Alkene polymerization by a cationic zirconium diamide complex formed by ligand cyclometallation

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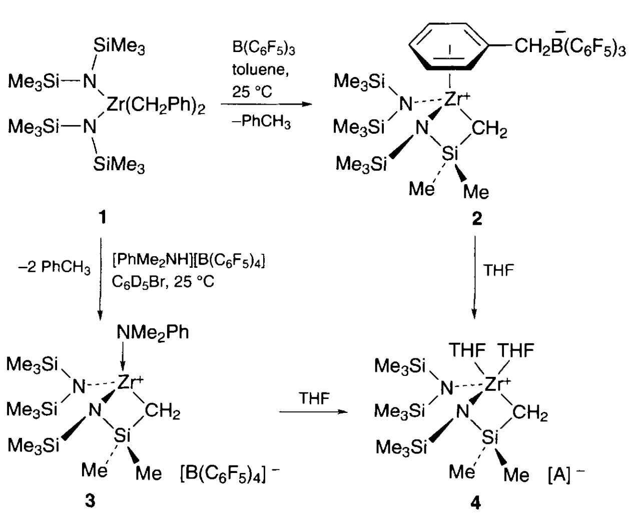
Reaction of $\{(Me_3Si)_2N\}_2Zr(CH_2Ph)_2$ 1 with $B(C_6F_5)_3$ gives a cationic benzyl complex, which at −25 °C, expels toluene to afford $\{(Me_3Si)_2N\}\overline{Zr(CH_2SiMe_2N}SiMe_3)\{\eta^n\text{-}PhCH_2\text{-}B(C_6F_5)_3\}$ 2; strong anion coordination to zirconium in cyclometallation product 2 suppresses alkene polymerization, whereas the analogous cationic NMe_2Ph adduct 3, formed by protonolysis of 1, polymerizes both ethene and propene.

Metallocene[1] and cyclopentadienyl-amide catalysts[2] based on Group 4 metals are applied in kiloton-scale ethene copolymerization processes, but diamide complexes,[3] which represent the next family in this series, have received little attention.[4] This is surprising considering the facile synthesis of neutral diamide complexes[3,5] as potential catalyst precursors and the expected increased electrophilicity of putative diamide cations compared to cyclopentadienyl analogues. We recently reported the first alkene polymerization catalysts based on a cationic Group 4 diamide complex.[6] We postulated that the very low propene reactivity of this system may reflect hindered coordination and insertion of alkenes larger than ethene due to the tridentate nature of the (amino diamide) ligand. In an attempt to obtain a potentially more reactive three-coordinate zirconium cation, we investigated a precursor containing two very bulky amide ligands,[5] $\{(Me_3Si)_2N\}_2Zr(CH_2Ph)_2$ **1**. We now report that initial alkyl abstraction in this system is followed by amide ligand cyclometallation under mild conditions (−25 °C) giving cations which are alkene polymerization catalysts.

The new crystalline dibenzyl complex, **1**, may be prepared by treatment of the dichloride[5] with $Mg(CH_2Ph)_2(dioxane)_{0.5}$ in Et_2O solvent. Mixing pentane solutions of complex **1** and $B(C_6F_5)_3$ at 25 °C results in the instantaneous precipitation of yellow complex **2** in quantitative yield (Scheme 1); analytically pure crystals may be obtained from dichloromethane–hexane solution at −40 °C. Solutions of **2** in toluene, bromobenzene or 1,1,2,2-tetrachloroethane are stable (21 h, 25 °C); in dichloromethane decomposition occurs over several hours. Pseudotetrahedral complex **2**, has been shown by ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopy to contain a four-membered Zr–C–Si–N ring, an amide ligand, $N(SiMe_3)_2$, and coordinated benzylborate anion.†



Scheme 1

Confirmation of amide cyclometallation[7] in **2** is provided by the observation of a 1 : 1 : 9 pattern of Si*Me* resonances (CD_2Cl_2, 25 °C; two coincident) together with diastereotopic $ZrCH_2$ resonances (δ 2.20 and 1.86, $^2J_{HH}$ 14.0 Hz). Coordination[8] of $[PhCH_2B(C_6F_5)_3]^-$ to the asymmetric zirconium centre leads to broad resonances for a diastereotopic BCH_2 group (δ 3.37 and 3.19) and five inequivalent phenyl hydrogens, which resonate far downfield of the free anion [in brackets]: *m*, δ_H 7.67, 7.59 [6.88]; *p*, δ_H 7.49 [6.78]; *o*, δ_H 7.37, 7.26 [6.74]. Interestingly, in C_7D_8 solution, the *meta* and *para* phenyl resonances are found upfield of the free anion: *m*, δ_H 6.41 (accidentally equivalent); *p*, δ_H 6.11; *o*, δ_H 7.21, 7.10.[8] The downfield benzyl *ipso* carbon resonance at δ_C 160.9 (free anion: δ_C 148.5) and the large value of $\Delta\delta$ (*m,p*-F) of 4.1 ppm (free anion: 2.7 ppm) in the ^{19}F NMR spectrum‡ are also consistent with anion coordination. On warming (C_7D_8) the anion ^1H NMR resonances broaden, and at 70 °C a 2 : 2 : 1 phenyl resonance pattern and a single broad BCH_2 resonance may be observed, whilst the cation resonance pattern remains unchanged. These results are consistent with anion dissociation giving a contact ion pair (without inversion at zirconium) at high temperatures.[9]

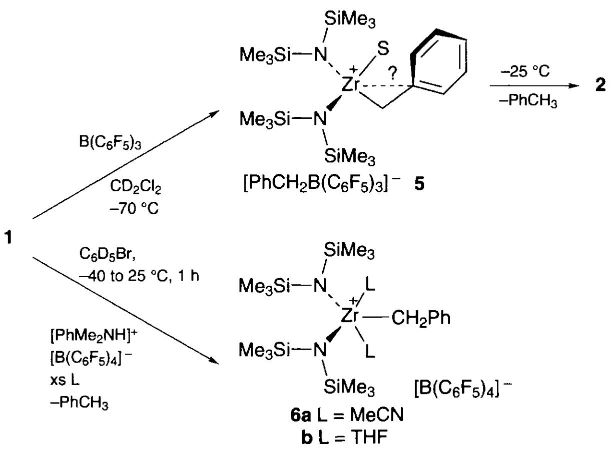
Protonolysis of **1** with $[PhMe_2NH][B(C_6F_5)_4]$ in C_6D_5Br solution cleanly affords complex **3**, in which NMe_2Ph coordinates to the cyclometallated cation (Scheme 1). The complex is deposited as a pale yellow oil on hexane addition, but decomposes on attempted crystallization. Similar to **2**, the complex exhibits resonances for diastereotopic $ZrCH_2$ and $SiMe_2$ groups (−25–50 °C, C_6D_5Br).† Although coordination of NMe_2Ph *via* the nitrogen[10] is supported by the observation of inequivalent N*Me* resonances and 2 : 1 : 2 N*Ph* resonances (^1H and ^{13}C NMR), participation of the benzene ring in bonding,[8] in a fluxional structure analogous to **2**, cannot be ruled out. The coordinated anion in **2**, or base in **3** is displaced by excess THF giving bis-THF adduct **4** (^1H, ^{13}C NMR), isolated as a colourless oil

An intensely coloured yellow intermediate in the formation of **2** may be generated by careful addition of $B(C_6F_5)_3$ to a CD_2Cl_2 solution of complex **1** at −70 °C in an NMR tube. The cationic benzyl complex **5** (Scheme 2), is stable at −70 °C, but is cleanly converted to **2**, with elimination of equimolar toluene, over 2 h at −25 °C. Intermediate **5** exhibits ^1H and ^{19}F NMR resonances indicative of non-coordination of the $[PhCH_2B(C_6F_5)_3]^-$ anion to the benzylzirconium cation, particularly characteristic being the low value of $\Delta\delta$ (*m,p*-F) of 3.0 ppm (^{19}F NMR).†,‡ The upfield location of the Zr-benzyl *ortho* hydrogen resonance at δ_H 6.98 is consistent with η^1-benzyl coordination.[11] The formally 10-electron cation may, perhaps, be stabilized by dichloromethane coordination.§

The benzyl cation may also be trapped as base adducts, **6a** and **6b**, by protonolysis of **1** in the presence of excess MeCN or THF, respectively (Scheme 2). Preliminary ^1H NMR studies indicate that the stable cations (C_6D_5Br, 25 °C), isolated by precipitation with hexane, coordinate two molecules of Lewis base and exhibit η^1-benzyl coordination (o-H: δ_H 6.81 and > 6.9, respectively, for **6a** and **6b**).

Preliminary studies have shown that **3** exhibits higher alkene reactivity than **2**. In ethene polymerization, respective rates of 34 000 and 1000 g/mol Zr bar h were observed (7.1 bar, 25 °C).¶ Complex **3** affords polypropene [$CH_2=C(Me)R$ end groups], with rates of 4600 g/mmol Zr bar h at 25 °C (6.5 bar, M_n 50 000) and 980 g/mol Zr bar h at 60 °C (6.5 bar; M_n 7300), whereas **2** is inert.¶ The atactic polymer structure contrasts to patent claims of isotactic polypropene formation using a related catalyst.[4] In NMR tube experiments (25 °C, C_6D_5Br) excess ethene (< 1 bar) is instantaneously polymerized by **3**, but slowly consumed (hours) by **2**. Similarly, propene (30 equiv.) is rapidly polymerized by **3** (< 5 min), but shows no reaction with **2**. Slower initiation than propagation is reflected in the high proportion of unreacted complex in these reactions: only in the reaction of **3** with propene (75 equiv.), is conversion of the complex (to unidentified products) > 50%. Possible initiation mechanisms include alkene insertion into the metallacycle 4-ring (with eventual β-hydrogen elimination–transfer), and a σ-bond metathesis reaction[12] of $RCH=CH_2$ with the Zr–CH_2 bond giving $[\{(Me_3Si)_2N\}_2Zr(CH=CHR)]^+$.

Although cyclometallation is a persistent feature of the chemistry of the $N(SiMe_3)_2$ ligand,[8] we have found that cation generation accelerates this process. For comparison, preliminary results indicate that the neutral complex, $\{(Me_3Si)_2N\}_2ZrBn_2$, undegoes ligand activation on thermolysis (60 °C, 1 h).[7] Conversion of the initially formed benzyl cation to **2** or **3** is expected to be thermodynamically favoured by stronger coordination of crowded $[PhCH_2B(C_6F_5)_3]^-$ or NMe_2Ph, respectively, to the cyclometallated cation than to the more crowded intermediate.[8,10] Cyclometallation is suppressed by strong base coordination, reflecting the necessity for a vacant coordination site for σ-bond metathesis.[12] The first ionic diamide catalyst for propene polymerization has been identified. Differences in the strength of ligand coordination to zirconium [NMe_2Ph < $\{PhCH_2B(C_6F_5)_3\}^-$] may help to explain the greater alkene reactivity of **3** than **2**. This study has shown that ligand degradation[13] does not necessarily lead to catalyst deactivation in d^0 metal polymerization chemistry.



Scheme 2

Footnotes

† *Selected NMR data* (^1H NMR assignments based on 2-D COSY experiments). For **2**: ^1H NMR (CD_2Cl_2, 25 °C): δ_H 0.36, 0.33 (3 H, Si*Me*$_2$), 0.24 (27 H, Si*Me*$_3$). ^{13}C NMR ($C_2D_2Cl_4$, −30 °C): δ_C 131.1, 130.8 (2 C, Bn), 124.5 (p-Bn), 69.7 (t, $^1J_{CH}$ 125 Hz, $ZrCH_2$), 36 (vbr, BCH_2), 5.0, 4.8 (3 C, 6 C, $SiMe_3$), 3.6, 3.3 (1 C, $SiMe_2$). ^{19}F NMR (CD_2Cl_2, 25 °C): δ_F −133.03 (d), −163.43 (t), −167.47 (m). For **3**: ^1H NMR (C_6D_5Br, −25 °C): δ_H 7.19 (2 H, m-Ph), 6.60 (1 H, p-Ph), 6.39 (2 H, o-Ph), 2.64, 2.61 (3 H, NMe_2), 1.34, 1.12 (d, $^2J_{HH}$ 14.0 Hz, 1 H, $ZrCH_2$), 0.21 (3 H, $SiMe_2$), 0.08. 0.05 (9 H, 18 H, $SiMe_3$), 0.01 (3 H, $SiMe_2$). ^{13}C NMR ($C_2D_2Cl_4$, −25 °C): δ_C 132.9, 128.6 (o/m-PhN), 113.2 (p-PhN), 66.7 (t, $^1J_{CH}$ 129 Hz, $ZrCH_2$), 42.0, 41.7 (NMe_2), 4.8, 4.6 (6 C, 3 C, $SiMe_3$), 4.3, 3.1 (1 C, $SiMe_2$). For **5**: ^1H NMR (CD_2Cl_2, −70 °C): δ_H 7.74 (2 H, m-BnZr), 7.44 (1 H, p-BnZr), 6.98 (2 H, o-BnZr), 6.84 (2 H, m-BnB), 6.79 (1 H, p-BnB), 6.63 (2 H, o-BnB), 3.30 (2 H, $ZrCH_2$), 2.68 (br, 2 H, BCH_2), 0.21 (36 H, $SiMe_3$). ^{19}F NMR (CD_2Cl_2, −70 °C): δ_F −131.93 (m), −163.97 (m) and −166.99 (m).

‡ The value of $\Delta\delta$ (m,p-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 non-coordination): A.D. Horton, unpublished results.

§ In C_7D_8 solution (−60 to −25 °C) two benzyl intermediates are formed [4 : 1; distinct $N(SiMe_3)_2$, BCH_2Ph and $ZrCH_2Ph$ resonances] and converted to **2** at −25 °C (1 h).

¶ Polymerization conditions: 0.2 mmol catalyst, 200 ml toluene, 1 l jacket-cooled steel autoclave, 30 min (ethene) or 180 min (propene). **3**/Ethene: exotherm of 34 °C. Polyethene GPC analysis: for **2** M_w = 284 000, M_n = 16 300, M_w/M_n = 17.4. For **3**: M_w = 414 000, M_n = 49 000, M_w/M_n = 8.4.

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