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Communications

Unusual Weakly Coordinating Anion Reactivity in Metallocene Chemistry. Formation of Tantalocene Cation−Dinuclear Anion Pairs

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Summary: *Unlike the clean reaction of group 4 metallocene alkyls with $B(C_6F_5)_3$, the reaction of Cp_2TaMe_3 with $M(C_6F_5)_3$ ($M = B, Al$) in benzene or toluene produces an oily product mixture containing the expected $Cp_2TaMe_2^+CH_3M(C_6F_5)_3^-$ as well as the unexpected $Cp_2TaMe_2^+$-$[(C_6F_5)_3MCH_3M(C_6F_5)_3]^-$ in equilibrium, along with unreacted Cp_2TaMe_3. The surprising reactivity of weakly coordinating anions $CH_3M(C_6F_5)_3^-$ in the abstractive metallocene chemistry renders formation of novel μ-Me-bridged dinuclear anions. Subsequently, the reaction of Cp_2TaMe_3 with 2 equiv of $Al(C_6F_5)_3$ cleanly generates the tantalocene cation−dinulcear anion ion pair $Cp_2TaMe_2^+$-$[(C_6F_5)_3AlCH_3Al(C_6F_5)_3]^-$ as colorless crystals in a quantitative yield. A crystallographic study confirms the structure, which reveals unassociated cation−anion pairs with nearly symmetrical μ-CH_3 bridging in the anion portion.*

Reactions of group 4 metallocene alkyl or diene complexes with strong organo-Lewis acids such as $B(C_6F_5)_3$ and a number of its derivatives have attracted increasing attention because the cationic species derived therefrom are isolable and often X-ray crystallographically characterizable.[1] In addition, they are typically highly active, single-site olefin polymerization catalysts.[2] In sharp contrast, the product of the analogous reaction with tantalocenes such as tris(cyclopentadienyl)Ta(butadiene) has proven difficult to isolate in the

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(1) For recent reviews, see: (a) Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem.* **2000**, 2131−2142. (b) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434. (c) Lupinetti, A. J.; Strauss, S. H. *Chemtracts-Inorg. Chem.* **1998**, *26*, 565−595. (d) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345−354.

(2) For recent leading references, see: (a) Stockland, R. A., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 6315−6316. (b) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499−5509. (c) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841−1849. (d) Corradi, M. M.; Pindado, G. J.; Sarsfield, M. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **2000**, *19*, 1150−1159. (e) Lieber, S.; Prosenc, M.-H.; Brintzinger, H.-H. *Organometallics* **2000**, *19*, 377−387. (f) Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *J. Am. Chem. Soc.* **1999**, *121*, 9483−9484. (g) Dahlmann, M.; Erker, G.; Nissinen, M.; Fröhlich, R. *J. Am. Chem. Soc.* **1999**, *121*, 2820−2828. (h) Doerrer, L.; Green, M. L. H.; Häussinger, D.; Sassmannshausen, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2111−2118. (i) Pellecchia, C.; Pappalardo, D.; Gruter, G.-J. *Macromolecules* **1999**, *32*, 4491−4493. (j) Stephan, D. W.; Stewart, J. C.; Guerin, F.; v. H. Spence, R. E.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116−1118. (k) Cowley, A. H.; Hair, G. S.; McBurnett, B. G.; Jones, R. A. *Chem. Commun.* **1999**, 437−438. (l) Wright, J. M.; Landis, C. R.; Ros, M. A. M. P.; Horton, A. D. *Organometallics* **1998**, *17*, 5031−5040. (m) Barsan, F.; Karam, A. R.; Parent, M. A.; Baird, M. C. *Macromolecules* **1998**, *31*, 8439−8447. (n) Grassi, A.; Saccheo, S.; Zambelli, A.; Laschi, F. *Macromolecules* **1998**, *31*, 5588−5591. (o) Chen, E. Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6787−6305.

(3) (a) Strauch, H. C.; Wibbeling, B.; Frohlich, R.; Erker, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 3802−3812. (b) Strauch, H. C.; Erker, G.; Frohlich, R. *Organometallics* **1998**, *17*, 5746−5757.

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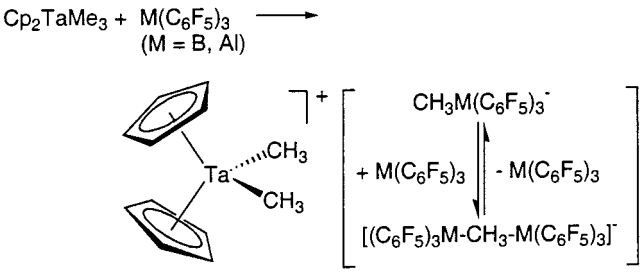
Scheme 1



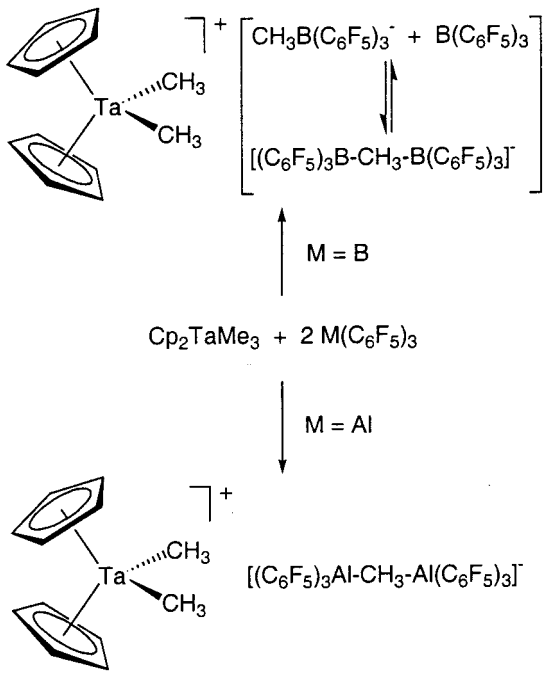
pure state, and the structure of the resulting counteranion remains unclear.[3]

Consequently, Erker et al.[3] developed a new cation-generating method to obtain the (butadiene)tantalocene cation using the ion pair $Cp_2ZrMe^+MeB(C_6F_5)_3^-$,[4] instead of $B(C_6F_5)_3$[5] or other metallocene cation generating agents such as $[Ph_3C]^+[B(C_6F_5)_4]^-$[6] and $[HNRR'_2]^+$-$[B(C_6F_5)_4]^-$.[7] Zwitterionic tantalocene derivatives can also be obtained from the reaction of tantalocene methyl methylidene $Cp_2Ta(=CH_2)(CH_3)$ and $B(C_6F_5)_3$, as recently reported by Piers et al.[8] We communicate here the unusual weakly coordinating anion reactivity in the reaction of tantalocene trimethyl with $B(C_6F_5)_3$ and $Al(C_6F_5)_3$[9] as well as the synthesis of a new class of tantalocene cations paired with novel μ-Me-bridged dinuclear anions.

Unlike the reaction of Cp'_2ZrMe_2 with $B(C_6F_5)_3$, which cleanly generates the corresponding cationic complexes $Cp'_2ZrMe^+MeB(C_6F_5)_3^-$ (Cp′ = Cp and substituted derivatives),[4] the reaction of Cp_2TaMe_3[10] with 1 equiv of $M(C_6F_5)_3$ (M = B, Al) in benzene or toluene produces an oily product mixture containing $Cp_2TaMe_2^+CH_3M(C_6F_5)_3^-$ and $Cp_2TaMe_2^+[(C_6F_5)_3MCH_3M(C_6F_5)_3]^-$ in equilibrium, along with unreacted Cp_2TaMe_3 (Scheme 1; see Supporting Information for experimental and characterization details). Observation of changes in the monoanion/dinuclear anion ratio vs time[11] in the reaction with $B(C_6F_5)_3$ reflects the instability of the diboron anion, while such a ratio is kept at ca. 1:1 in the reaction with $Al(C_6F_5)_3$ for the same study.

A very interesting aspect of this reaction is that due to the *weakly coordinating feature of the* $Cp_2TaMe_2^+$ *countercation*, the enhanced nucleophilicity of the free anion $CH_3M(C_6F_5)_3^-$, once generated, attacks $M(C_6F_5)_3$ to form μ-Me-bridged dinuclear anions $[(C_6F_5)_3MCH_3M(C_6F_5)_3]^-$.[12] This chemistry is different from what has been demonstrated for the group 4 metallocenes where the *weakly coordinating feature of the anion* promotes the reactivity of the countercation to form μ-Me-bridged dinuclear cations $[Cp'_2MMeCH_3MeMCp'_2]^+$ (M = Zr, Ti).[13] All ^1H NMR signals are broad at room temperature, indicative of dynamic exchange processes as shown in Scheme 1; ^1H NOESY experiments confirm this finding. To our knowledge, this is the first report of weakly coordinating anion reactivity in metallocene chemistry that renders formation of μ-Me-bridged dinuclear anions.

Scheme 2



In an attempt to isolate the tantalocene cation−dinuclear anion pair and characterize it in the pure state rather than in the above equilibrium mixture, 2 equiv of $B(C_6F_5)_3$ was used in the reaction with Cp_2TaMe_3. Interestingly, the reaction still produced an oily product mixture containing a significant amount of unreacted $B(C_6F_5)_3$ (Scheme 2; see Supporting Information for experimental and characterization details). Next the use of the sterically more accessible, stronger organo-Lewis acid $Al(C_6F_5)_3$ was tried, but it profoundly changed the reaction outcome as well as the stability of the resulting μ-Me-bridged dinuclear anion. Thus, mixing Cp_2TaMe_3 with 2 equiv of $Al(C_6F_5)_3$ in benzene

(4) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623−3625.

(5) (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250. (b) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212−212.

(6) (a) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571. (b) Ewen, J. A.; Elder, M. J. Eur. Pat. Appl. EP 0,426,637, 1991.

(7) (a) Hlatky, G. G.; Upton, D. J.; Turner, H. W. PCT Int. Appl. WO 91/09882, 1991. (b) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840−842. (c) Turner, H. W. Eur Pat. Appl. EP 0 277 004 A1, 1988.

(8) Cook, K. S.; Piers, W. E.; Rettig, S. J.; McDonald, R. *Organometallics* **2000**, *19*, 2243−2245.

(9) Biagini, P.; Lugli, G.; Abis, L.; Andreussi, P. U. S. Pat. 5,602269, 1997. ***Extra caution should be exercised when handling this material due to its thermal and shock sensitivity.***

(10) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389−2399.

(11) Mixing Cp_2TaMe_3 and $B(C_6F_5)_3$ in a 1:1 ratio at room temperature for 15 min, NMR spectra indicated formation of a mixture of $Cp_2TaMe_2^+CH_3B(C_6F_5)_3^-$ and $Cp_2TaMe_2^+[(C_6F_5)_3BCH_3B(C_6F_5)_3]^-$ in ca. 1:2 ratio, along with unreacted Cp_2TaMe_3. However, this ratio became ca. 2:1 after sitting in the NMR tube at room temperature for 1 h.

(12) Preparation of trityl, ammonium, or $[CpIrH(C_8H_{12})]^+$ salts of dinuclear anions having a general formula of $[(C_6F_5)_3M\text{-}LG\text{-}M(C_6F_5)_3]^-$ where linking group LG = cyanide and M = B,[12a] LG = cyanide, azide, dicyanamide, and imidazolide and M = B, Al,[12b,c] and LG = μ-OH and M = B[12d] has been recently reported: (a) Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533−1534. (b) LaPointe, R. E. PCT Int. Appl. WO 99/42465. (c) LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560−9561. (d) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. H.; Cafferkey, S.; Doerrer, L. H.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529−2530.

(13) (a) Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451−12452. (b) Beck, S.; Prosenc, M.-H.; Brintzinger, H.-H.; Goretzki, R.; Herfert, N.; Fink, G. *J. Mol. Catal.* **1996**, *111*, 67−79. (c) Bochmann, M.; Lancaster, S. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634−1637. (d) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1−C5.

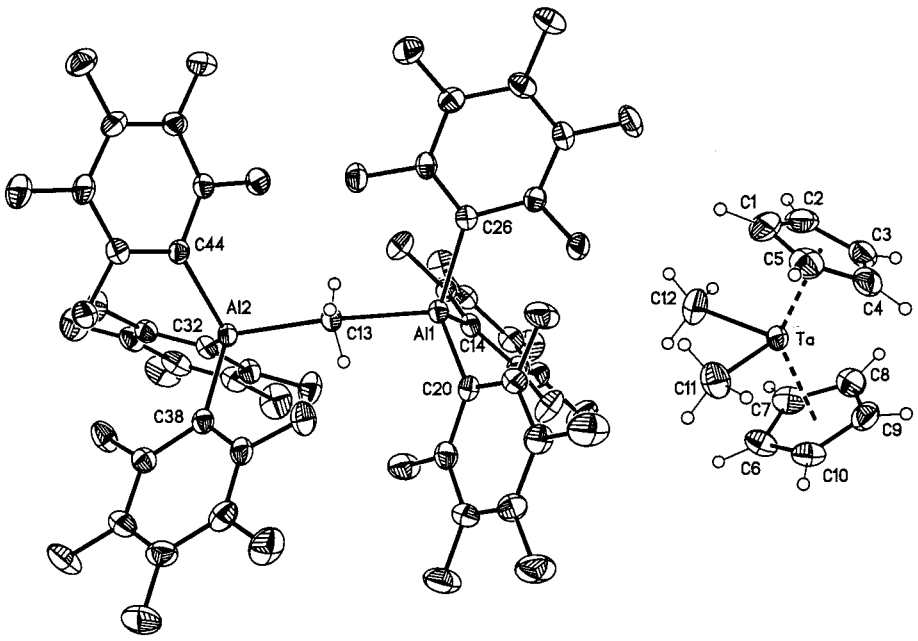


Figure 1. Thermal ellipsoid drawing of $Cp_2TaMe_2^+[(C_6F_5)_3AlCH_3Al(C_6F_5)_3]^-$ shown at the 50% probability level. The F atoms of the anion portion are not labeled for clarity. Selected bond lengths and angles (Å, deg): Ta−C11 = 2.188(3); Ta−C12 = 2.166(3); Al1−C13 = 2.109(3); Al2−C13 = 2.060(3); Al1−C13−Al2 = 174.7(2); C12−Ta−C11 = 96.6(1); Cp(centroid)−Ta−Cp(centroid) = 133.8(1).

or toluene results in immediate precipitation of a clean product as colorless crystals in quantitative yield. Spectroscopic data and analytical analysis[14] suggest the formation of the desired ion pair $Cp_2TaMe_2^+[(C_6F_5)_3AlCH_3Al(C_6F_5)_3]^-$ (Scheme 2). In bromobenzene-d_5 solution at room temperature, ^{1}H NOESY experiments indicated no dynamic exchange between the cation $Cp_2TaMe_2^+$ methyl and the anion $[(C_6F_5)_3AlCH_3Al(C_6F_5)_3]^-$ methyl.

A crystallographic study confirms the structure of $Cp_2TaMe_2^+[(C_6F_5)_3AlCH_3Al(C_6F_5)_3]^-$ (Figure 1),[15] which reveals unassociated tantalocene cation−dinuclear anion pairs with the distances between tantalum and aluminum atoms of 6.861 Å (Ta to Al1), 7.312 Å [Ta to Al2 ($1+x$, $-1+y$, z)], 7.618 Å [Ta to Al2 ($2-x$, $-1-y$, $2-z$)]. The dinuclear anion features a nearly symmetrical μ-CH_3 bridging between two aluminum centers. The Al1- - -C13- - -Al2 vector is nearly linear with an angle of 174.7(2)°, and the geometry at the Al centers is that of a slightly distorted tetrahedron with the sum of C(arene)−Al−C (arene) angles of 333.4° and 334.9°. The Al−CH_3 distances of 2.109(3) and 2.060(3) Å are comparable to those in the anion (μ-CH_3)-Al(C_6F_5)$_3^-$ (2.084(2) and 2.059(2) Å) in a "doubly activated" *ansa*-zirconocene complex,[16] but are noticeably longer than that in the anion (μ-CH_3)-Al(C_6F_5)$_3^-$ (2.033(3) Å) in a "constrained geometry" Ti complex.[16b] The geometry of the $Cp_2TaMe_2^+$ cation with Cp(centroid)−Ta−Cp(centroid) and C11−Ta−C12 angles of 133.8(1)° and 96.6(1)°, respectively, compares well with those of the isoelectronic neutral Cp_2ZrMe_2,[17] but having appreciably shorter M−CH_3 distances for the tantalocene cation (Ta−C11 = 2.188(3) Å; Ta−C12 = 2.166(3) Å) than those for Cp_2ZrMe_2 (2.280(5) and 2.273 (5) Å) without correcting for differences in Ta/Zr ionic radii. However, the metrical parameters of the $Cp_2TaMe_2^+$ cation are very similar to those of the $CpCp^*TaMe_2^+$ cation paired with trifluoromethylsulfonate anion.[18]

These results demonstrate for the first time the surprising reactivity of weakly coordinating anions $CH_3M(C_6F_5)_3^-$ in abstractive chemistry involving reactions of group 5 metallocenes and strong organo-Lewis acids $M(C_6F_5)_3$. Further exploratory studies on other bridging functionalities as well as potential applications of these ion pairs are in progress.

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Supporting Information Available: Experimental details and complete X-ray crystallographic data for $Cp_2TaMe_2^+[(C_6F_5)_3Al-CH_3-Al(C_6F_5)_3]^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) ^{1}H NMR (C_6D_6, 23 °C): δ 4.96 (s, 10 H, C_5H_5), −0.40 (s, 6 H, Ta−CH_3); C_7D_8: δ 5.11 (s, C_5H_5), 0.61 (s, br, Al−CH_3−Al), −0.32 (s, Ta−CH_3); bromobenzene-d_5: δ 5.51 (s, C_5H_5), 1.61 (s, br, Al−CH_3−Al), −0.05 (s, Ta−CH_3).^{19}F NMR (bromobenzene-d_5, 23 °C): δ −122.83 (d, $^3J_{F-F}$ = 18.3 Hz, 12 F, *o*-F), −154.39 (s, br, 6 F, *p*-F), −162.19 (t, $^3J_{F-F}$ = 18.1 Hz, 12 F, *m*-F). ^{13}C NMR (bromobenzene-d_5, 23 °C): δ 112.10 (C_5H_5, $^1J_{CH}$ = 175.5 Hz), 57.05 (Ta−CH_3, $^1J_{CH}$ = 125.3 Hz). Anal. Calcd for $C_{49}H_{19}Al_2F_{30}Ta$: C, 41.67; H, 1.36. Found: C, 41.99; H, 1.47.

(15) Crystallographic data for $C_{49}H_{19}Al_2F_{30}Ta\cdot C_6H_6$: triclinic, space group $P\bar{1}$ (No. 2); a = 12.9456(6) Å, b = 13.2896(6) Å, c = 16.1621(7) Å, α = 74.166(1)°, β = 82.767(1)°, γ = 88.123(1)° at 173(2) K; V = 2647.9(2) Å^3; Z = 2. A benzene molecule was located in the asymmetric unit in addition to the cation and anion. The structure was solved by the direct methods and refined by full-matrix least-squares techniques using 9837 reflections having $I > 2\sigma(I)$ and resulting in R1 = 0.0274, wR2 = 0.0560. The μ-CH_3 hydrogen atoms of C13 were located and refined without any constraints.

(16) (a) Chen, E. Y.-X. PCT Int. Appl. WO 00/09524. (b) Chen, E. Y.-X.; Kruper, W. J.; Roof, G.; Wilson, D. R. Manuscript submitted for publication.

(17) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750−755.

(18) Schaefer, W. P.; Quan, R. W.; Bercaw, J. E. *Acta Cryst.* **1992**, *C48*, 1610−1612.