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PAPER

Titanium "constrained geometry" complexes with pendant arene groups†

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The synthesis of the proligands $C_5Me_4HSiMe_2N(H)R)$ (R = CMe_2Ph **1**, 2-C_6H_4Ph **2**) was accomplished *via* a straightforward salt metathesis reaction of the appropriate lithium amide and $ClSiMe_2(C_5Me_5H)$. Generation of the dilithio salt and reaction with $TiCl_3{\cdot}(THF)_3$ followed by oxidation gave $C_5Me_4SiMe_2N(C_6H_4Ph)TiCl_2$ (**3**) in low yield. In contrast, deprotonation of **1** and **2** and reaction with $(Me_2N)_2TiCl_2$ afforded $C_5Me_4(SiMe_2NR)Ti(NMe_2)_2$ (R = CMe_2Ph **4**, 2-C_6H_4Ph **5**), respectively, in good yields Treatment with MeI gave the analogs $C_5Me_4(SiMe_2NR)TiI_2$ (R = CMe_2Ph **6**, 2-C_6H_4Ph **7**). Reduction of **7** with potassium graphite afforded $C_5Me_4(SiMe_2NC_6H_4Ph)Ti$ **8**. Treatment of **6** and **7** with MeMgBr afforded $C_5Me_4(SiMe_2NR)TiMe_2$ (R = CMe_2Ph **9**, 2-C_6H_4Ph **10**). Complexes **9** and **10** in combination with the activator $[Ph_3C][B(C_6F_5)_4]$ catalyzed the polymerization of styrene and ethylene. Copolymerization was also investigated. While the catalyst derived from **10** showed poor activity, compound **9** showed markedly higher activity than **10** and $(C_5Me_4)SiMe_2(N\mathit{t}Bu)]TiMe_2$.

Introduction

While metallocenes of the type Cp'_2MR_2 (M = Ti or Zr; R = alkyl) remain precursors of the most active and well understood olefin polymerisation catalysts systems, new catalysts are continually sought to provide new polymer microstructures and circumvent existing patents.[1,2] Soon after Bercaw and coworkers reported the synthesis and olefin polymerization activity of an *ansa*-bridged cyclopentadienyl-amido (Cp-amido) scandium complex, (Fig. 1(a)),[3,4] Okuda reported the synthesis of a related complex of titanium (Fig. 1(b),(c)),[5] and patents for processes utilizing similar group IV systems in ethylene homo- and copolymerisations were filed.[6,7] Such Cp-amido systems have been dubbed "constrained geometry catalysts" (CGCs), as the *ansa*-bridge necessitates an "opening-up" of the metal centre that is believed to enhance monomer coordination.

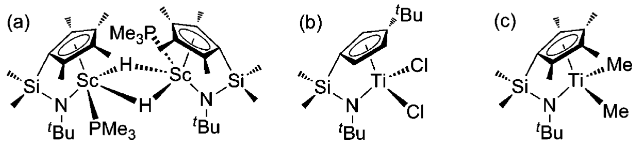

Fig. 1 CGC Complexes.

The prototypical CGC is a titanium catalyst incorporating a permethylated Cp′ group and a *tert*-butyl group on the nitrogen centre (Fig. 1), but the term CGC has been applied to a wide variety of ligand scaffolds that incorporate an assortment of main group elements bonded to various early transition metals.[8] An application where the use of CGCs offers enhanced productivity over classical group IV metallocenes is that of ethylene copolymerisations with α-olefins.[9] CGCs have been shown to effect superior comonomer incorporation in copolymerisations of ethylene and styrene, in contrast to copolymersations with classical metallocenes.[7,10] This is surprising considering typical CGCs demonstrate poor activities in the homopolymerisation of styrene.[7] In this case, catalyst deactivation is believed to result from intramolecular coordination of the phenyl ring of a 2,1 inserted monomer.[11] This seems plausible given the intramolecular arene coordination observed in related CGC benzyl cations.[12]

Marks and coworkers have developed catalyst systems with higher activities than prototypical CGC systems for the polymerization of styrene. They have found that binuclear CGC systems are more active in these polymerizations and hypothesized that arene coordination of the growing polymer chain occurs at the opposite metal centre, thereby allowing for monomer coordination to the metal centre that is the site of propagation.[11] This group has also demonstrated that typical CGC catalysts can be used to promote the polymerization of styrene in the presence of multiple equivalents of secondary and tertiary silanes; here amplification of the polymerization activity is believed to be a result of displacement of Ti···Ph interactions *via* the formation of weak Ti···H–SiR_3 contacts.[13] A variety of substituted CGC-based catalysts have been developed and examined.[14,15] For example, Waymouth and co-workers have explored the impact of electron-withdrawing substituents on N,[16] while Yang *et al.* have employed sterically demanding arene substituents on N.[17] While in these cases the arene fragment modifies the donor capacity, the groups of Hessen[18–27] and Bochmann[28,29] have probed the interactions of

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early metal systems with pendant arenes on Cp ligands. Arriola and coworkers have developed CGC polymerization catalysts with arene systems extending from the Cp unit (Fig. 1).[30] These catalysts were found to increase styrene incorporation in ethylene–styrene copolymerisations presumably a result of interaction of the extended π-system with the phenyl ring of an incoming monomer.[31] The Stephan group showed that the pendant arene in biphenylphosphinimide complexes of group IV metals stabilized metal cations.[32] The synthesis of CGC-type precatalysts with pendant phenyl groups on the nitrogen substituent were targeted with these precedents in mind. Synthetic methods to obtain these species have been developed and an initial assessment of the derived catalysts in ethylene and styrene polymerization is described.

Experimental section

General considerations

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glove box. Solvents (pentane, hexanes, toluene, diethyl ether, THF and methylene chloride) were purified employing a Grubbs' type column systems manufactured by Innovative Technology and stored over either a potassium mirror (toluene, diethyl ether, and pentane) or molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 200 °C under vacuum for 3 h prior to use. Deuterated solvents were dried over Na/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br) and vacuum distilled prior to use. All common organic reagents were purified by conventional methods unless otherwise noted. ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-400 spectrometer at 300 K unless otherwise noted. ^{1}H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR experiments were referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. Combustion analyses were performed in-house employing a Perkin Elmer CHN Analyzer. $[Ph_3C][B(C_6F_5)_4]$ and $[(C_5Me_4)SiMe_2(N\mathit{t}Bu)]TiCl_2$ were generously donated by NOVA Chemicals Corporation. $PhCMe_2NH_2$ was purchased from TCI Chemicals and used as received. $ClSiMe_2(C_5Me_5H)$ and $PhC_6H_4NH_2$ were purchased from Aldrich chemicals and used as received. $(Me_2N)_2TiCl_2$[33] and $[(C_5Me_4)SiMe_2(N\mathit{t}Bu)]TiMe_2$[7] were synthesized *via* literature procedures. High temperature GPC data were provided by the Department of Chemistry, Cornell University, Ithaca, NY.

Synthesis of ($C_5Me_4HSiMe_2N(H)R$) (R = CMe_2Ph 1, 2-C_6H_4Ph 2). These compounds were synthesized *via* a similar procedure, therefore only one synthesis is described. A solution of $PhMe_2CN(H)Li$ (prepared *via* the 1 : 1 reaction of *n*BuLi and cumyl amine: 4.5 g, 4.25 mmol) in THF (100 mL) was cooled to –78 °C and added slowly, *via* cannula, to a solution of $Cp'Me_2SiCl$ (9.131 g, 4.25 mL), also at –78 °C. After the addition was complete the solvent was removed *in vacuo* and the product distilled under vacuum to afford a bright yellow-green oil (12.0 g, 94%). ^{1}H NMR (CD_2Cl_2) : 7.50 (d, 2H $^{3}J_{H-H}$ = 8 Hz, *o*-C_6H_4); 7.32 (t, 2H, $^{3}J_{H-H}$ = 7 Hz, *m*-C_6H_4); 7.21 (tt, 1H, $^{3}J_{H-H}$ = 8 Hz, $^{4}J_{H-H}$ = 1 Hz, *p*-C_6H_4); 2.86 (s, 1H, Cp′*H*); 2.03 (s, 6H, Cp′*Me*); 1.89 (s, 6H, Cp′*Me*); 1.51 (s, 6H, CMe_2Ph); 0.91 (s, 1H, N*H*); 0.06 (s, 6H, SiMe_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 153.0, 135.9, 133.8, 128.4, 128.4, 126.3, 126.0, 57.5, 54.6, 34.1 (CMe_2Ph), 15.2 (Cp′*Me*), 11.6 (Cp′*Me*), 1.8 (SiMe_2).

2: White crystalline solid, 2.15 grams, 65%. ^{1}H NMR (CD_2Cl_2): 7.4 (t, 2H, $^{3}J_{H-H}$ = 7 Hz, *m-Ph*), 7.3 (m, 3H), 7.2 (t, 1H, $^{3}J_{H-H}$ = 7 Hz), 7.1 (dd, 1H, $^{3}J_{H-H}$ = 7 Hz,$^{4}J_{H-H}$ = 2 Hz), 6.9 (d, 1H, $^{3}J_{H-H}$ = 8 Hz), (td, 1H, $^{3}J_{H-H}$ = 7 Hz,$^{4}J_{H-H}$ = 1 Hz), 3.6 (s, 1H, N*H*), 3.0 (s, 1H Cp′*H*), 1.8 (s, 6H, Cp′*Me*), 1.7 (s, 6H, Cp′*Me*), 0.2 (s, 6H, SiMe_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 145.0, 140.4, 136.8, 132.7, 131.1, 130.3, 129.8, 129.4, 128.8, 127.7, 118.0 (*Cp′*), 116.0 (*Cp′*), 55.0 (*Cp′*), 14.5 (Cp′*Me*), 11.4 (Cp′*Me*), –1.5 (SiMe_2). EA calc'd for $C_{23}H_{29}NSi$ (347.577) C, 79.48; H, 8.41; N, 4.03; Found: C, 79.25, H, 9.24, N, 3.95. X-ray quality crystals were grown by slow cooling of a solution in pentane.

Synthesis of $C_5Me_4SiMe_2N(C_6H_4Ph)TiCl_2$ (3). A solution of **2** (815 mg, 2.34 mmol) in THF (250 mL) was cooled to –78 °C, at which point *n*BuLi (1.5 mL, 4.8 mmol) was added dropwise while the reaction mixture was stirred with a magnetic stirrer bar. After the addition was complete the reaction mixture was warmed to room temperature with a water bath, then subsequently cooled to –78 °C. This mixture was then transferred dropwise, *via* cannula, to a stirring slurry of $TiCl_3(THF)_3$ (869 mg, 2.34 mmol) in THF (200 mL) which had also been cooled to –78 °C. After the addition was complete, the reaction mixture was warmed to room temperature and the solvent removed *in vacuo*. The reaction mixture was then transferred to the glovebox, where the mixture was re-dissolved in diethyl ether (200 mL) and filtered through Celite, at which point silver chloride (336 mg, 2.34 mmol) was added. The solvent was removed under reduced pressure and the mixture extracted into toluene (100 mL) and filtered through Celite. The solution was cooled to –35 °C after which the supernatant liquid was removed from yellow, needle-like crystals (105 mg, 10%). Removal of solvent *in vacuo* from the supernatant liquid afforded an oil that contained little of **3**, evidenced by ^{1}H NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): 7.5 (dm, 2H, $^{3}J_{H-H}$ = 7 Hz), 7.3–7.2 (m, 5H), 7.2–7.1 (m, 2H), 2.3 (s, 6H, Cp′*Me*), 2.1 (s, 6H, Cp′*Me*), 0.1 (s, 6H, SiMe_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 148.9, 143.9, 141.5, 139.0, 134.9, 132.1, 128.54, 128.46, 127.5, 125.8, 125.4, 106.5, 16.7 (Cp′*Me*), 13.7 (Cp′*Me*), 2.2 (SiMe_2). EA calc'd for $C_{23}H_{27}NSiCl_2Ti$ (464.345) C, 59.49; H, 5.86; N, 3.02; Found: C, 59.0, H, 5.82, N, 2.59.

Synthesis of $C_5Me_4(SiMe_2NR)Ti(NMe_2)_2$ (R = CMe_2Ph 4, 2-C_6H_4Ph 5). These compounds were synthesized *via* a similar procedure, therefore only one synthesis is described. A solution of **1** (544 mg, 1.8 mmol) in THF (20 mL) was cooled to –35 °C at which point *n*BuLi (2.25 mL, 1.6 M in hexanes) was added dropwise, with stirring, over a period of 3 min, during which time the solution went from colourless to a clear, deep yellow. This solution was allowed to warm to room temperature over a period of 45 min after which it was cooled to –35 °C and added dropwise to a solution of $(Me_2N)_2TiCl_2$[33] (373 mg, 1.8 mmol) in THF (35 mL) which was also at –35 °C. The reaction mixture changed from a dark red solution to an orange/white slurry over the course of the addition. The reaction was warmed to room temperature and stirred for an additional hour. The solvent was removed under reduced pressure after which dichloromethane was added (10 mL) and the mixture filtered through Celite. Removal of the solvent *in vacuo* and subsequent washing with cold (–35 °C) pentane (2 × 3 mL) afforded an orange crystalline solid (632 mg, 78%) ^{1}H NMR (CD_2Cl_2) (300.048 MHz): 7.39 (m, 2H, *o*-C_6H_4); 7.24 (m, 2H, *m*-C_6H_4); 7.16 (m, 1H, *p*-C_6H_4); 3.11 (s, 12H, N*Me*$_2$); 2.10 (s, 6H, Cp′*Me*); 2.02 (s, 3H, Cp′*Me*); 1.70 (s, 6H, C*Me*$_2$Ph); 0.07 (s, 6H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): 153.00(*ipso*-Ph); 128.03 (Ph); 127.78 (Cp′); 127.39 (Cp′); 126.99(Ph); 126.20 (Ph); 101.30 (*ipso*-Cp′); 64.36 (*C*Me$_2$); 50.44 (N*Me*$_2$); 33.49 (C*Me*$_2$); 14.11 (Cp′*Me*); 12.59 (Cp′*Me*); 5.89 (Si*Me*$_2$). EA calc'd for $C_{24}H_{41}N_3SiTi$ (447.576) C, 64.01; H, 9.23; N, 9.39. Found: C, 64.18, H, 9.24, N, 9.27. X-ray quality crystals were grown by slow cooling of a solution in pentane.

5: Bright orange crystals, 731 mg, 94%. ^{1}H NMR (CD_2Cl_2): 7.4 (dm, 2H, $^3J_{H-H}$ = 7 Hz), 7.3 (t, 2H, $^3J_{H-H}$ = 7 Hz), 7.2 (tm, 1H, $^3J_{H-H}$ = 7 Hz), 7.1 (tm, 2H, $^3J_{H-H}$ = 7 Hz), 6.9 (td, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 1 Hz), 6.8 (d, 1H, $^3J_{H-H}$ = 8 Hz), 2.9 (s, 12H, N*Me*$_2$); 2.2 (s, 6H, Cp′*Me*); 2.1 (s, 3H, Cp′*Me*); 0.2 (s, 6H, Si*Me*$_2$).^{13}C{^{1}H} NMR (CD_2Cl_2): 153.8, 143.5, 136.1, 131.6, 131.0, 130.9, 129.4, 128.2, 128.0, 127.9, 127.5, 126.6, 121.6, 102.2, 48.2 (N*Me*$_2$), 14.6 (Cp′*Me*), 12.1 (Cp′*Me*), 3.96 (Si*Me*$_2$). EA calc'd for $C_{27}H_{39}N_3SiTi$ (481.593) C, 67.34, H, 8.16; N, 8.73. Found: C, 67.42, H, 8.42, N, 8.82. X-ray quality crystals were grown by slow cooling of a solution in pentane.

Synthesis of $C_5Me_4(SiMe_2NR)TiI_2$ (R = CMe_2Ph 6, 2-C_6H_4Ph 7). These compounds were synthesized *via* a similar procedure, therefore only one synthesis is described. **6**: To a solution of **4** (1.525 g, 3.4 mmol) in CH_2Cl_2 (10 mL) was added iodomethane (0.5 mL, 80.2 mmol) in one portion. The solution darkened from yellow orange to dark red, concomitant with the formation of a white precipitate. The mixture was stirred for 12 h, after which the solution was filtered through Celite and the solvent removed from the filtrate *in vacuo*. The resulting solid was washed with cold pentane (2 × 5 mL) to afford a red microcrystalline solid (2.01 g, 96%). ^{1}H NMR (CD_2Cl_2) (300.048 MHz): 7.5 (dm, 2H, $^3J_{H-H}$ = 8 Hz, *o-Ph*), 7.3 (tm, 2H, $^3J_{H-H}$ = 8 Hz, *m-Ph*), 7.2 (tm, 1H, $^3J_{H-H}$ = 8 Hz, *p-Ph*), 2.6 (s, 6H, Cp′*Me*), 2.3 (s, 6H, C*Me*$_2$), 2.1 (s, 6H, Cp′*Me*), 0.1 (s, 6H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): 150.8, 146.6, 143.0, 130.9, 129.8, 129.0, 107.9 (*ipso*-Cp′); 69.5 (*C*Me$_2$), 35.3 (C*Me*$_2$), 21.6 (Cp′*Me*), 18.7 (Cp′*Me*), 6.2 (Si*Me*$_2$). EA calc'd for $C_{20}H_{29}NSiTiI_2$(613.232) C, 39.17; H, 4.77; N, 2.28 Found: C, 39.21; H, 4.86; N, 2.50. X-ray quality crystals were grown by slow evaporation of a solution in dichloromethane.

7: Bright red crystals, 935 mg, 98%. ^{1}H NMR (CD_2Cl_2): 7.7 (dd, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz), 7.6 (m, 2H), 7.4–7.2 (m, 6H), 2.6 (s, 6H, Cp′*Me*), 2.1 (s, 6H, Cp′*Me*), 0.1 (s, 6H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): 149.2, 146.4, 141.4, 133.7, 132.5, 131.9, 128.6, 128.4, 128.3, 127.5, 125.9, 106.8, 19.4 (Cp′*Me*), 16.9 (Cp′*Me*), 2.4 (Si*Me*$_2$). EA calc'd for $C_{23}H_{27}NSiTiI_2$ (647.249) C, 42.68; H, 4.20; N, 2.16. Found: C, 42.45, H, 4.48, N, 2.06. X-ray quality crystals were grown by slow evaporation of a solution in dichloromethane.

Synthesis of $C_5Me_4SiMe_2N(C_6H_4Ph)Ti$ (8). Potassium graphite (122 mg, 0.9 mmol) was added to a solution of **7** (292 mg, 0.45 mmol) in THF (35 mL) in portions over a period of 5 min during which time the red solution became a dark brown slurry. This reaction mixture was stirred for an additional 2 h after which the solvent was removed *in vacuo*. Hexanes (15 mL) were added and the mixture filtered through Celite to afford a dark brown solution, which was concentrated under reduced pressure to approximately half the original volume. This solution was cooled to −35 °C overnight to afford dark brown crystals (55 mg, 31%). The supernatant hexanes were concentrated and cooled to −35 °C overnight to afford a second crop of crystals (17 mg) for an overall yield of 41%. ^{1}H NMR (C_6D_6): 6.92 (dd, 1H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz), 6.84 (td, 1H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz), 6.30 (td, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz), 6.24 (dm, 1H, $^3J_{H-H}$ = 8 Hz), 3.99 (dd, 2H, $^3J_{H-H}$ = 6 Hz, $^4J_{H-H}$ = 1 Hz), 3.22 (dd, 2H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 6 Hz), 2.43 (s, 6H, Cp′*Me*), 1.63 (tt, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz), 0.99 (s, 6H, Cp′*Me*), 0.49 (s, 6H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 156.0, 144.2, 126.4, 124.6, 124.4, 121.2, 117.5, 114.1, 113.0, 111.0, 34.8, 23.1, 16.8 (Cp′*Me*), 14.6, 11.0 (Cp′*Me*), 4.5 (Si*Me*$_2$). EA calc'd for $C_{23}H_{27}NSiTi$ (393.440) C, 70.22; H, 6.92; N, 3.56. Found: C, 69.80, H, 7.45, N, 3.58.

Synthesis of $C_5Me_4SiMe_2N(R)TiMe_2$ (R = CMe_2Ph 9, 2-C_6H_4Ph 10). These compounds were synthesized *via* a similar procedure, therefore only one synthesis is described. A solution of **6** (382 mg, 0.63 mmol) in THF (30 mL) was cooled to −35 °C and MeMgBr (3 M in diethyl ether, 0.436 mL) was added in one portion. The ethereal solution changed from a dark orange to a yellow solution with a white precipitate. The solvent was removed under reduced pressure and the product was extracted with pentane (20 mL) and filtered through a plug of Celite. The pentane was removed *in vacuo* to afford a yellow solid (215 mg, 89%). ^{1}H NMR (C_6D_6): 7.5 (dm, 2H, $^3J_{H-H}$ = 8 Hz, *o-Ph*), 7.2–7.1 (m), 7.1 (tt, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz, *p-Ph*), 2.05 (s, 6H, C*Me*$_2$), 2.0 (s, 6H, Cp′*Me*), 1.9 (s, 6H, Cp′*Me*), 0.5 (s, 6H, Ti*Me*$_2$) 0.1 (s, 6H, Si*Me*$_2$). ^{13}C{^{1}H} (C_6D_6, partial) : 149.2, 132.2, 128.0, 124.9, 124.8, 97.0, 60.1, 50.3, 32.0, 13.4, 10.3, 3.4. EA calc'd for $C_{22}H_{35}NSiTi$ (389.493) C, 67.84; H, 9.06; N, 3.60 Found: C, 67.32; H, 8.65; N, 3.12.

10: Pale yellow crystals, 122 mg, 82%.^{1}H NMR (CD_2Cl_2): 7.4 (dm, 2H, $^3J_{H-H}$ = 8 Hz), 7.3 (dd, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz), 7.3–7.2 (m, 4H), 7.1 (td, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz), 6.9 (dd, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz), 2.2 (s, 6H, Cp′*Me*), 1.9 (s, 6H, Cp′*Me*), 0.3 (s, 6H, Ti*Me*$_2$) 0.03 (s, 6H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): 149.8, 142.2, 137.0, 135.9, 131.7, 130.8, 130.3, 128.5, 128.1, 128.1, 127.0, 126.9, 123.6, 98.0, 56.3, 15.4, 12.4, 2.8 (Si*Me*$_2$). EA calc'd for $C_{25}H_{33}NSiTi$ (423.510) C, 70.90; H, 7.85; N, 3.31; Found: C, 70.42, H, 8.37, N, 3.06. X-ray quality crystals were grown by slow cooling of a solution in pentane.

Styrene polymerizations. In the glovebox, a 500 mL round-bottom Schlenk flask was charged with a magnetic stir bar, toluene (50 mL), and styrene (10 g) that had been filtered though activated neutral alumina immediately prior to use. The flask was removed from the glovebox and attached to a Schlenk line *via* Tygon© tubing which was evacuated and flushed with N_2 (5×) before the flask was opened to one atmosphere of N_2. In the glovebox, the titanium precatalyst (11 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (10 μmol) were combined in toluene (4 mL) and loaded into a plastic syringe, removed from the glovebox and injected into the stirring toluene–styrene mixture. After one hour, acidified methanol (10 mL) was injected to quench the reaction, and methanol (400 mL) was added to precipitate the polymer. The polymeric solids were collected by vacuum filtration and dried in a vacuum oven at 60 °C for 48 h.

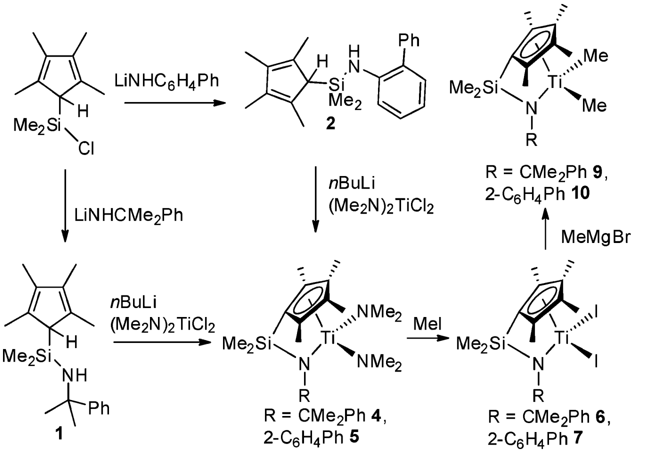
Ethylene polymerizations. In the glovebox, a 500 mL round-bottom Schlenk flask was charged with a magnetic stir bar, toluene (50 mL), and tri-iso-butylaluminium (40 mg). The flask was removed from the glovebox and attached to a Schlenk line *via* Tygon© tubing which was evacuated and flushed with N_2 (5×) before the flask evacuated and refilled with ethylene (3×). In the glovebox, the titanium precatalyst (10 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (10 μmol) were separately dissolved in toluene (3 mL) and loaded into separate plastic syringes, removed from the glovebox and the precatalyst solution was injected into the toluene–styrene mixture immediately followed by the activator solution. After ten minutes, acidified methanol (10 mL) was injected to quench the reaction, and methanol (400 mL) was added to precipitate the polymer. The polymeric solids were collected by vacuum filtration and dried in a vacuum oven at 60 °C for 72 h.

X-ray data collection and reduction. Crystals were manipulated and suspended in Paratone inside a glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data for crystals were collected on a Bruker Apex II diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multi-scan method (SADABS). Subsequent solution and refinement were performed using the SHELXTL solution package.

Structure solution and refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[34] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function $\omega(F_o - F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the supplementary data.†

Results and discussion

Synthesis of the proligands $C_5Me_4HSiMe_2N(H)R)$ (R = CMe_2Ph **1**, 2-C_6H_4Ph **2**) was accomplished *via* a straightforward salt metathesis reaction of the appropriate lithium amide and $ClSiMe_2(C_5Me_5H)$ (Scheme 1). Complex **1** was isolated in good yield as a yellow oil, similarly to the related $(C_5Me_4H)SiMe_2(N(H)tBu)$.[3,35] Complex **2** was isolated in moderate yield as a waxy crystalline solid and the formulation was confirmed crystallographically (Fig. 2 and Table 1). The metrical parameters of this species are unexceptional. Complexation of these ligands with titanium was initially attempted by reaction of $TiCl_4{\cdot}(THF)_2$ with the dilithio species generated by the *in situ* deprotonation of **1** and **2** with *n*BuLi. This reaction generated a mixture of unidentified products, which is not surprising as low yields were reported in the synthesis of related Cp-amido titanium complexes synthesized in this fashion.[5,36] In a modified synthetic attempt, the Me_3Si-derivatives of **1** or **2** were generated *in situ* by deprotonation with two equivalents of *n*BuLi followed by treatment with Me_3SiCl, but treatment of these species with $TiCl_4{\cdot}(THF)_2$ also resulted in mixtures of unidentified products.



Scheme 1 Synthesis of **1**, **2** and **4–7**, **9** and **10**.

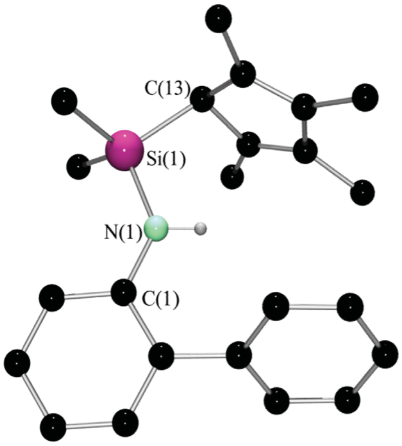


Fig. 2 POV-Ray depiction of **2**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Si(1)–N(1), 1.7312(19); Si(1)–C(22), 1.859(3); Si(1)–C(23), 1.867(3); Si(1)–C(13), 1.896(2); N(1)–Si(1)–C(13), 102.74(10); C(1)–N(1)–Si(1), 131.04(14).

An alternative metathetical avenue to such complexes is treatment of the dilithio ligand precursor with $TiCl_3{\cdot}(THF)_3$ followed by subsequent oxidation to the desired Ti(IV) precatalyst with AgCl or $PbCl_2$.[7] This synthetic strategy was attempted using **2** and afforded the desired titanium dichloride species $C_5Me_4SiMe_2N(C_6H_4Ph)TiCl_2$ (**3**) albeit in low yield (10%).

Seeking a higher yield synthetic strategy to titanium complexes, deprotonation of **1** and **2** *in situ* followed by treatment with $(Me_2N)_2TiCl_2$ afforded $C_5Me_4(SiMe_2NR)Ti(NMe_2)_2$

(R = CMe_2Ph **4**, 2-C_6H_4Ph **5**), respectively, in good yield (Scheme 1). These compounds were isolated as highly soluble, large crystals; the solid state molecular structures were determined *via* X-ray analysis (Fig. 3). The constrained-geometry ligand Ti–N distances were found to be 1.985(2) Å and 2.013(2) Å and the average Ti–N bond distances for the NMe_2 groups were 1.927(2) Å and 1.925(2) Å in **4** and **5**. These are longer than 1.972(4) Å and 1.915(5) Å seen for the corresponding distances in $C_5H_4SiMe_2N(tBu)Ti(NMe_2)_2$ Interestingly, the centroid–Ti distances in **4** and **5** are found to be 2.104(3) and 2.065(3) Å, bracketing that found in $C_5H_4SiMe_2N(tBu)Ti(NMe_2)_2$ (Ti–Ct, 2.083 Å).[35]

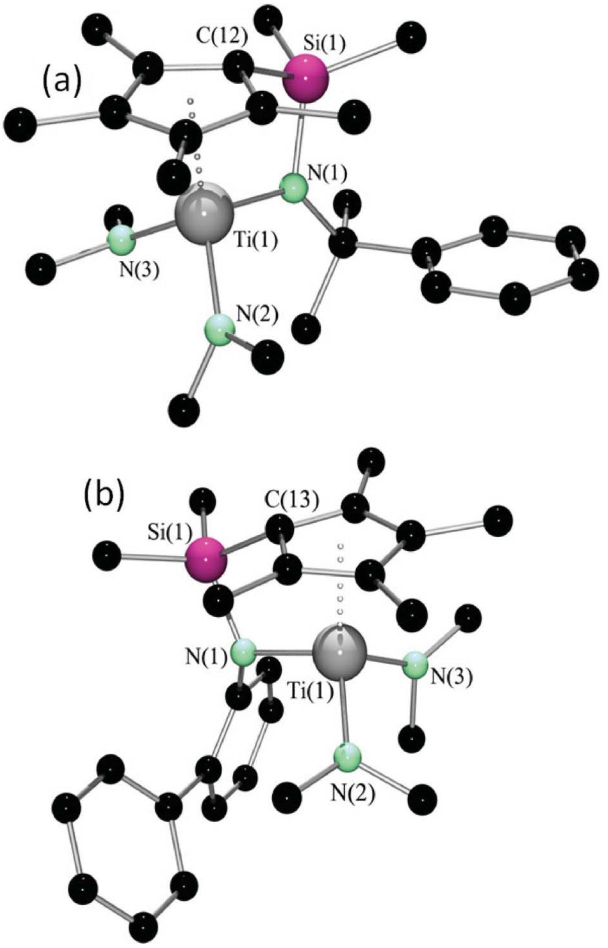


Fig. 3 POV-Ray depiction of (a) **4** and (b) **5**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) **4**: Ti(1)–Ct, 2.104(3); Ti(1)–N(1), 1.985(2); Ti(1)–N(2), 1.942(2); Ti(1)–N(3), 1.915(2); Si(1)–N(1), 1.730(2); Si(1)–C(12), 1.861(3); N(1)–Ti(1)–Ct, 106.18(10); N(1)–Si(1)–C(12), 93.63(12); N(3)–Ti(1)–N(2), 100.48(10). **5**: Ti(1)–Ct, 2.065(3); Ti(1)–N(1), 2.013(2); Ti(1)–N(2), 1.925(2); Ti(1)–N(3), 1.925(2); Si(1)–N(1), 1.732(2); Si(1)–C(13), 1.869(3); N(1)–Ti(1)–Ct, 105.12(10); N(1)–Si(1)–C(13), 93.10(11); N(2)–Ti(1)–N(3), 99.76(11).

Cummins and coworkers have previously reported the cleavage of Ti–N bonds with MeI to give TiI_2 derivatives.[37] Analogous treatment of either **4** or **5** with >20 equivalents of MeI in CH_2Cl_2 afforded $C_5Me_4(SiMe_2NR)TiI_2$ (R = CMe_2Ph **6**, 2-C_6H_4Ph **7**). The ^1H NMR spectra of these reactions in CD_2Cl_2 revealed these reactions to be quantitative and these products were isolated in 96 and 98% yield, respectively. X-ray diffraction studies allowed for the determination of the solid-state molecular structures of both **6** and **7** (Fig. 4). The metrical parameters of these complexes are unexceptional, although, to the best of our knowledge, the molecular structures of similar (Cp-amido)TiI_2 complexes have not been reported. "Constrained geometry" titanium diiodides have been reported in the literature, but these complexes were synthesized from impure (Cp-amido)$TiMe_2$ and reconverted to such dialkyl complexes as a purification strategy.[38]

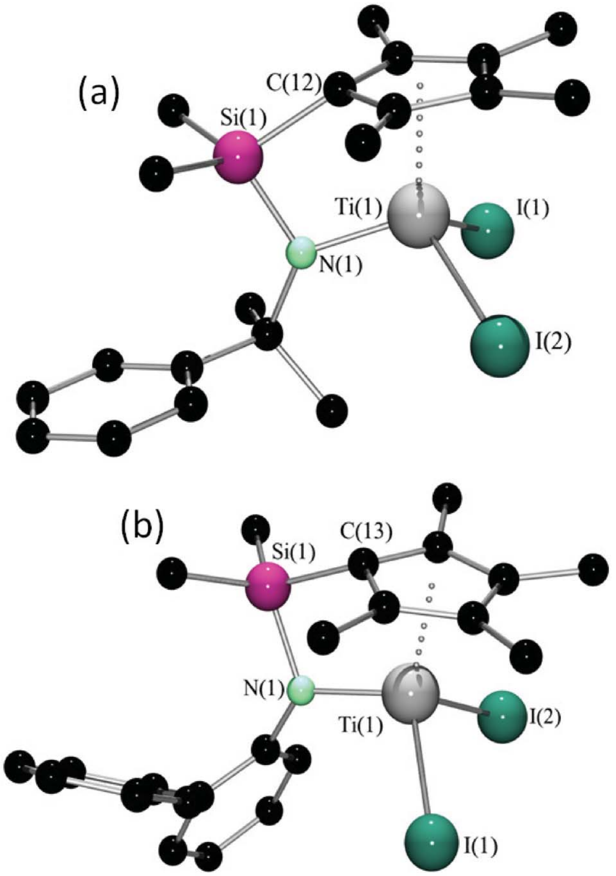
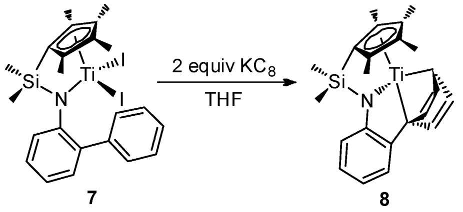


Fig. 4 POV-Ray depiction of (a) **6** and (b) **7**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) **6**: Ti(1)–Ct, 2.045(8); Ti(1)–N(1), 1.919(5); I(1)–Ti(1), 2.6544(12); I(2)–Ti(1), 2.6812(13); Si(1)–N(1), 1.764(5); Si(1)–C(12), 1.889(8); N(1)–Ti(1)–Ct, 108.70(10); N(1)–Si(1)–C(12), 90.8(3); I(1)–Ti(1)–I(2), 105.70(4). **7**: Ti(1)–Ct, 2.025(7); Ti(1)–N(1), 1.946(7); I(1)–Ti(1), 2.6390(16); I(2)–Ti(1), 2.6495(18); Si(1)–N(1), 1.773(7); Si(1)–C(13), 1.866(9); N(1)–Ti(1)–Ct, 107.23(10); N(1)–Si(1)–C(13), 89.4(3); I(1)–Ti(1)–I(2), 100.73(5).

Previous work in the Stephan group with biphenyl-phosphinimide ligands has shown that reduction of titanium complexes of this ligand results in reoxidation of the metal centre *via* activation of this pendant arene.[39] Treatment of **7** with two equivalents of potassium graphite afforded a similar arene-activation product, $C_5Me_4(SiMe_2N\ C_6H_4Ph)Ti$, **8** (Scheme 2). X-ray quality crystals of **8** could not be obtained after repeated recrystallizations but the ^1H NMR spectrum contained resonances at 4.0, 3.2, and 1.6 ppm in a 2 : 2 : 1 ratio attributable to the hydrogens from the former phenyl substituent (Fig. 5). The relative ratios and multiplicity of these resonances verify the



Scheme 2 Synthesis of **8**.

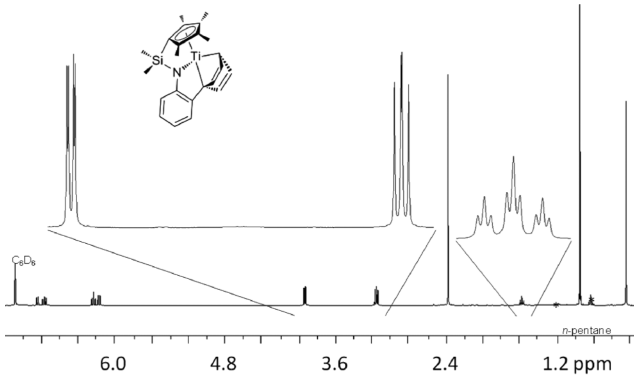


Fig. 5 ^1H NMR spectrum of **8** in C_6D_6.

formulation of **8**. Attempts to effect analogous reduction of **6** with potassium graphite afforded a mixture of products which were not identified.

In order to generate the dialkyl precatalysts required for polymerization, **6** and **7** were treated with two equivalents of MeMgBr in THF, affording $C_5Me_4(SiMe_2NR)Ti(NMe_2)_2$ (R = CMe_2Ph **9**, 2-C_6H_4Ph **10**), respectively (Scheme 1). The solid-state molecular structure of **9** was not determined, but a resonance at 0.1 ppm attributable to two equivalent titanium methyl groups verified the alkylation had proceeded to completion. Single crystals of **10** were obtained. X-ray data did confirm the structure of **10** (Fig. 6) although the poor quality of the crystals precluded a meaningful discussion of metrical parameters.

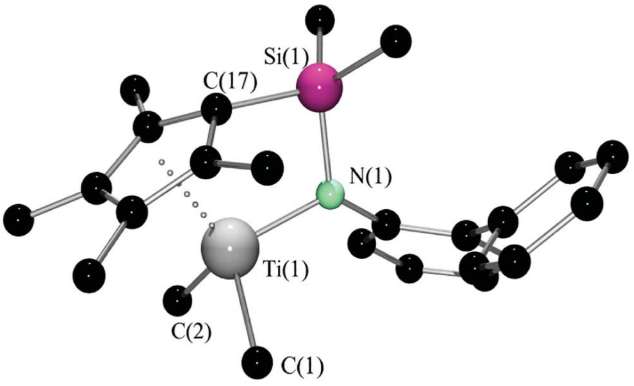


Fig. 6 POV-Ray depiction of **10**. Hydrogen atoms are omitted for clarity.

Reactions of **9** and **10** with $[Ph_3C][B(C_6F_5)_4]$ generated cations that were used as catalysts in polymerisation reactions of styrene and ethylene (Table 2). Polymerisations were also conducted using $[(C_5Me_4)SiMe_2(N\textit{t}Bu)]TiMe_2$ under identical conditions for comparative purposes. Cations derived from $[(C_5Me_4)SiMe_2(N\textit{t}Bu)]TiMe_2$ have been shown to exhibit very poor productivities in the polymerization of styrene,[7] a result that was reproduced here. Polymerization of styrene using **9** as a precatalyst afforded higher activity than the catalyst derived from complex **10**, while this latter catalyst exhibited similar activity to $[(C_5Me_4)SiMe_2(N\textit{t}Bu)]TiMe_2$ under these conditions. While use of these catalysts in the polymerisation of ethylene gave higher activities as expected, the catalyst derived from **9** exhibited good activity. The resulting polyethylene has polydispersity that is consistent with a single-site catalyst. In contrast, the catalyst derived from **10** was inactive. It is interesting to note that the catalyst derived from

Table 1 Crystallographic data

	2	4	5	6	7	10
Formula	$C_{23}H_{29}NSi$	$C_{24}H_{41}N_3SiTi$	$C_{27}H_{39}N_3SiTi$	$C_{20}H_{29}I_2NSiTi$	$C_{23}H_{27}I_2NSiTi$	$C_{25}H_{33}NSiTi$
Formula weight	347.56	447.59	481.60	613.23	647.25	423.51
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	Cc	$P2_1/c$	$P\bar{1}$
a (Å)	9.3969(19)	8.9918(18)	8.7355(17)	19.434(4)	15.316(3)	7.5742(15)
b (Å)	10.297(2)	32.057(6)	12.022(2)	8.4193(17)	7.7666(16)	11.756(2)
c (Å)	12.440(3)	9.6600(19)	12.655(3)	14.943(3)	21.150(4)	13.062(3)
α (°)	68.91(3)	90	85.17(3)	90	90	80.73(3)
β (°)	82.78(3)	117.73(3)	82.55(3)	111.49(3)	108.64(3)	85.90(3)
γ (°)	64.73(3)	90	79.94(3)	90	90	83.85(3)
V (Å^3)	1015.0(4)	2464.8(8)	1295.0(4)	2275.0(8)	2383.9(8)	1139.5(4)
Z	2	4	2	4	4	2
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
d_{calc} (g cm^{-1})	1.137	1.206	1.235	1.790	1.803	1.234
R_{int}	0.121	0.411	0.396	3.147	3.009	0.438
μ (cm^{-1})	4542	22 740	12 539	7620	16 159	10 730
Total data	0.0426	0.0799	0.0586	0.0313	0.0929	0.1237
Data > $3\sigma(F_o^2)$	3144	5597	5897	3837	5413	5127
Variables	226	274	299	226	253	261
R (>3σ)	0.0600	0.0552	0.0548	0.0333	0.0590	0.1179
R_w	0.1644	0.1575	0.1551	0.0775	0.1364	0.3469
GOF	1.090	0.996	1.028	1.096	1.021	1.070

Data collected with Mo Kα radiation (λ = 0. 0.71073 Å).

Table 2 Polymerization and copolymerization data

Precatalyst	Olefin(s)	Act.[a]	M_w	PDI
CGC	Styrene	3	13 620	1.64
9	Styrene	16	11 650	1.52
10	Styrene	3	11 360	1.51
CGC	Ethylene	308	158 400	2.06
9	Ethylene	770	177 000	2.91
10	Ethylene	0	—	—
9	Ethylene/Styrene	Negligible	—	—

[a] polyolefin: g $mmol^{-1}$ h^{-1} atm^{-1} polystyrene : g $mmol^{-1}$ h^{-1}. CGC = $[(C_5Me_4)SiMe_2(N\textit{t}Bu)]TiMe_2$.

the related species $[(C_5Me_4)SiMe_2(NPh)]TiMe_2$ is active for the polymerization of ethylene, although less so than the N-alkylated congener.[7] Given the large variance in the activities for styrene and ethylene polymerization using the precatalyst **9**, it is perhaps not surprising that trials for ethylene/styrene copolymerization produced negligible amounts of polymer.

The cause of inactivity of the catalyst derived from **10** in ethylene polymerization is unknown, although it is conceivable that intramolecular coordination of the pendant arene inhibits reaction with the olefin. Efforts to confirm this were undertaken by monitoring the reaction of **10** with $[Ph_3C][B(C_6F_5)_4]$ using ^1H NMR spectroscopy. While the abstraction of methyl from Ti was evident by the observation of Ph_3CMe, NMR data for these Ti-cations did not confirm an interaction with the pendant arene substituent. Nonetheless, this postulate is supported to some extent by the preparation of **8**, where the generation of unsaturation at the Ti center prompts interaction with the arene fragment.

Conclusions

A new, high yielding, synthetic route to titanium constrained geometry precatalysts has been developed in the synthesis of CGCs with pendant arene groups. While the complex bearing a biphenyl substituent demonstrated generally low activities in the polymerisation of styrene and ethylene, the complex bearing a cumyl substituent exhibited moderately increased activities in comparison to the benchmark CGC under similar conditions. Nonetheless, this catalyst was inactive in coplymerization of ethylene/styrene.

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