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Monoalkyl, chiral-at-metal 'constrained geometry' complexes as efficient α-olefin and methyl methacrylate polymerisation catalysts

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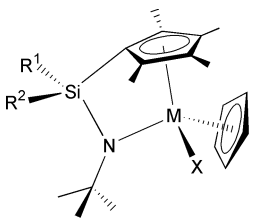
A new class of monoalkyl or monochloro constrained geometry group 4 complexes has been synthesized; upon activation with aluminium activators they serve as efficient catalysts for olefin polymerisation and for polymerisation of methyl methacrylate.

Constrained geometry complexes such as $Me_2Si(C_5Me_4)(t\text{-BuN})–MX_2$ (CGC–MX_2, M = Ti, Zr; X = Cl, alkyl) are currently of great scientific and technological interest as highly active Ziegler–Natta-type coordination catalysts for copolymerization of ethylene and α-olefins.[1] It has been reported that the pre-activated form of group 4 metallocene and related complexes must have two or more alkyl (or halide or other suitable) groups so that there is a remaining metal–alkyl bond for monomer to insert into after one of the metal–alkyl groups is abstracted to form the activated species.[2]

We have previously reported that a doubly activated constrained geometry Ti complex, which does not contain a free alkyl ligand in its activated form, is also a highly active olefin polymerisation catalyst.[3] Most recently, Royo *et al.*[4] reported that, when activated with methylaluminoxane (MAO),[5] a doubly silylamido-bridged cyclopentadienyl zirconium benzyl complex is active for ethylene polymerisation. These reports prompted us to disclose here a new class of monoalkyl or monochloro, chiral-at-metal[6] constrained geometry complexes (**1**–**6**) and their use as precursors to efficient catalysts, upon activation with aluminium activators, for olefin polymerisation and for polymerisation of methyl methacrylate (MMA).



1, M = Ti, X = Cl, $R^1 = R^2$ = Me
2, M = Zr, X = Cl, $R^1 = R^2$ = Me
3, M = Ti, X = Cl, R^1 = Me, R^2 = Ph
4, M = Zr, X = Cl, R^1 = Me, R^2 = Ph
5, M = Ti, X = Me, $R^1 = R^2$ = Me
6, M = Zr, X = Me, $R^1 = R^2$ = Me

Complexes **1** and **2** were prepared from the reaction of sodium cyclopentadienide in THF with the corresponding dichloride precursors in greater than 80% yield.[7] Complexes **3** and **4** were synthesized in the same manner, however, the products are a mixture of two isomers in ~1:1 ratio as a result of dissymmetric silyl bridging. These two isomers can be separated by fractional recrystallization from a solvent mixture of toluene and hexanes. Both ^1H and ^{13}C NMR data indicate the Cp ligand is η^5-bonded to the metal for complexes **1**–**6**, all of which have been characterized spectroscopically and analytically, and complex **6** has also been characterized crystallographically (Fig. 1).†

Reaction of **1** with MeLi in diethyl ether produced a 6:1 ratio of the monomethyl derivative (**5**) and the unexpected dimethyl derivative CGC–$TiMe_2$ (**7**).[8] Formation of **7** can be avoided by replacing MeLi with MeMgBr, and thus a clean formation of **5** was observed which was isolated in 84% yield.‡ The analogous reaction of **2** with MeLi in diethyl ether cleanly produced the Zr derivative **6** which was isolated in 91% yield. In contrast to the formation of **7**, the dimethyl Zr complex was not observed, even upon addition of a one-fold excess of MeLi.

While the dimethyl CGC titanium complex **7** is active for MMA polymerization upon activation with both $B(C_6F_5)_3$[9] and $Al(C_6F_5)_3$,[10] producing syndiotactic PMMA of 80.7 and 66.0% syndiotacticity at 25 °C, respectively, the MMA polymerization by the monomethyl complex **5** strongly depends on the choice of activator: the borane-activated complex is inactive but the alane-activated complex is as active as **7**. Furthermore, when activated with a large excess of MAO, the monochloro Zr complex **2** is highly active for copolymerization of ethylene and 1-octene with activity reaching 1.8×10^8 g polymer (mol Zr)$^{-1}$ h^{-1} (conditions: 2.0 μmol **2**, MAO/Zr = 500, T_p = 120 °C, 740 g Isopar E, 118 g C_8, 450 psi C_2, 5 mmol H_2, t_p = 15 min, yield = 89.4 g). In contrast, the analogous Ti complex **1** is practically inactive yielding only 2.0 g of the copolymer even with 10 μmol catalyst loading. This trend holds true for propylene polymerisation: the monochloro Zr complex **4** is more active than the monomethyl Ti complex **5**, with both complexes producing essentially atactic polypropylene.

To seek for possible answers for the sharp difference in polymerisation activity between the Ti and Zr catalysts, **5** was reacted with $B(C_6F_5)_3$ yielding CGC–Ti^+(Cp)[$MeB(C_6F_5)_3$]$^-$ (**8**). The non-coordinating nature of the borate anion is suggested by the small $\delta(\delta_m - \delta_p)$ = 2.59 ppm in the ^{19}F NMR of the anion.[11] On the other hand, the reaction of the Zr complex **6** with $Al(C_6F_5)_3$ produces CGC–Zr^+(Cp)$MeAl(C_6F_5)_3^-$ (**9**) in which the aluminate anion is weakly coordinated to the Zr cation, as evidenced by the chemical shifts[3,12] of the CH_3 group of the anion in the ^1H NMR and of the C_6F_5 groups in the ^{19}F NMR (Fig. 2). An excess of the alane does not effect the abstraction of the Cp ligand.

On the basis of this study, the inactivity of the MMA polymerization by complex **5** when activated with $B(C_6F_5)_3$ can be attributed to the formation of the separated ion pair **8** in which there is no metal–alkyl group to initiate MMA polymer-

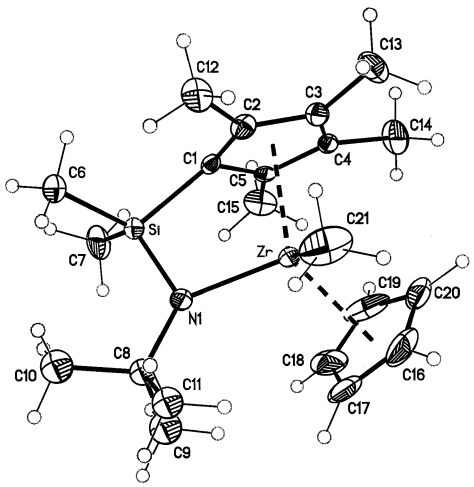


Fig. 1 The molecular structure of **6**. Selected bond lengths and angles (Å, °): Zr–N 2.129(2), Zr–C(21) 2.283(8), Zr–Me_4Cp 2.225, Zr–Cp 2.281, N–Zr–Me_4Cp 101.2, N–Zr–Cp 111.4.

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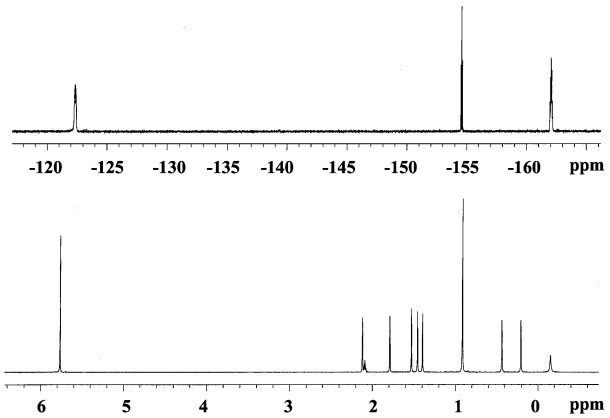
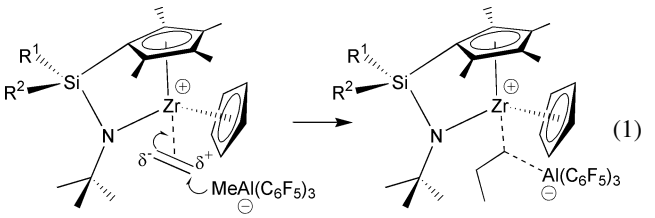


Fig. 2 NMR spectra of **9** in toluene-d_8, 23 °C. Top: ^{19}F NMR spectrum; bottom: ^{1}H NMR spectrum. Resonances at 2.10 (s) and 2.09 (m) are from toluene in the alane (used as a toluene adduct) and the NMR solvent, repectively.

isation.[13] The efficient MMA polymerization with the same complex, but activated with the alane, can be explained with a different mechanism *via* enolaluminates.[14] For olefin polymerisation by the Zr catalysts, the observations that excess of the alane does not effect the abstraction of the Cp ligand from **9** and that the olefinic region of a low molecular weight polypropylene sample by **4** shows only vinylidene (β-H elimination, 80%) and allyl (β-Me elimination, 20%) end groups argue that the olefin monomer is unlikely to be inserted into the Zr–Cp bond. The initiation step presumably involves nucleophilic attack on the polarized olefin (**10**) and formation of Zr···CH_2(R)···Al bonds (**11**) [eqn. (1)], a bimetallic mechanism resembling that originally proposed by Natta and Mazzanti.[15]



(1)

In summary, mono-alkyl or -chloro CGC Zr complexes demonstrate high olefin polymerisation activity when activated with aluminum activators. The current finding that group 4 metal complexes containing a *single* insertable or abstractable metal-alkyl bond can be activated for olefin polymerisation significantly expands the polymerisation catalyst library by including a class of monoalkyl and –chloro metal complexes.

Notes and references

† *Crystal data* for complex **6**: $C_{21}H_{35}NSiZr$, M = 420.81, orthorhombic, space group $Pna2_1$, a = 15.8874(7) , b = 10.2802(4) , c = 13.2006(6) Å, V = 2156.0(2) Å^3, Z = 4, D_c = 1.296 Mg m^{-3}, T = 173(2) K, μ(Mo-Kα) = 0.568 mm^{-1}; 15448 reflections measured, 4674 unique (R_{int} = 0.0349), F^2 refinement, R_1 = 0.0351 ($I > 2\sigma(I)$), wR_2 = 0.993 (all data). CCDC reference number is 179845. See http:/www.rsc.org/suppdata/ccb2/b201346k/ for crystallographic data in CIF or other electronic format.

‡ $Me_2Si(Me_4C_5)$(*t*BuN)Ti(Cp)Cl (**1**): NMR: ^{1}H (300 MHz, C_6D_6): δ 5.86 (s, 5H, Cp), 2.48, 1.82, 1.77, 1.59 (s, 3H, Me_4C_5), 1.35 (s, 9H, *t*Bu), 0.61, 0.25 (s, 3H, Me_2Si). ^{13}C{^{1}H} (75 MHz, C_6D_6): δ 137.7, 135.5, 129.6, 125.4, 114.3, 109.4, 63.7, 34.2, 16.8, 15.1, 12.9, 12.8, 9.7, 6.1. Anal. $C_{20}H_{32}NClSiTi$, found (calc.): C, 60.09 (60.37); H, 7.95 (8.11); N, 3.34 (3.52%).

$Me_2Si(Me_4C_5)$(*t*BuN)Zr(Cp)Cl (**2**): NMR: ^{1}H (300 MHz, C_6D_6): δ 5.97 (s, 5H, Cp), 2.36, 1.85, 1.81, 1.67 (s, 3H, Me_4C_5), 1.29 (s, 9H, *t*Bu), 0.61, 0.38 (s, 3H, Me_2Si). ^{13}C{^{1}H} (75 MHz, C_6D_6): δ 132.7, 130.2, 126.1, 122.9, 112.9, 106.2, 57.7, 35.2, 15.6, 14.5, 12.3, 12.2, 10.1, 6.7. Anal. $C_{20}H_{32}NClSiZr$, found (calc.): C, 54.25 (54.44); H, 7.18 (7.31); N, 2.97 (3.17%).

Ph(Me)Si(Me_4C_5)(*t*BuN)Ti(Cp)Cl (**3**, isomer A): NMR: ^{1}H (300 MHz, C_6D_6): δ 7.61 (m, 2H, Ph), 7.24 (m, 3H, Ph), 5.95 (s, 5H, Cp), 2.59, 1.83, 1.46, 1.24 (s, 3H, Me_4C_5), 1.47 (s, 9H, *t*Bu), 0.94 (s, 3H, *Me*PhSi). ^{13}C{^{1}H} (75 MHz, C_6D_6): δ 142.88, 138.07, 137.39, 135.52, 130.02, 129.70, 128.32, 127.16, 115.43 (Cp), 110.56, 64.46, 34.32, 17.13, 14.65, 13.45, 13.30, 8.35. **3**, isomer B: NMR: ^{1}H (300 MHz, C_6D_6): δ 7.98 (m, 2H, Ph), 7.05 (m, 3H, Ph), 5.97 (s, 5H, Cp), 2.02, 1.72, 1.65, 1.52 (s, 3H, Me_4C_5), 1.47 (s, 9H, *t*Bu), 0.70 (s, 3H, *Me*PhSi). Anal. $C_{25}H_{34}ClNSiTi$, found (calc.): C, 65.17 (65.28); H, 7.39 (7.45); N, 2.88 (3.05%).

Ph(Me)Si(Me_4C_5)(*t*BuN)Zr(Cp)Cl (**4**, isomer A): NMR: ^{1}H (300 MHz, C_6D_6): δ 7.96, (dd, 2H, Ph), 7.27 (m, 3H, Ph), 6.06 (s, 5H, Cp), 1.84, 1.83, 1.71, 1.55 (s, 3H, Me_4C_5), 1.38 (s, 9H, *t*Bu), 0.83 (s, 3H, *Me*PhSi). ^{13}C (C_6D_6): δ 143.76, 137.27, 136.29, 130.50, 129.72, 128.90, 128.24, 125.20, 113.31 (Cp), 104.64, 58.58, 36.09, 15.64, 14.62, 13.12, 11.68, 6.66. **4**, isomer B: NMR: ^{1}H (300 MHz, C_6D_6): δ 7.72 (dd, 2H, Ph), 7.27 (m, 3H, Ph), 6.06 (s, 5H, Cp), 2.46, 1.86, 1.55, 1.30 (s, 3H, Me_4C_5), 1.39 (s, 9H, *t*Bu), 0.94 (s, 3H, *Me*PhSi). ^{13}C (C_6D_6): δ 143.51, 135.51, 133.18, 132.23, 129.68, 126.22, 125.34, 121.28, 113.80 (Cp), 106.86, 58.47, 35.45, 16.02, 14.27, 12.79, 12.65, 8.33. Anal. $C_{25}H_{34}ClNSiZr$, found (calc.): C, 59.49 (59.66); H, 7.05 (6.81); N, 2.60 (2.78%).

$Me_2Si(Me_4C_5)$(*t*BuN)Ti(Cp)Me (**5**): NMR: ^{1}H (300 MHz, C_6D_6): δ 5.67 (s, 5H, Cp), 2.22, 1.83, 1.56, 1.42 (s, 3H, Me_4C_5), 1.27 (s, 9H, *t*Bu), 0.59, 0.47 (s, 3H, Me_2Si), 0.20 (s, 3H, MeTi). ^{13}C{^{1}H} (75 MHz, C_6D_6): δ 131.25, 129.96, 124.18, 119.92, 111.41 (Cp), 104.84, 61.31, 35.56, 33.82, 15.93, 16.36, 12.85, 11.44, 8.84, 8.38. Anal. $C_{21}H_{35}NSiTi$, found (calc.) C, 66.59 (66.82); H, 9.10 (9.34); N, 3.58 (3.71%).

$Me_2Si(Me_4C_5)$(*t*BuN)Zr(Cp)Me (**6**): NMR: ^{1}H (300 MHz, C_6D_6): δ 5.80 (s, 5H, Cp), 2.25, 1.93, 1.61, 1.60 (s, 3H, Me_4C_5), 1.20 (s, 9H, *t*Bu), 0.60, 0.48 (s, 3H, Me_2Si), −0.07 (s, 3H, MeZr). ^{13}C{^{1}H} (75 MHz, C_6D_6): δ 128.81, 124.20, 123.69, 120.42, 110.64 (Cp), 103.18, 56.55, 35.96, 22.82, 15.84, 14.66, 12.52, 11.62, 10.35, 7.69. Anal. $C_{21}H_{35}NSiZr$, found (calc.): C, 59.65 (59.94); H, 8.12 (8.38); N, 2.77 (3.33%).

$Me_2Si(Me_4C_5)$(*t*BuN)Ti$^+$(Cp)MeB$(C_6F_5)_3^-$ (**8**): NMR: ^{1}H (300 MHz, C_7D_8): δ 5.75 (s, 5H, Cp), 1.78, 1.47, 1.21, 1.10 (s, 3H, Me_4C_5), 1.23 (s, 9H, *t*Bu), 0.54, 0.12 (s, 3H, Me_2Si), 0.47 (s, 3H, MeB). ^{19}F (282 MHz, C_7D_8): δ −131.78 (d, 6F, *o*-F), −164.25 (t, 3F, *p*-F), −166.84 (m, 6F, *m*-F).

$Me_2Si(Me_4C_5)$(*t*BuN)Zr$^+$(Cp)MeAl$(C_6F_5)_3^-$ (**9**): NMR: ^{1}H (300 MHz, C_7D_8): δ 5.76 (s, 5H, Cp), 1.79, 1.52, 1.45, 1.39 (s, 3H, Me_4C_5), 0.91 (s, 9H, *t*Bu), 0.43, 0.20 (s, 3H, Me_2Si), −0.15 (s, 3H, MeAl). ^{19}F (282 MHz, C_7D_8): δ –122.35 (d, 6F, *o*-F), −154.58 (t, 3F, *p*-F), −162.07 (m, 6F, *m*-F).

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