). ¹⁹F NMR (470.3 MHz, C_6D_5Br): δ –131.9 (br d, o-F), –161.7 (t, J = 21, p-F), –165.8 (br d, m-F).

NMR-Scale Synthesis of {[η⁶-Ar-CMe₂-η⁵-C₅H₄]Ta(C₅H₉)}[B-(C₆F₅)₄] (3). A solution of 2 (ca. 8.7 μmol) in C₆D₅Br was degassed on a vacuum line by three freeze–pump–thaw cycles. Subsequently, ca. 1.1 equiv of cyclopentene was condensed into the tube using a calibrated gas bulb (9.4 mL, ~20 mmHg) and the reaction was monitored by ¹H NMR spectroscopy. Full conversion was achieved in 5 h, and NMR spectroscopy was consistent with the formation of 3. Layering the C₆D₅Br solution with cyclohexane afforded a small amount of dark green crystals, and X-ray analysis confirmed the proposed formulation. ¹H NMR (500 MHz, C₆D₅Br, -30 °C): δ 4.52 (s, 1H), 4.44 (s, 1H), 4.25 (s, 1H), 4.21 (s, 1H), 4.18 (s, 1H), 4.12 (s, 1H), 2.03 (s, 1H), 1.81 (s, 3H, ArMe), 1.65 (s, 3H, ArMe), 0.52 (s, 3H, CMe₂), 0.40 (s, 3H, CMe₂), -0.69 (br, 1H, β-CHH'), -7.04 (br, 1H, β-CHH'), broad overlapped signals between 1.9 and 1.0 ppm due to C₅H₉.

NMR-Scale Synthesis of {[η^6 -Ar-CMe₂- η^5 -C₅H₄]Ta-(CH₂CH₂CH₂CHMe₂)}[B(C₆F₅)₄] (4). A solution of 2 (ca. 3.6 μ mol) in C₆D₅Br was degassed on a vacuum line by three freeze–pump– thaw cycles. Subsequently, ca. 10 equiv of 2-methyl-2-pentene was condensed into the tube using a calibrated gas bulb (9.4 mL, ~70 mmHg) and the reaction was monitored by ¹H NMR spectroscopy. NMR spectroscopy was consistent with the formation of 4. ¹H NMR (500 MHz, C₆D₅Br, -30 °C): δ 4.52 (s, 2H, Cp + Ar o-H), 4.51 (s, 1H, Cp), 4.32 (s, 1H, Cp), 4.24 (s, 1H, Ar o-H), 4.18 (s, 1H, Cp), 2.14 (s, 1H, Ar pH), 1.83 (s, 3H, ArMe), 1.75 (s, 3H, ArMe), 1.37 (m, 1H, TaCH₂CH₂CH₂CHMe₂), 1.25 (m, 1H, TaCH₂CH₂CHH'CHMe₂),

0.78 (d, J = 6.7, 3H, TaCH₂CH₂CH₂CHMe₂), 0.77 (d, J = 6.7, 3H, TaCH₂CH₂CH₂CHMe₂), 0.62 (m, 1H, TaCHH'CH₂CH₂CHMe₂), 0.56 (s, 3H, CMe₂), 0.52 (m, 1H, TaCH₂CH₂CHMe₂), 0.41 (s, 3H, CMe₂), -0.46 (m, 1H, TaCHH'CH₂CH₂CHMe₂), -1.3 (br, 1H, TaCH₂CHH'CH₂CHM'CH₂CHMe₂), -6.6 (br, 1H, TaCH₂CHH'CH₂CHMe₂). ¹³C NMR³⁸ (125.7 MHz, C₆D₅Br, -30 °C): δ 127.7 (s, Ar *m*-C), 128.2 (s, Ar *m*-C), 103.5 (d, $J \approx 185$, Cp CH), 100.6 (d, $J \approx 180$, Cp CH), 96.9 (d, $J \approx 176$, Ar *o*-CH), 93.9 (d, $J \approx 178$, Ar *p*-CH), 93.6 (d, $J \approx 188$, Cp CH), 60.4 (s, Ar *ipso*-C), 40.2 (t, $J \approx 129$, TaCH₂CH₂CH₂CHMe₂), 36.2 (s, CMe₂), 29.6 (d, $J \approx 124$, TaCH₂CH₂CH₂CHMe₂), 21.1, 20.7 (q, $J \approx 129$, ArMe), 20.3, 19.9 (q, $J \approx 127$, CMe₂), 9.7 (t, $J \approx 145$, TaCH₂CH₂CH₂CHMe₂), 1.6 (TaCH₂CH₂CH₂CHMe₂).

 $\{[\eta^{6}-Ar-CMe_{2}-\eta^{5}-C_{5}H_{4}]TaCH(Me)Ph\}[B(C_{6}F_{5})_{4}]$ (5). A solution of 1 (38.1 mg, 30.0 μ mol) in 1 mL of bromobenzene was degassed on a vacuum line by three freeze-pump-thaw cycles. The reaction vessel was pressurized with 1 bar of H₂, and the mixture was stirred at room temperature for 15 min. The excess H₂ was pumped off. To the red solution was added 3.8 μ L of styrene (33 μ mol) by microsyringe, and the mixture was allowed to react at -30 °C overnight. The product was precipitated by addition of pentane and the supernatant decanted. The yellow-brown product was washed with toluene and then pentane and subsequently dried in vacuo to give 23.8 mg of brownish microcrystalline 5 (20.2 μmol, 67%). ¹H NMR (500 MHz, C₆D₅Br, 20 °C): δ 7.20 (t, 1H, J = 7.6, Ph), 7.15 (t, 1H, J = 7.6, Ph), 6.67 (t, 1H, J = 7.5, Ph), 6.62 (d, 1H, J = 8.3, Ph o-H), 4.55 (s, 1H, Ar o-H), 4.25 (s, 1H, Ar o-H), 4.12 (s, 1H, Cp), 3.82 (s, 1H, Cp), 3.50 (s, 1H, Cp), 2.87 (s, 1H, Ar p-H), 2.39 (br, 1H, Ph o-H), 2.04 (s, 3H, ArMe), 1.72 (s, 3H, ArMe), 1.63 (s, 1H, Cp), 1.51 (d, 3H, J = 6.1, TaCH(Me)Ph, 0.58 (s, 3H, CMe₂), 0.44 (s, 3H, CMe₂), -0.22 (q, 1H, J = 6.1, TaCH(Me)Ph. ¹³C NMR (125.7 MHz, C₆D₅Br, 20 °C): δ 143.8 (d, J= 163, Ph CH), 137.2 (d, J = 161, Ph CH), 133.17 (s, Ar m-C), 133.15 (s, Ph ipso-C), ~126 (Ar m-C), 122.0 (d, overlapped, Ph CH), 121.9 (d, overlapped, Ph CH), 111.5 (d, J = 180, Cp CH), 107.3 (d, J = 179, Cp CH), 98.1 (d, J = 172, Ar o-CH), 96.8 (d, J = 168, Ar p-CH), 88.2 (d, J = 174, Ar o-CH), 75.3 (d, J = 183, Cp CH), 73.7 (d, J = 145, Ph o-CH), 72.2 (s, Cp ipso-C), 70.3 (d, J = 184, Cp CH), 61.4 (s, Ar ipso-C), 41.1 (d, J = 135, TaCH(Me)Ph), 34.5 (s, CMe_2), 20.9 (q, J = 128, ArMe), 20.8 (q, J = 128, ArMe), 20.6 (q, J = 128, CMe₂), 20.1 (q, J = 128, CMe₂). Anal. Calcd for C₄₈H₂₈BF₂₀Ta: C, 49.00; H, 2.40. Found: C, 48.78; H, 2.34.

 $[\eta^{6}-\text{Ar-CMe}_{2}-\eta^{5}-\text{C}_{5}\text{H}_{4}]\text{Ta}(\text{Pr})\text{Br}$ (6). Solid 1 (123.4 mg, 0.0971 mmol) and Bu₄NBr (32.9 mg, 0.101 mmol) were mixed in the glovebox, and 2 mL of cold $(-30 \, ^\circ \text{C})$ bromobenzene was added. While it was warmed to room temperature, the mixture was shaken to dissolve all starting materials. The resulting brownish yellow solution was allowed to react overnight at room temperature. Upon addition of 5 mL of pentane, a white precipitate was formed, from which the supernatant was decanted. The residue was washed with 10 mL of a toluene/pentane (1/1) mixture. The combined filtrate was evaporated to dryness, yielding 6 as a brown-green microcrystalline material (41.3 mg, 0.0802 mmol, 83%). ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 5.69 (s, 1H, Cp), 5.05 (s, 1H, Cp), 4.36 (s, 1H, Cp), 4.33 (s, 1H, Ar p-H), 3.85 (s, 1H, Cp), 3.36 (s, 1H, Ar o-H), 3.27 (s, 1H, Ar o-H), 2.02 (s, 3H, ArMe), 1.52 (s, 3H, ArMe), 1.41 (m, 1H, TaCH₂CHH'Me), 1.40 (ps t, overlapped, 1H, TaCHH'CH₂Me), 1.21 (t, J = 7.1, 3H, TaCH₂CH₂Me), 0.96 (m, 1H, TaCH₂CHH'Me), 0.53 (s, 3H, CMe₂), 0.43 (ps t, J = 13.6, 1H, TaCHH'CH₂Me), 0.20 (s, 3H, CMe₂). ¹³C NMR (data taken from HSQC/HMBC experiments, $C_6 D_{62}$ 25 °C): δ 134.9, 129.9, 115.3 (Cp CH), 106.7 (Cp CH), 100.8 (Ar o-CH), 95.4 (Ar p-CH), 85.6 (Ar o-CH), 78.2 (Cp ipso-C), 72.8 (Cp CH), 71.4 (Cp CH), 58.4 (Ar ipso-C), 33.4 (CMe₂), 30.4 (TaCH₂CH₂Me), 23.8 (TaCH₂CH₂Me), 22.3 (CMe₂), 21.4 (ArMe), 21.3 (CMe₂), 20.1 (ArMe), 15.1 (TaCH₂CH₂Me). Anal. Calcd for C₁₉H₂₆BrTa: C, 44.29; H, 5.09. Found: C, 44.52; H, 5.12.

NMR-Scale Synthesis of $\{[\eta^6-Ar-CMe_2-\eta^5-C_5H_4]Ta(C_6D_5Br)_x\}[B-(C_6F_5)_4]_2$ (7). An NMR tube containing a solution of 1 (3.0 mg, 2.4 μ mol) in 0.4 mL of C_6D_5Br was degassed on a vacuum line by three

freeze–pump–thaw cycles. The tube was frozen in liquid N₂ and backfilled with 1 bar of H₂, after which the tube was closed. After it was warmed to room temperature, the resulting red solution was analyzed by ¹H NMR, showing full conversion to 2.⁸ Excess H₂ was pumped off, and [Ph₃C][B(C₆F₅)₄] (2.2 mg, 2.4 μ mol) was added in the glovebox. The reaction was complete after ca. 1 h, and NMR spectroscopy showed clean formation of Ph₃CH and 7. ¹H NMR (300 MHz, C₆D₅Br, 20 °C): δ 7.15–6.95 (Ph₃CH), 5.64 (s, 2H, Cp), 5.40 (Ph₃CH), 5.26 (s, 1H, Ar *p*-H), 4.86 (s, 2H, Ar *o*-H), 4.66 (s, 2H, Cp), 2.02 (s, 6H, ArMe), 0.50 (s, 6H, CMe₂).

 $\{[\eta^6 - \text{Ar-CMe}_2 - \eta^5 - \text{C}_5 \text{H}_4] \text{Ta}(\text{THF-}d_8)_2\} [B(\text{C}_6 \text{F}_5)_4]_2$ (7-THF). An NMR tube containing a solution of 1 (23.0 mg, 0.0181 mmol) in 0.4 mL of C₆D₅Br was degassed on a vacuum line by three freezepump-thaw cycles. The tube was frozen in liquid N2 and back-filled with 1 bar of H₂, after which the tube was closed. After it was warmed to room temperature, the resulting red solution was analyzed by ¹H NMR, showing full conversion to 2. Excess H₂ was pumped off, and $[Ph_3C][B(C_6F_5)_4]$ (16.7 mg, 0.0181 mmol) was added in the glovebox. A viscous dark oil precipitated over the course of 1 h, which was subsequently dissolved by addition of ca. 0.2 mL of THF- d_8 . NMR spectroscopy was consistent with the formation of Ph₃CH and 7-THF. ¹H NMR (500 MHz, C₆D₅Br/THF-d₈, 20 °C): δ 7.10 (t, 6H, *J* = 7.5, Ph₃CH *m*-H), 7.04 (t, 3H, *J* = 7.3, Ph₃CH *p*-H), 6.99 (d, 6H, *J* = 7.4, Ph₃CH o-H), 6.24 (2H, Cp), 5.40 (s, 1H, Ph₃CH), 5.32 (s, 1H, Ar p-H), 5.17 (s, 2H, Cp), 4.92 (s, 2H, Ar o-H), 1.99 (s, 6H, ArMe), 0.65 (s, 6H, CMe₂). ¹³C NMR (125.7 MHz, C₆D₅Br/THF-d₈, 20 °C): δ 144.1 (s, Ph₃CH ipso-C), 140.9 (s, Ar m-C), 129.6 (d, J = 160, Ph₃CH CH), 128.4 (d, J = 159, Ph₃CH CH), 126.4 (d, J = 159, Ph₃CH CH), 118.8 (d, *J* = 180, Cp CH), 102.9 (d, *J* = 173, Ar *p*-CH), 98.4 (d, J = 179, Ar o-CH), 94.5 (s, Cp ipso-C), 88.9 (s, Ar ipso-C), 78.9 (d, J = 185, Cp CH), 57.1 (d, J = 127, Ph₃CH), 33.2 (s, CMe₂), 22.1 (q, J = 130, ArMe), 20.2 (q, J = 128, CMe₂).

Diffusion of cyclohexane into the $C_6D_5Br/THF \cdot d_8$ solution precipitated a dark oil, from which the supernatant was decanted. Repeated trituration of the oil with pentane gave 7-THF as a sticky solid material (34.2 mg, 0.0181 mmol, 99%). Anal. Calcd for $C_{72}H_{35}B_2F_{40}O_2Ta$: C, 45.65; H, 1.86. Found: C, 46.33; H, 2.25. A small amount of the solid material was dissolved in THF, and pentane was layered on top of the solution. A dark oil precipitated, which slowly solidified in the course of several days to give dark blue needles of 7-THF.

X-ray Crystallography. Suitable crystals of 6 and 7-THF were mounted on top of a glass fiber in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. The final unit cell was obtained from the xyz centroids of 7262 (6) and 7391 (7-THF) reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, and decay and absorption: a multiscan absorption correction was applied, on the basis of the intensities of symmetry-related reflections measured at different angular settings (SADABS).³⁰ The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.³¹ The hydrogen atoms were generated by geometrical considerations and constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. For 6, the polarity of the structure of the molecule actually chosen was determined by Flack's refinement parameter³² (x = 0.016(14)). For 7-THF, refinement was frustrated by disorder in the position of C(124). A two-site occupancy model was applied to C(124), for which the displacement parameters were separately refined. The sof of the major fraction refined to a value of 0.55(4). All refinement and geometry calculations were performed with the program packages SHELXL³³ and PLATON.³⁴ Crystal data and details on data collection and refinement are presented in the Supporting Information.

Computational Studies. Calculations were performed with the Gaussian03 program using density functional theory (DFT).³⁵ Geometries were fully optimized starting from the X-ray structures using the B3LYP exchange-correlation functional with the LANL2DZ

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basis set on the metal center and 6-311G(d) basis sets on all other atoms. The anions were omitted in the calculations. Optimizations were performed without (symmetry) constraints, and the resulting structures were confirmed to be minima on the potential energy surface by frequency calculations (number of imaginary frequencies 0). For 7-**THF**_{calcd}, another stationary point (number of imaginary frequencies 0) was identified for which the orientation of the coordinated THF molecules was somewhat different: the structural features of the [Cp-arene]Ta fragment were virtually identical and the energies of these two minima were within 1 kJ/mol.

Charge decomposition analysis was performed using the CDA program by Dapprich and Frenking.³⁶ The input for the CDA program was generated from single-point calculations on the appropriate optimized geometry (without bridging atom, as described previously⁷) with double- ζ basis sets used throughout (LANL2DZ on the metal, 6-31G(d) on all nonmetal atoms). For visualization of the computed structures and molecular orbitals the program MOLEKEL 4.3 was used.³⁷

ASSOCIATED CONTENT

Supporting Information

Tables giving Cartesian coordinates for the optimized geometries of 1_{calcd} , 6_{calcd} , 7-THF_{calcd}, and $7_{calcd,opt}$ and tables, a figure, and CIF files giving crystallographic data for compounds 3, 6, and 7-THF. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: edwin.otten@rug.nl.

Notes

The authors declare no competing financial interest.

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