Tantalum(V)-Based Metallocene, Half-Metallocene, and Non-Metallocene Complexes as Ethylene−1-Octene Copolymerization and Methyl Methacrylate Polymerization Catalysts

Shaoguang Feng and Gordon R. Roof

The Dow Chemical Company, Chemical Sciences, Midland, Michigan 48674

Eugene Y.-X. Chen*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

Received August 3, 2001

The half-sandwich imido tantalum dichloride (η^5-C_5Me_4H)Ta(=N^tBu)Cl_2 is prepared directly from the reaction of the neutral constrained-geometry ligand $Me_2Si(C_5Me_4H)(^tBuNH)$ and $TaCl_5$ in refluxing toluene. The dichloride is cleanly converted to the corresponding imido tantalum dimethyl complex (η^5-C_5Me_4H)Ta(=N^tBu)Me_2 (**2**). Using the same synthetic strategy, the neutral bulky chelating diamine ligand $ArNH(CH_2)_3NHAr$ (Ar = 2,6-$^iPr_2C_6H_3$) is reacted with $TaCl_5$ in toluene under mild reflux conditions, affording the six-coordinate tantalum complex $[ArN(CH_2)_3NHAr]TaCl_4$, which is conveniently converted to the corresponding non-metallocene tantalum trimethyl complex $[ArN(CH_2)_3NAr]TaMe_3$ (**4**) on treatment with an excess of MeMgBr. Alternatively, **4** can be prepared in better than 70% overall yield based on the diamine ligand from a one-pot synthesis by mixing the neutral diamine ligand with $TaCl_5$ followed by addition of an excess of MeMgBr. Reaction of Cp_2TaMe_3 with 1 equiv of $B(C_6F_5)_3$ in benzene or toluene produces an oily mixture containing both $Cp_2TaMe_2^+CH_3B(C_6F_5)_3^-$ and $Cp_2TaMe_2^+[(C_6F_5)_3B{-}CH_3{-}B(C_6F_5)_3]^-$ in the solution phase. Subsequently, the reaction of Cp_2TaMe_3 with 2 equiv of $Al(C_6F_5)_3$ cleanly generates the tantalocene cation−binuclear anion ion pair $Cp_2TaMe_2^+[(C_6F_5)_3Al{-}CH_3{-}Al(C_6F_5)_3]^-$ (**5**) as colorless crystals. In bromobenzene-*d*$_5$, reactions of Cp_2TaMe_3 with Lewis acids $M(C_6F_5)_3$ (M = B, Al) in a 1:1 ratio afford the expected cationic species $Cp_2TaMe_2^+CH_3M(C_6F_5)_3^-$ as clean products. Reaction of the non-metallocene **4** with $M(C_6F_5)_3$ is similar to that of Cp_2TaMe_3. When it is activated with 2 equiv of $Al(C_6F_5)_3$, Cp_2TaMe_3 is active for syndiospecific MMA polymerization but inactive for olefin polymerization. In contrast, the non-metallocene **4** has no activity for MMA polymerization but is active for olefin polymerization. Most interestingly, the half-metallocene **2**, when activated with a suitable activator, is very active (with a catalytic efficiency of 1.2 × 10^6 g of polymer/((mol of metal) atm h)) for high-temperature (140 °C) olefin copolymerizations, producing low-density poly(ethylene-*co*-1-octene) copolymers with high molecular weight.

Introduction

The activated forms of the group 4 metallocene and related complexes are often structurally well-defined, typically highly active, single-site olefin polymerization catalysts[1] and, therefore, have attracted increasing attention from both academics and industry. On the other hand, group 5 metallocene and related complexes, especially tantalum and niobium complexes, have not been widely studied and used as effective homogeneous catalysts for polymerization of vinyl monomers. Nevertheless, noteworthy successes include the discovery by Mashima, Nakamura, and co-workers[2] that the half-sandwich Ta(III) and Nb(III) diene complexes, i.e., isoelectronic structures of the group 4 metallocenes, are living ethylene polymerization catalysts and are also active for methyl methacrylate (MMA) polymerization upon activation with suitable activators. Other types of group 5 complexes such as half-sandwich imido[3] and amidinate[4] compounds, tantalum aminopyridinato com-

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[1] For recent reviews, see: (a) Erker, G. *Acc. Chem. Res.* **2001**, *34*, 309−317. (b) Chum, P. S.; Kruper, W. J.; Guest, M. J. *Adv. Mater.* **2000**, *12*, 1759−1767. (c) Gladysz, J. A., Ed. *Chem. Rev.* **2000**, *100*, 1167−1682. (d) Marks, T. J., Stevens, J. C. *Top. Catal.* **1999**, *7*, 1−208. (e) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447. (f) Jordan, R. F., Ed. *J. Mol. Catal.* **1998**, *128*, 1−337. (g) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598. (h) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13−18. (i) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144−187. (j) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (k) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170.

[2] (a) Matsuo, Y.; Mashima, K.; Tani, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 960−962. (b) Mashima, K. *Macromol. Symp.* **2000**, *159*, 69−76. (c) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633−2640. (d) Mashima, K.; Fujikawa, S.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 10990−10991.

10.1021/om010702c CCC: $22.00
Publication on Web 02/05/2002

plexes,[5] and vanadium diimine/pyridine complexes[6] have also been found to be active for ethylene polymerization.

It is argued that the cationic forms of the group 5 catalysts are less electron deficient and thus less active for olefin polymerizations than the corresponding group 4 catalysts, but they are more tolerant toward polar functionalities. Therefore, it would be of great interest to synthesize new group 5 complexes with modified steric/electronic ligation as well as to investigate their catalytic activities for olefin polymerization and for polymerization of polar vinyl monomers. We report here (a) a convenient approach toward the synthesis of new half-sandwich imido Ta and bulky chelating diamide Ta alkyl complexes, (b) methide abstraction reactions[7] of Ta(V)-based trimethyl complexes with the strong organo-Lewis acids $B(C_6F_5)_3$[8] and $Al(C_6F_5)_3$,[9] and (c) studies using Ta(V) imido complexes as effective catalysts for olefin copolymerization and using tantalocenes(V) for polymerization of MMA.[10,11]

Experimental Section

General Remarks. All syntheses and manipulations of air-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line or in an argon-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed sample J. Young tubes. Solvents were first saturated with nitrogen and then dried by passage through activated alumina and Q-5 catalyst (Englehardt Chemicals Inc.) prior to use. Deuterated hydrocarbon NMR solvents were dried over sodium/potassium alloy and distilled and/or filtered prior to use, whereas $CDCl_3$ and C_6D_5Br were dried over activated Davison 4 Å molecular sieves. Methyl methacrylate (MMA) monomer was degassed and dried over CaH_2 overnight and then freshly vacuum-distilled before use. NMR spectra were recorded on either a Varian Inova 300 (FT: 300 MHz, ^1H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) or a Varian Inova 400 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and reported relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external $CFCl_3$. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, and by the CHN Lab at the University of Michigan, Ann Arbor, MI.

Tris(perfluorophenyl)borane, $B(C_6F_5)_3$, was obtained as a solid from Boulder Scientific Inc. and was used without further purification for preparative reactions or purified by recrystallization from hexane at −35 °C for NMR-scale reactions. Trimethylaluminum (TMA) in toluene or hexanes, $TaCl_5$ (99.99%), $ZnMe_2$ (1.0 M heptane solution), CpTl, MeMgBr in diethyl ether, *n*-BuLi in hexane, 2,6-diisopropylaniline, TMEDA, and 1,3-dibromopropane were purchased from Aldrich Chemical Co. and used as received. PMAO-IP was purchased from Akzo-Nobel. Cp_2TaMe_3,[12] $Me_2Si(C_5Me_4H)(^tBuNH)$ (CGC-H_2),[13] and CGC-$TiMe_2$[14] were prepared according to the literature procedures, respectively. The bulky chelating diamine ligand $ArNH(CH_2)_3NHAr$ ($Ar = 2,6\text{-}{}^iPr_2C_6H_3$) was prepared from LiNHAr and 1,3-dibromopropane according to a literature procedure.[15] $[HNMe(C_{18}H_{37})_2]^+[(C_6F_5)_3AlNC_3H_3NAl(C_6F_5)_3]^-$ (Al imidazolide) was prepared from 2 equiv of $Al(C_6F_5)_3$ with 1 equiv each of imidazole and dioctadecylmethylamine in toluene.[16] $Ph_3C^+[B(C_6F_5)_4]^-$ was prepared according to literature procedures.[17]

Polymerization Procedures and Polymer Characterizations. Ethylene−1-Octene Copolymerization. A 2 L Parr reactor was used in the polymerizations. All feeds were passed through columns of alumina and Q-5 catalyst prior to introduction into the reactor. Catalyst and activator solutions were handled in the glovebox. A 2 L reactor was charged with about 740 g of mixed alkanes solvent (Isopar E, ExxonMobil Co.) and 118 g of 1-octene comonomer, and the contents were stirred. Hydrogen was added as a molecular weight control agent by differential pressure expansion from a 75 mL addition tank at 300 psig. The reactor contents were heated to the polymerization temperature of 140 °C and saturated with ethylene at 500 psig. Catalysts and activators, as dilute solutions in toluene, were premixed and transferred to a catalyst addition tank and injected into the reactor. The polymerization conditions were maintained for 15 min with ethylene added on demand. Heat was continuously removed from the reaction through an internal cooling coil. The resulting solution was removed from the reactor, quenched with isopropyl alcohol, and stabilized by an addition of 10 mL of a toluene solution containing approximately 67 mg of a hindered

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(3) (a) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Little, I. R.; Marshall, E. L.; da Costa, M. H. R.; Mastroianni, S. *J. Organomet. Chem.* **1999**, *591*, 78−87. (b) Witte, P. T.; Meetsma, A.; Hessen, B. *Organometallics* **1999**, *18*, 2944−2946. (c) Antonelli, D. M.; Leins, A.; Stryker, J. M. *Organometallics* **1997**, *16*, 2500−2502.

(4) Decker, J. M.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4417−4420.

(5) Kakala, K.; Löfgren, B.; Polamo, M.; Leskelä, M. *Macromol. Rapid Commun.* **1997**, *18*, 635−638.

(6) Reardon, D.; Conan, F.; Gambarottta, S.; Yap, G.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318−9325.

(7) (a) Methide abstraction of Cp_2TaMe_3 with organo-Lewis acids was communicated earlier: Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 5541−5543. (b) Piers et al. reported that the reaction of $Cp_2Ta({=}CH_2)(CH_3)$ with $B(C_6F_5)_3$ leads to zwitterionic tantalocene complexes: Cook, K. S.; Piers, W. E.; Rettig, S. J.; McDonald, R. *Organometallics* **2000**, *19*, 2243−2245. (c) Erker et al. developed a new cation generating method to obtain the (butadiene)tantalocene cation by reacting the ion pair $Cp_2ZrMe^+MeB(C_6F_5)_3^-$ with (η^5-cyclopentadienyl)(η^1-cyclopentadienyl)(η^2-butadiene)tantalum: Strauch, H. C.; Erker, G.; Frohlich, R. *Organometallics* **1998**, *17*, 5746−5757.

(8) (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.

(9) (a) Lee, C. H.; Lee, S. J.; Park, J. W.; Kim, K. H.; Lee, B. Y.; Oh, J. S. *J. Mol. Catal., A: Chem.* **1998**, *132*, 231−239. (b) Biagini, P.; Lugli, G.; Abis, L.; Andreussi, P. U.S. Patent 5,602,269, 1997.

(10) For recent references on polymerization of MMA by lanthanocenes, see: (a) Yasuda, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1955−1959. (b) Nodono, M.; Tokimitsu, T.; Tone, S.; Makino, T.; Yanagase, A. *Macromol. Chem. Phys.* **2000**, *201*, 2282−2288. (c) Qian, C.; Nie, W.; Sun, J. *Organometallics* **2000**, *19*, 4134−4140. (d) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276−3277. (e) Boffa, L. S.; Novak, B. M. *Macromolecules* **1994**, *27*, 6993−6995. (f) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134−7143. (g) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908−4909.

(11) For recent references on polymerization of MMA by group 4 metallocenes, see: (a) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7943−7944. (b) Frauenrath, H.; Keul, H.; Höcker, H. *Macromolecules* **2001**, *34*, 14−19. (c) Bandermann, F.; Ferenz, M.; Sustmann, R.; Sicking, W. *Macromol. Symp.* **2001**, *174*, 247−253. (d) Cameron, P. A.; Gibson, V.; Graham, A. J. *Macromolecules* **2000**, *33*, 4329−4335. (e) Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875−1883. (f) Deng, H.; Shiono, T.; Soga, K. *Macromolecules* **1995**, *28*, 3067−3073. (g) Collins, S.; Ward, S. G. *J. Am. Chem. Soc.* **1992**, *114*, 5460−5462.

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

(13) (a) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. (b) Piers, W. E.; Shapiro, P. J.; Bunnel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74−84.

(14) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Pat. Appl. EP 416 815-A2, 1991.

(15) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415−4420.

(16) (a) LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560−9561. (b) LaPointe, R. E. PCT Int. Appl. WO 9942467, 1999.

(17) (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.

phenol antioxidant (Irganox 1010 from Ciba Geigy Corp.) and 133 mg of a phosphorus stabilizer (Irgafos 168 from Ciba Geigy Corp.).

Between polymerization runs a wash cycle was conducted in which 850 g of Isopar-E was added to the reactor and the reactor was heated to 150 °C. The reactor was then emptied of the heated solvent immediately before beginning a new polymerization run.

Polymers were recovered by drying for about 20 h in a vacuum oven set at 140 °C. Density values were derived by determining the polymer's mass when in air and the volume displaced when immersed in methyl ethyl ketone. Micro melt index values (MMI) were obtained using a Custom Scientific Instrument Inc. Model CS-127MF-015 apparatus at 190 °C and calibrated using a series of known I_2 (melt index: grams of PE extruded in 10 min at 190 °C, 2.16 kg) commercial PE standards. Melting and crystallization temperatures of polymers were measured by differential scanning calorimetry (DSC 2910, TA Instruments, Inc.). Samples were first heated from room temperature to 180 °C at 100 °C/min. After being held at this temperature for 4 min, the samples were cooled to −40 °C at 10 °C/min and were then heated to 160 °C at 10 °C/min after being held at −40 °C for 4 min. High-temperature gel permeation chromatography (GPC) analyses of polymer samples were carried out in 1,2,4-trichlorobenzene at 135 °C on a Waters 150C high-temperature instrument. A polystyrene/polyethylene universal calibration was carried out using narrow molecular weight distribution polystyrene standards from Polymer Laboratories with 2,6-di-*tert*-butyl-4-methylphenol (BHT) as the flow marker.

Methyl Methacrylate Polymerization. MMA polymerizations were performed in 50 mL Schlenk tubes with a septum and an external temperature-controlled bath on a Schlenk line or in a glovebox. In a typical procedure, Cp_2TaMe_3 (46.7 μmol) and the activator $M(C_6F_5)_3$ (M = B, Al) in a desired ratio were loaded into the tube in a glovebox and toluene was added (10 mL total volume). The tube was removed from the box and put on the Schlenk line. MMA (1.00 mL, 0.936 g, 9.35 mmol) was added through the septum via a gastight syringe after stirring the catalyst and activator mixture for 10 min. The polymerization was quenched by adding 2 mL of acidified methanol after the measured time interval. The polymer product was precipitated into 50 mL of methanol, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Glass transition temperatures of polymers were measured by differential scanning calorimetry (DSC 2920, TA Instruments, Inc.). Samples were first heated from room temperature to 180 °C. After being held at this temperature for 4 min, the samples were cooled to −20 °C at 10 °C/min and were then heated to 160 °C at 10 °C/min after being held at −20 °C for 4 min. Gel permeation chromatography analyses of polymer samples were carried out at room temperature using THF as eluent on a Waters 150C instrument and calibrated using monodispersed PMMA standards at a flow rate of 1.0 mL/min. Number-average molecular weights and polydispersities of PMMA were given relative to PMMA standards. ^{1}H and ^{13}C spectra for the analysis of PMMA microstructures were recorded in $CDCl_3$ and analyzed according to the literature.[18]

Modified Synthesis of Tris(perfluorophenyl)alane ($Al(C_6F_5)_3$ as a 0.5 Toluene Adduct). This reagent was prepared by modification of literature procedures[9b] (*Extra caution should be exercised when handling this material due to its thermal and shock sensitivity. Preparation of the unsolvated form of this reagent should be avoided.*). In a glovebox, $B(C_6F_5)_3$ (3.00 g, 5.86 mmol) was slurried in a solvent mixture (10 mL of toluene and 30 mL of hexanes) and $AlMe_3$ (2.0 M in hexanes, 2.93 mL, 5.86 mmol) was added via syringe. The suspension became clear after being stirred for 5 min at room temperature, and crystalline solids started to precipitate. The mixture was stirred at room temperature for 2 h and then filtered. The crystalline solid collected was washed with hexanes and dried in vacuo to produce 1.98 g of the product in a pure state. Slow cooling of the combined filtrates at −35 °C gave an additional 1.20 g of the pure product as a white crystalline solid, after washing with hexanes and drying in vacuo. The total yield is 3.18 g (95.0%). ^{1}H NMR (C_6D_6, 23 °C): δ 7.09−6.98 (m, 5H, C_6H_5), 2.09 (s, 3H, CH_3). ^{19}F NMR (C_6D_6, 23 °C): δ −123.20 (d, $^3J_{F-F}$ = 18.7 Hz, 6F, *o*-F), −150.76 (t, $^3J_{F-F}$ = 18.3 Hz, 3F, *p*-F), −160.62 (m, 6F, *m*-F). ^{1}H NMR (C_6D_5Br, 23 °C): δ 7.37−7.24 (m, 5H, C_6H_5), 2.38 (s, 3H, CH_3). ^{19}F NMR (C_6D_5Br, 23 °C): δ −120.85 (d, $^3J_{F-F}$ = 18.0 Hz, 6F, *o*-F), −149.58 (t, $^3J_{F-F}$ = 21.2 Hz, 3F, *p*-F), −159.87 (m, 6F, *m*-F).

Synthesis of (η^5-C_5Me_4H)Ta(=N^{t}Bu)Me_2 (2). In a glovebox, $Me_2Si(C_5Me_4H)(^tBuNH)$ (CGC-H_2, 0.50 g, 2.00 mmol) and $TaCl_5$ (0.72 g, 2.00 mmol) were mixed in 20 mL of toluene and the mixture was refluxed for 12 h. The reaction mixture was filtered, and the solvent of the filtrate was removed under reduced pressure to give a yellow solid. ^{1}H NMR spectra of the crude material indicated formation of a mixture of the products containing $(C_5Me_4H)Ta(=N^tBu)Cl_2$ as a major product. Recrystallization of the crude product mixture from toluene at −40 °C afforded a mixture of yellow and orange crystals. Yellow crystals were combined with the yellow mother liquor, and the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL) and filtered. The solvent of the yellow filtrate was removed under reduced pressure to afford 0.40 g of $(C_5Me_4H)Ta(=N^tBu)Cl_2$ (**1**) as a yellow solid; yield 45.5%. ^{1}H NMR (C_6D_6, 23 °C): δ 5.79 (s, 1H, C_5Me_4*H*), 1.91, 1.80 (s, 12H, C_5*Me*$_4$H), 1.21 (s, 9H, ^{t}Bu).

In a glovebox, **1** (0.40 g, 0.90 mmol) was dissolved in 20 mL of diethyl ether and the solution was cooled to −40 °C. MeMgBr in diethyl ether (0.60 mL, 1.80 mmol) was added via syringe, and the mixture was stirred for 2 h at room temperature. The solvent was removed, and the residue was extracted with hexanes (20 mL) and filtered through Celite. The concentrated solution (10 mL) was left in a freezer at −40 °C for several days, and no crystals were formed. The cloudy solution was filtered through Celite, and the solvent of the filtrate was then removed under reduced pressure and the residue was dried in vacuo for 2 h to afford 0.33 g of **2** as a yellow-green oil; yield 91.7%. Anal. Calcd for $C_{15}H_{28}NTa$: C, 44.67; H, 6.99; N, 3.47. Found: C, 44.28; H, 7.23; N, 3.25.

Spectroscopic data for **2** are as follows. ^{1}H NMR (C_6D_6, 23 °C): δ 5.22 (s, 1H, C_5Me_4*H*), 1.81, 1.75 (s, 12H, C_5*Me*$_4$H), 1.42 (s, 9H, ^{t}Bu), 0.16 (s, 6H, Ta−CH_3). ^{13}C NMR (C_6D_6, 23 °C): δ 119.34, 115.91, 100.51 (*C*$_5$Me$_4$H), 72.95 (Me$_3$*C*N=), 42.71 (Ta−*C*H$_3$), 33.73 (*Me*$_3$CN=), 13.12, 10.56 (C$_5$*Me*$_4$H).

Synthesis of [ArN(CH_2)$_3$NAr]TaMe_3 (4). In a glovebox, the neutral diamine ligand ArNH(CH_2)$_3$NHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (1.55 g, 3.93 mmol) was dissolved in 40 mL of toluene and cooled to −40 °C. $TaCl_5$ (1.41 g, 3.93 mmol) was added in small portions, and the mixture was gradually warmed to room temperature and then heated to 90 °C for 2 h. The orange suspension was filtered and the solid collected and dried to produce 1.86 g of yellow solid. The red filtrate was cooled to −40 °C for 12 h, producing 0.25 g of orange crystals. All peaks in the ^{1}H NMR spectra of the orange crystals are broad at room temperature but are sharp and well resolved at 80 °C, indicating the formation of the six-coordinate tantalum complex [ArN(CH_2)$_3$NHAr]TaCl_4 (**3**). ^{1}H NMR (C_6D_6, 80 °C): δ 7.23−7.02 (m, 6H, Ar), 5.25 (s br, NH), 4.92 (s br, 2H, −NH*CH*$_2$CH$_2$), 3.78−3.66 (m, 2H, −N*CH*$_2$CH$_2$), 3.65−3.59 (m, 4H, −*CH*Me$_2$), 1.78−1.76 (m, 2H, −NCH$_2$*CH*$_2$), 1.46 (d, *J* = 6.6 Hz, 6H, −CH*Me*$_2$), 1.28 (d, *J* = 6.6 Hz, 12H, −CH*Me*$_2$), 1.08 (d, *J* = 6.6 Hz, 6H, −CH*Me*$_2$).

The yellow solid (1.86 g) initially collected after the filtration was extracted with 100 mL of toluene and filtered. The filtrate was cooled to −40 °C for 24 h, affording an additional 0.18 g

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[18] Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: San Diego, CA, 1996.

of **3**. The combined mother liquors were concentrated and cooled again to −40 °C, producing a third crop of **3** (0.15 g). The total yield is 0.58 g (20.2%).

Complex **3** (0.188 g, 0.25 mmol) was suspended in 15 mL of diethyl ether and cooled to −40 °C. MeMgBr (0.425 mL, 3.0 M in Et_2O, 1.27 mmol) was added via syringe, and large precipitates formed during the addition. The mixture was stirred at room temperature for 45 min after the addition, and the solvent of the resulting yellow suspension was removed under reduced pressure to leave a solid residue. The residue was extracted with hexanes (15 mL) and filtered through Celite to produce a yellow solution which was filtered again through Celite. The filtrate was cooled to −40 °C in a freezer inside the box, and no crystals were obtained. The solvent was then removed and the residue was dried in vacuo to afford the crude product as a yellow solid. Further purification was made by redissolving the solid in hexane, filtering through Celite, and drying in vacuo to produce the desired product **4** in quantitative yield. Anal. Calcd for $C_{30}H_{49}N_2Ta$: C, 58.24; H, 7.98; N, 4.53. Found: C, 57.59; H, 7.64; N, 4.23.

Alternatively, **4** can be prepared in better than 70% overall yield based on the diamine ligand from a one-pot approach by mixing the neutral diamine ligand with $TaCl_5$ at −30 °C and stirring at room temperature for another 2 h, followed by an addition of 5 equiv of MeMgBr.

Spectroscopic data for **4** are as follows. ^{1}H NMR (C_6D_6, 23 °C): δ 7.18−7.11 (m, 6H, Ar), 3.61−3.50 (m, 8H, $-CH$Me$_2$, $-NCH_2CH_2$), 2.15 (m, 2H, $-NCH_2CH_2$), 1.37 (d, J = 6.9 Hz, 12H, $-CHMe_2$), 1.25 (d, J = 6.9 Hz, 12 H, $-CHMe_2$), 1.02 (s, 9H, Ta$-CH_3$). ^{1}H NMR (C_6D_6, 80 °C): δ 3.65 (t, 4H, $-NCH_2CH_2$), 3.57 (sept, 4H, $-CH$Me$_2$).^{1}H NMR (C_6D_5Br, 23 °C): δ 7.34 (m, 6H, Ar), 3.89 (t, J = 5.7 Hz, 4H, $-NCH_2CH_2$), 3.70 (sept, J = 6.9 Hz, 4H, $-CH$Me$_2$), 2.66 (m, 2H, $-NCH_2CH_2$), 1.53 (d, J = 6.6 Hz, 12H, $-CHMe_2$), 1.45 (d, J = 6.6 Hz, 12H, $-CHMe_2$), 1.04 (s, 9H, Ta$-CH_3$). ^{13}C NMR (C_6D_6, 23 °C): δ 144.87, 127.40, 126.82, 124.56 (Ar), 65.55 ($-NCH_2CH_2$), 55.94 (Ta$-CH_3$), 28.34, 27.02, 25.99, 24.72 ($-CH$Me$_2$, $-CHMe_2$, $-NCH_2CH_2$).

Reaction of Cp_2TaMe_3 with 2 Equiv of $Al(C_6F_5)_3$ and Isolation of $Cp_2TaMe_2^+[(C_6F_5)_3Al-CH_3-Al(C_6F_5)_3]^-$ (5). NMR-scale reactions were carried out in J. Young NMR tubes, the samples being loaded into the NMR tubes in a glovebox after mixing Cp_2TaMe_3 (0.02 mmol) and $Al(C_6F_5)_3$·0.5(toluene) (11.4 mg, 0.04 mmol) in 0.7 mL of C_6D_6. The mixture was allowed to react at room temperature for 10 min before the NMR spectra were recorded. The solution became cloudy immediately, and colorless crystals started to precipitate onto the wall of NMR tubes. NMR spectra of the solution phase indicated formation of the clean product **5**. ^{1}H NMR (C_6D_6, 23 °C): δ 4.96 (s, 10H, C_5H_5), 1.77 (s, br, Al$-CH_3-$Al), −0.40 (s, 6H, Ta$-CH_3$). ^{19}F NMR (C_6D_6, 23 °C): δ −122.66 (d, $^3J_{F-F}$ = 18.3 Hz, 12F, *o*-F), −154.58 (s, br, 6F, *p*-F), −162.35 (m, 12F, *m*-F). The crystals collected were redissolved in bromobenzene-d_5, and the NMR spectra indicated a species identical with that in the solution (vide infra).

This reaction was repeated in bromobenzene-d_5 (0.01 mmol scale) to afford a clear solution. NMR spectra indicated formation of the clean product **5**. ^{1}H NMR (C_6D_5Br, 23 °C): δ 5.78 (s, 10H, C_5H_5), 2.21 (s, br, 3H, Al$-CH_3-$Al), 0.23 (s, 6H, Ta$-CH_3$). ^{19}F NMR (C_6D_5Br, 23 °C): δ −122.83 (d, $^3J_{F-F}$ = 18.3 Hz, 12F, *o*-F), −154.39 (s, br, 6F, *p*-F), −162.19 (t, $^3J_{F-F}$ = 18.1 Hz, 12F, *m*-F). ^{13}C NMR (C_6D_5Br, 23 °C): δ 112.10 (C_5H_5, $^1J_{CH}$ = 175.5 Hz), 57.05 (Ta$-CH_3$, $^1J_{CH}$ = 125.3 Hz).

The preparative isolation of the complex was carried out in the glovebox by mixing Cp_2TaMe_3 (0.018 g, 0.05 mmol) and $Al(C_6F_5)_3$·0.5(toluene) (0.057 g, 0.1 mmol) in 10 mL of toluene and stirring at room temperature for 5 min. The solvent was removed under reduced pressure, and the residue was washed with 2 mL of hexane and dried in vacuo, affording 0.067 g of the clean product as a white crystalline solid. Yield: 94.9%. Anal. Calcd for $C_{49}H_{19}Al_2F_{30}Ta$: C, 41.67; H, 1.36. Found: C, 41.99; H, 1.47.

Reaction of Cp_2TaMe_3 with 1 Equiv of $Al(C_6F_5)_3$. In a small vial, Cp_2TaMe_3 and $Al(C_6F_5)_3$·0.5(toluene) were mixed in 0.7 mL of bromobenzene-d_5 in a 1:1 ratio (0.01 mmol scale), and the mixture was loaded into a J. Young NMR tube in a glovebox. The mixture was allowed to react at room temperature for 10 min before the NMR spectra were recorded. A clear solution was obtained immediately after mixing, and the NMR spectra indicated the clean formation of the corresponding cationic species $Cp_2TaMe_2^+CH_3Al(C_6F_5)_3^-$. ^{1}H NMR ($C_6D_5Br$, 23 °C): δ 5.79 (s, 10H, C_5H_5), 0.38 (s, br, 3H, Al$-CH_3$), 0.21 (s, br, 6H, Ta$-CH_3$). ^{19}F NMR (C_6D_5Br, 23 °C): δ −120.96 (dd, 6F, *o*-F), −158.02 (t, 3F, *p*-F), −163.09 (m, 6F, *m*-F). The same reaction in benzene-d_6 or toluene-d_8 produced initially a yellow suspension which gradually turned to oily precipitates at the bottom of the NMR tube. NMR spectra of the solution phase showed a mixture of species, including the unreacted Cp_2TaMe_3. The ^{1}H and ^{19}F NMR chemical shifts are very sensitive to the concentration and temperature, and the spectra are difficult to reproduce.

Reaction of Cp_2TaMe_3 and $B(C_6F_5)_3$. In a glovebox, Cp_2TaMe_3 and $B(C_6F_5)_3$ were mixed in 0.7 mL of benzene-d_6 in a 1:1 ratio (0.02 mmol scale), and the solution was loaded into a J. Young NMR tube. The mixture was allowed to react at room temperature for 15 min before the NMR spectra were recorded. The initially formed light yellow suspension turned gradually to yellow oily precipitates at the bottom of the tube. NMR spectra of the solution phase indicated formation of a mixture of two products, $Cp_2TaMe_2^+CH_3B(C_6F_5)_3^-$ and $Cp_2TaMe_2^+[(C_6F_5)_3B-CH_3-B(C_6F_5)_3]^-$, in a ca. 1:2 ratio, along with unreacted Cp_2TaMe_3. However, this ratio became ca. 2:1 after this phase stood in the NMR tube at room temperature for 1 h. ^{1}H NMR (C_6D_6, 23 °C): δ 5.05 (s, br, 10H, C_5H_5), 1.33 (s, br, 3H, B$-CH_3-$B), 0.95 (s, br, 3H, B$-CH_3$), −0.40 (br, Ta$-CH_3$). ^{19}F NMR (C_6D_6, 23 °C): δ −131.99 (d, $^3J_{F-F}$ = 21.2 Hz, 12F, *o*-F, binuclear anion), −132.30 (d, $^3J_{F-F}$ = 21.2 Hz, 6F, *o*-F, mononuclear anion), −163.98 (t, $^3J_{F-F}$ = 21.4 Hz, 6F, *p*-F, binuclear anion), −164.05 (t, $^3J_{F-F}$ = 21.4 Hz, 3F, *p*-F, mononuclear anion), −166.57 (t, 12F, *m*-F, binuclear anion), −166.64 (t, 6F, *p*-F, mononuclear anion). The 1:2 Cp_2TaMe_3/$B(C_6F_5)_3$ reaction produced a yellow oil containing the same mixture of species in the solution phase but with substantially sharper peaks for the Cp and Ta$-CH_3$ resonances. A substantial amount of the unreacted $B(C_6F_5)_3$ was also present in the solution.

The reactions were repeated in bromobenzene-d_5 (0.01 mmol scale) to afford clear solutions. NMR spectra of the 1:1 ratio reaction indicated formation of $Cp_2TaMe_2^+CH_3B(C_6F_5)_3^-$. ^{1}H NMR ($C_6D_5Br$, 23 °C): δ 5.78 (s, 10H, C_5H_5), 1.29 (s, br, 3H, B$-CH_3$), 0.21 (s, 6H, Ta$-CH_3$). ^{19}F NMR (C_6D_5Br, 23 °C): δ −131.95 (d, $^3J_{F-F}$ = 21.2 Hz, 6F, *o*-F), −163.50 (t, $^3J_{F-F}$ = 21.0, 3F, *p*-F), −166.12 (m, 6F, *m*-F). NMR spectra of the 1:2 reaction showed formation of the same product, along with unreacted $B(C_6F_5)_3$ and a small amount of $MeB(C_6F_5)_2$.

Reaction of Cp_2TaMe_3 and $Ph_3C^+[B(C_6F_5)_4]^-$. In a small vial, Cp_2TaMe_3 and $Ph_3C^+[B(C_6F_5)_4]^-$ were mixed in 0.7 mL of bromobenzene-d_5 in a 1:1 ratio (0.01 mmol scale) and the mixture was loaded into a J. Young NMR tube in a glovebox. The mixture was allowed to react at room temperature for 10 min before the NMR spectra were recorded. A clear yellow solution was obtained immediately after the mixing. NMR spectra indicated the clean formation of the corresponding cationic species $Cp_2TaMe_2^+[B(C_6F_5)_4]^-$ and 1 equiv of Ph_3CCH_3. ^{1}H NMR (C_6D_5Br, 23 °C): δ 5.78 (s, 10H, C_5H_5), 2.24 (s, 3H, Ph_3CCH_3), 0.21 (s, 6H, Ta$-CH_3$). ^{19}F NMR (C_6D_5Br, 23 °C): δ −131.62 (s, br, 6F, *o*-F), −161.40 (t, $^3J_{F-F}$ = 21.0, 3F, *p*-F), −165.35 (s, br, 6F, *m*-F). The 1:2 reaction produced the same product, even after heating at 100 °C.

Reaction of $[ArN(CH_2)_3NAr]TaMe_3$ (4) and $B(C_6F_5)_3$. In a small vial, $[ArN(CH_2)_3NAr]TaMe_3$ and $B(C_6F_5)_3$ were mixed in 0.7 mL of bromobenzene-d_5 in a 1:1 ratio (0.01 mmol scale) and the mixture was loaded into a J. Young NMR tube in a glovebox. The mixture was allowed to react at room temperature for 10 min before the NMR spectra were recorded. A clear pale yellow solution was obtained immediately after the mixing. NMR spectra indicated the clean formation of the corresponding cationic species $[ArN(CH_2)_3NAr]TaMe_2^+CH_3B(C_6F_5)_3^-$ (**6**). ^{1}H NMR (C_6D_5Br, 23 °C): δ 7.49−7.32 (m, 6H, Ar), 4.24 (t, J = 6.0 Hz, 4H, −NCH_2CH$_2$), 3.09 (sept, J = 6.9 Hz, 4H, −CHMe$_2$), 2.53 (m, 4H, −NCH$_2$$CH_2$), 1.39 (d, J = 6.6 Hz, 12H, −CHMe_2), 1.35 (d, J = 6.6 Hz, 12H, −CHMe_2), 1.31 (s, br, 3H, −BCH_3), 1.12 (s, 6H, Ta−CH$_3$). ^{19}F NMR (C_6D_5Br, 23 °C): δ −131.95 (d, $^3J_{F-F}$ = 18.5 Hz, 6F, o-F), −164.10 (t, $^3J_{F-F}$ = 20.9 Hz, 3F, p-F), −166.62 (m, 6F, m-F).

The reaction of $[ArN(CH_2)_3NAr]TaMe_3$ and $B(C_6F_5)_3$ in a 1:2 ratio produced the same product, along with unreacted $B(C_6F_5)_3$ and a small amount of $MeB(C_6F_5)_2$.

Reaction of $[ArN(CH_2)_3NAr]TaMe_3$ (4) and $Al(C_6F_5)_3$. In a small vial, $[ArN(CH_2)_3NAr]TaMe_3$ and $Al(C_6F_5)_3\cdot 0.5$(toluene) were mixed in 0.7 mL of bromobenzene-d_5 in a 1:1 ratio (0.01 mmol scale) and the mixture was loaded into a J. Young NMR tube in a glovebox. The mixture was allowed to react at room temperature for 10 min before the NMR spectra were recorded. A clear pale yellow solution was obtained immediately after the mixing. ^{1}H NMR spectra indicated the clean formation of the cation $[ArN(CH_2)_3NAr]TaMe_2^+$, but ^{19}F NMR spectra showed the presence of both the mononuclear and binuclear anions $CH_3Al(C_6F_5)_3^-$ (**7**; ∼80%) and $[(C_6F_5)_3Al-CH_3-Al(C_6F_5)_3]^-$ (**8**; ∼20%). ^{1}H NMR (C_6D_5Br, 23 °C): δ 7.38−7.24 (m, 6H, Ar), 4.31 (t, J = 6.0 Hz, 4H, −NCH_2CH$_2$), 2.93 (sept, J = 6.9 Hz, 4H, −CHMe$_2$), 2.49 (m, 4H, −NCH$_2$$CH_2$), 1.36 (d, J = 6.6 Hz, 12H, −CHMe_2), 1.33 (d, J = 6.6 Hz, 12H, −CHMe_2), 1.15 (s, 6H, Ta−CH$_3$), 0.50 (s, br, 3H, −AlCH_3). ^{19}F NMR (C_6D_5Br, 23 °C) for **7**: δ −121.30 (d, $^3J_{F-F}$ = 18.3 Hz, 6F, o-F), −158.00 (s, br, 3F, p-F), −163.25 (m, 6F, m-F). ^{19}F NMR (C_6D_5Br, 23 °C) for **8**: δ −121.63 (d, $^3J_{F-F}$ = 18.3 Hz, 6F, o-F), −157.10 (t, $^3J_{F-F}$ = 19.5 Hz, 3F, p-F), −163.25 (m, 6F, m-F).

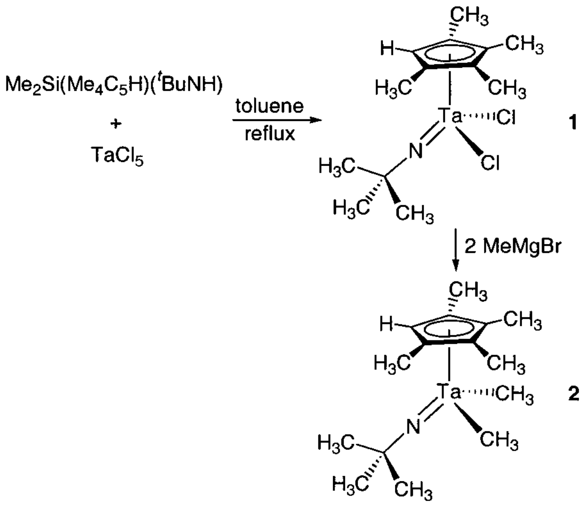
The same reaction, but with 2 equiv of $Al(C_6F_5)_3$, generated a clear pale yellow solution, and NMR spectra indicated the clean formation of the corresponding cation paired with a binuclear anion, $[ArN(CH_2)_3NAr]TaMe_2^+[(C_6F_5)_3Al-CH_3-Al(C_6F_5)_3]^-$ (**8**). The ^{1}H NMR spectrum is identical with that obtained from the 1:1 reaction, except that the broad Al−CH_3−Al signal is now shifted to 0.19 ppm.

Results and Discussion

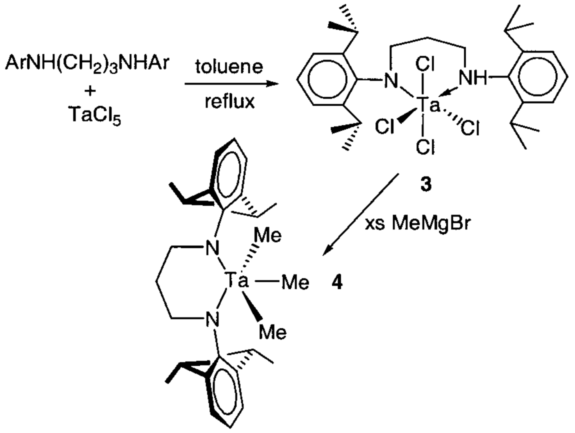
Synthesis of (η^5-C_5Me_4H)Ta(=N^{t}Bu)Me$_2$ (2). In a one-step fashion, reaction of the neutral constrained-geometry ligand $Me_2Si(C_5Me_4H)(^tBuNH)$ with $TaCl_5$ in refluxing toluene conveniently affords the half-sandwich imido tantalum dichloride **1** in better than 45% yield (Scheme 1).[19] Details about the reaction mechanism are currently unknown. Nevertheless, the dichloride **1** can be cleanly converted to the corresponding dimethyl complex **2** using 2 equiv of MeMgBr. Spectroscopic features of **1** and **2** are similar to those structurally related imido tantalum complexes reported in the literature.[3c,20]

Synthesis of $[ArN(CH_2)_3NAr]TaMe_3$ (Ar = 2,6-$^iPr_2C_6H_3$) (4). To avoid the potential reduction of Ta(V) species to lower valent species when organometallic reagents such as organolithium reagents are used for the synthesis, the neutral bulky chelating diamine ligand $ArNH(CH_2)_3NHAr$ (Ar = 2,6-$^iPr_2C_6H_3$)[15] was used to directly react with $TaCl_5$ in toluene under mild reflux conditions (Scheme 2). The six-coordinate, toluene-soluble complex **3** was isolated as orange crystals. All peaks in the ^{1}H NMR spectrum of **3** are very broad and unassignable at room temperature but are well-resolved at high temperatures. Thus, the ^{1}H NMR spectrum of **3** at 80 °C shows two doublets for the inequivalent isopropyl methyl groups on the phenyl ring at the covalent bond (Ta−N) site but only one doublet for equivalent isopropyl methyl groups at the dative bond (Ta←NH) site, presumably due to dissociation and

Scheme 1



Scheme 2



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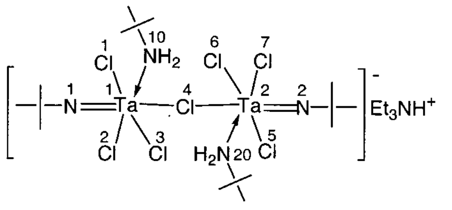
[19] When carried out in the presence of 2 equiv of Et_3N, the same reaction produced an ammonium salt of a chloride-bridged dimeric tantalum anion in low yield, the structure of which was confirmed by X-ray diffraction analysis but was only partially refined with the following selected bonding distances (Å) for the structure:



Ta1-N1 = 1.727; Ta1-N10 = 2.278
Ta1-Cl1 = 2.408; Ta1-Cl2 = 2.372
Ta1-Cl3 = 2.379;Ta1-Cl4 = 2.770
Ta2-Cl4 = 2.763; Ta2-Cl5 = 2.397
Ta2-Cl6 = 2.372; Ta2-Cl7 = 2.381
Ta2-N2 = 1.747; Ta2-N20 = 2.245

[20] (a) Royo, P.; Sánchez-Nieves, J. *J. Organomet. Chem.* **2000**, *597*, 61−68. (b) Gibson, V. C.; Poole, A. D.; Siemeling, U.; Williams, D. N.; Clegg, W.; Hockless, D. C. R. *J. Organomet. Chem.* **1993**, *462*, C12−C14.

recombination of the Ta←NH bond at this temperature resulting in racemization at the nitrogen center. In an attempt to increase the yield of **3** by refluxing the neutral ligand and $TaCl_5$ in toluene in the presence of 2 equiv of triethylamine, only the unreacted ligand was recovered.

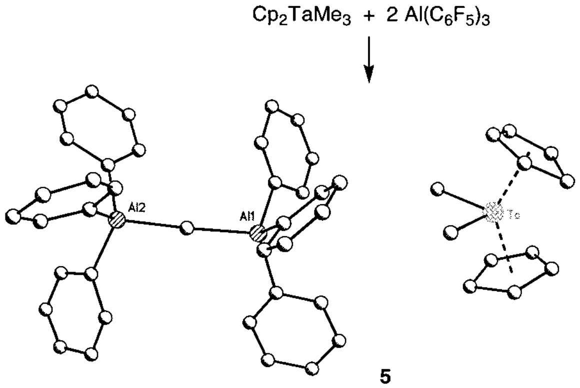
The six-coordinate complex **3** can be quantitatively converted to the corresponding Ta trimethyl species **4** by reacting **3** with an excess of MeMgBr. Alternatively, **4** can be prepared in better than 70% overall yield from a one-pot approach by mixing the neutral diamine ligand with $TaCl_5$ at −30 °C and stirring at room temperature for another 2 h, followed by addition of an excess of MeMgBr.

Isopropyl methyl groups on the phenyl ring in **4** appear as two doublets, attributable to the restricted rotations about the $N-C_{ipso}$ bond (assuming the two nitrogen centers are sp^2 hybridized). However, three tantalum methyl groups have the same chemical shift, in sharp contrast to Cp_2TaMe_3, in which two lateral methyl groups are separated from the central methyl group by +0.04 ppm (downfield shift) in benzene-d_6 and +0.18 ppm in bromobenzene-d_5. The equivalency of the three Ta methyl groups in **4** is not disrupted down to −80 °C, presumably due to fast interconversion on the NMR time scale between two prototype structures (trigonal bipyramid and square pyramid) for a five-coordinate complex.

Methide Abstraction of Cp_2TaMe_3 and 4 with the Strong Organo-Lewis Acids $M(C_6F_5)_3$ (M = B, Al) and $Ph_3C^+[B(C_6F_5)_4]^-$. The product of the reactions of Cp_2TaMe_3 with Lewis acids $M(C_6F_5)_3$ is very sensitive to the reaction medium. In toluene or benzene, unlike the reaction of Cp'_2ZrMe_2 with $B(C_6F_5)_3$, which cleanly generates the corresponding isolable and X-ray crystallographically characterizable cationic complexes $Cp'_2ZrMe^+MeB(C_6F_5)_3^-$ (Cp′ = Cp and substituted derivatives),[21] the reaction of Cp_2TaMe_3 with 1 equiv of $B(C_6F_5)_3$ produces an oily product mixture containing both $Cp_2TaMe_2^+CH_3B(C_6F_5)_3^-$ and $Cp_2TaMe_2^+[(C_6F_5)_3B-CH_3-B(C_6F_5)_3]^-$ in the solution phase, along with unreacted Cp_2TaMe_3.

An interesting aspect of this reaction is that, due to the weakly Lewis acidic $Cp_2TaMe_2^+$ countercation, the enhanced nucleophilicity of the free anion $CH_3B(C_6F_5)_3^-$, once generated, attacks $B(C_6F_5)_3$ to form the Me-bridged binuclear anion $[(C_6F_5)_3B-CH_3-B(C_6F_5)_3]^-$.[22] 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 the Me-bridged dinuclear cations $[Cp'_2ZrMe-CH_3-MeZrCp'_2]^+$.[23] Subsequently, 2 equiv of $B(C_6F_5)_3$ was used in the reaction with Cp_2TaMe_3 in an attempt to isolate the tantalocene cation−dinuclear anion pair and characterize it in the pure state. However, the reaction still produced an oily product mixture containing a significant amount of the unreacted $B(C_6F_5)_3$. Next, the use of the sterically more accessible, stronger organo-Lewis acid $Al(C_6F_5)_3$[24] was tried, but it profoundly changed the reaction outcome as well as the stability of the resulting Me-bridged binuclear anion. Thus, mixing Cp_2TaMe_3 with 2 equiv of $Al(C_6F_5)_3$ in benzene or toluene results in immediate precipitation of a clean product as colorless crystals in quantitative yield. Spectroscopic and analytical data as well as X-ray crystal diffraction studies confirm the formation of the desired ion pair $Cp_2TaMe_2^+[(C_6F_5)_3Al-CH_3-Al(C_6F_5)_3]^-$ (**5**)[7a] (Scheme 3).

Scheme 3



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The 1:1 reactions of Cp_2TaMe_3 with Lewis acids $M(C_6F_5)_3$ (M = B, Al) in polar NMR solvents such as bromobenzene-d_5 afford clear solutions and produce the expected cationic species $Cp_2TaMe_2^+CH_3M(C_6F_5)_3^-$ as clean products. The reaction with 2 equiv of the borane produces the same product along with the unreacted borane, whereas the reaction with 2 equiv of the alane cleanly generates the tantalocene cation−binuclear anion pair (**5**). The reaction of Cp_2TaMe_3 with $Ph_3C^+[B(C_6F_5)_4]^-$ produces the corresponding cationic species $Cp_2TaMe_2^+[B(C_6F_5)_4]^-$. Attempts to abstract the second $Ta-CH_3$ group for generating possibly a tantalum dication with 2 equiv of $Ph_3C^+[B(C_6F_5)_4]^-$ afforded the same product as in the 1:1 ratio reaction, even with heating at 100 °C.

Reaction of the nonmetallocene Ta complex **4** with strong Lewis acids $M(C_6F_5)_3$ (M = B, Al) in toluene-d_8 results in oily precipitates, and the NMR spectra of the solution phase showed formation of a mixture of several cationic species. However, the reactions in bromobenzene-d_5 are clean and afford clear solutions. Thus, reaction of **4** with $B(C_6F_5)_3$ in C_6D_5Br cleanly generates the corresponding cationic species **6** (Scheme 4). In comparison with the neutral species **4**, the $-CH$Me$_2$ resonance in **6** is substantially high-field shifted by 0.61 ppm, while the resonances for $-NCH_2CH_2$ and $Ta-CH_3$ are downfield shifted by 0.35 and 0.08 ppm, respectively, suggesting the cationic nature around the metal center. The observed large high-field shift in chemical shifts for the meta fluorines and especially for the para fluorines,

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[21] (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.

[22] The preparation of trityl or ammonium salts of dinuclear anions having a general formula of $[(C_6F_5)_3M-LG-M(C_6F_5)_3]^-$, where the linking group LG = cyanide and M = B[22a] and LG = cyanide, azide, dicyanamide, imidazolide and M = B, Al,[22b] has been recently reported: (a) Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533−1534. (b) See ref 16.

[23] (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.

[24] Chen, E. Y.-X.; Kruper, W. J.; Roof, G.; Wilson, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 745−746.

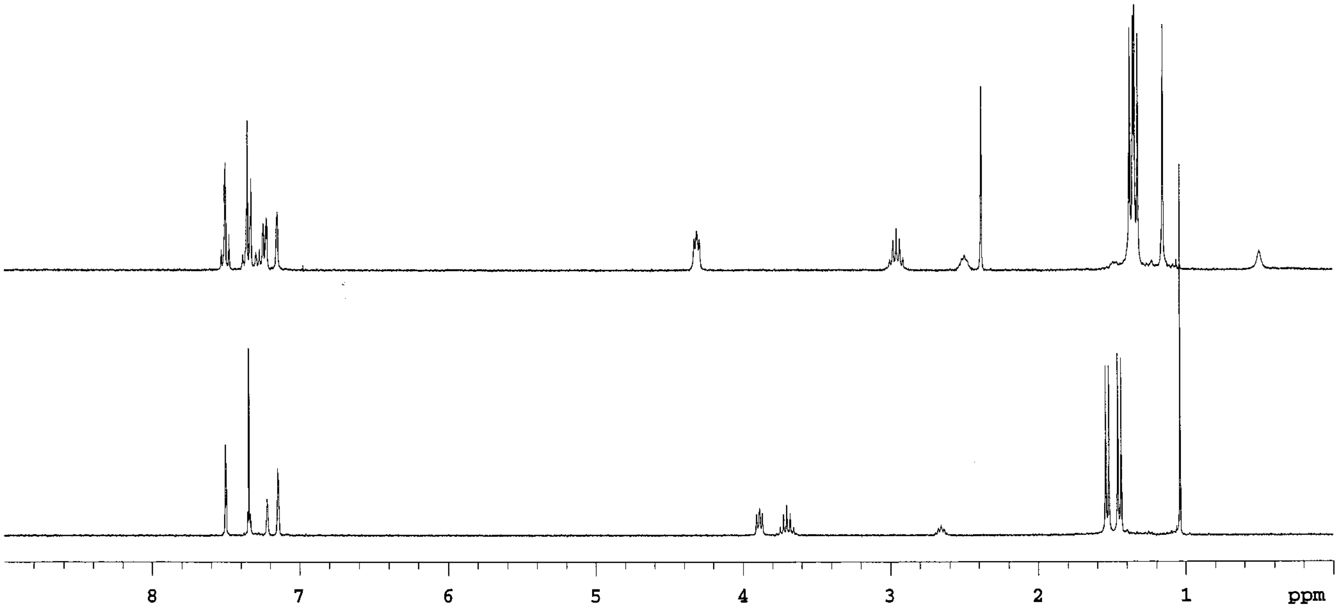
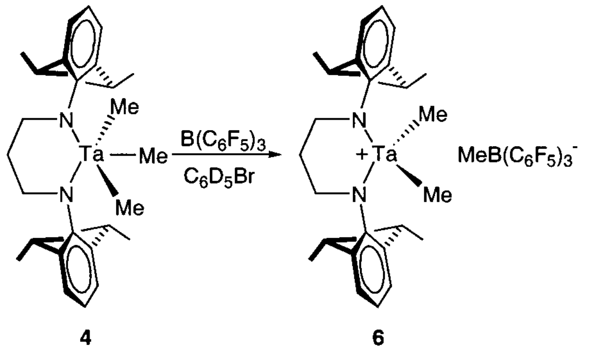
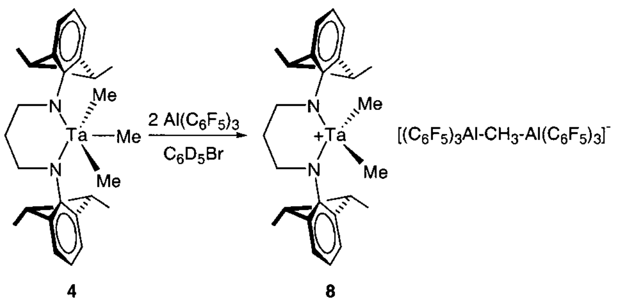


Figure 1. ^{1}H NMR of **4** (bottom) and the reaction product of **4** and Al(C_6F_5)$_3$·toluene (top) bromobenzene-d_5 at 23 °C. See Experimental for peak assignments.

Scheme 4



Scheme 5



as well as the small $\Delta\delta$ ($\delta_m - \delta_p$) value of 2.52 ppm in ^{19}F NMR chemical shifts of the anion, indicate the solvent-separated, nonassociated free anion MeB(C_6F_5)$_3^-$.[25] Reaction of **4** with 2 equiv of B(C_6F_5)$_3$ does not effect the abstraction of the second tantalum methyl group, forming the same product as the 1:1 reaction except for the presence of the unreacted borane.

The products of the reaction between **4** and Al(C_6F_5)$_3$ in C_6D_5Br depend on the ratio of the two reactants. In a 1:1 ratio, the reaction at room temperature produces Ta cations with a mixture of the mononuclear anion $CH_3Al(C_6F_5)_3^-$ (**7**, ~80%) and the binuclear anion [(C_6F_5)$_3$-Al−CH_3−Al(C_6F_5)$_3$]$^-$ (**8**, ~20%). Due to the nonassociative nature between the cation and anion, the cation portion is spectroscopically identical in ^{1}H NMR for both species, whereas in ^{19}F NMR two different anions can be seen. When a second equivalent of Al(C_6F_5)$_3$ is added, **8** is formed quantitatively by NMR (Scheme 5). The spectroscopic features of the tantalum cation are similar to those observed from the reaction with the borane, and the sharp differences between the neutral **4** and the cation in **7** or **8** are illustrated in Figure 1.

Polymerization Studies. Results from high-temperature ethylene−1-octene copolymerization studies using the three distinctive classes of Ta(V) complexes activated with various activators are summarized in Table 1. It can be seen from the table that Cp_2TaMe_3 has no olefin polymerization activity (but is active for MMA polymerization with suitable activators; vide infra) even with an excess of Lewis acid activators (runs 2 and 3). The non-metallocene Ta complex **4** is active but exhibits low polymerization activity toward copolymerization of ethylene and 1-octene upon activation with [HNMe($C_{18}H_{37}$)$_2$]$^+$[(C_6F_5)$_3$AlNC$_3$H$_3$NAl(C_6F_5)$_3$]$^-$ or PMAO-IP (runs 4 and 5). The most active catalyst of this series is the half-sandwich imido Ta dimethyl complex **2**. Thus, upon activation with [HNMe($C_{18}H_{37}$)$_2$]$^+$-[(C_6F_5)$_3$AlNC$_3$H$_3$N(Al(C_6F_5)$_3$]$^-$, 50 g of copolymer was produced within 15 min using 5.0 μmol of **2**, giving an activity of 1.2 × 10^6 g of polymer/((mol of Ta) atm h) (run 6). This copolymer has a low density of 0.898, a high molecular weight of 127 000, and a molecular weight distribution of 2.29, indicative of large octene incorporation in the copolymer. Complex **2** is still very active at a polymerization temperature of 160 °C, giving an activity of 5.4 × 10^5 g of polymer/((mol of Ta) atm h) (run 7). Other activators such as PMAO-IP give lower polymerization activity (run 8).

Half-sandwich Ta(III) and Nb(III) diene complexes are active for controlled MMA polymerization when activated with suitable activators,[2] whereas the non-metallocene Ta(V) complex **4** exhibits no polymerization activity upon activation with various activators. The

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(25) (a) Klosin, J.; Roof, G.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684−4686. (b) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672−2674.

Table 1. High-Temperature Ethylene and 1-Octene Copolymerization Results and Polymer Properties Catalyzed by Ta(V) Complexes with Various Activators[a]

entry	catalyst	activator	amt of catalyst/ activator (μmol)	exotherm (°C)	yield (g)	efficiency (g of polymer/ ((mol of metal) atm h))	density (g/mL)	MMI (micro melt index)	M_w[b]	M_w/M_n
1[c]	CGC-$TiMe_2$	$B(C_6F_5)_3$	2.0/2.0	8.1	138.0	8 288 000	0.892	3.7	77 500	1.94
2	Cp_2TaMe_3	$B(C_6F_5)_3$	1.0/4.0	0.5	trace	0				
3	Cp_2TaMe_3	$Al(C_6F_5)_3$	1.0/4.0	0.4	trace	0				
4	**4**	Al imidazolide[d]	2.0/2.0	1.3	3.0	180 000	0.900	0.2		
5	**4**	PMAO-IP	20/10 000	1.1	1.9	11 000				
6	**2**	Al imidazolide	5.0/5.0	1.4	50.2	1 206 000	0.898	0.9	127 000	2.29
7[e]	**2**	Al imidazolide	5.0/5.0	1.3	22.4	538 000	0.900	1.8		
8[f]	**2**	PMAO-IP	20/10000	1.2	14.8	89 000	0.917	0.2	125 000	2.72

[a] Conditions: 140 °C, 118 g of octene, 5 mmol of H_2, 500 psig of ethylene, 740 g of isopar-E, 15 min. [b] GPC relative to polystyrene standards. [c] A control run. [d] $[HNMe(C_{18}H_{37})_2]^+[(C_6F_5)_3AlNC_3H_3N(Al(C_6F_5)_3]^-$. [e] Carried out at 160 °C. [f] Carried out at 130 °C.

Table 2. MMA Polymerization Results[a]

entry	complex	T_p (h)	yield (%)	M_n[b]	M_w/M_n	I^*[c] (%)	T_g (°C)	$[rr]$[d] (%)	$[mr]$ (%)	$[mm]$ (%)
1	$Cp_2TaMe_3/B(C_6F_5)_3$	12	0							
2	$Cp_2TaMe_3/Al(C_6F_5)_3$	12	0							
3	$Cp_2TaMe_3/2Al(C_6F_5)_3$	10	100	158 600	5.42	12.6	120.5	72.9	25.8	1.3
4	(i) $2Al(C_6F_5)_3$ (ii) Cp_2TaMe_3	10	100	347 300	3.22	5.7		75.9	23.4	0.7
5	$Cp_2TaMe_3/2B(C_6F_5)_3$	12	0							

[a] Polymerization conditions: 46.7 μmol of initiator (I); mole ratio MMA/I = 200 with target M_n = 20 000; 10 mL of toluene; 25 °C. Catalyst and activator are mixed in situ the the ratio indicated in the complex column. For run 4, MMA monomer was first mixed with $Al(C_6F_5)_3$ followed by addition of Cp_2TaMe_3. [b] GPC relative to polystyrene standards. [c] Initiator efficiency: $I^* = M_n(\text{calcd})/M_n(\text{exptl})$. [d] Determined by ^1H NMR spectroscopy.

metallocene complex Cp_2TaMe_3 is also inactive for MMA polymerization in toluene when activated with 1 equiv of $B(C_6F_5)_3$ or $Al(C_6F_5)_3$. However, active polymerization systems are generated if 2 equiv of $Al(C_6F_5)_3$ was used for the activation, regardless of addition sequence. Thus, the activated catalyst polymerization by first mixing Cp_2TaMe_3 with 2 equiv of $Al(C_6F_5)_3$ before adding MMA produced PMMA in 100% yield at a MMA/initiator ratio of 200 for 10 h (Table 2, run 3). A similar activity is observed via activated monomer polymerization by first mixing MMA with 2 equiv of $Al(C_6F_5)_3$ before adding Cp_2TaMe_3 (run 4). Interestingly, activation with 2 equiv of $B(C_6F_5)_3$ did not generate an active MMA polymerization system (run 5). These findings seem to be consistent with the observations that the reactions of Cp_2TaMe_3 with 1 equiv of $Al(C_6F_5)_3$ or with 1 or 2 equiv of $B(C_6F_5)_3$ in toluene produce a mixture of species, while the reaction with 2 equiv of $Al(C_6F_5)_3$ cleanly generates $Cp_2TaMe_2{}^+[(C_6F_5)_3Al-CH_3-Al(C_6F_5)_3]^-$ (vide supra).

Number-average molecular weights of the PMMA produced from the tantalocene system are significantly higher than the calculated values, and molecular weight distributions are also broad (PDI from 3.22 to 5.42). Initiator efficiencies are low (from 5.6% to 12.6%), and the polymers are syndiotactic, with [*rr*] triads ranging from 73 to 76%.

In summary, neutral routes by direct reaction of the neutral ligands with $TaCl_5$ have been developed for the synthesis of half-metallocene and non-metallocene tantalum complexes. Activation of tantalum trimethyl complexes with 1 equiv of strong Lewis acids $M(C_6F_5)_3$ affords the corresponding cationic species paired with anions $MeM(C_6F_5)_3{}^-$ in polar solvents; however, the reaction in benzene or toluene produces a mixture of products. The reaction of Cp_2TaMe_3 with 2 equiv of $Al(C_6F_5)_3$ cleanly generates a cation paired with a binuclear anion, $Cp_2TaMe_2{}^+[(C_6F_5)_3Al-CH_3-Al(C_6F_5)_3]^-$, which is active for MMA polymerization. Among the three classes of complexes included in this study, the half-sandwich imido complex was established as an efficient olefin copolymerization catalyst. These results extend the olefin copolymerization catalyst library for producing low-density elastomers by including group 5 half-metallocene imido complexes.

Acknowledgment. We thank Drs. J. Klosin, W. J. Kruper, and P. N. Nickias of The Dow Chemical Co. for helpful discussions and Dr. Khalil A. Abboud of the University of Florida for X-ray diffraction analysis.

OM010702C