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Cationic Alkylzirconium Complexes Based on a Tridentate Diamide Ligand: New Alkene Polymerization Catalysts

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Summary: Alkyl abstraction from $\{Me_3SiN(CH_2CH_2NSiMe_3)_2\}ZrR_2$ (N_3ZrR_2; $R = CH_2Ph$, *Me) using* $B(C_6F_5)_3$ *affords cationic alkyl complexes stabilized by a diamide ligand. The ionic* η^2*-benzyl adduct decomposes slowly to give a cationic cyclometalation product, which coordinates the* $[PhCH_2B(C_6F_5)_3]^-$ *anion; the methyl cation coordinates the anion* $[MeB(C_6F_5)_3]^-$ *via a* $Zr\cdots Me-B$ *interaction. The complexes exhibit moderate ethene polymerization activity.*

The search for alternatives to group 4 metallocenes as electrophilic "uniform site" catalysts for alkene polymerization is currently of great interest.[1,2] Much attention has focused on nitrogen-containing ligands ($[L]^-$ or $[L_2]^{2-}$), such as porphyrins,[3] tetraaza[14]-annulenes,[4] tetradentate Schiff base ligands,[5] (hydroxyphenyl)oxazolines,[6] and benzamidinates.[7] Unfortunately ethene polymerization activities (for L_2MCl_2/methylaluminoxane or $[L_2MR]^+$; M = Ti, Zr, Hf) have been generally disappointing.[4−7] In contrast, and despite the application of dicyclopentadienyl and cyclopentadienylamide catalysts in kiloton-scale industrial processes, diamide complexes (the next family in this series) have received little attention in the patent[8] or scientific literature.[9−14] This is surprising considering the facile synthesis of diamide complexes as catalyst precursors[9−14] and the expected increased electrophilicity of diamide cations compared to analogues with polydentate nitrogen ligands. A program to probe the potential of diamide ligands in polymerization has now lead to the first alkene polymerization catalysts based on cationic diamide complexes. Recent reports[13,14] of *neutral* group 4 adducts of the new tridentate ligand $[Me_3SiN(CH_2CH_2NSiMe_3)_2]^{2-}$ lead us to report here our work involving *cationic* group 4 alkyl adducts of this ligand.

New crystalline dialkyl precursors of putative cationic complexes have been prepared from the readily available dichlorozirconium complex **1**[15,16] using standard alkylation methodology (Scheme 1).[17,18] The observation of ^{1}H NMR resonances (C_6D_5Br) for inequivalent benzyl (**2**, −20 °C) or methyl groups (**3**, 25 °C), as well as four different backbone dimethylene hydrogens,[19] is consistent with coordination of the amino nitrogen to zirconium in a trigonal bipyramidal structure. Fluxional exchange of the environments of the axial and equato-

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[11] For recent work on complexes of other d^0 metals with chelating diamide or triamide ligands, see the following and references therein: (a) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 11015. (b) Freundlich, J. S.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

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[15] Preparation of **1** proceeds via reaction of $Me_3SiN(CH_2CH_2NLiSiMe_3)_2$ (N_3Li_2) with $ZrCl_4$ in Et_2O (44% yield). The triamine, N_3H_2, is very easily prepared (>95% purity) by reaction of a small excess of Me_3SiCl with $HN(CH_2CH_2NH_2)_2$ in hexane, followed by removal of the amine hydrochloride byproduct by filtration and reduction to dryness.[13]

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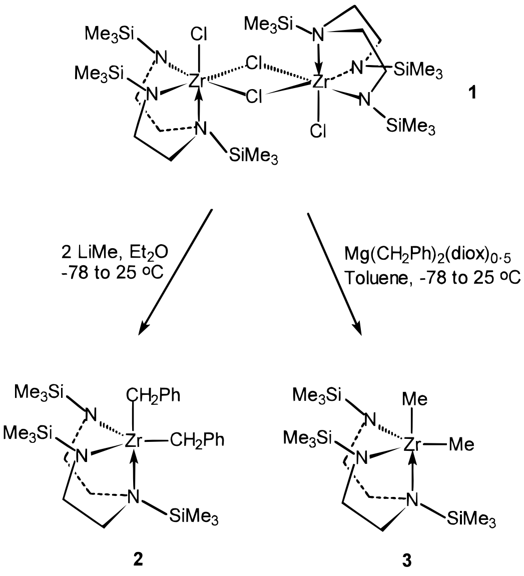
[17] Synthesis of **2**: Toluene (20 mL) at −78 °C was added to a mixture of **1** (3.1 mmol) and $Mg(CH_2Ph)_2(dioxane)_{0.5}$ (3.9 mmol). After the solution was warmed to 25 °C, the solvent was removed and **2** crystallized from pentane at −40 °C (0.84 g, 45%). Synthesis of **3**: To a suspension of **1** (0.41 mmol) in Et_2O (10 mL) at −78 °C was added an Et_2O solution of LiMe (0.83 mmol). After the solution was warmed to 25 °C, the solvent was removed and **3** crystallized from hexane at −40 °C (0.104 g, 58%). Synthesis of **5**: Toluene (0.5 mL) and bromobenzene (0.1 mL) were added to a mixture of **2** (0.19 mmol) and $B(C_6F_5)_3$ (0.19 mmol) at −30 °C. After the solution was stirred at 25 °C for 16 h, hexane (5 mL) addition afforded a precipitate, which was washed with hexane and dried, giving pure **5**. Typical NMR experiment: C_6D_5Br (0.7 mL) at −30 °C was added to a mixture of **2** or **3** and $B(C_6F_5)_3$ (each 0.01 mmol) in a 10 mL bottle at −30 °C, followed by rapid warming to 0 °C and transfer to an NMR tube. Although **4**, **6**, and **9** are formed quantitatively (>95% NMR purity), attempts to isolate the complexes in analytically pure crystalline form have not been successful.

[18] Reaction of **1** with LiMe in Et_2O was recently reported to give an intractable mixture.[13]

[19] The complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy and (for **2**) elemental analysis. The NMR data supports η^1-benzyl coordination in **2**: *ipso* C, δ 146.8 ppm; $ZrCH_2$, δ 72.1, 64.0 ppm ($^1J_{CH}$ = 120, 124 Hz); *ortho* H, δ 6.86, 6.78 ppm.

S0276-7333(96)00073-8 CCC: $12.00

Scheme 1



rial benzyls and of the dimethylene hydrogens in **2**, observed at 25 °C, presumably involves dissociation of the amino nitrogen, inversion at nitrogen, and recoordination.[14] The greater lability of the amino nitrogen in **2** than in dimethyl **3** (two sharp Zr*Me* ^{1}H NMR resonances at 25 °C: δ 0.55 and 0.46 ppm) might reflect stabilization of the 4-coordinate species by η^2-benzyl coordination.[19]

Abstraction of a benzyl group from **2** with $B(C_6F_5)_3$ in C_6D_5Br or $C_2D_2Cl_4$ solution cleanly affords a soluble product, **4**;[17] in toluene **4** is deposited as a yellow precipitate. The complex has been shown by ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy[20] to consist of a benzylzirconium cation[21] and a noncoordinated $[PhCH_2B(C_6F_5)_3]^-$ anion (Scheme 2).[22] The pseudotetrahedral complex is stabilized by η^2-coordination of the benzyl ligand (giving a maximum 14-electron count at Zr), as shown by the large $^1J_{CH}$ value of 142 Hz for the ZrCH_2 group (δ 68.7 ppm) and the upfield *ipso* carbon (δ 137.5 ppm) and *ortho* hydrogen resonances (δ 6.38 ppm).[23] An identical cation (in addition to free NMe_2Ph or Ph_3CCH_2Ph) is obtained using $[PhMe_2NH][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$.

Solutions of **4** (with $[PhCH_2B(C_6F_5)_3]^-$ as anion) decompose slowly (16 h, 25 °C), with elimination of 1 equiv of toluene, to give a single organometallic product,[17] which may be precipitated with hexane. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy[20] and elemental analysis have confirmed that orange solid **5** is the product of C−H activation of one of the amido $SiMe_3$ groups in **4** (Scheme 2). Ligand activation is reflected in the observation of four different Si*Me* resonances (1:1:3:3) and a diastereotopic SiCH_2Zr group (δ 0.70, 0.37, $^2J_{HH}$ = 13.2 Hz). The zirconium cation is stabilized by coordination of the benzylborate anion,[22] as shown, in particular, by the downfield *ipso* carbon resonance (δ 161.0 ppm; free anion, δ 148.6 ppm) and the large value of $\Delta\delta(m,p\text{-F})$ of 3.9 ppm (free anion, 2.7 ppm) in the ^{19}F NMR spectrum.[24]

In contrast to ionic **4**, the methyl complex **6**, obtained from the reaction of dimethyl **3** with $B(C_6F_5)_3$ in C_6D_5Br,[17] exhibits a covalent bonding interaction between the cation, $[N_3ZrMe]^+$, and the $[MeB(C_6F_5)_3]^-$ anion (Scheme 3).[25] Anion cordination is reflected in the downfield location of the B*Me* resonance (δ 1.38 ppm; free anion δ 1.13 ppm) and the large value of $\Delta\delta(m,p\text{-F})$ of 4.4 ppm.[24] The Zr*Me* group resonates at δ 0.65 ppm (^{1}H NMR) and at δ 55.1 ppm (^{13}C NMR), slightly upfield of dimethyl **3**.

Analogous methyl cations may be obtained by protonolysis (**7**) or reaction with the trityl reagent (**8**) in C_6D_5Br solution (Scheme 3).[17,20] Cation **7** is stabilized by NMe_2Ph coordination (downfield *ortho* and *para* hydrogen resonances).[17,26] For complex **8**, it is not possible to distinguish between possible weak solvent and anion coordination to the zirconium cation. The location of the Zr*Me* resonance in the complexes (**7**, δ 0.77 ppm; **8**, δ 0.75 ppm), slightly downfield from **6**, may reflect increased metal electrophilicity (compared to the THF adduct of **6**: δ 0.48 ppm).

Formation of methyl cations **7** and **8** proceeds via an intermediate species, **9**, cleanly obtained using 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ (Scheme 3).[17,20] Further reaction of **9** with another 0.5 equiv of the reagent affords **8** (20 min, 25 °C). Complex **9** exhibits two Zr*Me* resonances (δ 0.51, 2 Me; δ 0.48 ppm, 1 Me), as well as resonances for two equivalent and symmetric $\{N_3Zr\}$ fragments (2:1 ratio of $SiMe_3$ groups, four backbone methylene hydrogens). These data are consistent with a structure in which a methyl group bridges two $[N_3ZrMe]^+$ fragments, similar to recently reported metallocene complexes, $[\{Cp'_2ZrMe\}_2(\mu\text{-}Me)]^+$.[27] Again, it is clear that a methyl group of a group 4 dimethyl complex can act as an effective donor for an electrophilic metal center.

Preliminary reactivity studies of the cationic complexes have revealed moderate ethene polymerization activity but very low propene activity. A 20-fold excess of ethene is rapidly polymerized (<5 min, 25 °C) by C_6D_5Br solutions of **4** or **6**−**8** in an NMR tube; the conversion of 20 equiv of propene (to propene oligomers) is incomplete after 15 min. In all cases only a small

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(20) Selected NMR data (see also text) (^{1}H NMR, C_6D_5Br, 25 °C, unless otherwise stated) are as follows. **4**: δ 7.24 (*p*-BzZr), 7.19 (*m*-BzZr), 3.36 (BCH_2), 3.17, 2.99, 2.81 (4H, 2H, 2H, NCH_2), 2.69 (ZrCH_2), 0.22, −0.21 (18H, 9H, SiMe_3). ^{13}C NMR ($C_2D_2Cl_4$, −35 °C): δ 136.1, 130.5 (2C, *o,m*-BzZr), 129.3 (*p*-BzZr), 52.7, 49.6 (2C, NCH_2), 32 (1C, BCH_2), 0.7, −1.2 (6C, 3C, SiMe_3). ^{19}F NMR: δ −131.63 (d), −165.13 (t), −167.85 (m). **5**: δ 7.2 (*o,m*-Bz), 6.68 (*p*-Bz), 3.6−2.2 (NCH_2, BCH_2), 0.16, 0.12, −0.02, −0.03 (3H, 9H, 3H, 9H, SiMe_3). ^{13}C NMR: δ 161.0 (1C, *ipso*-Bz), 50.9, 50.1, 50.0, 49.9 (1C, NCH_2), 34.5 (ZrCH_2), 0.9 (1C, Si*Me*), −0.6, −0.7, −1.1 (3C, 3C, 1C, Si*Me*). ^{19}F NMR: δ −131.96 (d), −162.09 (t), −165.98 (m). **6**: δ 3.65 (2H, NCH_2), 3.1−2.8 (4H, NCH_2), 2.47 (2H, CH_2), 0.00, −0.01 (18H, 9H, SiMe_3). ^{13}C NMR (C_6D_5Br, −25 °C): δ 15.7 (B*Me*). ^{19}F NMR: δ −133.68 (d), −161.26 (t), −165.64 (m). **7**: δ 7.24 (*m*-Ph), 7.12 (*p*-Ph), 6.88 (*o*-Ph), 2.69 (s, 6H, NMe_2). ^{13}C NMR ($C_2D_2Cl_4$, −25 °C): δ 61.5 (Zr*Me*). **9**: δ 3.55, 3.16, 2.84, 2.48 (4H, NCH_2), 0.15, −0.07 (36H, 18H, SiMe_3).

(21) Schematic representation of one of two possible trigonal bipyramidal isomers (axial/equatorial groups exchanged) for **4** and **6**−**9** is arbitrary. A single species is observed spectroscopically.

(22) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

(23) (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (b) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633.

(24) The value of $\Delta(m,p\text{-F})$ (^{19}F NMR) is a good probe of coordination of $[RB(C_6F_5)_3]^-$ (R = Me, CH_2Ph) to cationic d^0 metals (values 3−6 ppm indicate coordination; <3 ppm indicates noncoordination): Horton, A. D. Unpublished results.

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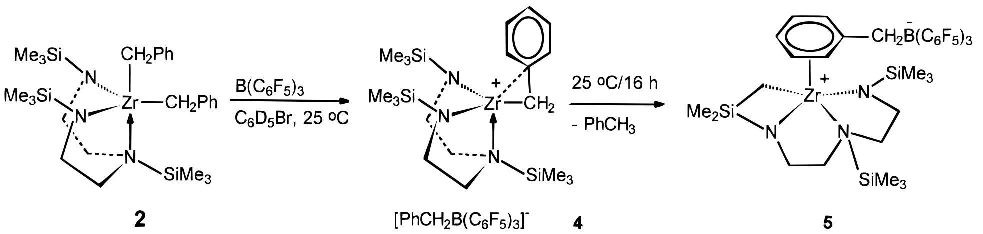
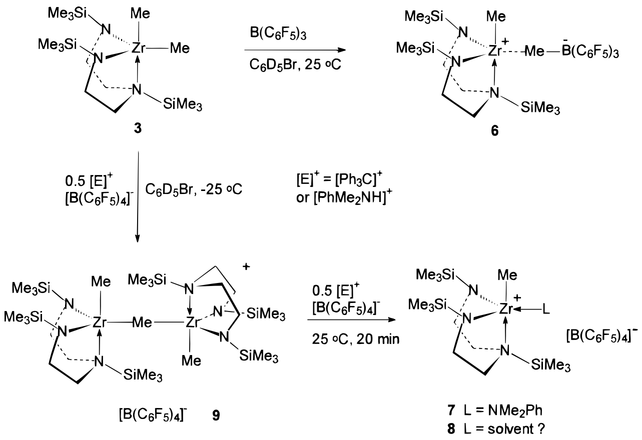
(26) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910.

(27) The proximity of the two Zr*Me* resonances is surprising as in $[\{(C_5H_5)_2ZrMe\}_2(\mu\text{-}Me)]^+$ the μ-Me resonates ca. 1 ppm upfield of the terminal methyl: Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

Scheme 2



Scheme 3



amount of the cation reacts (giving unidentified products), reflecting slower initiation than propagation in polymerization. In an autoclave experiment, benzyl cation **4** (0.2 mmol, 7.1 bar ethene, 200 mL toluene, 25 °C, 1 L autoclave) afforded 11.0 g of polyethene in 10 min (rate 3600 g/g of Zr•h; GPC analysis, $M_w = 230\,000$, $M_n = 52\,200$). The deviation of the polydispersity ($M_w/M_n = 4.4$) from the ideal uniform site value of 2 is partly ascribed to the nonisothermal nature of the polymerization (exotherm of +55 °C within 90 s). A similar reaction with propene (6.6 bar, 60 min) gave 0.45 g of atactic propene oligomers (^{1}H NMR: $CH_2{=}C(R)Me$ end groups, $M_n = 5600$), corresponding to a rate of 20 g/g Zr•h.

The new tridentate diamide ligand affords a relatively robust framework for cationic group 4 alkyl complexes. Although the ligand is subject to degradation by C−H activation of a $SiMe_3$ group adjacent to zirconium, the reaction is much slower than that found by us for other amide ligands.[28] Similar to the situation for cationic alkylmetallocenes, the cationic η^2-benzyl adduct of the tridentate ligand is a rather weak electrophile,[23b] whereas the methyl cation coordinates the $[MeB(C_6F_5)_3]^-$ anion, NMe_2Ph, or even N_3ZrMe_2. This work has shown that cationic diamide systems can function as effective ethene polymerization catalysts. The low propene reactivity may reflect a general inertness of four-coordinate diamide cations toward coordination and insertion of alkenes larger than ethene. In other studies, we have found that three-coordinate analogues exhibit higher activity toward propene.[28]

Supporting Information Available: Text and a table providing full details of the preparation, characterization, and alkene reactivity of the compounds (11 pages). Ordering information is given on any current masthead page.

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(28) Horton, A. D.; de With, J. *Chem. Commun.*, in press.