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The Synthesis and Olefin Reactivity of Neutral and Cationic Tantalum Amidinate−Pentamethylcyclopentadienyl Complexes

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$Cp^*[MeC(NPr^i)_2]TaCl_3$, **1**, was prepared in a 60% yield by the reaction of Cp^*TaCl_4 with 1 equiv of $Li[MeC(NPr^i)_2]$ in THF. The structure is pseudo-octahedral with a plane of symmetry containing the amidinate ligand and bisecting the Cp*. Reaction of **1** with excess MeMgCl yielded the trimethyl derivative $Cp^*[MeC(NPr^i)_2]TaMe_3$. Reaction of **1** with $AgSbF_6$ yielded the cation $[Cp^*[MeC(NPr^i)_2]TaCl_2][SbF_6]$. The amidinate orientation is changed with respect to **1** such that the amidinate and the Cp* are nearly parallel. Complex **1** polymerizes ethylene upon treatment with MAO in isobutane (470 (g PE)(mmol Ta)$^{-1}$ h^{-1} atm^{-1}).

Although the cyclopentadienyl ligand and its derivatives have proved to be exceedingly useful ligands for early transition metal Ziegler−Natta catalysts, recently there has been an increasing interest in the exploration of other ancillary ligands that offer different combinations of electronic and steric properties.[1] In many cases these "new" ligands are actually well-known but underexploited. Amidinates fall into this category. While there are, in fact, amidinate complexes known for nearly all early metals,[2−4] there are still few enough examples that their unique behavior as ancillary ligands is not fully understood. Herein, we add a significant piece to the puzzle by describing the synthesis, structures, and ethylene reactivity of mixed amidinate−Cp* tantalum complexes ($Cp^* = C_5Me_5$).[5,6]

Results and Discussion

$Cp^*[MeC(NPr^i)_2]TaCl_3$, **1**, was prepared in a 60% yield by the reaction of Cp^*TaCl_4 with 1 equiv of $Li[MeC(NPr^i)_2]$ in THF (Scheme 1). The red-orange compound exhibited ^1H NMR, ^{13}C NMR, and analytical data consistent with the proposed formulation. The molecule possesses a plane of symmetry as shown by the presence of only two isopropyl methyl resonances. The observation of two methine resonances, separated by 0.5 ppm, was consistent with an orientation in which the CNC face of the amidinate defines a plane that includes the Ta−Cp* (centroid) "bond".

A single-crystal X-ray diffraction study of **1** confirmed this orientation; the amidinate CNC face lies in a crystallographic plane that bisects the molecule (Figure 1, Table 1, Table 2). The overall structure can either be viewed as distorted octahedral with the Cp* ligand situated *trans* to one of the amidinate nitrogens or as a four-legged piano-stool structure with the perpendicular amidinate occupying a single leg site. The amidinate is bound unsymmetrically with C−N distances of 1.352(9) and 1.285(9) Å and Ta−N distances of 2.094(5) and 2.194(6) Å, respectively. The more unsaturated C═N is located *trans* to the Cp*. Other high-valent early metal amidinates that exhibit localized bonding have distances in this range.[2,6] Attempts to prepare the *N-tert*-butyl derivative of **1** by an analogous procedure failed, ostensibly due to steric saturation.

The trimethyl derivative of **1** was prepared by reaction with excess MeMgCl (4 equiv). The orange-yellow product $Cp^*[MeC(NPr^i)_2]TaMe_3$, **2**, was isolated in a 60% yield from the reaction mixture. Use of fewer equivalents of alkylating agent produced mixtures that resisted purification. The trimethyl derivative exhibited two resonances for the methyl groups attached to tantalum at δ −0.29 and −0.74 in a 2:1 ratio. ^1H NMR, ^{13}C NMR, and analytical data establish that trimethyl **2** is isostructural with trichloride **1**. X-ray structural data proved the accuracy of the assignment (Figure 2, Table 3). Trimethyl **2** has a single plane of symmetry, coinciding with the plane of the amidinate ligand. The amidinate is bound unsymmetrically as before with the same C−N distances as **1**. The tantalum−nitrogen distances are distinct, however. At 2.155(5) and 2.275(5) Å, they are an average of 0.07 Å longer than the comparable bonds of complex **1**. The more donating

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(1) Britovsek, G. J.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428−447, and references therein.

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(3) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300.

(4) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481.

(5) A series of benzamidinate−Cp* complexes of tantalum was previously reported: Schrumpf, F.; Roesky, H. W.; Subrahmanyan, T.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1990**, *583*, 124−132.

(6) Mixed amidinate−Cp zirconium complexes have been previously reported and their polymerization activities determined: (a) Chernega, A. N.; Gómez, R.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1415−1417. (b) Gómez, R.; Green, M. L. H.; Haggitt, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2607−2608. (c) Gómez, R.; Duchateau, R.; Hernega, A. N.; Teuben, J. H.; Edelmann, F. T.; Green, M. L. H. *J. Organomet. Chem.* **1995**, *491*, 153−158.

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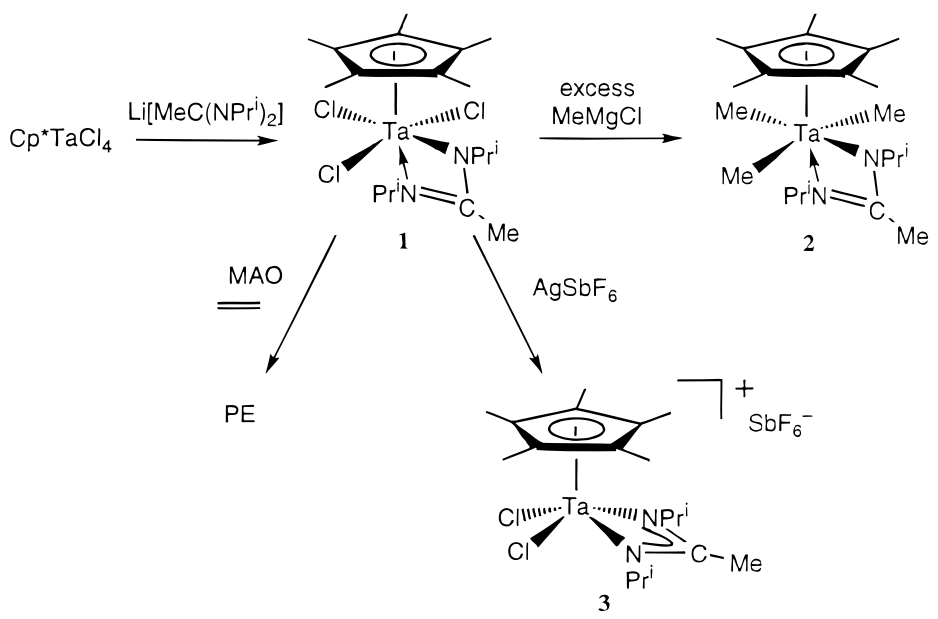
Scheme 1



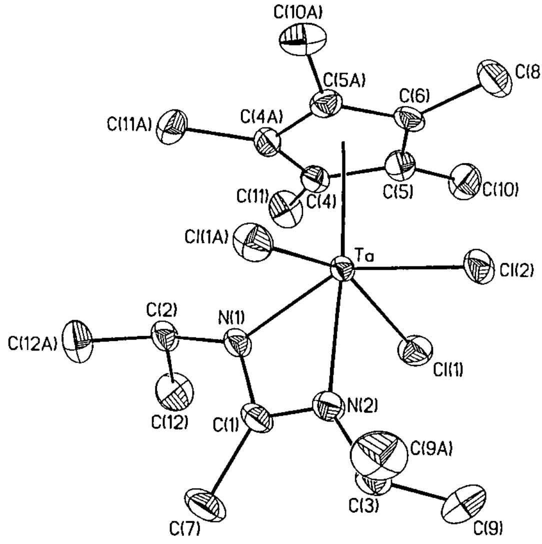


Figure 1. ORTEP drawing of Cp*[MeC(NPr^i)$_2$]TaCl$_3$, **1**, with 50% probability ellipsoids. H's omitted for clarity.

nature of the Me compared with Cl explains the lengthened bonds.

The cationic derivative of **1** was prepared by reaction with AgSbF$_6$. The deep red solid was isolated in a 64% yield from the CH$_2$Cl$_2$ mother liquor after filtration. Spectral and analytical data suggest that the correct formulation is [Cp*[MeC(NPr^i)$_2$]TaCl$_2$][SbF$_6$], **3**. The ^{1}H NMR spectrum shows a single resonance for the isopropyl methyl groups, indicating that the geometry around tantalum differs from that observed for **1** and **2**. Single-crystal diffractometry confirms both the cationic nature of the compound and the change in geometry (Figure 3, Table 4). The structure can be envisioned as a three-legged piano-stool with the amidinate ligand oriented such that the CNC face lies nearly parallel to the plane of the Cp*. In contrast with **1** and **2**, the amidinate is symmetric, with delocalized C−N bond distances of 1.325(12) Å. This distance falls between the "double" and "single" bonded distances observed for compound **1**. The tantalum nitrogen distances are identical and relatively short at 2.108(9) Å, comparable to the smaller of the two Ta−N distances of complex **1**. The cationic nature of the compound can also be seen in the Ta−Cl distances, which are 0.11 Å shorter than the average Ta−Cl distance in the neutral complex, **1**. There are no close contacts with the counterion in the lattice packing diagram of **3**. Given the diastereotopic relationships of the isopropyl methyls in this structure, the observation of a single methyl resonance implies that there is a facile process, such as amidinate rotation, for their equilibration. Low-temperature ^{1}H NMR studies confirm the fluxionality of the amidinate. Below the coalescence temperature of ~258 K ($k_c = 120$ s^{-1}) the isopropyl resonances appear as two doublets.

The orientational difference of the amidinate ligand between complexes **1** and **3** is intriguing. It is particularly interesting to note that the only other structurally characterized neutral tantalum amidinate−Cp* complex, Cp*Ta[p-MeOC$_6$H$_4$C(NSiMe$_3$)$_2$]F$_3$, which was prepared by Roesky and co-workers,[5] differs from **1** in amidinate orientation; one of the F ligands occupies the position *trans* to the Cp* and the amidinate is situated parallel to the Cp*. Although no cations have been reported for these group V complexes, isoelectronic analogues of **3** can be found in the neutral group IV amidinate−Cp* complexes such as CpZr[PhC(NSiMe$_3$)$_2$]Cl$_2$, which was prepared by Green and co-workers.[6c] This complex exhibits a parallel amidinate−Cp* orientation such that it is approximately isostructural with tantalum cation **3**. Orientation differences have also been noted in bis(amidinate) systems. There are instances of both coplanar[7] and noncoplanar[2g] orientations of the amidinates of tantalum, while only noncoplanar orientations have been reported for zirconium.[8,9] Although the barriers to rotation can be low, as we observed with cation **3**, the orientational differences are potentially relevant to the reactivity of these compounds.

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[8] Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307−314.

[9] Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 3087−3096.

Table 1. X-ray Data and Collection Parameters for Complexes 1, 2, and 3

	1	2	3
chemical formula	$C_{18}H_{32}N_2Cl_3Ta$	$C_{21}H_{41}N_2Ta$	$C_{18}H_{32}N_2Cl_2TaSbF_6$
temp (K)	200(2)	200(2)	200(2)
space group	*Pnma*	*Pnma*	$P2_1/m$
crystal dimens (mm)	0.20 × 0.20 × 0.30	0.32 × 0.24 × 0.18	0.33 × 0.24 × 0.06
a (Å)	17.522(4)	17.567(4)	7.307(15)
b (Å)	12.348(3)	12.760(3)	14.052(3)
c (Å)	9.758(2)	9.848(2)	12.276(3)
α (deg)	90	90	90
β (deg)	90	90	100.20(3)
γ (deg)	90	90	90
crystal system	orthorhombic	orthorhombic	monoclinic
Z, volume (Å)	4, 2111.3(7)	4, 2207.4(8)	2, 1240.6(4)
density (calcd) (Mg/m^3)	1.774	1.512	2.045
abs coeff (mm^{-1})	5.589	4.984	5.764
F(000)	1112	1016	732
θ range for data collection (deg)	2.32−25.00	2.32−27.50	2.22−25.00
limiting indices	$0 \le h \le 20$	$-22 \le h \le 22$	$0 \le h \le 8$
	$-14 \le k \le 0$	$-16 \le k \le 0$	$0 \le k \le 16$
	$0 \le l \le 11$	$0 \le l \le 12$	$-14 \le l \le 14$
no. of reflns collected	1955	5195	2209
no. of indepdt reflns	1955	2643	2068
goodness-of-fit	1.050	1.031	1.161
final *R* indices: R,[a] R_w[b] ($I > 2\sigma(I)$)	0.0254, 0.0603	0.0272, 0.0620	0.0538, 0.1405

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_2^2 - F_c^2)/F_o^4]^{1//2}$, $w = [\sigma^2 F_o^2 + (0.1F_o)^2]^{-1}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*[MeC(NPr^i)_2]TaCl_3$ (1)

Ta−N(1)	2.094(5)	Ta−N(2)	2.194(6)
Ta−Cl(1)	2.4372(13)	Ta−Cl(2)	2.3821(17)
N(1)−C(1)	1.352(9)	N(2)−C(1)	1.285(9)
N(1)−C(1)−N(2)	109.3(6)	N(1)−Ta−N(2)	60.2(2)
N(2)−Ta−Cl(1)	77.78(3)	Cl(1)−Ta−Cl(2)	88.66(3)
N(1)−Ta−Cl(1A)	84.02(4)	Cl(1)−Ta−Cl(1A)	155.55(7)

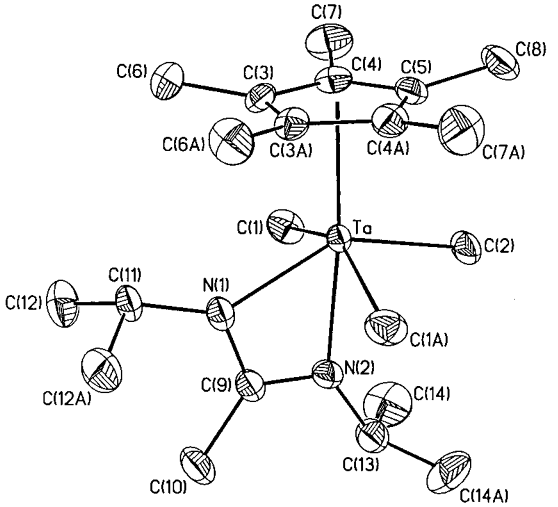

Figure 2. ORTEP drawing of $Cp^*[MeC(NPr^i)_2]TaMe_3$, **2**, with 50% probability ellipsoids. H's omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*[MeC(NPr^i)_2]TaMe_3$ (2)

Ta−N(1)	2.155(5)	Ta−N(2)	2.275(5)
Ta−C(1)	2.266(5)	Ta−C(2)	2.216(6)
N(1)−C(9)	1.350(7)	N(2)−C(9)	1.285(7)
N(1)−C(9)−N(2)	110.5(5)	N(1)−Ta−N(2)	58.43(19)
N(2)−Ta−C(1A)	75.25(13)	C(1)−Ta−C(2)	89.68(13)
N(1)−Ta−C(1)	81.03(12)	C(1)−Ta−C(1A)	150.3(3)

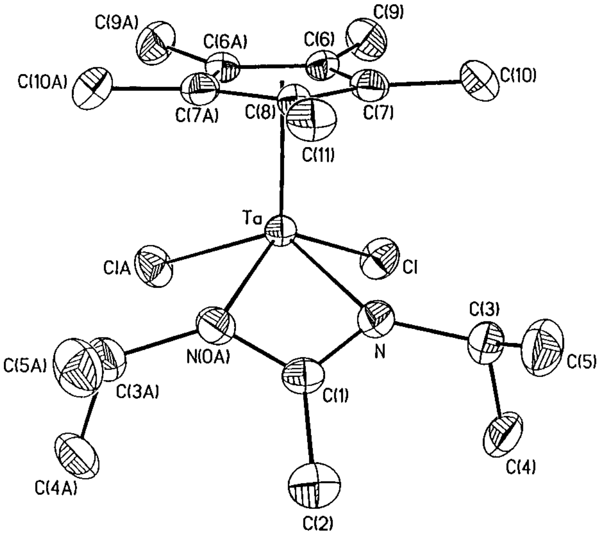

Figure 3. ORTEP drawing of $[Cp^*[MeC(NPr^i)_2]TaCl_2]$-$[SbF_6]$, **3**, with 50% probability ellipsoids. Counterion and H's omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Cp^*[MeC(NPr^i)_2]TaCl_2]^+SbF6^-$ (3)

Ta−N	2.108(9)	C(1)−N	1.325(12)
Ta−Cl	2.308(3)	C(1)−C(2)	1.52(2)
N−C(1)−N	107.2(12)	N−Ta−N	60.8(5)
N−Ta−Cl	86.3(2)	Cl−Ta−Cl	93.33(15)

The facility of cation preparation suggested that the reactivity with ethylene should be investigated. When the trichloride **1** was treated with a large excess of MAO, a polymerization activity of 470 (g PE)(mmol Ta)$^{-1}$ h^{-1} atm^{-1} at 60 °C was observed. GPC analysis shows a monomodal distribution centering at a M_n of ~80 K (PDI = 1.85). Increasing the temperature to 100 °C did not improve the yield, but rather resulted in lower molecular weight and a slightly broader distribution of chain lengths (M_n = ~50 K, PDI = 1.94). This reactivity is promising in that it falls into the "high" activity category on the scale proposed by Gibson et al.[1] Typically, nonmetallocene tantalum catalysts have reported activities significantly below 50 (g PE)(mmol Ta)$^{-1}$ h^{-1} atm^{-1}.[1,10] Only the bis(amidinate) complexes reported by Polamo and co-workers have higher activities (~1000 (g PE)(mol Ta)$^{-1}$ h^{-1} atm^{-1} at 60 °C).[11] Trimethyl **2** was also treated in situ with both $B(C_6F_5)_3$ and $[H(OEt_2)_2]^+$-

$[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$. Curiously, in neither case did the unisolated mixtures polymerize ethylene. Future isolation and characterization of the putative cations may indicate if strong anion association is responsible for inhibiting the reaction.

In summary, we have prepared and characterized a series of mixed amidinate−Cp* tantalum complexes that are useful starting materials for the exploration of the chemistry of this unique coordination environment. Furthermore, we have found that the trichloride **1** is a "highly" active precursor for Ziegler−Natta polymerization of ethylene.

Experimental Section

General Methods. Unless otherwise noted, all manipulations were carried out under an inert nitrogen atmosphere in a Vacuum Atmospheres drybox or with standard Schlenk or vacuum line techniques. Reagent grade tetrahydrofuran and toluene were distilled from Na/benzophenone under nitrogen. Reagent grade hexanes were washed with sulfuric acid, passed through a column of activated alumina, and distilled from Na/benzophenone under nitrogen. Methylene chloride, methylene chloride-d_2, and chloroform-d_1 were distilled or vacuum transferred from P_4O_{10}. Tantalum(V) chloride (resublimed, 99.99%) and tris(pentafluorophenyl)boron were obtained from Strem and used without further purification. Methylmagnesium chloride, methyllithium, and silver hexafluoroantimonate were purchased from Aldrich and used as received. 1,3-Diisopropylcarbodiimide was purchased from Aldrich and vacuum distilled prior to use. Cp*TaCl$_4$ was prepared according to literature methods.[12] Li[MeC(NPr^i)$_2$] was prepared by reaction of C(NPr^i)$_2$ and MeLi. ^{1}H and ^{13}C{H} NMR spectra were obtained on a Bruker AF spectrometer at 300 MHz and 25 °C, and chemical shifts were referenced to solvents. Elemental analyses were performed by Atlantic Microlab, Inc.

Cp*[MeC(NPr^i)$_2$]TaCl$_3$ (1). A THF solution of Li[MeC(NPr^i)$_2$] (1.32 g, 8.90 mmol) was added to a solution of Cp*TaCl$_4$ (4.06 g, 8.86 mmol) in THF at −30 °C. After stirring at RT for 6 h, the THF was removed in vacuo, and the resulting red-orange solid was extracted with toluene and filtered through Celite. Concentration and cooling of the filtrate yielded 3.01 g of crystalline solid (yield 60%). Recrystallization from THF gave analytically pure material. ^{1}H NMR (CDCl$_3$): δ 5.10 (m, 1H, CH), 4.70 (m, 1H, CH), 2.45 (s, 15H, C$_5$*Me*$_5$), 2.10 (s, 3H, C*H*$_3$), 1.56 (d, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$): δ 175.4, 129.5, 52.4, 51.1, 26.6, 21.6, 19.7, 13.0. Anal. Calcd for $C_{18}H_{32}N_2Cl_3Ta$: C, 38.35; H, 5.72; N, 4.97. Found: C, 38.36; H, 5.78; N, 4.73.

Cp*[MeC(NPr^i)$_2$]TaMe$_3$ (2). A 25 mL Schlenk flask was charged with **1** (300 mg, 0.532 mmol, 1 equiv) and 15 mL of THF. After cooling to −78 °C, an excess of MeMgCl (710 μL of a 3.0 M solution, 2.13 mmol, 4 equiv) was slowly added via syringe to the rapidly stirring solution. The cold reaction mixture was stirred for 5 min, slowly warmed to ambient temperature, and allowed to react for 24 h. The THF was removed in vacuo, and the resulting solid was extracted with toluene and filtered through Celite. The orange-yellow filtrate was concentrated under vacuum to a volume of 2 mL, carefully layered with hexanes, and stored at −30 °C overnight to yield 160 mg (60%) of pure crystalline product. ^{1}H NMR (CDCl$_3$): δ 4.70 (m, 1H, C*H*(CH$_3$)$_2$), 3.72 (m, 1H, C*H*(CH$_3$)$_2$), 1.97 (s, 15H, C$_5$*Me*$_5$), 1.90 (s, 3H, C*H*$_3$), 1.51 (d, 6H, CH(C*H*$_3$)$_2$), 1.08 (d, 6H, CH(C*H*$_3$)$_2$), −0.29 (br s, 6H, Ta−*Me*), −0.74 (br s, 3H, Ta−*Me*). ^{13}C NMR (CDCl$_3$): δ 167.2, 119.1, 50.2, 49.1 (2 overlapping peaks), 42.8, 23.5, 23.2, 19.9, and 11.6. Anal. Calcd for $C_{21}H_{41}N_2Ta$: C, 50.19; H, 8.22; N, 5.57. Found: C, 49.98; H, 8.20; N, 5.74.

[Cp*[MeC(NPr^i)$_2$]TaCl$_2$]$^+$[SbF$_6$]$^-$ (3). **1** (172.7 mg, 0.306 mmol) and AgSbF$_6$ (105.2 mg, 0.306 mmol) were each dissolved in 5 mL of CH$_2$Cl$_2$ and cooled to −30 °C. The AgSbF$_6$ solution was added to the solution of **1** while stirring; immediate precipitation of AgCl was noted. The reaction mixture was allowed to come to ambient temperature and stir for 10 min, upon which the precipitate was removed by filteration. The deep red filtrate was concentrated under vacuum to a volume of 1 mL and stored at −30 °C for 7 days. The crystalline product was collected by filtration to yield 150 mg (64%) of pure solid. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 3.90 (m, 2H, C*H*(CH$_3$)$_2$), 2.66 (s, 15H, C$_5$*Me*$_5$), 2.51 (s, 3H, C*H*$_3$), 1.40 (d, 12H, CH(C*H*$_3$)$_2$). ^{1}H NMR (CD$_2$Cl$_2$, 238 K): δ 3.79 (m, 2H, C*H*(CH$_3$)$_2$), 2.59 (s, 15H, C$_5$*Me*$_5$), 2.30 (s, 3H, C*H*$_3$), 1.40 (d, 6H, CH(C*H*$_3$)$_2$), 1.26 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ 173.4, 132.8, 54.6, 23.0, 19.8, 13.4. Anal. Calcd for $C_{18}H_{32}N_2Cl_2TaSbF_6$: C, 28.30; H, 4.22; N, 3.67. Found: C, 28.33; H, 4.38; N, 3.60.

Polymerization of Ethylene. Ethylene reactivities and GPC data were determined by Exxon, Baytown, TX. Conditions: 1 L steel autoclave, 5 mg of **1**, continuous ethylene pressure of 125 psi, 400 mL of isobutane solvent, 10 mL of 30 wt % MAO, 200 μL of triisobutyl aluminum, 30 min, 60 °C. GPC data (TCB solvent) are referenced to a polyethylene standard.

X-ray Structural Analyses. Crystals were coated with Fluorolube and mounted on a glass fiber with epoxy cement. The crystal was then placed in a cold N$_2$ stream. Single-crystal X-ray diffraction experiments were performed on a Siemens P3 diffractometer with graphite-monochromated Mo Kα (λ = 0.71772 Å) radiation. Structures were solved using SHELXTLPLUS software (version 5.02). An empirical absorption correction, based on azimuthal scans of six reflections, was performed. All data were corrected for Lorentz and polarization effects. The heavy atoms of the complex were located using direct methods; remaining atoms were located from subsequent difference Fourier syntheses and refined anisotropically. Hydrogen atom positions were computed by fixing the C−H distance to 0.96 Å. Details of the data collection for each complex are summarized in Table 1.

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Supporting Information Available: GPC data for polymerizations and details of the X-ray structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Caution must be used when comparing reactivity data from multiple laboratories. Changes in reaction conditions may dramatically affect the data.

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(12) Sanner, R. D.; Carter, S. T.; Bruton, W. J. *J. Organomet. Chem.* **1982**, *240*, 157−162.