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Ethylene Polymerization with Half-Sandwich Allyl Imido Complexes of Tantalum

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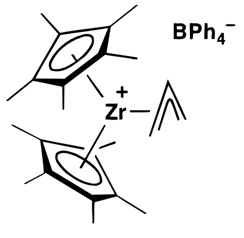
*Summary: The imido-based half-sandwich complex Cp*Ta(═N(2,6-diisopropylphenyl))(η^1-C_3H_5)(η^3-C_3H_5)* **(3)** *polymerizes ethylene in the presence of* $[(C_6H_5)_3C]^+[(C_6F_5)_4B]^-$ *or* $B(C_6F_5)_3$*, while chloride and alkyl derivatives are inactive in the presence of MAO or alkyl abstraction reagents. In contrast, however, Cp*Ta(═NSi(tert-butyl)₃)Cl₂* **(5)** *polymerizes ethylene in the presence of MAO while Cp*Ta(═NSi(tert-butyl)$_3$)(η^1-C_3H_5)(η^3-C_3H_5)* **(6)** *and Cp*Ta(═NSi(tert-butyl)$_3$)Me_2* **(4)** *are essentially inactive in the presence of alkyl abstractors.*

Since the first synthesis in the early 1980s,[1] there have been numerous suggestions that half-sandwich imido complexes of the group 5 metals would display chemistry similar to that observed for the group 4 bent metallocenes.[2,3] This has been attributed to the isolobal relationship between the two compound classes,[4] and indeed, several observations of structural and reactivity similarities have been reported for half-sandwich imido complexes of tantalum and niobium.[4,5] Despite two recent reports of olefin polymerization activity for imido complexes of vanadium, however, no reports of active catalysts derived from the heavier group 5 elements have been published.[6] Because of its small size and relative inertness, the imido ligand is an attractive alternative to many other dianionic cyclopentadienyl ligand equivalents, such as dicarbollide,[7] borollide,[8] trimethylenemethane,[9] and butadiene,[10] which have been used for Ziegler−Natta olefin polymerization. Since the imido ligand has seen extensive use in ring-opening metathesis polymerization (ROMP) chemistry[11] as a stable ancillary ligand at early transition metal centers, it might be expected to function as such in Ziegler−Natta systems.

Previous attempts to develop a niobium or tantalum half-sandwich imido catalyst for polymerization of olefins have been largely unsuccessful.[12,13] Complexes of the type [CpTa(═NR)Cl_2] and Cp*M(═NR)Cl_2 (Cp = C_5H_5; Cp* = C_5Me_5; R = *tert*-butyl, 2,6-diisopropyl; M = Nb, Ta) are not olefin polymerization catalysts in the presence of excess methylalumoxane (MAO).[14] Furthermore, it has not been possible to generate related half-sandwich alkyl cations[12b] from dialkyl precursors using a wide variety of alkyl abstraction reagents.[15] The reason for the inaccessibility of these species is not understood, but may be related to the propensity for imido transmetalation[16] or bridging to form inactive dimeric complexes.[12b]

To extend our previous investigations of group 4 metallocene bis(allyl) rearrangements[17] and the reactions of cationic permethylmetallocene allyl complexes,[18] the chemistry of the isoelectronic group 5 half-sandwich imido template was targeted for development. For zirconium, the crystalline, thermally, stable 16-electron complex $[Cp^*_2Zr(C_3H_5)]^+[BPh_4]^-$ **1** was shown to be a single-component catalyst for the polymerization of ethylene.[18a,19] The permethylzirconocene methyl and hydride cations are intractable solids or oils.[15b] Polymerization catalysis is presumably initiated by isomer-



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(1) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651.

(2) Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1994**, *11*, 1607.

(3) Antonelli, D. M.; Mountford, P.; Green, M. L. H. *J. Organomet. Chem*. **1992**, *438*, C4.

(4) (a) Gibson, V. C.; Williams, D. N.; Clegg, W.; Hockless, D. C. R. *Polyhedron* **1986**, *8*, 1819. (b) Siemling, U.; Gibson, V. C. *J. Organomet. Chem*. **1992**, *426*, C5. (c) Poole, A. D.; Gibson, V. C.; Clegg, W. *J. Chem. Soc., Chem. Commun*. **1992**, *237*. (d) Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemling, U.; Clegg, W.; Hockless, D. C. R., O'Neil, P. A.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, *9*, 739.

(5) (a) Poole, A. D.; Williams, D. N.; Kenwright, A. M.; Gibson, V. C.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A. *Organometallics* **1993**, *12*, 2549. Gibson, V. C.; Poole, A. D. *J. Chem. Soc., Chem. Commun.* **1995**, 2261.

(6) (a) CpV(═Ntol)Cl_2 (tol = toluyl) in conjunction with MAO or diethylaluminum chloride, see: Coles, M. P.; Gibson, V. C. *Polym. Bull.* **1994**, *33*, 529. An analogous niobium complex showed but marginal activity. (b) Hydrotris(pyrazolyl)borato imido complexes of vanadium, see: Scheuer, S.; Fischer, J.; Kress, J. *Organometallics* **1995**, *14*, 2627. (c) Bis(imido) complexes of chromium are also active, see: Poole, A. D.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1995**, 2261.

(7) (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126.

(8) (a) Herberich, G. E. *J. Organomet. Chem.* **1987**, *319*, 9. (b) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489.

(9) Bazan, G. C.; Rodriguez, G.; Cleary, B. P. *J. Am. Chem. Soc.* **1994**, *116*, 4489.

(10) Mashima, K.; Fujikawa, S.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 10990. Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633.

(11) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Torecki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448. (c) Parshall, G. W.; Nugent, W. A. *Chemtech* **1988**, *18*, 184.

(12) (a) Antonelli, D. M.; Mountford, P.; Green, M. L. H. *J. Organomet. Chem.* **1992**, *438*, 13. (b) Antonelli, D. M.; Gomes, P. T.; Mountford, P.; Green, M. L. H. *J. Chem. Soc. Dalton*, in press.

(13) Gibson, V. C. Personal communication to D.A., 1992.

(14) Coles, P. M.; Dalby, C. I.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1709.

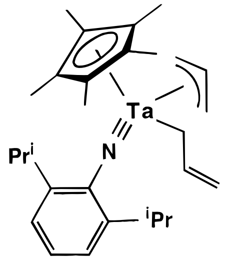
(15) (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 13, 763. (c) Turner, H. W. Eur. Patent Application 277004, 1988. (d) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991** *113*, 8570. (e) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(16) Mitchell, J. P. Ph.D. Thesis, University of Durham, Durham, U.K., 1992.

S0276-7333(97)00349-X CCC: $14.00

ization of the fluxional allyl ligand in complex **1** from η^3- to η^1-coordination to generate an active 14-electron complex. Nucleophilic addition to this complex occurs at the central carbon of the allyl ligand, supporting a bonding picture in which positive charge from the highly electrophilic metal center is delocalized onto the central carbon.[18a] These results suggested that cationic allyl complexes of the group 5 metals might be more stable than the corresponding alkyl derivatives, providing sufficient electronic stabilization to be isolated or, at a minimum, to be prepared *in situ* and used as polymerization catalysts.

Treatment of Cp*Ta(=N(2,6-diisopropylphenyl))Cl_2[4d] (**2**) with allylmagnesium bromide (2 equiv) leads to the formation of the fluxional bis(allyl) complex **3**.[20,21] Complex **3** reacts with $[Ph_3C]^+[B(C_6F_5)_4]^-$[15d] in fluorobenzene under 80 psi of ethylene to yield an orange solution. Within a few minutes formation of polyethylene is evident and after approximately 0.5 h stirring completely stops. Workup using HCl/MeOH, followed by filtration and washing of the resultant white solid with acetone, gives polyethylene, pure by infrared spectroscopy and elemental analysis.[22] An active catalyst is also obtained from complex **3** upon treatment with $B(C_6F_5)_3$[15e] (1 equiv) in fluorobenzene under ethylene. No significant polymerization is observed using this template in toluene.



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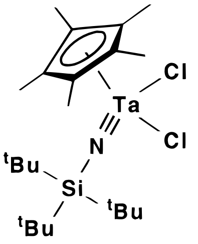
In contrast to the permethylzirconocene system, all attempts to isolate a stable cationic allyl complex from the reaction between complex **3** and $[Ph_3C]^+[B(C_6F_5)_4]^-$ lead only to the formation of intractable oils, as do other standard approaches to cation generation. The reaction between **3** and $[Cp_2Fe]^+[B(C_6F_5)_4]^-$,[23] for example, gives a paramagnetic green oil with no catalytic activity. Protonolysis using anilinium salts or treatment with $[(C_6F_5)_3B]$ leads to the isolation of intractable mixtures, which also show no catalytic activity.

To improve our understanding of the chemistry of this template, a second half-sandwich imido system was constructed. The bulky (tri-*tert*-butylsilyl)imido ligand sterically shields low-coordinate metal centers, preventing dimerization by blocking the γ-sphere of the metal while maintaining a reasonably unencumbered region in the immediate vicinity of the metal center.[24] On this basis, we anticipated that complexes of the type [Cp*M(=NSi(*tert*-butyl)$_3$)R]$^+$ (M = Nb, Ta; R = allyl, alkyl, H) would be more stable toward deactivation than those arylimido and alkylimido systems studied previously. Analogous to a previously developed procedure,[1] yellow crystalline [Cp*Ta(=NSi(*tert*-butylsilyl)$_3$)Me_2] (**4**) was prepared in 87% yield by heating Cp*TaMe$_3$Cl[25] and LiNHSi(*tert*-butyl$_3$)[24] in toluene overnight at 100 °C, followed by removal of the solvent *in vacuo*, trituration with pentane and crystallization from cold pentane.[20,21] Heating complex **4** with 2 equiv of $[^iPr_2EtNH]^+Cl^-$ in THF at 70 °C gave [Cp*Ta(=NSi(*tert*-butyl)$_3$)Cl_2] (**5**) in 84% yield after crystallization from pentane/toluene.[20,21]



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In contrast to the arylimido system, in the presence of MAO, complex **5** is an ethylene polymerization catalyst.[26] Qualitatively, it is more active than the catalyst derived from bis(allyl) complex **3**, although the

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[17] (a) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2083. (b) Casty, G. C.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7814.

[18] (a) Tjaden, E. B.; Casty, G. L.; Stryker, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 9814. See also: Tjaden, E. B. Ph.D. Dissertation, Indiana University, Bloomington, IN, 1993. (b) Antonelli, D. M.; Tjaden, E. B.; Stryker, J. M. *Organometallics* **1994**, *13*, 763.

[19] Erker has recently demonstrated that zirconocene butadiene complexes upon treatment with strong Lewis acids polymerize ethylene, a reaction proposed to proceed via intermediate formation of a cationic, boron-substituted η^3-allylic intermediate, see: Temme, B.; Erker, G.; Karl, J.; Heinrich, L.; Frolich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755.

[20] Experimental procedures and compound characterization data are included as Supporting Information.

[21] Preparative details.[20] Complex **3**: To a slurry of Cp*Ta(=N-(2,6-diisopropylphenyl))Cl_2,[4d] **2** (1.36 g, 2.42 mmol), in Et_2O (50 mL) at room temperature was added allyl magnesium chloride (2.4 mL, 2.0 M in THF, 4.8 mmol) dropwise by syringe under a nitrogen atmosphere. The resulting light yellow suspension was stirred for 2 h, diluted with pentane (50 mL), filtered through Celite, and evaporated *in vacuo* to dryness. The residue was taken up in warm pentane (30 mL), filtered through Celite, and cooled to −78 °C overnight to yield pale yellow crystals. Yield: 0.968 g (73%). Anal. Calcd for $C_{28}H_{42}NTa$: C, 58.63; H, 7.32. Found: C, 58.11; H, 7.41. ^1H NMR (C_6D_6): δ 1.38 (d, J = 8.4 Hz, 12H, CH*Me*$_2$), 1.70 (s, 15H, Me_5C_5), 3.19 (br s, 8H, H_t), 3.87 (sept J = 8.4 Hz, 2H, C*H*Me$_2$), 6.13 (quint J = 11.3 Hz, 2H, H_c), 6.96−7.28 (m, 3H, phenyl). ^1H NMR (C_7D_8, −40 °C): 3.19 (d, J = 11.3 Hz, 8H). Complex **5**: A toluene suspension (100 mL) of Cp*TaMe$_3$Cl (5.30 g, 13.33 mmol) and LiN(H)Si(^{t}Bu)$_3$[24] (2.95 g, 13.33 mmol) under nitrogen was stirred at 70 °C for 24 h, until all the lithium salt had dissolved. The solvent was removed *in vacuo*, and the orange residue was washed with pentane (2 × 10 mL), concentrated, and cooled to −40 °C to yield orange microcrystals of Cp*Ta[=NSi(^{t}Bu)$_3$]Me_2 (**4**). Yield: 4.70 g, (89%). Anal. Calcd for $C_{24}H_{48}NSiTa$: C, 51.46; H, 8.64; N, 2.50. Found: C, 51.17; H, 8.46; N, 2.44. A mixture of complex **4** (1.53 g, 2.73 mmol) and $[^iPr_2Et\ NH]^+Cl^-$ (1.13 g, 6.84 mmol) were heated to reflux in tetrahydrofuran (50 mL) for 24 h. The solvent was removed under reduced pressure, and the residue was triturated with toluene and filtered through Celite. Concentration, layering with pentane, and cooling to −40 °C gave 1.38 g (84%) Cp*Ta[=NSi(^{t}Bu)$_3$]Cl_2 (**5**) as bright yellow crystals. Anal. Calcd for $C_{22}Cl_2H_{42}NSiTa$: C, 43.96; H, 7.04; N, 2.33. Found: C, 44.59; H, 7.30; N, 2.46. ^1H NMR (C_6D_6): δ 1.95 (s, 15H, Me_5C_5), 1.34 (s, 27H, ^{t}Bu).

[22] The catalyst generated from complex **3** and $[Ph_3C]^+[B(C_6F_5)_4]^-$ in fluorobenzene at room temperature functions modestly, with an activity of 38 000 g of polyethylene per mol of catalyst per hour. The polymer obtained was completely soluble in 1,2,4-trichlorobenzene at 140 °C, giving an average molecular weight of 1.29 × 10^6 and polydispersity (D) of 17.4 by GPC analysis.[20] The broad molecular weight distribution strongly suggests that this system does not produce a single-site catalyst.

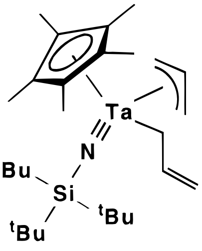
[23] Campbell, R. E., Jr. Eur. Pat. Appl. EP 421659; *Chem. Abstr.* **1991**, *115*, 72440j. The blue crystalline reagent is prepared by precipitation of the ferricinium cation from water on addition of LiB-$(C_6F_5)_4$, a procedure completely analogous to the preparation of the tetraphenylborate salt.

[24] See, for example: (a) Schaller, C. P.; Bonanno, J. B.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 4133. (b) Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

[25] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2396.

very different polymerization procedures preclude any direct comparison. Why complex **5** is active under these conditions and the other half-sandwich imido complexes in this series are not is poorly understood, but it can be tentatively attributed to the bulkiness of the *tert*-butyl groups, which may prevent dimerization of the active catalyst or inhibit MAO attack on the basic imido nitrogen center.

For comparison, the bis(allyl) silylimido complex **6** was prepared by treatment of complex **5** with allylmagnesium bromide (2 equiv) in diethyl ether.[20] The ^{1}H-NMR spectrum of **6** exhibits two signals in a 1:4 ratio for the central and terminal protons, respectively, of the allyl ligands, indicative of rapid equilibration between η^3- and η^1-allyl coordination modes.[18a] An X-ray crystal structure determination of complex **6** confirms that the allyl ligands are η^1- and η^3-coordinated in the solid state (Figure 1) and shows that the Ta−N−Si bond angle is a nearly linear 175.7(3)°,[20] similar to that observed in related complexes.[27]



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Surprisingly and in contrast to the closely analogous complex **3**, however, bis(allyl) complex **6** is not an ethylene polymerization catalyst in the presence of $[Ph_3C]^+[B(C_6F_5)_4]^-$ or $B(C_6F_5)_3$. Dimethyl complex **4** is also inactive in the presence of a variety of alkyl abstraction reagents previously used to activate dimethylzirconocene complexes toward olefin polymerization. These results are, at present, most difficult to rationalize.

In summary, imido-based Ziegler−Natta catalysts have been prepared through the use of ligands known to stabilize highly reactive, coordinatively unsaturated, Lewis acidic metal centers. Although some interesting but as yet difficult to understand observations have been made, these results demonstrate that the imido ligand can provide an alternative to other dianionic cyclopentadienyl analogues in the construction of group 5 olefin polymerization catalysts. This work also demonstrates that the allyl ligand is capable of supporting polymerization activity in a catalyst system for which the corresponding alkyl derivatives fail. Taken together, these results reveal that very subtle changes in precatalyst structure and activation can lead to dramatic differences in the resulting catalyst structure and activity. Further investigation is intended to define the specific function of the allyl ligand and evaluate its potential application to other catalyst systems.

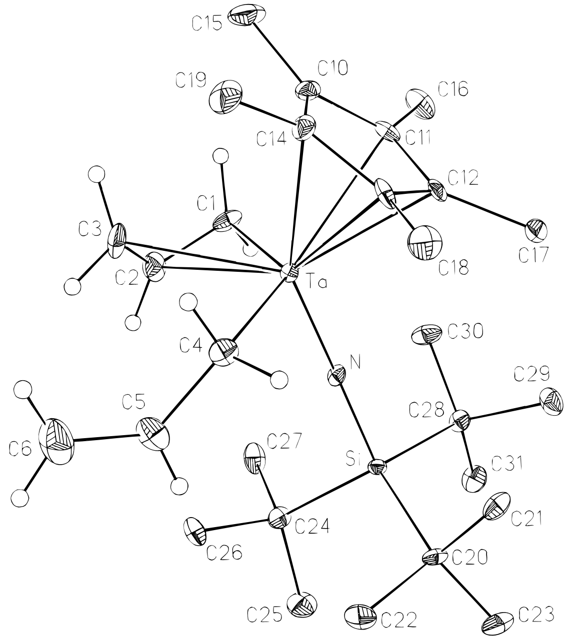

Figure 1. ORTEP diagram of Cp*Ta(=NSi(*tert*-butyl)$_3$)(η^1-C_3H_5)(η^3-C_3H_5), **6** (most hydrogen atoms omitted for clarity).[20] Selected bond distances (Å): Ta−N, 1.799(5); N−Si, 1.735(5); Ta−C1, 2.307(7); Ta−C2, 2.400(7); Ta−C3, 2.492(7); Ta−C4, 2.265(7); C1−C2, 1.406(11); C2−C3, 1.381(11); C4−C5, 1.470(11); C5−C6, 1.309(11). Selected bond angles (deg): Ta−N−Si, 175.7(3); C1−C2−C3, 121.6(8); Ta−C1−C2, 76.3(4); Ta−C3−C2, 70.0(4); C4−C5−C6, 128.2(9); Ta−C4−C5, 119.8(5). Final residuals: $R_1 = 0.0308$, $wR_2 = 0.0738$.

Acknowledgment. We are particularly grateful to Dr. Peter Hoang and NOVA Chemicals, Ltd., of Calgary, Alberta, for the GPC analyses of polymer products. We also thank Dr. Bob McDonald of the University of Alberta Structure Determination Laboratory for the X-ray crystallography. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta Department of Chemistry is gratefully acknowledged.

Supporting Information Available: Text giving the experimental, spectroscopic, and analytical data for complexes **3**−**6**, the polymerization experiments, and the crystallographic details for complex **6** and tables of the GPC experimental conditions, calibration procedure, molecular weight in polystyrene equivalents, and crystallographic data, atomic coordinates, bond distances, and bond angles for **6** (11 pages). Ordering information is given on any current masthead page.

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(26) Polymerization procedure: To a Fischer−Porter bottle containing MAO (200 equiv) in toluene (5 mL) at room temperature under ethylene pressure (65 psi) was added a solution of compound **5** (50.6 mg, 0.083 mmol) in 5 mL of toluene. Polymerization was stopped after 20 min by addition of 6N HCl−MeOH (1:1, 20 mL). The recovered polyethylene was washed with MeOH and dried *in vacuo* to a constant weight (1.686 g). The activity under these conditions was 61 000 g of polyethylene per mol of catalyst per h. A significant portion of the material obtained was insoluble in 1,2,4-trichlorobenzene at 140 °C, reflecting the production of high molecular weight polymer. The soluble portion was analyzed by GPC, giving an average molecular weight = 1.09×10^6 and $D = 3.6$.

(27) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley Interscience: New York, 1988.