

Synthesis and Reactivity of Tantalocene Zwitterions Stabilized by Ground-State α -Agostic Interactions via Reaction of $B(C_6F_5)_3$ with $Cp'_2Ta(=CH_2)(CH_3)$ ($Cp' = C_5H_5, C_5H_4Me$)

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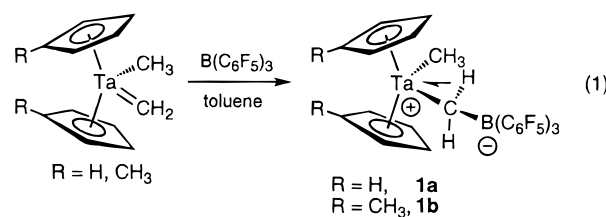
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Summary: Zwitterionic tantalocene derivatives are formed when the perfluorophenyl-substituted borane $B(C_6F_5)_3$ is reacted with the tantalocene methyl methylenide complexes $Cp'_2Ta(=CH_2)(CH_3)$ ($Cp' = C_5H_5, C_5H_4Me$). The products arise from borane attack of the methylenide ligand and are characterized by a strong, ground-state α -agostic interaction, and insertion of tert-butyl isocyanide occurs exclusively into the agostic Ta–C bond, producing iminoacyl zwitterions.

We have been studying the fundamental chemistry involved in the reactions of early-transition-metal organometallic compounds with highly electrophilic, perfluorophenyl-substituted boranes.² While the main impetus for these studies stems from the role these boranes play in the activation of olefin polymerization catalysts,³ a detailed understanding of the interaction of boranes with simple hydrocarbyl ligands has additional relevance to catalytic hydroboration⁴ and diboration⁵ processes. We recently reported⁶ preliminary results on the reactions of $HB(C_6F_5)_2$ ⁷ with Schrock's methyl methylenide compound $Cp_2Ta(=CH_2)CH_3$;⁸ here we disclose the reactions of this organometallic compound with the tertiary borane $B(C_6F_5)_3$.⁹ The products are zwitterionic

tantalocene¹⁰ derivatives exhibiting rare ground-state α -agostic interactions.

As a classic example of a nucleophilic carbene, $Cp_2Ta(=CH_2)CH_3$ reacts rapidly with electrophiles at the methylene ligand.⁸ Predictably, therefore, reaction of $Cp'_2Ta(=CH_2)CH_3$ ($Cp' = C_5H_5, C_5H_4Me$) with $B(C_6F_5)_3$ proceeds rapidly in toluene to afford the zwitterionic tantalocene complexes $Cp'_2Ta[CH_2B(C_6F_5)_3]CH_3$ (**1a,b**) in excellent yield (eq 1). Borane attack at the meth-



ylidene carbon is signaled by the upfield shift of the now boron-broadened resonances for the methylene protons (2.10 ppm) and carbon atom (150.3 ppm) of **1a** in comparison to $Cp_2Ta(=CH_2)CH_3$ (10.14 and 224.0 ppm, respectively). A resonance at –9.4 ppm in the ¹¹B NMR spectrum and a meta–para chemical shift difference of 4.7 ppm in the ¹⁹F NMR spectrum¹¹ are indicative of borate formation and a significant degree of charge separation in the zwitterions **1**.

The tantalum centers in compounds **1** are stabilized by a strong α -agostic interaction involving one of the C–H bonds of the electron-rich methylene unit, as evidenced by established criteria.¹² In solution, a low average ¹J_{CH} value of 98.7(5) Hz is observed for the CH₂ unit in **1a**, compared with a value of 129.1(5) Hz for the methyl C–H bonds. In the solid, a low-frequency stretch of 2742 cm^{–1} ($\nu_{CD} = 2026$ cm^{–1}) augments the findings of an X-ray structural analysis,¹³ in which both CH₂ hydrogens were located and refined, clearly establishing the presence of a ground-state α -agostic linkage (Figure 1). The agostic C(12)–H(14) bond is elongated by 0.27(4) Å compared to the conventional C(12)–H(15) bond, while the Ta–C(12) distance is notably shorter

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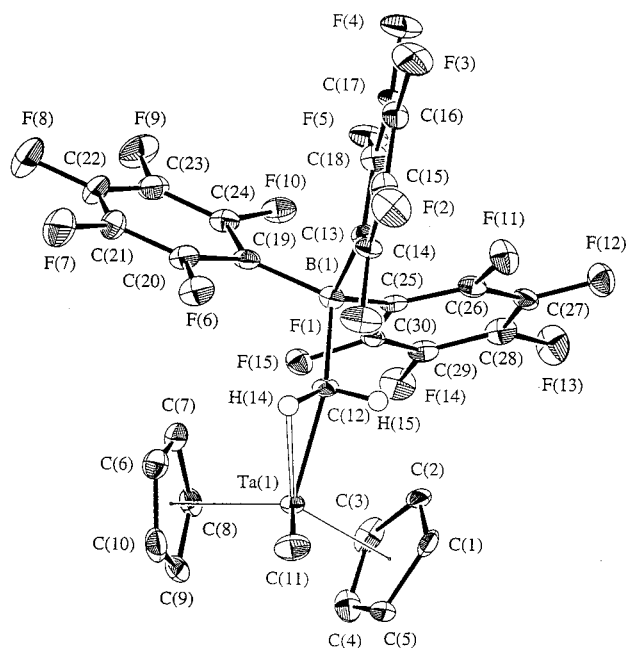


Figure 1. Molecular structure of **1a**. Selected bond distances (Å): Ta(1)–Cp(1), 2.107; Ta(1)–Cp(2), 2.113; Ta(1)–C(11), 2.218(5); Ta(1)–C(12), 2.141(5); Ta(1)–H(14), 2.26(4); C(12)–H(14), 1.26(4); C(12)–H(15), 0.99(5); B(1)–C(12), 1.661(7); B(1)–C(13), 1.675(7); B(10)–C(19), 1.643(8); B(1)–C(25), 1.649(6). Selected bond angles (deg): Cp(1)–Ta(1)–Cp(2), 131.9; C(11)–Ta(1)–C(12), 97.0(2); C(11)–Ta(1)–H(14), 68.6(11); Ta(1)–C(12)–H(14), 78.7(19); Ta(1)–C(12)–B(1), 145.6(3); Ta(1)–C(12)–H(15), 95.1(29); B(1)–C(12)–H(14), 123.6(20).

(2.141(5) Å) than the Ta–C(11) length of 2.218(5) Å. The Ta–C(12)–H(14) angle is only 78.7(19)°.

Since no evidence exists for an α -agostic stabilization in the related compounds $\text{Cp}_2\text{Ta}[\text{CH}_2\text{Al}(\text{CH}_3)_3]\text{CH}_3$ ($^1J_{\text{CH}} = 128 \text{ Hz}^8$) and $[\text{Cp}_2\text{Ta}(\text{CH}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($^1J_{\text{CH}} = 126 \text{ Hz}$), its presence in **1a** is a consequence of more extensive charge separation and subsequent delocalization of borate charge onto the methylene carbon, making its C–H bonds better donors. Structural observation of α -agostic interactions are of interest due to the role these structures play in the olefin chemistry of metallocenes.¹⁵ As they are usually associated with transition-state structures, well-characterized ground-state α -agostic interactions are rare and usually imposed by steric factors which preclude β -agostic structures.¹⁶ In **1a**, the agostic interaction occurs for electronic reasons, despite

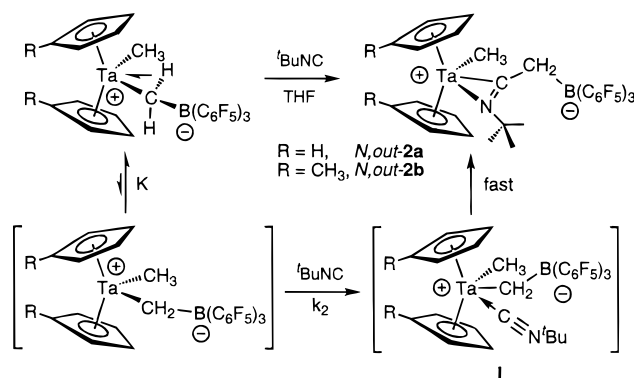
(13) Crystals of **1a** were grown from dichloroethane and form as a solvate. Crystal data for **1a**: $\text{C}_{34}\text{H}_{23}\text{F}_{15}\text{BCl}_4\text{Ta}$, $0.12 \times 0.25 \times 0.30 \text{ mm}$, triclinic, $P\bar{1}$ (No. 2), $a = 10.6312(10) \text{ Å}$, $b = 11.7797(9) \text{ Å}$, $c = 15.4744(15) \text{ Å}$, $\alpha = 100.8110(12)^\circ$, $\beta = 90.9989(9)^\circ$, $\gamma = 108.215(2)^\circ$, $V = 1802.1(3) \text{ Å}^3$, $Z = 2$, $fw = 1050.10$, $D_{\text{calc}} = 1.935 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 61.0^\circ$, Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ Å}$, $T = -93^\circ\text{C}$, 16 290 measured reflections, 8283 unique, 6426 reflections with $I_{\text{net}} > 3.0\sigma(I_{\text{net}})$, $\mu = 34.46 \text{ cm}^{-1}$, minimum/maximum transmission 0.7040 and 1.0000, residuals on F^2 (all data) $R = 0.069$, $R_w = 0.072$, GOF = 1.39, 530 parameters.

(14) See the Supporting Information for details on the synthesis and characterization of this compound and its $^t\text{BuNC}$ insertion product.

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Scheme 1



engendering unfavorable steric interactions between the $-\text{B}(\text{C}_6\text{F}_5)_3$ moiety and a Cp ring as the agostic C–H bond strives to align with the plane bisecting the rings. In fact, the agostic C–H vector is about 30° out of this plane, illustrating the effect a bulky substituent can have on the geometry of such an interaction. It is nonetheless strong enough to stabilize **1a** against potential decomposition to neutral products by $-\text{C}_6\text{F}_5$ transfer to tantalum.¹⁷

Compounds **1** are zwitterionic analogues of neutral group 4 bis(alkyl)metallocenes, and we have begun to examine their chemistry for comparative purposes. Thus, insertion of *tert*-butyl isocyanide proceeds smoothly in tetrahydrofuran with excess isocyanide to give the N-out iminoacyl zwitterions **2a,b** (Scheme 1) as metastable kinetic isomers (vide infra). Interestingly, the insertion occurs regioselectively into the Ta–CH₂ bond, as indicated by the more pronounced downfield shift of the boron-broadened methylene resonance (to 3.75 ppm from 2.10 ppm) in comparison to the slight upfield change in the methyl resonance (to 0.37 ppm from 0.55 ppm) upon insertion. Selective CO and RNC insertions into the metallocene M–C bond of the more sterically demanding R group are generally the norm.¹⁸ ^{11}B ($\delta = -10.9 \text{ ppm}$) and ^{19}F ($\Delta_{m,p} = 4.3 \text{ ppm}$) NMR spectroscopy shows that the $-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3$ borate fragment remains intact during insertion under these conditions.¹⁹ A resonance at 219.8 ppm for the iminoacyl carbon atom is characteristic of η^2 -binding for this ligand, a common bonding mode in high-valent early-d-block metals.²⁰ We assign the kinetically formed isomer the “N-out” configuration on the basis of a 2D ROESY experiment, which shows cross-peaks between the *tert*-butyl and methylene protons and between the methylene and methyl resonances, with no cross-peak between the *tert*-

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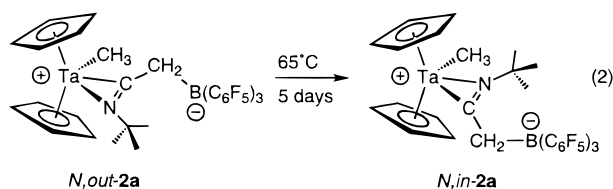
(18) Approach of the isocyanide from the lateral position of the metallocene wedge associated with the sterically more bulky alkyl group pushes this group into the central position of the wedge, the sterically less demanding site: (a) Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, 174, C35. (b) Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593. (c) Erker, G. *Acc. Chem. Res.* **1984**, 17, 103 and references therein.

(19) (a) In other solvents, such as benzene, formation of the $^t\text{BuNC}$ adduct of $\text{B}(\text{C}_6\text{F}_5)_3$ ^{19b} is competitive with insertion. Presumably, dissociation of $\text{B}(\text{C}_6\text{F}_5)_3$ from **1** is more facile in this solvent. (b) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, 18, 1724.

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butyl and methyl protons present. This assignment was confirmed by an X-ray structural analysis of the 1,1'-dimethyl analogue **2b**, which crystallizes as two independent molecules in the unit cell, one of which is disordered over two conformations with 65:35 occupancies.²¹ An ORTEP diagram of the nondisordered molecule (A) is shown in Figure 2, clearly showing the *N-out* orientation of the iminoacyl ligand. Metrical parameters are comparable to those of related compounds,^{22,23} although **2b** has the lowest value of Δ ²⁴ (-0.061 Å) of any tantalum iminoacyl compound reported to date, consistent with the fact that it is a more electron deficient tantalum center.

Typically, *N-in* isomers are more thermodynamically stable than *N-out* structures in metallocene and related iminoacyl complexes.²¹ Indeed, the *N-out* isomers of **2** can be converted quantitatively to the *N-in* derivatives by heating at 65 °C for several days (eq 2). These



relatively harsh conditions are presumably required due to the stronger Ta–N interaction present in zwitterions **2** (manifested in the low value of Δ , vide supra). The opportunity to observe and characterize both insertion isomers, and study their interconversion, is rare.²³

Mechanistically, the formation of the kinetic insertion products *N-out-2* appears to proceed as shown in Scheme 1. Dissociation of the α -agostic C–H bond is required, as indicated by a substantial inverse isotope effect of 0.84(4) at 30 °C on the rate of the reaction for **1a** vs **1a-d₅**.²⁵ Inverse isotope effects have been observed in other reactions where dissociation of an agostic interaction is the initial step,²⁶ reflecting the inverse equilibrium isotope effect (EIE) for the agostic/nonagostic preequilibrium (i.e., $K_D > K_H$). Furthermore, the rate of insertion of ^tBuNC into $[\text{Cp}_2\text{Ta}(\text{CH}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, which does not feature an α -agostic interaction, is much faster than that observed for **1a**.¹⁴ Thus, in this chem-

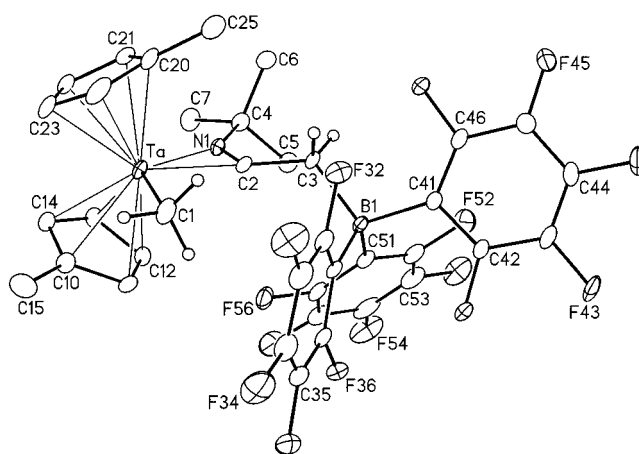


Figure 2. Molecular structure of **2b**. Selected bond distances (Å): Ta–C(1), 2.259(7); Ta–C(2), 2.182(6); Ta–N(1), 2.121(5); C(2)–N(1), 1.264(8); C(4)–N(1), 1.501(9); C(2)–C(3), 1.500(9); B(1)–C(3), 1.698(9). Selected bond angles (deg): C(1)–Ta–C(2), 80.6(3); C(1)–Ta–N(1), 114.7(2); C(2)–Ta–N(1), 34.1(2); Ta–C(2)–C(3), 156.3(5); C(3)–C(2)–N(1), 131.2(6); C(2)–C(3)–B(1), 124.1(6); C(3)–B(1)–C(31), 110.8(5); C(3)–B(1)–C(41), 110.1(5); C(3)–B(1)–C(51), 107.6(5).

istry, the presence of a ground-state α -agostic interaction hampers insertion chemistry, in contrast to the facilitating role such interactions play in stabilizing transition states for olefin insertion reactions.¹⁵ Disengagement of the α -agostic interaction in zwitterions **1** frees up a metallocene orbital to accommodate incoming ^tBuNC, which presumably approaches via the lateral site next to the $-\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3$ group, forming intermediate **I**.¹⁸ This intermediate was not detected even at low temperature (-80 °C), indicating that insertion to give the kinetic *N-out* isomer of **2a** is rapid. That isocyanide binding is rate-limiting is supported by the following observations: (1) the reaction rate increases when a larger concentration of ^tBuNC is employed (still pseudo-first-order conditions); (2) k_{obs} at 17 °C for the more basic isocyanide ^tBuNC ($7.34 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) is larger than for the less basic $\text{C}_6\text{H}_5\text{CH}_2\text{NC}$ ($3.61 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$); (3) k_{obs} for insertion of ^tBuNC in **1a** is larger than for the (slightly) more electron rich 1,1'-dimethyl derivative **1b** ($1.47 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$); (4) the activation entropy is $-31.4(5)$ eu, suggesting an associative rate-limiting step.

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Supporting Information Available: Text giving experimental details, figures giving representative kinetic plots, and full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, and complete bond distances and angles for **1a** and **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) Crystals of the 1,1'-dimethyltantalocene derivative **2b** suitable for X-ray analysis were grown from CH_2Cl_2 . Crystal data for **2b**: $\text{C}_{38}\text{H}_{30}\text{F}_{15}\text{BCl}_2\text{NTa}$, $0.28 \times 0.26 \times 0.11$ mm, triclinic, $P\bar{1}$ (No. 2), $a = 14.223(4)$ Å, $b = 16.875(5)$ Å, $c = 18.026(5)$ Å, $\alpha = 107.887(5)^\circ$, $\beta = 109.932(5)^\circ$, $\gamma = 96.671(5)^\circ$, $V = 3751.1(18)$ Å³, $Z = 4$, $\text{fw} = 1048.29$, $D_{\text{calc}} = 1.856 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 51.5^\circ$, Mo K α radiation, $\lambda = 0.71073$ Å, $T = -80$ °C, 27 577 measured reflections, 14 270 unique, 11 320 reflections with $I_{\text{net}} > 2.0\sigma(I_{\text{net}})$, $\mu = 3.179 \text{ mm}^{-1}$, minimum/maximum transmission 0.3255 and 0.6783, final R indices $R1 = 0.0521$, $wR2 = 0.1410$, GOF = 1.028, 1087 parameters.

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(24) $\Delta = d(\text{Ta}–\text{N}) - d(\text{Ta}–\text{C})$. The lower this parameter, the more electron deficient the metal center.²⁰

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