

Neutral Group V Bent Metallocene Analogs Containing the Tribenzylidenemethane Dianion

George Rodriguez and Guillermo C. Bazan*

Department of Chemistry, University of Rochester
Rochester, New York 14627

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While the synthesis and reactivity of trimethylenemethane (TMM) complexes containing late transition metals is well documented,¹ the chemistry of high-oxidation-state, early-transition-metal counterparts remains virtually unexplored. The few known examples display a range of bonding modes; the TMM ligand in $\text{Cp}^*(\text{TMM})\text{TaMe}_2$ ² ($\text{Cp}^* = \text{Me}_5\text{C}_5$) and $[\text{Cp}^*(\text{TMM})\text{Zr}(\mu\text{-Cl})_2\text{Li}(\text{TMEDA})]$ ³ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) is η^4 bound, while in $\text{Cp}^*_2\text{Zr}(\text{TMM})$ ⁴ an η^3 coordination is observed. Sterically significant substituents on the periphery of the TMM skeleton exert a strong influence. For example, tribenzylidenemethane (TBM) complexes of zirconium, i.e., $[\text{Cp}^*(\text{TBM})\text{ZrCl}_2]^- [\text{Li}(\text{TMEDA})_2]^+$, are discrete salts instead of zwitterions and have distorted (intermediate between η^3 and η^4) TBM–Zr bonding.³

The electronic relationship between the TMM and cyclopentadienyl fragments motivates our early-metal studies: both ligands are formally six-electron donors but differ in their respective charges. Substitution of a cyclopentadienyl ligand for a dianionic six-electron donor is a strategy of current interest in the general area of homogeneous Ziegler–Natta polymerization as it permits construction of neutral group IV counterparts of catalytically important cationic metallocene alkyls as well as incorporation of group V metals into metallocene-like molecules. To this end, $(\text{C}_5\text{H}_4\text{Me})(\text{C}_2\text{B}_9\text{H}_{11})\text{TaMe}_2$,⁵ $\text{Cp}^*(\eta^4\text{-1,3-butadiene})\text{TaMe}_2$,⁶ and $\text{Cp}^*(\text{C}_4\text{H}_4\text{BN}^+\text{Pr}_2)\text{TaMe}_2$,⁷ containing the dianionic dicarbollide, diene, and aminoborollide ligands, respectively, have been prepared. The activities of dicarbollide complexes toward olefin insertion suffer from the hydridic B–H ligand cage constituents, which can bind to electrophilic metal sites.⁸ Aminoborollide and diene complexes are significantly less active than group IV metallocenes, perhaps as a result of the “reduced” and therefore less electrophilic nature of the metal (Ta(III) resonance contribution). The TBM ligand is an attractive alternative since it provides considerable steric protection, has no extraneous functionalities, and is strictly dianionic. In this communication we report the synthesis, characterization, and reactivity of (TBM)TaMe₃ and complexes of general composition $\text{Cp}(\text{TBM})\text{TaMe}_2$ ($\text{Cp} = \text{C}_5\text{H}_5$).

Slow addition of $\text{Li}_2(\text{TBM})(\text{TMEDA})_2$ to Me_3TaCl_2 in benzene results in the formation of (TBM)TaMe₃. Isolation from residual $\text{LiCl}(\text{TMEDA})_x$ species requires efficient removal of TMEDA by three xylene condensation–evaporation cycles on the crude reaction mixture. Extraction with benzene yields (TBM)TaMe₃ as an orange powder in 44% isolated yield

(Scheme 1). Similar results are obtained using $\text{Li}_2(\text{t-Bu-TBM})(\text{TMEDA})_2$. These 12-electron complexes are thermally and chemically robust (compare with explosive WMe_6).^{9,10} Structural determination of $(\text{t-Bu-TBM})\text{TaMe}_3$ revealed a C_3 symmetric molecular geometry (neglecting the *tert*-butyl group) as shown in Scheme 1.¹¹ Tantalum is seven coordinate with a “domed” TBM framework containing the three phenyl rings in a typical propeller-like arrangement. An unusual molecular trait is the eclipsed, trigonal-prismatic-like (neglecting TBM’s inner carbon), arrangement of the TBM framework relative to the three methyls.

Since a staggered, octahedral-like, arrangement is preferred on steric grounds,¹² the observed conformation must have an electronic origin. Note that the lone pair orbitals of three methyl ligands have energetic and nodal properties similar to those of TMM, namely, an e and an a₁ set.¹³ Therefore, the molecular orbital description of (TMM)TaMe₃, and by extension (TBM)TaMe₃, is closely related to that of hypothetical $[\text{TaMe}_6]^-$ and both compounds should have analogous geometries. Both WMe_6 and $[\text{ZrMe}_6]^{2-}$ are known to have trigonal-prismatic (D_{3h}) geometries on the basis of electron diffraction¹⁴ and crystallographic¹⁵ characterization. The preference for D_{3h} over O_h geometry in d⁰ MX₆ complexes has been accounted in terms of a Jahn–Teller distortion that occurs when there is a low electron count at the metal, the M–X bond is sufficiently covalent, and X is a small strong σ donor.¹⁶ Similar reasoning can be applied to $[\text{TaMe}_6]^-$ and therefore (TMM)TaX₃ molecules.¹⁷

(TBM)TaMe₃ converts quantitatively to (TBM)TaMe₂Cl by reaction with excess ZnCl_2 in THF/ C_6H_6 or by photolysis in CH_2Cl_2 (AlCl_3 works similarly but at a much slower rate).¹⁸ Structural characterization (Scheme 1) confirms an eclipsed geometry similar to that of $(\text{t-Bu-TBM})\text{TaMe}_3$.¹⁹ Further reaction with LiCp and LiCp* yields $\text{Cp}(\text{TBM})\text{TaMe}_2$ and $\text{Cp}^*(\text{TBM})\text{TaMe}_2$ (Scheme 1 shows reaction for Cp). Despite the near-quantitative yield determined by ¹H NMR spectroscopy, the Cp* derivative is isolated in only 50% yield as an oil that is difficult to crystallize. In sharp contrast, $\text{Cp}(\text{TBM})\text{TaMe}_2$ has limited

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(10) Other complexes containing dianionic Cp analogs are robust, for example, the benzyne complex $(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{CpTa}(\eta^2\text{-C}_6\text{H}_4)(\text{PMe}_3)$, isoelectronic to $\text{Cp}_2\text{Zr}(\eta^2\text{-C}_6\text{H}_4)(\text{PMe}_3)$, is air and moisture stable; see: (a) Houseknecht, K. L.; Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 1163. (b) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(11) Crystal data for $(\text{t-Bu-TBM})\text{TaMe}_3$: space group $P2_1$ (No. 4) with $a = 10.361(3)$ Å, $b = 8.846(3)$ Å, $c = 13.935(3)$ Å, $\beta = 100.62(3)^\circ$, $Z = 2$, $\text{FW} = 564.57$, and $\rho = 1.49$ g/cm³. A total of 2505 reflections ($h \pm l$) were collected in the range $4^\circ < 2\theta < 50^\circ$ with the 1420 having $I > 3\sigma(I)$ being used in the structural refinement by full-matrix least-squares techniques (171 variables) using the TEXSAN crystallographic package from Molecular Structures Corporation. Final $R = 0.051$, $R_w = 0.045$.

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(18) Reaction with acids is nonselective. Careful addition of 1 equiv of triflic acid to (TBM)TaMe₃ results in (TBM)TaMe₂(OTf) contaminated with (TBM)TaMe(OTf)₂; Rodriguez, G. Unpublished results.

(19) Crystal data for $(\text{TBM})\text{TaClMe}_2$: space group $R\bar{3}$ (No. 148) with $a = b = c = 18.123(8)$ Å, $\alpha = \beta = \gamma = 115.56(3)^\circ$, $Z = 6$, $\text{FW} = 528.85$, and $\rho = 1.69$ g/cm³. A total of 8168 reflections ($h \pm k \pm l$) were collected in the range $4^\circ < 2\theta < 50^\circ$ with the 2467 having $I > 3\sigma(I)$ being used in the structural refinement by full-matrix least-squares techniques (236 variables) using the TEXSAN crystallographic package from Molecular Structures Corporation. Final $R = 0.026$, $R_w = 0.030$.

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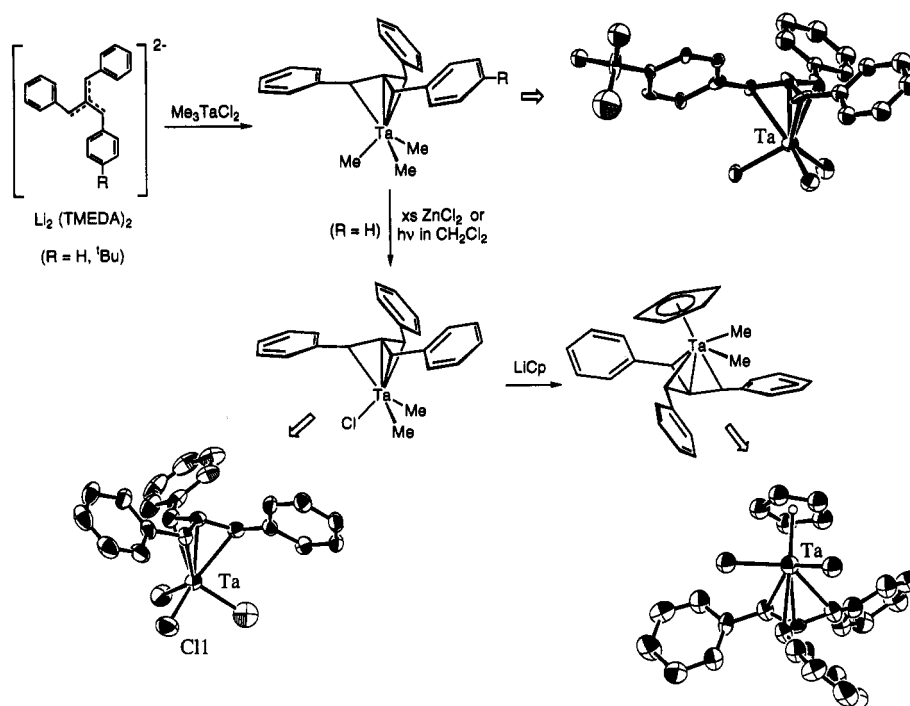
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Scheme 1



solubility and is isolated by performing the reaction in THF and collecting the resulting red precipitate. Single crystals suitable for X-ray crystallography formed when THF solutions of the two reactants were layered at -30°C and allowed to react over a period of 2 weeks. Solution and refinement of the structure proved nontrivial with a $P31c$ space group and four molecules in the unit cell. In such a structure two independent molecules must each lie on a 3-fold axis with disorder involving the two methyl and Cp ligands. Only a brief discussion is presented here as the complete details have been published independently.²⁰ Note the metallocene-like arrangement with a $\text{syn-}\eta^4$ bound TBM ligand (Scheme 1) and that the angle defined by $\text{C}_{21}\text{--Ta--Cp}_{\text{cent}}$ ($131.5(9)^\circ$) is similar to the $\text{Cp}_{\text{cent}}\text{--Zr--Cp}_{\text{cent}}$ angle in Cp_2ZrMe_2 (132.5°).²¹ Unlike ($t\text{Bu-TBM}$) TaMe_3 and $(\text{TBM})\text{TaMe}_2\text{Cl}$, the TBM framework in $\text{Cp}(\text{TBM})\text{TaMe}_2$ is staggered relative to the tripod defined by the other ligands as expected on the basis of both increased steric interference and higher electron count.

Ethylene polymerization activities of 12 kg PE/h[Ta]mol at 25°C and 40 kg PE/h[Ta]mol at 60°C were measured by activating $\text{Cp}^*(\text{TBM})\text{TaMe}_2$ with methylaluminoxane (MAO) in toluene ($\text{Cp}(\text{TBM})\text{TaMe}_2$ cannot be dissolved in aromatic solvents).²² These rates are significantly higher than those reported with other group V metallocene mimics such as Cp^* -

$(\eta^4\text{-1,3-butadiene})\text{TaMe}_2$ (1.9 kg PE/h[Ta]mol at 25°C) or $\text{Cp}^*(\text{C}_4\text{H}_4\text{BNR}_2)\text{TaMe}_2$ (0.6 kg PE/h[Ta]mol at 25°C) but fall well below those observed using group IV metallocenes. Attempts to use typical activators such as $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{H}(\text{OEt}_2)]^+[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$ have not given catalytically active mixtures.

In summary, tantalum-TBM complexes have been prepared. The stability of the parent complex $(\text{TBM})\text{TaMe}_3$ is remarkable when compared to the stabilities of other 12-electron organometallic species. $\text{Cp}(\text{TBM})\text{TaMe}_2$ and $\text{Cp}^*(\text{TBM})\text{TaMe}_2$ are similar to group IV metallocenes, in terms of geometry and electron count, but are not as active when activated with MAO and are resistant to activation using other reagents. Our current thinking is that the Ta-C bond is less polarized than Zr-C and therefore less reactive toward either protic or Lewis acids.

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Supporting Information Available: Experimental procedures for the preparation of all compounds and tables of crystal data, positional parameters, bond distances, and anisotropic thermal parameters for ($t\text{Bu-TBM}$) TaMe_3 and $(\text{TBM})\text{TaMe}_2\text{Cl}$ (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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