Journal of Organometallic Chemistry 695 (2010) 1464–1471

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Silylium–metallocenium dications derived from hydrosilyl-bridged metallocenes and roles in polymerization of polar and nonpolar vinyl monomers

Yuetao Zhang, Eugene Y.-X. Chen *

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, USA

ARTICLE INFO

Article history:
Received 11 February 2010
Accepted 28 February 2010
Available online 3 March 2010

Keywords:
Dication
Double activation
Metallocene catalyst
MMA polymerization
Propylene polymerization

ABSTRACT

Hydrosilyl-bridged half-metallocene (^{H}CGC)TiMe$_2$ (**1**) [^{H}CGC = Me(H)Si(η^5-C$_5$Me$_4$)(η^1-N^{t}Bu)] and *ansa*-metallocene *rac*-(^{H}SBI)ZrMe$_2$ (**2**) [^{H}SBI = Me(H)Si(η^5-indenyl)$_2$] are doubly activated with 2 equiv of Al(C$_6$F$_5$)$_3$, through methide abstractions from both M–Me bonds, to generate homo-dications **1**-Ti^{2+} and **2**-Zr^{2+}, or with 2 equiv of Ph$_3$CB(C$_6$F$_5$)$_4$, through unique simultaneous hydride and methide abstractions from the Si–H and M–Me bonds, to produce a novel class of silylium–metallocenium hetero-dications **1**-Si^{+}Ti^{+} and **2**-Si^{+}Zr^{+}. Analogous chloride-derivatives of hetero-dications can also be produced starting from the dichloride precursors, but the chloride abstraction occurs through a transit silylium ion. An opposite activity trend has been observed for the influence of the hetero-dication formation on polymerizations of polar (MMA) and nonpolar (propylene) vinyl monomers. In MMA polymerization, the activity of the hetero-dications, especially the metallocene-based **2**-Si^{+}Zr^{+}, is substantially lower than the corresponding monocations. In marked contrast, the propylene polymerization activity of hetero-dications has seen 100% and 40% enhancements for **1**-Si^{+}Ti^{+} and **2**-Si^{+}Zr^{+}, respectively, over their respective monocations.

1. Introduction

Cationic group 4 metallocene and related complexes [1] have been widely used as highly active catalysts for coordination-insertion polymerization of nonpolar vinyl monomers (α-olefins in particular) [2] and coordination-addition polymerization of polar vinyl monomers [3]. The continuing interest in the study of such catalysts, typically in their cationic form, is attributed to their high catalytic activity and remarkable ability to precisely control the stereochemistry of the polymerization and the architecture of the resulting polymers as well as the ability to produce new classes of polymeric materials unattainable by other means of polymerization [3].

In 2001, one of us discovered that double activation of group 4 metallocene and half-metallocene dimethyl complexes with two equiv of the highly Lewis acidic alane, Al(C$_6$F$_5$)$_3$, leads to formation of doubly activated, dicationic metallocene complexes [4]. Significantly, such doubly activated complexes show a considerably higher activity in large-scale runs of ethylene and 1-ocetene copolymerizations than the singly activated (monocation) analogous. Another remarkable polymerization feature of the doubly activated catalyst is its much larger initial polymerization exothermicity (by ~30 °C), a desirable feature for continuous polymerization processes, than otherwise singly activated, cationic catalysts [4]. Reactions with multiple equiv of the analogous borane B(C$_6$F$_5$)$_3$ or trityl borate Ph$_3$CB(C$_6$F$_5$)$_4$ did not generate the dicationic complexes. Most recently, we revealed novel living/controlled methyl methacrylate (MMA) [5] and acrylate [6] polymerizations using a combination of a silyl ketene acetal (SKA) with a catalytic amount of the ubiquitous olefin polymerization activator Ph$_3$CB(C$_6$F$_5$)$_4$, readily producing PMMA of low to high number-average molecular weight (M_n > 10^5) with narrow molecular weight distributions (MWDs = 1.04–1.12) at ambient temperature [5]. An intriguing, "monomer-less" initiation step involves oxidative activation of dimethylketene methyl trimethylsilyl acetal, Me$_2$C=C(OMe)OSiMe$_3$ (^{Me}SKA), by Ph$_3$CB(C$_6$F$_5$)$_4$, leading to the Me$_3$Si^{+}-activated (silylated) MMA derived from vinylogous hydride abstraction of ^{Me}SKA with Ph$_3$C^{+}; subsequent Michael addition of ^{Me}SKA to the activated MMA affords the highly active, bifunctional active species containing both nucleophilic SKA and electrophilic silylium cation catalyst sites, Me$_3$SiOC(OMe)=CMeCH$_2$CMe$_2$C(OMe)=O···SiMe$_3$][B(C$_6$F$_5$)$_4$] [5]. The use of the borane B(C$_6$F$_5$)$_3$ did not effect hydride abstraction of SKA. A propagation "catalysis" cycle in the MMA polymerization consists of a fast step of recapturing the silylium catalyst from the ester group of the growing polymer chain by the incoming MMA, followed by a rate-determining step of the C–C bond formation via intermolecular Michael addition of the polymeric SKA to the silyl cation-activated MMA. Hence, both activation methodology and fundamental steps involved in the chain initiation and propagation of the

* Corresponding author. Tel.: +1 970 491 5609; fax: +1 970 491 1801.
E-mail address: eugene.chen@colostate.edu (E.Y.-X. Chen).

0022-328X/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.02.030

silylium-catalyzed living polymerization are mechanistically different from the classic group-transfer polymerization [7], commonly considered involving reductive activation and associative propagation.

In this contribution, we explored the possibility of generating novel silylium–metallocenium hetero-dicationic catalysts based on hydrosilyl-bridged [Me(H)Si<] *ansa*-metallocene and half-metallocene dimethyl complexes. We reasoned that such complexes bearing both M–Me and Si–H ligands can be activated by $Ph_3CB(C_6F_5)_4$, which is known for its ability to abstract the methide group from the metallocene M–Me bond [8] and the hydride from the silyl Si–H bond [9]. The end result would be the formation of a novel class of hetero-dicationic metallocene complexes consisting of the Si^+M^+ (M = Ti, Zr) core fragment, generated through simultaneous hydride and methide abstractions by the potent abstractor $Ph_3CB(C_6F_5)_4$. Overall, the motivation of this study is twofold: first, we are driven to develop a new class of silylium–metallocenium hetero-dicationic catalysts; second, we are interested in knowing how such dications would affect polymerization of polar and nonpolar vinyl monomers, specifically MMA and propylene.

2. Experimental

2.1. Materials and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line (typically from 10^{-5} to 10^{-7} Torr), or in an argon-filled glovebox (typically <1.0 ppm oxygen). NMR-scale reactions (typically in a 0.02 mmol scale) were conducted in Teflon-valve-sealed J. Young-type NMR tubes. HPLC grade organic solvents were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through activated alumina (for Et_2O, THF, and CH_2Cl_2) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene-d_6, and toluene-d_8 were dried over sodium/potassium alloy and vacuum-distilled or filtered, whereas C_6D_5Br, CD_2Cl_2, and $CDCl_3$ were dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) or a Varian Inova 400 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to $SiMe_4$, whereas ^{19}F NMR spectra were referenced to external $CFCl_3$. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

Methyl methacrylate (MMA; Aldrich Chemical Co.) was degassed and dried over CaH_2 overnight, distilled under reduced pressure, titrated with neat tri(*n*-octyl)aluminum (Strem Chemicals) to a yellow end point [10], and finally distilled under reduced pressure. The purified monomer was stored in a brown bottle inside a −30 °C glovebox freezer. Propylene (polymer purity, Metheson) was purified by passage through the mixed stainless steel column of the activated alumina and Q-5 supported copper catalyst. Butylated hydroxytoluene (BHT-H, 2,6-di-*tert*-butyl-4-methylphenol, Aldrich Chemical Co.) was recrystallized from hexanes prior to use. Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ [11] and trityl tetrakis(pentafluorophenyl)borate $Ph_3CB(C_6F_5)_4$ [12] were obtained as a research gift from Boulder Scientific Co., $B(C_6F_5)_3$ was purified by recrystallization from hexanes at −30 °C, whereas $Ph_3CB(C_6F_5)_4$ was used as received. Tris(pentafluorophenyl)alane $Al(C_6F_5)_3$ [13], as a 0.5 toluene adduct $Al(C_6F_5)_3{\cdot}(C_7H_8)_{0.5}$, was prepared by the reaction of $B(C_6F_5)_3$ and $AlMe_3$ in a 1:3 toluene/hexanes solvent mixture in quantitative yield [14]. Although we have experienced no incidents when handling this material, *extra caution should be exercised*, especially when dealing with the unsolvated form, because of its thermal and shock sensitivity. Dimethylketene methyl trimethylsilyl acetal (^{Me}SKA), 1,2,3,4-tetramethyl-1,3-cyclopentadiene, diisopropylamine (⩾99%), methyl isobutyrate, chlorotrimethylsilane, dichloromethylsilane, and isopropyl isobutyrate were purchased from Aldrich and dried over CaH_2, followed by vacuum distillation, whereas $ZrCl_4$, $TiCl_4$ (in CH_2Cl_2), indene, ^{n}BuLi (1.6 M in hexanes), and MeMgBr (3.0 M in diethyl ether) were purchased from Aldrich and used as received. Literature procedures were employed for the preparation of the following compounds and metallocene complexes: $ZrCl_4{\cdot}(THF)_2$ [15], (CGC)$TiMe_2$ [16] [CGC = $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^1\text{-}N^tBu)$], *rac*-(SBI)$ZrMe_2$ [17] [SBI = $Me_2Si(\eta^5\text{-indenyl})_2$], *rac*-(SBI)$ZrMe^+MeM(C_6F_5)_3^-$ (M = B, Al) [4], *rac*-(^{H}SBI)$ZrCl_2$ (**4**) [^{H}SBI = $Me(H)Si(\eta^5\text{-indenyl})_2$] [18], (^{H}CGC)$TiCl_2$ (**3**) [^{H}CGC = $Me(H)Si(\eta^5\text{-}C_5Me_4)(\eta^1\text{-}N^tBu)$] [19], and (^{H}CGC)$TiMe_2$ (**1**) [19].

2.2. Preparation of rac-(^{H}SBI)$ZrMe_2$ (**2**)

In a glovebox, MeMgBr (0.48 mL, 3.0 M in Et_2O, 1.44 mmol) was added to a solution of *rac*-(^{H}SBI)$ZrCl_2$ (**4**) (0.25 g, 0.58 mmol) in Et_2O (25 mL) at room temperature. The mixture was stirred overnight, after which all volatiles were removed in vacuo. Toluene (~50 mL) was added to the residue, and the resulting precipitates were filtered through a pad of Celite. The solvent of the filtrate was removed in vacuo to afford 0.19 g (84 %) of the pure title complex as a brown powder. Anal. Calc. for $C_{21}H_{22}SiZr$: C, 64.06; H, 5.63. Found: C, 63.78; H, 5.57%.

^1H NMR (CD_2Cl_2, 300 MHz, 23 °C): δ 7.65–7.62 (m, 2H, C_6 ring), 7.45–7.42 (m, 1H, C_6 ring), 7.38–7.35 (m, 1H, C_6 ring), 7.30–7.25 (m, 2H, C_6 ring), 7.04–6.97 (m, 2H, C_6 ring), 6.86 (d, J = 3.3 Hz, 1H, C_5 ring), 6.82 (d, J = 3.3 Hz, 1H, C_5 ring), 5.94 (d, J = 3.3 Hz, 1H, C_5 ring), 5.93 (d, J = 3.3 Hz, 1H, C_5 ring), 5.44 (q, J = 3.9 Hz, 1H, Si*H*), 1.01 (d, J = 3.9 Hz, 3H, Si*Me*), −1.41 (s, 3H, Zr*Me*), −1.42 (s, 3H, Zr*Me*). ^1H NMR (C_6D_6, 400 MHz, 23 °C): δ 7.38–7.55 (m, 2H, C_6 ring), 7.23 (d, J = 8.4 Hz, 1H, C_6 ring), 7.09–7.03 (m, 3H, C_6 ring), 6.79–6.71 (m, 2H, C_6 ring), 6.61 (d, J = 3.2 Hz, 1H, C_5 ring), 6.58 (d, J = 3.2 Hz, 1H, C_5 ring), 5.72 (d, J = 3.2 Hz, 1H, C_5 ring), 5.57 (d, J = 3.6 Hz, 1H, C_5 ring), 5.26 (q, J = 4.0 Hz, 1H, Si*H*), 0.50 (d, J = 4.0 Hz, 3H, Si*Me*), −1.04 (s, 3H, Zr*Me*), −1.05 (s, 3H, Zr*Me*). ^{13}C NMR (C_6D_6, 100 MHz, 23 °C): δ 131.1, 130.6, 128.5, 128.3, 126.8, 126.6, 126.5, 126.2, 125.5, 125.4, 125.0, 124.9 (C_6 ring), 119.3, 117.5, 112.1, 111.5, 80.78, 80.22 (C_5 ring), 38.27, 37.73 ($ZrMe_2$), −5.22 (Si*Me*).

2.3. Activation of (^{H}CGC)$TiMe_2$ (**1**) with 1, 2, and 3 equiv of $Al(C_6F_5)_3$

These reactions were carried out by the same manner as described for the reaction with the dimethylsilyl derivative (CGC)$TiMe_2$ [4]. The reaction of **1** with 1 equiv of $Al(C_6F_5)_3$ in toluene-d_8 at room temperature cleanly generates the corresponding μ-methyl bridged ion pair, (^{H}CGC)$TiMe(\mu\text{-Me})Al(C_6F_5)_3$ (**1a-**Ti^+ and **1b-**Ti^+) as a yellow solution, which can be readily characterized by NMR as two isomers in a 2:3 ratio. The isolated product in quantitative yield was spectroscopically and analytically pure. Anal. Calc. for $C_{34}H_{31}AlF_{15}NSiTi$: C, 48.53; H, 3.71; N, 1.66. Found: C, 48.33; H, 3.56; N, 1.57%.

^1H NMR (toluene-d_8, 300 MHz, 23 °C): δ 5.21, 5.14 (q, J = 3.0 Hz, 1H, Si*H*), 1.71, 1.75 (s, 3H, Cp*Me*), 1.68, 1.44 (s, 3H, Cp*Me*), 1.59, 1.55 (s, 6H, Cp*Me*), 1.13, 1.12 (s, 9H, N^t*Bu*), 0.83, 0.80 (s, 3H, Ti*Me*), 0.22, 0.32 (d, J = 3.0 Hz, 3H, Si*Me*), 0.08, 0.15 (s, br, 3H, Al-μ-*Me*). ^{19}F NMR (toluene-d_8, 282 MHz, 23 °C): δ −122.7 (m, 6F, *o*-F of C_6F_5), −153.9 (t, J = 19.9 Hz, 3F, *p*-F of C_6F_5), −161.8 (m, 6F, *m*-F of C_6F_5). ^{13}C NMR (toluene-d_8, 100 MHz, 23 °C): δ 150.3 (d, J_{C-F} = 235.0 Hz), 141.7 (d, J_{C-F} = 249.5 Hz), 137.3 (d, J_{C-F} = 236.8 Hz), and 116.5 (s, br) for C_6F_5 groups, 141.6, 141.1, 139.1, 138.7, 137.9, 137.8, 136.3, 135.8, 101.8, and 100.8 for C_5Me_4, 68.54, 66.26 (Ti*Me*),

62.47, 62.42 ($NCMe_3$), 32.64 ($NCMe_3$), 19.47 (s, br, Al-μ-*Me*), 15.57, 14.15, 13.84, 12.68, 11.84, 11.73, 11.48, and 11.24 for C_5Me_4, 1.24, 1.08 (Si*Me*).

Activation of **1** with 2 equiv of $Al(C_6F_5)_3$ cleanly affords the corresponding dicationic complex, (^{H}CGC)Ti[(μ-Me)$Al(C_6F_5)_3$]$_2$ (**1**-Ti^{2+}), as an orange-yellow solution, which can be readily characterized by NMR. The isolated dication is unstable at room temperature and thus not suitable for elemental analysis. ^{1}H NMR (toluene-d_8, 300 MHz, 23 °C): δ 5.17 (q, *J* = 3.0 Hz, 1H, Si*H*), 1.67 (s, 3H, Cp*Me*), 1.65 (s, 3H, Cp*Me*), 1.60 (s, 3H, Cp*Me*), 1.51 (s, 3H, Cp*Me*), 1.13 (s, 9H, N^t*Bu*), 0.53 (s, br. 3H, Al*Me*), 0.41 (s, br. 3H, Al*Me*), 0.28 (d, *J* = 3.0 Hz, 3H, Si*Me*). ^{19}F NMR (toluene-d_8, 282 MHz, 23 °C): δ −122.9 (m, 6F, *o*-F of C_6F_5), −152.4 (m, 3F, *p*-F of C_6F_5), −161.3 (m, 6F, *m*-F of C_6F_5). ^{13}C NMR (toluene-d_8, 100 MHz, 23 °C): δ 150.2 (d, J_{C-F} = 234.9 Hz), 142.0 (d, J_{C-F} = 249.5 Hz), 137.3 (d, J_{C-F} = 249.6 Hz), and 114.6 (s, br) for C_6F_5 groups, 141.2, 140.2, 137.9, 137.4, 101.6 for C_5Me_4, 62.87 ($NCMe_3$), 32.64 ($NCMe_3$), 32.24, 31.75 (s, br, Al-μ-*Me*), 14.61, 13.64, 11.73, 11.46 for C_5Me_4, 1.10 (Si*Me*).

Activation of **1** with 3 equiv of $Al(C_6F_5)_3$ forms the same dication as above, leaving 1 equiv of $Al(C_6F_5)_3$ unreacted. This result shows that the alane does not abstract the hydride from the bridging hydrosilyl group.

2.4. Activation of (^{H}CGC)$TiMe_2$ (**1**) with 1, 2, and 3 equiv of $B(C_6F_5)_3$

These reactions were carried out by the same manner as described for the reaction with the dimethylsilyl derivative (CGC)$TiMe_2$ [4]. The reaction of **1** with 1 equiv of $B(C_6F_5)_3$ in toluene-d_8 at room temperature cleanly generates the corresponding μ-methyl bridged ion pair, (^{H}CGC)TiMe(μ-Me)$B(C_6F_5)_3$, as a yellow-green solution, which can be readily characterized by NMR as two isomers in a 2:3 ratio. The isolated product in quantitative yield was spectroscopically and analytically pure. Anal. Calc. for $C_{34}H_{31}BF_{15}NSiTi$: C, 49.48; H, 3.79; N, 1.70. Found: C, 50.07; H, 3.81; N, 1.54%.

^{1}H NMR (toluene-d_8, 300 MHz, 23 °C): δ 5.08, 5.17 (q, *J* = 3.0 Hz, 1H, Si*H*), 1.77, 1.72 (s, 3H, Cp*Me*), 1.55, 1.53 (s, 3H, Cp*Me*), 1.46, 1.49 (s, 3H, Cp*Me*), 1.44, 1.43 (s, 3H, Cp*Me*), 1.01, 0.98 (s, 9H, N^t*Bu*), 0.95, 0.93 (s, 3H, Ti*Me*), 0.61, 0.68 (s, br. 3H, B*Me*), 0.16, 0.30 (d, *J* = 3.0 Hz, 3H, Si*Me*). ^{19}F NMR (toluene-d_8, 282 MHz, 23 °C): δ −133.5 (m, 6F, *o*-F of C_6F_5), −159.1 (m, 3F, *p*-F of C_6F_5), −164.3 (m, 6F, *m*-F of C_6F_5). ^{13}C NMR (toluene-d_8, 100 MHz, 23 °C): δ 148.73 (d, J_{C-F} = 233.1 Hz), 139.6 (d, J_{C-F} = 245.9 Hz), 137.5 (d, J_{C-F} = 235.5 Hz), and 123.1 (s, br) for C_6F_5 groups, 141.5, 140.7, 139.6, 139.3, 139.1, 138.9, 136.9, 136.4, 103.4, and 102.3 for C_5Me_4, 68.77, 66.33 (Ti*Me*), 63.33, 63.22 ($NCMe_3$), 32.29, 32.26 ($NCMe_3$), 15.72, 14.32, 13.39, 12.10, 11.90, 11.77, 11.46, 11.20 for C_5Me_4, 1.19, 0.89 (Si*Me*).

Activation of **1** with 2 or 3 equiv of $B(C_6F_5)_3$ affords the same ion pair as above, leaving 1 or 2 equiv of $B(C_6F_5)_3$ unreacted. This result shows that the borane abstracts neither the second Zr–Me group from the mono-cation nor the hydride from the bridging hydrosilyl group.

2.5. Activation of (^{H}CGC)$TiMe_2$ (**1**) with 2 equiv of $Ph_3CB(C_6F_5)_4$

The NMR reaction of **1** and $Ph_3CB(C_6F_5)_4$ in 0.7 mL of toluene-d_8 in a 1:2 ratio (0.02 mmol scale) was carried out in a J-Young NMR tube, the sample being loaded into the NMR tube in a glovebox. The mixture was allowed to react for 20 min at room temperature before the NMR spectra were recorded. A solution and red oily precipitates were observed immediately upon mixing of the reagents. The NMR spectra of the solution show the formation of Ph_3CH and Ph_3CMe, while the NMR spectra of the red oil upon dissolution in CD_2Cl_2 indicate the formation of the dicationic complex (^{H}CGC)$^+$TiMe$^+$$[B(C_6F_5)_4]_2^-$ (**1**-Si^+Ti^+), a result of both methyl and hydride abstractions from the Ti–Me and Si–H bonds. This reaction was repeated directly in CD_2Cl_2, obtaining the same result. The isolated dication is unstable at room temperature and thus not suitable for elemental analysis. ^{1}H NMR for Ph_3CH and Ph_3CMe (toluene-d_8, 300 MHz, 23 °C): δ 2.01 (s, 3H, Ph_3CMe), 5.37 (s, 1H, Ph_3CH), 6.98–7.10 (m, 30H, Ph_3CH and Ph_3CMe). ^{1}H NMR for (CGC)$^+$TiMe$^+$$[B(C_6F_5)_4]_2^-$ (CD_2Cl_2, 300 MHz, 23 °C): δ 2.61 (s, 3H, Cp*Me*), 2.56 (s, 3H, Cp*Me*), 2.49 (s, 3H, Cp*Me*), 2.14 (s, 3H, Cp*Me*), 1.50 (s, 9H, N^t*Bu*), 1.03 (s, 3H, Ti*Me*), 0.91 (s, 3H, Si*Me*). ^{19}F NMR (CD_2Cl_2, 282 MHz, 23 °C): δ −131.5 (d, *J* = 11.0 Hz, 8F, *o*-F of C_6F_5), −161.7 (t, *J* = 20.3 Hz, 4F, *p*-F of C_6F_5), −165.6 (t, *J* = 18.2 Hz, 8F, *m*-F of C_6F_5).

2.6. Activation of rac-(^{H}SBI)$ZrMe_2$ (**2**) with 1, 2, and 3 equiv of $Al(C_6F_5)_3$

These reactions were carried out by the same manner as described for the reaction with the dimethylsilyl derivative *rac*-(SBI)$ZrMe_2$ [4]. The reaction of **2** with 1 equiv of $Al(C_6F_5)_3$ in toluene-d_8 at room temperature cleanly generates the corresponding μ-methyl bridged ion pair, *rac*-(^{H}SBI)ZrMe(μ-Me)$Al(C_6F_5)_3$ (**2a**-Zr^+ and **2b**-Zr^+)), as yellow solution, which can be readily characterized by NMR as two isomers in a 1:1 ratio. The isolated product in quantitative yield was spectroscopically and analytically pure. Anal. Calc. for $C_{39}H_{22}AlF_{15}SiZr$: C, 50.81; H, 2.41. Found: C, 51.05; H, 2.53%.

^{1}H NMR (toluene-d_8, 300 MHz, 23 °C): δ 7.50, 7.53 (d, 1H, C_6 ring), 6.33–7.19 (m, 9H, Ind), 5.57, 5.66 (d, *J* = 3.3 Hz, 1H, C_5 ring), 5.01, 5.16 (d, *J* = 3.3 Hz, 1H, C_5 ring), 4.96, 5.13 (q, *J* = 3.9 Hz, 1H, Si*H*), 0.36, 0.43 (d, *J* = 3.9 Hz, 3H, Si*Me*), −0.77, −0.76 (s, 3H, Zr*Me*), −1.00, −0.99 (s, 3H, Al*Me*). ^{19}F NMR (toluene-d_8, 282 MHz, 23 °C): δ −122.7 (m, 6F, *o*-F of C_6F_5), −153.9 (m, 3F, *p*-F of C_6F_5), −161.7 (m, 6F, *m*-F of C_6F_5). ^{13}C NMR (toluene-d_8, 100 MHz, 23 °C): δ 150.3 (d, J_{C-F} = 231.3 Hz), 141.5 (d, J_{C-F} = 249.5 Hz), 137.2 (d, J_{C-F} = 251.3 Hz), and 117.3 (s, br) for C_6F_5 groups, 137.8, 137.2, 132.7, 132.3, 132.1, 131.8, 128.4, 127.6, 127.5, 127.3, 127.2, 126.8, 126.4, 126.3, 125.8, 125.6, 124.0, 123.5, 122.1, 120.0, 118.6, 117.1, 115.8, 114.7, 112.9, 112.2, 83.56, 82.96, 82.87, 82.36 for Ind, 49.65, 49.03 (Zr*Me*), 6.07 (Zr-*Me*-Al), −6.08, −7.01 (Si*Me*).

Activation of **2** with 2 equiv of $Al(C_6F_5)_3$ cleanly affords the corresponding dicationic complex, *rac*-(^{H}SBI)Zr[(μ-Me)$Al(C_6F_5)_3$]$_2$ (**2**-Zr^{2+}), as a red solution, which can be readily characterized by NMR as a single isomer. The isolated dication decomposes in 30 min at room temperature and is not suitable for elemental analysis. ^{1}H NMR (toluene-d_8, 300 MHz, 23 °C): δ 7.33 (s, br. 1H, Ind), 6.85 (d, *J* = 8.7 Hz, 1H, Ind), 6.62–6.65 (m, 1H, Ind), 6.74 (d, *J* = 8.7 Hz, 1H, Ind), 6.51–6.56 (m, 6H, Ind), 5.41 (s, br. 1H, C_5 ring), 5.05 (q, *J* = 3.9 Hz, 1H, Si*H*), 0.40 (d, *J* = 3.9 Hz, 3H, Si*Me*), –0.80 (s, 6H, Al*Me*). ^{19}F NMR (toluene-d_8, 282 MHz, 23 °C): δ −122.8 (m, 6F, *o*-F of C_6F_5), −152.1 (m, 3F, *p*-F of C_6F_5), −161.2 (m, 6F, *m*-F of C_6F_5).

Activation of **2** with 3 equiv of $Al(C_6F_5)_3$ forms the same dication as above, leaving 1 equiv of $Al(C_6F_5)_3$ unreacted. This result shows again that the alone does not abstract the hydride from the bridging hydrosilyl group.

2.7. Activation of rac-(^{H}SBI)$ZrMe_2$ (**2**) with 2 equiv of $Ph_3CB(C_6F_5)_4$

The NMR reaction of **2** and $Ph_3CB(C_6F_5)_4$ in 0.7 mL of toluene-d_8 in a 1:2 ratio (0.02 mmol scale) was carried out in a J-Young NMR tube, the sample being loaded into the NMR tube in a glovebox. The mixture was allowed to react for 20 min at room temperature before the NMR spectra were recorded. A solution and red oily precipitates were observed immediately upon mixing of the reagents. The NMR spectra of the solution show the formation of Ph_3CH and

Ph_3CMe, and the repeated reaction in CD_2Cl_2 indicates the formation of the dicationic complex (^{H}SBI)$^{+}$ZrMe^{+}[$B(C_6F_5)_4$]$_2^-$ (**2**-Si^{+}Zr^{+})), a result of both methyl and hydride abstractions from the Zr–Me and Si–H bonds. The isolated dication is unstable at room temperature and thus not suitable for elemental analysis. ^{1}H NMR (CD_2Cl_2, 300 MHz, 23 °C) for most diagnostic resonances due to limited solubility and stability: δ 0.20 (s, Zr*Me*), 1.67 (s, Si*Me*), 2.17 (s, Ph_3CMe), 5.54 (s, Ph_3CH), 7.07–7.33 (m, *Ph*$_3$CH and *Ph*$_3$CMe). ^{19}F NMR (CD_2Cl_2, 282 MHz, 23 °C): δ −131.3 (s, br, 8F, *o*-F of C_6F_5), −161.8 (t, J = 20.3 Hz, 4F, *p*-F of C_6F_5), −165.7 (t, J = 18.2 Hz, 8F, *m*-F of C_6F_5).

2.8. Activation of (^{H}CGC)$TiCl_2$ (**3**) with $Ph_3CB(C_6F_5)_4$

NMR-scale reactions were carried out in J-Young NMR tubes, the samples being loaded into the NMR tubes in a glove box after mixing the two reagents in 0.7 mL of CD_2Cl_2 in a 1:0.5 ratio (0.02 mmol scale). The mixture was allowed to react at room temperature overnight before the NMR spectra were recorded. A yellow solution was observed, and the NMR data are consistent with the formation of Ph_3CH, (^{Cl}CGC)$TiCl_2$ (**5**) [19], and (^{H}CGC)TiCl^{+}[$B(C_6F_5)_4$]$^-$ (**3**-Ti^{+}). ^{1}H NMR for **5** (CD_2Cl_2, 300 MHz, 23 °C): δ 2.30 (s, 3H, Cp*Me*), 2.28 (s, 3H, Cp*Me*), 2.27 (s, 3H, Cp*Me*), 2.18 (s, 3H, Cp*Me*), 1.48 (s, 9H, N^t*Bu*), 1.07 (s, 3H, Si*Me*). ^{1}H NMR for **3**-Ti^{+} (CD_2Cl_2, 300 MHz, 23 °C): δ 5.53 (d, J = 3.9 Hz, 1H, Si*H*), 2.59 (s, 3H, Cp*Me*), 2.54 (s, 3H, Cp*Me*), 2.46 (s, 3H, Cp*Me*), 2.39 (s, 3H, Cp*Me*), 1.59 (s, 9H, N^t*Bu*), 1.06 (d, J = 3.9 Hz, 3H, Si*Me*). ^{19}F NMR (CD_2Cl_2, 282 MHz, 23 °C): δ −131.3 (s, br, 8F, *o*-F of C_6F_5), −161.8 (t, J = 20.3 Hz, 4F, *p*-F of C_6F_5), −165.7 (t, J = 17.5 Hz, 8F, *m*-F of C_6F_5).

The reaction of **3** and 1 equiv of $Ph_3CB(C_6F_5)_4$ was carried out in the same manner as described in the above reaction. A light yellow solution was observed and the NMR data are consistent with the formation of Ph_3CH, **5** [19], **3**-Ti^{+}, and (^{H}CGC)$^{+}$TiCl^{+}[$B(C_6F_5)_4$]$_2^-$ (**3**-Si^{+}Ti^{+}). ^{1}H NMR for **3**-Si^{+}Ti^{+} (CD_2Cl_2, 300 MHz, 23 °C): δ 2.66 (s, 3H, Cp*Me*), 2.61 (s, 3H, Cp*Me*), 2.48 (s, 3H, Cp*Me*), 2.42 (s, 3H, Cp*Me*), 1.67 (s, 9H, N^t*Bu*), 1.54 (s, 3H, Si*Me*). ^{19}F NMR (CD_2Cl_2, 282 MHz, 23 °C): δ −131.4 (s, br, 8F, *o*-F of C_6F_5), −161.9 (t, J = 20.3 Hz, 4F, *p*-F of C_6F_5), −165.8 (t, J = 17.5 Hz, 8F, *m*-F of C_6F_5).

2.9. Activation of rac-(^{H}SBI)$ZrCl_2$ (**4**) with $Ph_3CB(C_6F_5)_4$

NMR reactions were carried out in J-Young NMR tubes, the samples being loaded into the NMR tubes in a glovebox after mixing the two reagents in 0.7 mL of CD_2Cl_2 in a 1:1 ratio (0.02 mmol scale). The mixture was allowed to react at room temperature overnight before the NMR spectra were recorded. A solution and red precipitates were formed. Only the Ph_3CH resonances can be seen in the NMR due to the insolubility of the precipitates. ^{1}H NMR (CD_2Cl_2, 300 MHz, 23 °C): δ 7.11–7.32 (m, 15H, *Ph*$_3$CH), 5.55 (s, 1H, Ph_3CH).

2.10. General polymerization procedures

MMA polymerizations were performed either in 30 mL, oven-dried glass reactor inside the glovebox, or in 25 mL oven- and flame-dried Schlenk flasks interfaced to the dual-manifold Schlenk line. Two different polymerization procedures were employed for comparative studies. In the pre-activation methodology (method A), the precatalyst (metallocene dimethyl complexes) and the activator were premixed in a predetermined ratio in toluene or CH_2Cl_2 and stirred for 10 min (to generate in situ the active species), followed by addition of monomer to start the polymerization. In the in-reactor activation methodology (method B), the precatalyst and the monomer were premixed and the polymerization was started by addition of the activator. After the measured time interval, the polymerization was quenched by addition of 5 mL of 5% HCl-acidified methanol. The quenched mixture was precipitated into 100 mL of methanol, stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Propylene polymerizations were performed in 100 mL oven- and flame-dried Schlenk flasks that was charged with 20 mL solvent (CH_2Cl_2 or toluene) and the desired amounts of the pre catalyst (10 μmol) in glovebox and then interfaced to the high-vacuum line. The flask was degassed at −78 °C and warmed to room temperature. The propylene feed (15 psi) was introduced into this rapidly stirred flask with an external temperature bath equilibrated at the desired polymerization temperature, followed by addition of a solution of $Ph_3CB(C_6F_5)_4$ via a gas-tight syringe to start the polymerization. The pressure of propylene during the polymerization was regulated at 1.0 atm throughout the polymerization. The polymerization was quenched and the polymer product was isolated using the above procedure described for the MMA polymerization.

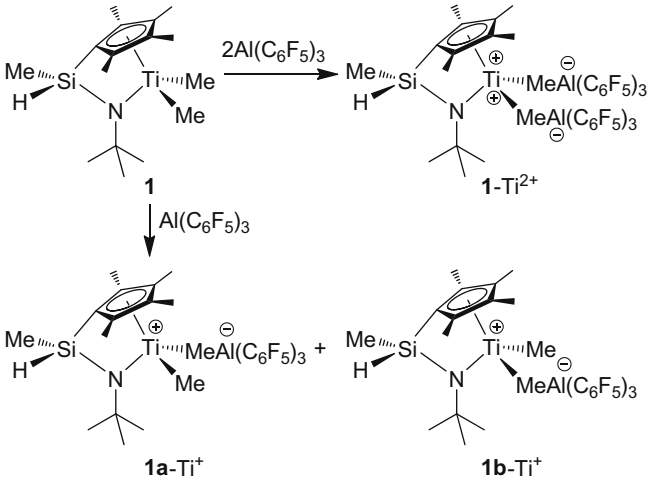
2.11. Polymer characterizations

Molecular weights and molecular weight distributions of PMMA were measured by gel permeation chromatography (GPC) analyses carried out at 40 °C and a flow rate of 1.0 mL/min, with $CHCl_3$ as the eluent on a Waters University 1500 GPC instrument equipped with four 5 μm PL gel columns (Polymer Laboratories). The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Empower software (version 2002); number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were given relative to PMMA standards. ^{1}H NMR spectra for the analysis of PMMA microstructures were recorded in $CDCl_3$ and analyzed according to the literature [20].

3. Results and discussion

3.1. Mono- and di-cations from activation with $E(C_6F_5)_3$ (E = B, Al)

The reaction of (^{H}CGC)$TiMe_2$ (**1**) with 1 equiv of $Al(C_6F_5)_3$ cleanly generates the corresponding cationic complex as two stereo-isomers, **1a**-Ti^{+} and **1b**-Ti^{+} (Scheme 1), a result of the asymmetric substitution at the bridging Si. On the other hand, the reaction of **1** with 2 equiv of $Al(C_6F_5)_3$ affords the corresponding



Scheme 1. Generation of (^{H}CGC)Ti-based mono- and di-cations via activation with $Al(C_6F_5)_3$.

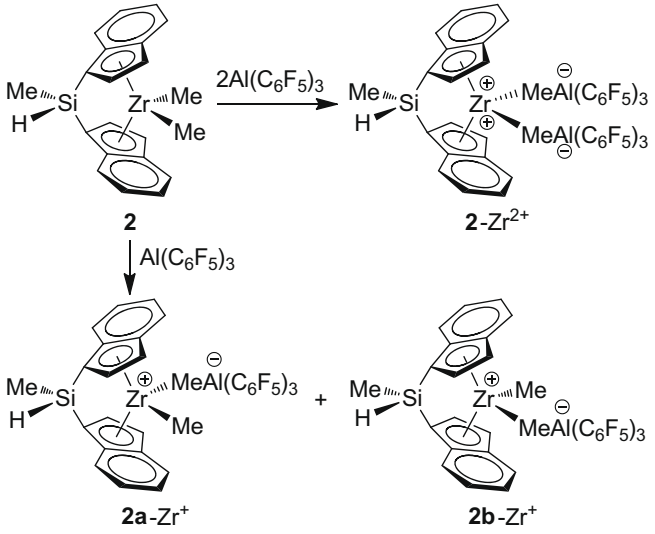
dicationic complex **1**-Ti^{2+} (Scheme 1). Addition of excess $Al(C_6F_5)_3$ does not effect hydride abstraction from the hydrosilyl bridging group in **1**. Furthermore, unlike $Al(C_6F_5)_3$, multiple equiv of $B(C_6F_5)_3$ does not effect the methide abstraction from the second Ti–Me bond, producing only the monocations, analogous to **1a**-Ti^+ and **1b**-Ti^+ (see Section 2). Overall, these activation chemistry results are the same as those seen for the parent (CGC)$TiMe_2$ activated with one or multiple equiv of $E(C_6F_5)_3$, [4] except for the two isomers observed for the monocation derived from **1**.

Likewise, activation of (^{H}SBI)$ZrMe_2$ (**2**) with 1 equiv of $Al(C_6F_5)_3$ cleanly produces the corresponding cationic complex also as two isomers, **2a**-Zr^+ and **2b**-Zr^+, whereas activation with 2 equiv of $Al(C_6F_5)_3$ generates the corresponding dicationic complex **2**-Zr^{2+} (Scheme 1). Activation of **2** with 1 or 2 equiv of $B(C_6F_5)_3$ forms the same monocation as two isomers, analogous to **2a**-Zr^+ and **2b**-Zr^+ (see Section 2). These results are also consistent with the activation of the parent (SBI)$ZrMe_2$ using 1 or multiple equiv of $E(C_6F_5)_3$ [4]. Again, addition of excess $Al(C_6F_5)_3$ does not effect hydride abstraction from the hydrosilyl bridging group in **2** (see Scheme 2).

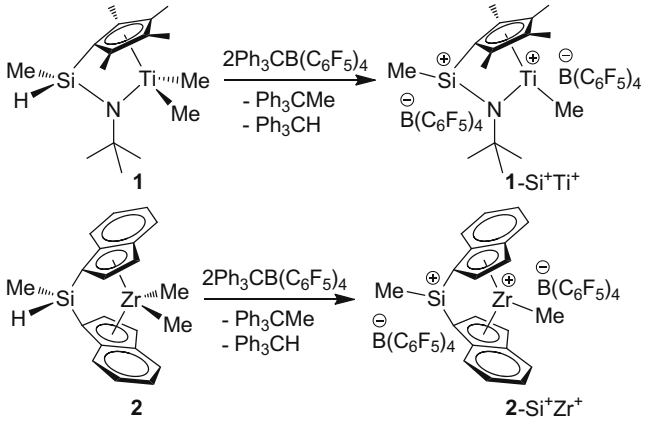
3.2. Hetero-dications from activation with $Ph_3CB(C_6F_5)_4$

As strong Lewis acids $E(C_6F_5)_3$ did not effect the hydride abstraction from the bridging hydrosilyl group, next we examined the oxidative cleavage pathway enabled by $Ph_3CB(C_6F_5)_4$ to potentially generate hetero-dications on the bridging Si and the metal center. Excitingly, treatment of **1** with 2 equiv of $Ph_3CB(C_6F_5)_4$ in toluene-d_8 resulted in spontaneous formation of a red solution accompanied by red oily precipitates; the solution phase is readily shown to be Ph_3CH and Ph_3CMe, and NMR data (see Experimental) of the red precipitates, upon dissolution in CD_2Cl_2, indicate the formation of the dicationic complex **1**-Si^+Ti^+ (Scheme 3), a result of both methide and hydride abstractions from the Ti–Me and Si–H bonds in **1**. The same products were formed when the reaction was carried out directly in CD_2Cl_2. This methodology can be extended to hydrosilyl-bridged zirconocene **2**, the reaction of which with 2 equiv of $Ph_3CB(C_6F_5)_4$ likewise forms the corresponding dicationic complex **2**-Si^+Zr^+ (Scheme 3), with concomitant formation of Ph_3CH and Ph_3CMe co-products.

Interestingly, activation of the dichloride complex (^{H}CGC)$TiCl_2$ (**3**) with 0.5 equiv of $Ph_3CB(C_6F_5)_4$ in CD_2Cl_2 produced a yellow solution consisting of Ph_3CH, (^{Cl}CGC)$TiCl_2$ (**5**), and (^{H}CGC)$TiCl^+$ $[B(C_6F_5)_4]^-$ (**3**-Ti^+, Scheme 4). As outlined in Scheme 4, the reaction is proposed to proceed with the transit silyl cation, **3**-Si^+, with concomitant formation of Ph_3CH, and subsequent chloride abstraction from another 0.5 equiv of **3** by **3**-Si^+ gives both **5** and **3**-Ti^+. Accordingly, the reaction of **3** with 1 equiv of $Ph_3CB(C_6F_5)_4$ further converts **3**-Ti^+ to dication **3**-Si^+Ti^+. Activation of *rac*-(^{H}SBI)$ZrCl_2$ (**4**) with $Ph_3CB(C_6F_5)_4$ in CD_2Cl_2 gave a solution containing Ph_3CH and red precipitates. The reaction is assumed to follow the same pathway forming the corresponding dicationic complex, but the insolubility of this dication hampered its NMR characterizations.



Scheme 2. Generation of (^{H}SBI)Zr-based mono- and di-cations with $Al(C_6F_5)_3$.

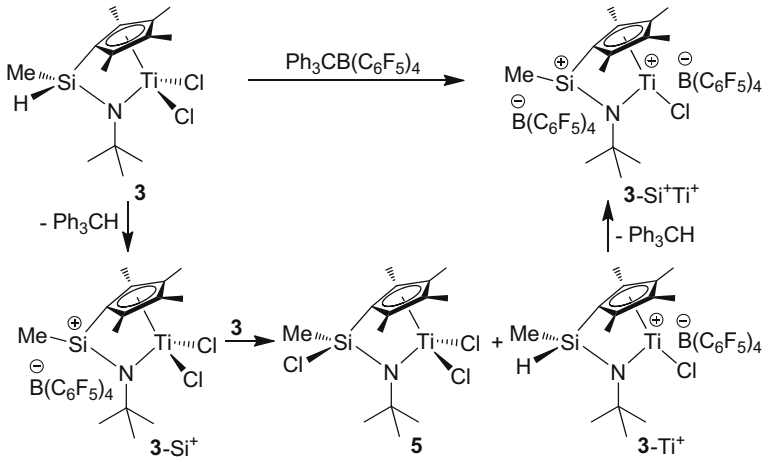


Scheme 3. Generation of silylium–metallocenium (Si^+M^+) dications with 2 equiv of $Ph_3CB(C_6F_5)_4$.

3.3. MMA polymerization

Table 1 summarizes the results of the MMA polymerization by (^{H}CGC)$TiMe_2$ activated with 1 and 2 equiv of $Ph_3CB(C_6F_5)_4$ in a fixed [MMA]:[catalyst] ratio = 400, but in different activation methods (pre-activation and in-reactor activation), solvents (toluene and CH_2Cl_2), and temperature (25 °C and 80 °C). A control run with the $B(C_6F_5)_3$ activation at 25 °C in toluene achieved quantitative monomer conversion in 40 h, producing PMMA with narrow MWD = 1.10 and $M_n = 4.10 \times 10^4$; this experimental M_n value is nearly identical to the calculated M_n value, thereby giving a near quantitative initiator efficiency of 97% (run 1). These results also show living characteristics of the MMA polymerization by this catalyst. The PMMA produced has a syndiotacticity (*rr*) of 75%, similar to that observed for the parent CGC complex (CGC)$TiMe_2$ activated with $B(C_6F_5)_3$ at room temperature [21]. The polymerization activity can be drastically increased by raising the reaction temperature, which reduced the time to achieve near quantitative monomer conversion from 80 h at 25 °C to 4 h at 80 °C while maintaining the living characteristics of the polymerization (run 2); however, the polymer syndiotacticity decreased from 75% *rr* at 25 °C to ~70% *rr* at 80 °C, which was also observed for the parent CGC catalyst [21a].

Turning to the polymerizations by (^{H}CGC)$TiMe_2$ pre-activated with $Ph_3CB(C_6F_5)_4$ in toluene, all polymerization characteristics (activity, control, efficiency, and syndiotacticity) were lowered when comparing the dication generated by 2 equiv of $Ph_3CB(C_6F_5)_4$ (run 4) to the monocation by 1 equiv $Ph_3CB(C_6F_5)_4$ (run 3). This intriguing observation was repeated when either switching to the in-reactor activation methodology (run 6 vs. 5) or raising the temperature to 80 °C (run 8 vs. 7). Also noteworthy is the considerably lower initiator efficiency by the catalyst generated with the $Ph_3CB(C_6F_5)_4$ activation than the catalyst generated with the $B(C_6F_5)_3$ activation, reflecting a consequence of the instability of



Scheme 4. Generation of Si^+Ti^+ dications with $Ph_3CB(C_6F_5)_4$.

Table 1
Selected MMA polymerization results by (^{H}CGC)$TiMe_2$ (**1**).[a]

Run No.	Activator (method)	Solvent	Temp (°C)	Time (h)	Conv. [b] (%)	$10^{-4}M_n$ [c] (g/mol)	MWD [c] (M_w/M_n)	I^* [d] (%)	[*mm*] [b] (%)	[*mr*] [b] (%)	[*rr*] [b] (%)
1	1 $B(C_6F_5)_3$ (A)	TOL	25	40	99	4.10	1.10	97	2.6	22.5	74.9
2	1 $B(C_6F_5)_3$ (A)	TOL	80	4	94	4.17	1.08	90	3.3	27.2	69.5
3	1TTPB (A)	TOL	25	40	96	5.22	1.09	74	2.8	21.2	76.0
4	2TTPB (A)	TOL	25	40	86	5.65	1.21	61	7.2	23.7	69.1
5	1TTPB (B)	TOL	25	40	94	6.40	1.12	59	3.0	20.9	76.1
6	2TTPB (B)	TOL	25	40	86	5.91	1.26	58	6.0	22.8	71.2
7	1TTPB (B)	TOL	80	2	78	5.22	1.10	60	2.1	26.6	71.3
8	2TTPB (B)	TOL	80	2	21	3.63	1.18	23	6.7	29.6	63.7
9	1TTPB (A)	DCM	25	48	23	6.01	1.28	15	2.2	20.3	77.5
10	2TTPB (A)	DCM	25	48	<1	5.51	1.12	<1	5.7	23.4	70.9
11	1TTPB (B)	DCM	25	48	100	6.94	1.12	58	2.0	20.5	77.5
12	2TTPB (B)	DCM	25	48	47	4.40	1.33	43	3.0	20.5	76.5

[a] Carried out in 10 mL toluene (TOL) or CH_2Cl_2 (DCM) at 25 °C or 80 °C; [Zr] = 2.34 mM; $[MMA]_0/[Zr]_0 = 400$; activator = $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$ (TTPB); activation method = pre-activation (the Ti complex and the activator were premixed and stirred for 10 min followed by addition of MMA, method A) or in-reactor activation (the Ti complex and MMA were premixed before addition of the activator, method B).
[b] Monomer conversion and tacticity (methyl triad distribution) determined by ^{1}H NMR spectroscopy.
[c] M_n and MWD determined by GPC relative to PMMA standards in $CHCl_3$.
[d] Initiator efficiency (I^*) = M_n(calc)/M_n(exptl), where M_n(calc) = MW(MMA) × $[MMA]_0/[I]_0$ × conversion (%) + MW of chain-end groups.

Table 2
Selected MMA polymerization results by *rac*-(^{H}SBI)$ZrMe_2$ (**2**).[a]

Run No.	Activator (method)	Solvent	Time (h)	Conv. (%)	$10^{-4}M_n$ (g/mol)	MWD (M_w/M_n)	I^* (%)	[*mm*] (%)	[*mr*] (%)	[*rr*] (%)
13	1TTPB (A)	TOL	4	85	20.3	1.71	17	89.6	6.0	4.4
14	2TTPB (A)	TOL	24	0						
15	1TTPB (A)	DCM	4	48	12.4	1.66	16	74.9	14.7	10.4
16	2TTPB (A)	DCM	24	14	4.80	1.45	12	75.9	14.7	9.4
17	1TTPB (B)	TOL	4	94	21.1	1.48	19	83.6	10.6	5.8
18	2TTPB (B)	TOL	24	2						
19	1TTPB (B)	DCM	4	81	14.1	1.51	23	71.1	17.3	11.6
20	2TTPB (B)	DCM	24	36	5.64	1.62	25	74.7	15.3	10.0

[a] See footnotes in Table 1 for conditions and explanations.

the cations paired with the non-coordinating anion $[B(C_6F_5)_4]^-$, a well-known phenomenon [8]. This instability issue associated with the cation paired with $[B(C_6F_5)_4]^-$ became more pronounced in the polar solvent CH_2Cl_2. Thus, the polymerization with the pre-formed catalyst in CH_2Cl_2 resulted in only 15% efficiency for the monocation (run 9) and <1% efficiency for the even less stable dication (run 10), suggesting most (for the monocation) or nearly all (for the dication) of the pre-formed catalyst have already decomposed before contacting the monomer. To back up this assertion, the same polymerization with the in-reactor activation methodology drastically improved their efficiencies to 58% for the monocation (run 11) and to 43% for dication (run 12).

Table 2 summarizes the results of the MMA polymerization by *rac*-(^{H}SBI)$ZrMe_2$ activated with $Ph_3CB(C_6F_5)_4$. In toluene, the pre-formed monocation exhibits good activity, achieving 85% monomer conversion in 4 h. The PMMA produced has an isotacticity (*mm*) of ~90%, but the polymerization is ill-controlled with a low initiator efficiency of only 17% (run 13), due to the slow initiation by the Zr–Me species [3]. The pre-formed dication showed no activity (run 14) because the dication **2**-Si^+Zr^+ is insoluble in tolu-

Table 3
Selected propylene polymerization results by metallocene catalysts.[a]

Run No.	Precatalyst (method)	[TTPB]/[precat]	Time (min)	Yield[b] (g)	Productivity (10^{-6} g PP/mol h atm)
21	(CGC)$TiMe_2$ (B)	1	10	1.70	1.02
22	(CGC)$TiMe_2$ (B)	2	10	1.69	1.01
23	*rac*-(SBI)$ZrMe_2$ (B)	1	5	3.48	4.18
24	*rac*-(SBI)$ZrMe_2$ (B)	2	5	3.84	4.60
25	(^{H}CGC)$TiMe_2$ (B)	1	10	0.88	0.53
26	(^{H}CGC)$TiMe_2$ (B)	2	10	1.78	1.07
27	*rac*-(^{H}SBI)$ZrMe_2$ (B)	1	5	2.34	2.81
28	*rac*-(^{H}SBI)$ZrMe_2$ (B)	2	5	3.23	3.88

[a] Carried out in 20 mL CH_2Cl_2 at 25 °C with 10 μmol Zr or Ti catalyst under 1 atm propylene using $Ph_3CB(C_6F_5)_4$ (TTPB) as activator using the in-reactor activation procedure.
[b] Average yield of 2–3 runs with typical errors of ⩽5%.

ene. Switching to CH_2Cl_2, the cation instability drastically lowered the polymerization activity for the monocation (run 15), but now the cation solubility gave some activity for the dication (run 16). Again, consistent with the instability of the cation paired with $[B(C_6F_5)_4]^-$, the in-reactor activation methodology improved polymerization performances by such catalysts (runs 17 and 18 vs. runs 13 and 14), especially for polymerizations carried out in CH_2Cl_2 (runs 19 and 20 vs. runs 15 and 16). However, complications using the in-reactor activation may arise from these slowly initiating cationic zirconocene alkyl catalysts due to a competing bimetallic pathway when the neutral zirconocene dimethyl co-exists with the cationic alkyl species, the consequence of which is the lowered overall isotacticity due to the contribution of the syndiotactic polymer produced by the bimetallic pathway [3].

3.4. Propylene polymerization

We first carried out several control runs to determine whether the "trityl effect" [22] (i.e., enhanced activity with increasing trityl borate activator concentration) applies to the current systems under current conditions (0.5 mM catalyst in CH_2Cl_2 at 25°), or not. Specifically, propylene polymerizations using (CGC)$TiMe_2$ activated with 1 or 2 equiv of $Ph_3CB(C_6F_5)_4$ gave an identical activity (run 21 vs. 22, Table 3), consistent with the formation of the same monocationic catalyst with 1 or 2 equiv of the activator. Likewise, the polymerization activity of *rac*-(SBI)$ZrMe_2$ differed only slightly between runs activated with 1 and 2 equiv of $Ph_3CB(C_6F_5)_4$ (run 23 vs. 24). Hence, both systems under the current conditions showed no or non-attributable "trityl effect", thereby establishing a basis for judging effects of the trityl borate activator equivalency on polymerization activity by catalyst structural changes (i.e., monocation vs. dication).

Indeed, the propylene polymerization activity of the dicationic catalyst **1**-Si^+Ti^+ derived from activation of (^{H}CGC)$TiMe_2$ with 2 equiv of $Ph_3CB(C_6F_5)_4$ was twice of that achieved by the monocationic catalyst (run 26 vs. 25). The propylene polymerization by *rac*-(^{H}SBI)$ZrMe_2$ activated with 2 equiv of $Ph_3CB(C_6F_5)_4$ was also seen a 40% activity enhancement over the monocation derived from activation with 2 equiv of $Ph_3CB(C_6F_5)_4$ (run 28 vs. 27). These consistent results argue that the silylium bridging within the dications **1**-Si^+Ti^+ and **2**-Si^+Zr^+ (Scheme 3) enhances the propylene polymerization activity of the respective cationic Ti and Zr metal centers by rendering the metal centers more electrophilic.

4. Conclusions

Hydrosilyl-bridged half-metallocene (^{H}CGC)$TiMe_2$ and metallocene *rac*-(^{H}SBI)$ZrMe_2$ provide a unique platform for generation of a novel class of silylium-metallocenium hetero-dications (Si^+M^+) through simultaneous hydride and methide abstractions from the Si–H and M–Me bonds by the potent abstractor $Ph_3CB(C_6F_5)_4$. On the other hand, homo-dications (M^{2+}) can be readily produced by the activation with 2 equiv of $Al(C_6F_5)_3$, but not with $B(C_6F_5)_4$ or $Ph_3CB(C_6F_5)_4$. Analogous chloride-derivatives of hetero-dications can also be produced starting from the dichloride precursors, but the chloride abstraction occurs through the transit silylium ion.

The formation of the silylium–metallocenium hetero-dications has shown a substantial impact mostly on the activity of polymerization of MMA and propylene. In MMA polymerization, the activity of the dications, especially the metallocene-based **2**-Si^+Zr^+, is substantially lower than the corresponding monocations. The instability and low solubility of the pre-formed cations paired with the non-coordinating anion $[B(C_6F_5)_4]^-$ are assumed to account for the observations. In sharp contrast, the propylene polymerization activity of the dication **1**-Si^+Ti^+, derived from activation of (^{H}CGC)$TiMe_2$ with 2 equiv of $Ph_3CB(C_6F_5)_4$, is twice of that for the monocation. The propylene polymerization by *rac*-(^{H}SBI)$ZrMe_2$ activated with 2 equiv of $Ph_3CB(C_6F_5)_4$ is also seen a 40% activity enhancement over the monocation. These considerably rate enhancements are contributable to the more electrophilic metal centers rendered by the silylium bridging within dications **1**-Si^+Ti^+ and **2**-Si^+Zr^+.

A currently unexplored interesting aspect of the polymerization of polar vinyl monomers is to use the chiral silylium ion within dications such as **1**-Si^+Ti^+ and **2**-Si^+Zr^+ as catalyst and the added ^{Me}SKA as initiator for promoting stereoregulation in silylium-catalyzed polymerization. However, the dications in their present form would present complications due to the presence of two reactive sites within the same complex (i.e., interplay between the silylium-catalyzed bimolecular process and metallocenium-catalyzed unimolecular process). The chloride-derivative **3**-Si^+Ti^+ is seemingly a more suitable candidate, but it co-exists with two other species in a mixture. The work to explore this aspect of the polymerization and develop new approaches to access such isolable dications is in progress.

Acknowledgments

This work was supported by the National Science Foundation (NSF-0848845). We thank Boulder Scientific Co., for the research gifts of $B(C_6F_5)_3$ and $Ph_3CB(C_6F_5)_4$.

Reference

[1] Selected reference works and reviews: (a) E.Y.-X. Chen, A. Rodriguez-Delgado, in: M. Bochmann (Vol. Ed.), M.P. Mingos, R.H. Crabtree (Chief Eds.), Comprehensive Organometallic Chemistry III, Elsevier, Oxford, 2007, vol. 4, pp. 759–1004.;
(b) T. Cuenca, in: M. Bochmann (vol. Ed.), M.P. Mingos, R.H. Crabtree (Chief Eds.), Comprehensive Organometallic Chemistry III, Elsevier, Oxford, 2007, vol. 4, pp. 323–696.;
(c) M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255–270;
(d) R.F. Jordan, Adv. Organomet. Chem. 32 (1991) 325–387.

[2] (a) Selected books, reference works, or journal reviews: L.S. Baugh, J.A.M. Canich (Eds.), Stereoselective Polymerization with Single-Site Catalysts, CRC Press, Boca Raton, FL, 2008;
(b) L. Resconi, J.C. Chadwick, L. Cavallo, in: M. Bochmann (Vol. Ed.), M.P. Mingos, R.H. Crabtree (Chief Eds.), Comprehensive Organometallic Chemistry III, Elsevier, Oxford, 2007, vol. 4, pp. 1005–1166.;
(c) G.J. Domski, J.M. Rose, G.W. Coates, A.D. Bolig, M. Brookhart, Prog. Polym. Sci. 32 (2007) 30–92;
(d) T.J. Marks (Ed.), Proc. Natl Acad. Sci. USA 103 (2006) 15288–15354;
(e) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283–315;
(f) J.A. Gladysz (Ed.), Chem. Rev. 100 (2000) 1167–1681;
(g) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. 34 (1995) 1143–1170.
[3] E.Y.-X. Chen, Chem. Rev. 109 (2009) 5157–5214.
[4] E.Y.-X. Chen, W.J. Kruper, G. Roof, D.R. Wilson, J. Am. Chem. Soc. 123 (2001) 745–746.
[5] Y. Zhang, E.Y.-X. Chen, Macromolecules 41 (2008) 36–42.
[6] Y. Zhang, E.Y.-X. Chen, Macromolecules 41 (2008) 6353–6360.
[7] (a) O.W. Webster, Adv. Polym. Sci. 167 (2004) 1–34;
(b) D.Y. Sogah, W.R. Hertler, O.W. Webster, G.M. Cohen, Macromolecules 20 (1987) 1473–1488;
(c) O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham, T.V. RajanBabu, J. Am. Chem. Soc. 105 (1983) 5706–5708.
[8] E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391–1434.
[9] J.B. Lambert, S. Zhang, C.L. Stern, J.C. Huffman, Science 260 (1993) 1917–1918.
[10] R.D. Allen, T.E. Long, J.E. McGrath, Polym. Bull. 15 (1986) 127–134.
[11] (a) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623–3625;
(b) A.G. Massey, A.J. Park, J. Organomet. Chem. 5 (1966) 218–225;
(c) A.G. Massey, A.J. Park, J. Organomet. Chem. 2 (1964) 245–250.
[12] (a) M. Bochmann, S.J. Lancaster, J. Organomet. Chem. 434 (1992) C1–C5;
(b) J.C.W. Chien, W.-M. Tsai, M.D. Rausch, J. Am. Chem. Soc. 113 (1991) 8570–8571.
[13] (a) C.H. Lee, S.J. Lee, J.W. Park, K.H. Kim, B.Y. Lee, J.S. Oh, J. Mol. Catal. A: Chem. 132 (1998) 231–239;
(b) P. Biagini, G. Lugli, L. Abis, P. Andreussi, US Patent, 5602269, 1997.
[14] S. Feng, G.R. Roof, E.Y.-X. Chen, Organometallics 21 (2002) 832–839.
[15] L.E. Manzer, Inorg. Synth. 21 (1982) 135.
[16] (a) J.-F. Carpentier, V.P. Maryin, J. Luci, R.F. Jordan, J. Am. Chem. Soc. 123 (2001) 898–909;
(b) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S. Lai, Eur. Pat. Appl. EP (1991) 0416815A2.
[17] J.N. Christopher, G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4038–4044.
[18] J. Tian, Y. Soo-Ko, R. Metcalfe, Y. Feng, S. Collins, Macromolecules 34 (2001) 3120–3122.
[19] A.B. Vázquez, P. Royo, E. Herdtweck, J. Organomet. Chem. 683 (2003) 155–164.
[20] (a) A.D. Bolig, E.Y.-X. Chen, J. Am. Chem. Soc. 126 (2004) 4897–4906;
(b) F.A. Bovey, P.A. Mirau, NMR of Polymers, Academic Press, San Diego, CA, 1996;
(c) R.C. Ferguson, D.W. Ovenall, Polym. Prepr. 26 (1985) 182–183;
(d) R. Subramanian, R.D. Allen, J.E. McGrath, T.C. Ward, Polym. Prepr. 26 (1985) 238–240.
[21] (a) B. Lian, C.M. Thomas, C. Navarro, J.-F. Carpentier, Organometallics 26 (2007) 187–195;
(b) A. Rodriguez-Delgado, W.R. Mariott, E.Y.-X. Chen, Macromolecules 37 (2004) 3092–3100;
(c) J. Jin, D.R. Wilson, E.Y.-X. Chen, Chem. Commun. (2002) 708–709.
[22] (a) C. Alonso-Moreno, S.J. Lancaster, J.A. Wright, D.L. Hughes, C. Zuccaccia, A. Correa, A. Macchioni, L. Cavallo, M. Bochmann, Organometallics 27 (2008) 5474–5487;
(b) F. Song, R.D. Cannon, S.J. Lancaster, M. Bochmann, J. Mol. Catal. A: Chem. 218 (2004) 21–28.