Chemical Science

EDGE ARTICLE

Cite this: *Chem. Sci.*, 2023, **14**, 8514

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Rare earth dialkyl cations and monoalkyl dications supported by a rigid neutral pincer ligand: synthesis and ethylene polymerization†

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Received 10th April 2023
Accepted 15th July 2023

DOI: 10.1039/d3sc01830j

rsc.li/chemical-science

A palladium-catalyzed coupling reaction between 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene and 2 equiv. of 1,3-diisopropylimidazolin-2-imine afforded the rigid neutral 2,7-di-*tert*-butyl-4,5-bis(1,3-diisopropylimidazolin-2-imino)-9,9-dimethylxanthene (XII_2) pincer ligand. Reaction of XII_2 with $YCl_3(THF)_{3.5}$ provided $[(XII_2)YCl_3]$ (**1**). However, compound **1** failed to react cleanly with 3 equiv. of $LiCH_2SiMe_3$, and the reaction of XII_2 with $[Y(CH_2SiMe_3)_3(THF)_2]$ afforded a complex mixture of products. To access group 3 alkyl complexes without the intermediacy of $[(XII_2)M(CH_2SiMe_3)_3]$, the XII_2 ligand was protonated using $[H(OEt_2)_2][B(C_6F_5)_4]$ to form $[H(XII_2)][B(C_6F_5)_4]$, and subsequent reaction with $[M(CH_2SiMe_3)_3(THF)_2]$ (M = Y, Sc) directly afforded the cationic scandium and yttrium dialkyl complexes $[(XII_2)M(CH_2SiMe_3)_2][B(C_6F_5)_4]$ {M = Y (**2**) and Sc (**3**)}. Reaction of **3** with $B(C_6F_5)_3$ in C_6D_5Br afforded dicationic $[(XII_2)Sc(CH_2SiMe_2CH_2SiMe_3)][MeB(C_6F_5)_3][B(C_6F_5)_4]$ (**4**) featuring a $CH_2SiMe_2CH_2SiMe_3$ ligand, formed as a result of methyl anion abstraction from silicon, with concomitant migration of the neighbouring CH_2SiMe_3 group from scandium to silicon. The $MeB(C_6F_5)_3$ anion in **4** forms a contact ion pair. By contrast, reaction of **1** with $[CPh_3][B(C_6F_5)_3]$ in C_6D_5Br/toluene or *o*-$C_6H_4F_2$/toluene afforded dicationic $[(XII_2)Sc(CH_2SiMe_3)(\eta^x\text{-toluene})_n][B(C_6F_5)_4]_2$ (**5**). Compounds **2–4** showed negligible ethylene polymerization activity, whereas **5** is highly active (up to 870 kg mol^{-1} h^{-1} atm^{-1} in *o*-$C_6H_4F_2$/toluene under 1 atm of ethylene at room temperature).

Introduction

Homogeneous rare earth (and transition metal) catalysts for olefin insertion polymerization are primarily monocationic alkyl species, generated by electrophilic abstraction of an alkyl group from a neutral polyalkyl pre-catalyst (which may itself be generated *in situ*) in arene or alkane solvent.[1–3] Dicationic alkyl complexes, particularly those which are monometallic and can provide access to a vacant coordination site, offer new catalyst design possibilities and may afford particularly high polymerization activities due to enhanced electrophilicity of the metal centre. However, such complexes have rarely been described or utilized in catalysis (*vide infra*).

A handful of monometallic rare earth alkyl dications which are stabilized through coordination of THF and/or a crown ether have been reported: $[MR(THF)_x]^{2+}$ (x = 4–6; R = Me,[4,5] CH_2Ar,[6] or CH_2SiMe_3 [4,7]), $[M(CH_2SiMe_3)(THF)_x(12\text{-crown-}4)]^{2+}$ (x = 2 or 3),[7] $[MR(12\text{-crown-}4)_2]^{2+}$ (R = Me or CH_2SiMe_3),[7–9] and $[MMe(L)(THF)_x]^{2+}$ (L = 15-crown-5 or 18-crown-6; x = 1 or 2),[8,9] where M is a rare earth element.[10–12] These complexes were generated in THF, and have not been reported to be substantially active ethylene or α-olefin polymerization catalysts, presumably due to a high degree of coordinative saturation. However, highly active ethylene polymerization catalysts were accessed by treatment of toluene solutions of $[M(CH_2SiMe_3)_3(THF)_2]$ (M = Tm, Er, Y, Ho, Dy, Tb) with 5 equiv. of $[HNMe_2Ph][B(C_6F_5)_4]$ in the presence of excess $Al(CH_2SiMe_3)_3$ or Al^iBu_3; one equivalent of $[HNMe_2Ph][B(C_6F_5)_4]$ was insufficient to achieve high polymerization activities, suggesting that the active species is a coordinatively unsaturated alkyl dication. A similarly active ethylene polymerization catalyst was accessed *via* the reaction of $[Y(CH_2SiMe_3)_2(thf)_4][Al(CH_2SiMe_3)_4]$ with 5 equiv. of $[HNMe_2Ph][B(C_6F_5)_4]$ in toluene in the presence of Al^iBu_3. However, neither of the catalytically active species generated in toluene were spectroscopically or crystallographically characterized due to low solubility.[4]

Rare earth alkyl dications which are free from oxygen-donor solvent or crown ether ligands are shown in Fig. 1. The scandium alkyl dications (**A–B**) were generated *in situ via* reactions of a neutral trialkyl precursor with two equiv. of $[CPh_3][B(C_6F_5)_4]$ in chlorobenzene or dichloromethane (for **A**),[13,14] or bromobenzene or toluene (for **B**),[15] and were assigned on the basis of solution NMR studies, and because two equivalents of $[CPh_3]$

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† Electronic supplementary information (ESI) available: NMR spectra, the X-ray structure of compound **3**, and polyethylene GPC data. CCDC 2247081 (**2**) and 2247082 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: **https://doi.org/10.1039/d3sc01830j**

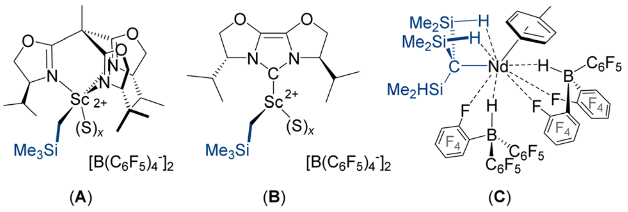


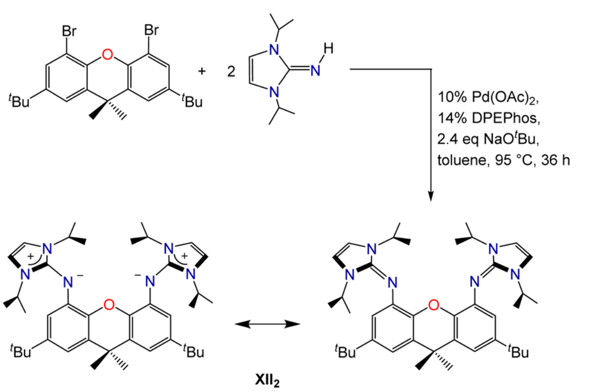
Fig. 1 Rare earth alkyl dications (S = arene solvent) free from oxygen-donor solvent or crown ether ligands: the scandium complexes (A–B) were characterized in solution, whereas neodymium complex C was characterized in solution and the solid state.

$[B(C_6F_5)_4]$ were required to generate an active α-olefin polymerization catalyst.[16] Neodymium complex **C** can be viewed as an alkyl dication with tight ion pairing of the two $HB(C_6F_5)_3^-$ anions. This compound was characterized in solution and by X-ray crystallography, and was found to be a highly active catalyst for butadiene polymerization.[17]

Herein we report the synthesis of a rigid neutral NON-donor pincer ligand, which has enabled the synthesis of scandium and yttrium dialkyl monocations, as well as the monoalkyl dications $[(XII_2)Sc(CH_2SiMe_2CH_2SiMe_3)][MeB(C_6F_5)_3][B(C_6F_5)_4]$ and $[(XII_2)Sc(CH_2SiMe_3)(\eta^x\text{-toluene})_n][B(C_6F_5)_4]_2$. These dications were characterized by solution NMR spectroscopy, and the latter was found to be highly active for ethylene polymerization.

Results and discussion

Palladium-catalyzed coupling of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene with 2 equiv. of 1,3-diisopropylimidazolin-2-imine afforded the neutral XII_2 ligand (2,7-di-*tert*-butyl-4,5-bis(1,3-diisopropylimidazolin-2-imino)-9,9-dimethylxanthene; Scheme 1), in which the ether donor of the xanthene backbone is flanked by imidazolin-2-imine donors. Two resonance structures for the XII_2 ligand are depicted in Scheme 1; the zwitterionic resonance structure is responsible for the high donor ability of the imidazolin-2-imine groups, and also provides a means for the imidazole rings to lie perpendicular to the plane of the xanthene backbone.



Scheme 1 Synthesis and resonance structures of the neutral XII_2 pincer ligand.

The XII_2 ligand is a neutral analogue of our recently reported AII_2 monoanion (4,5-bis(1,3-diisopropylimidazolin-2-imino)-2,7,9,9-tetramethylacridanide; Fig. 2).[18] It is also a close steric analogue of the dianionic XA_2 ligand (4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene; Fig. 2), which we reported in 2007.[19] This dianionic pincer ligand, and relatives with alternative aryl substituents on nitrogen, have been employed for the synthesis of a broad range of highly reactive early transition metal,[20] rare earth,[21,22] actinide,[19,23–30] and main group[31–45] species.

Reaction of XII_2 with $YCl_3(THF)_{3.5}$ cleanly generated $[(XII_2)YCl_3]$ (**1**; Scheme 2), which was isolated in 82% yield, and gave rise to ^1H and ^{13}C NMR spectra corresponding to the expected C_{2v} symmetry. However, compound **1** failed to react cleanly with 3 equiv. of $LiCH_2SiMe_3$ to afford $[(XII_2)Y(CH_2SiMe_3)_3]$. Furthermore, the reaction of XII_2 with $[Y(CH_2SiMe_3)_3(THF)_2]$ afforded a complex mixture of products. Based on these results, we reasoned that $[(XII_2)Y(CH_2SiMe_3)_3]$ may be unstable as a consequence of steric crowding. A related, albeit less-pronounced, situation was previously observed in the uranium chemistry of the dianionic XA_2 ligand, which shares a similar steric profile to XII_2: $[(XA_2)U(CH_2SiMe_3)_2]$ is thermally stable in solution at room temperature, whereas $[Li(THF)_x][(XA_2)U(CH_2SiMe_3)_3]$ decomposed over several days to afford $SiMe_4$ and unidentified paramagnetic products.[26]

To bypass potentially unstable $[(XII_2)Y(CH_2SiMe_3)_3]$, an alternative ligand attachment strategy was pursued (Scheme 2). Reaction of the XII_2 ligand with $[H(Et_2O)_2][B(C_6F_5)_4]$ in fluorobenzene, followed by the addition of hexanes provided $[H(XII_2)][B(C_6F_5)_4]\cdot 0.5$ hexane as a white solid in 86% yield, and subsequent reaction with $[M(CH_2SiMe_3)_3(THF)_2]$ (M = Y or Sc) afforded $[(XII_2)M(CH_2SiMe_3)_2][B(C_6F_5)_4]$ [M = Y (**2**) or Sc (**3**)] in greater than 90% yield. The room temperature ^1H and ^{13}C NMR spectra of **2** are consistent with apparent C_{2v} symmetry, with the MCH_2 signal at −0.77 ppm ($^1J_{C,H}$ 102 Hz) in the ^1H NMR spectrum and 37.2 ppm (d, $^1J_{C,Y}$ 41 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. The ^1H and ^{13}C NMR spectra of scandium complex **3** are similar, but with broadened signals from atoms located outside of the plane of the ligand backbone, indicative of a fluxional process involving migration of the alkyl groups between coordination sites within and above/below the plane of the ligand backbone (with concomitant flexing of the ligand backbone). Consistent with this explanation, a sharper $ScCH_2$ ^1H NMR signal was observed at 48 °C (−0.33 ppm), whereas upon cooling to −33 °C, this signal decoalesced to afford two broad peaks at 0.22 and −0.87 ppm. A similar fluxional process is

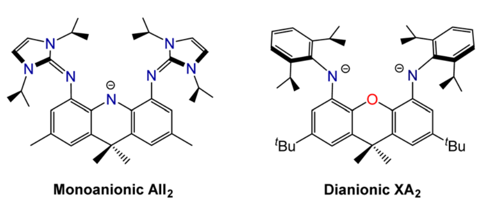
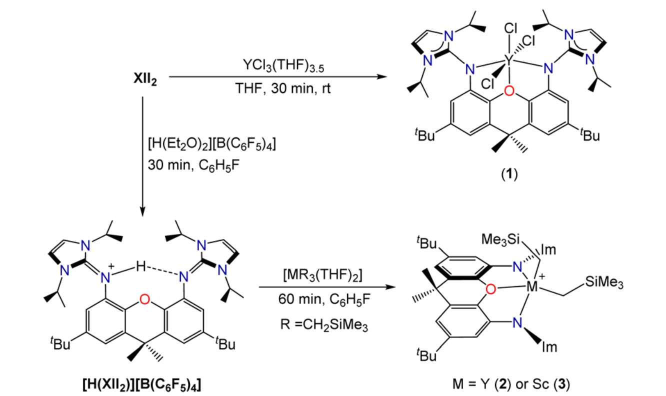


Fig. 2 Monoanionic AII_2 and dianionic XA_2 pincer ligands which are structurally related to the neutral XII_2 ligand in this work.



Scheme 2 Synthesis of complexes **1–3** (Im = 1,3-diisopropylimidazol-2-ylidene).

presumably operative for **2**, but would be expected to be more rapid due to reduced steric hindrance around the larger metal ion.

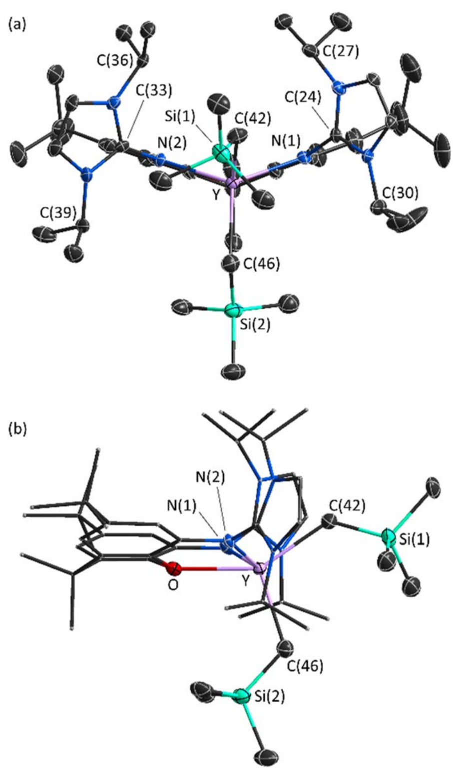


Fig. 3 Front (a) and side (b) views of the cationic portion of the X-ray crystal structure of $[(XII_2)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]\cdot2$hexane (**2**·2hexane). Ellipsoids are set to 30% probability, and hydrogen atoms are omitted for clarity. Both CMe_3 groups and one $SiMe_3$ group (attached to C(42)) are disordered, and only one orientation is shown. In view (b), all atoms of the XII_2 ligand, except for O, N(1) and N(2) are shown in wireframe. Selected bond lengths (Å) and angles (°): Y–N(1) 2.336(4), Y–N(2) 2.330(3), Y–O 2.425(3), Y–C(42) 2.393(5), Y–C(46) 2.385(5), N(1)–C(24) 1.367(5), N(2)–C(33) 1.378(5), C(27)···C(36) 4.80, C(30)···C(39) 8.43, N(1)–Y–N(2) 122.1(1), O–Y–C(42) 145.5(2), O–Y–C(46) 107.4(2), C(42)–Y–C(46) 107.0(2), Y–C(42)–Si(1) 126.3(4), Y–C(42)–Si(1A) 122.8(7), Y–C(46)–Si(2) 119.6(2).

X-ray quality crystals of **2**·2hexane were grown from flurobenzene/hexanes at −29 °C (Fig. 3). The XII_2 ligand is κ^3NON-coordinated, with a ligand backbone bend (the angle between the planes of the two aryl rings of the ligand backbone) of 38° (*cf.* 29° in $[(AII_2)Y(CH_2SiMe_3)_2]$,[18] and 25° in $[(XA_2)Y(CH_2SiMe_3)(THF)]$[21]).[46] One alkyl ligand is located above the plane of the XII_2 ligand backbone, whereas the other is located approximately in the plane, affording a distorted square pyramidal geometry.

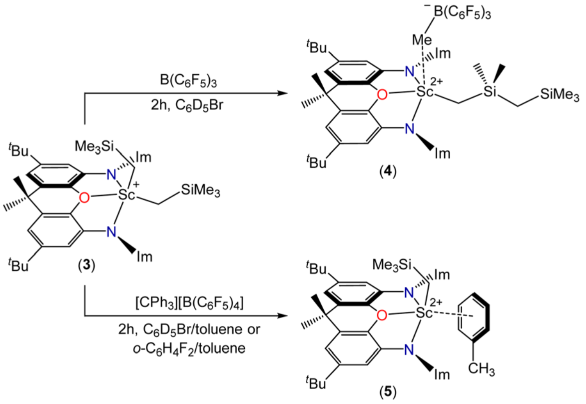
The flanking imidazole rings are oriented approximately perpendicular to the plane of the ligand backbone (with angles of 80° and 87° between the plane of each imidazole ring and the adjacent aryl ring). Furthermore, the imine N(1)–C(24) and N(2)–C(33) distances {1.367(5) and 1.378(5) Å} are significantly longer than those in free imidazolin-2-imines such as (NHC)=N{C_6H_4(OMe)-*p*} (1.308(2) Å; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)[47] and $[\{\kappa^2\text{-}2,6\text{-}C_5H_3N(CH_2N=\{NHC\})_2\}FeCl_2]$ (1.294(3) Å; NHC = 1,3-di-*tert*-butylimidazol-2-ylidene).[48] These observations are consistent with a substantial contribution from the zwitterionic resonance form of the imidazolin-2-imine donors.

Cationic **2** is qualitatively isostructural with neutral $[(AII_2)Y(CH_2SiMe_3)_2]$.[18] However, the Y–C distances of 2.385(5) and 2.393(5) Å in **2** are considerably shorter than those in $[(AII_2)Y(CH_2SiMe_3)_2]$ (2.434(2) and 2.482(2) Å). Similarly, the Y–N(1) and Y–N(2) distances of 2.330(3) Å and 2.336(4) Å in **2** are notably shorter than the $Y\text{–}N_{\text{imidazolin-2-imine}}$ distances in $[(AII_2)Y(CH_2SiMe_3)_2]$ (2.394(2), 2.421(2) Å).[49] These bond metrics are indicative of a significantly more electron deficient yttrium center in cationic **2** than in neutral $[(AII_2)Y(CH_2SiMe_3)_2]$.

X-ray quality crystals of **3**·2PhF were also obtained from fluorobenzene/hexanes at −29 °C (Fig. S44†). The structure of **3** is analogous to that of **2**, but with M–C and M–N bonds which are shorter by 0.14–0.18 Å, primarily reflecting the lower ionic radius of Sc^{III} (0.745 Å) *versus* Y^{III} (0.90 Å).[50] The ligand backbone bend angle is slightly more obtuse (41°) than that in **2**, and the N(1)–C(24) and N(2)–C(33) distances of 1.369(4) Å (for both) are equal within error to those in **2**.

Reactions of compound **2** with $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ in bromobenzene or toluene/bromobenzene afforded mixtures of unidentified products accompanied by $SiMe_4$. By contrast, the reaction of **3** with $B(C_6F_5)_3$ in bromobenzene (Scheme 3) cleanly produced a new C_s symmetric product with a ^{1}H NMR spectrum featuring Si*Me*$_x$ signals at −0.12 and −0.31 ppm, integrating to 9H and 6H respectively, accompanied by two C*H*$_2$ signals (2H each) at 0.85 and −0.66 ppm, and a broad singlet (3H) at 1.51 ppm (Fig. 4). These data point to the formation of dicationic $[(XII_2)Sc(CH_2SiMe_2CH_2SiMe_3)][MeB(C_6F_5)_3][B(C_6F_5)_4]$ (**4**), resulting from methyl anion abstraction from silicon, with concomitant migration of the neighbouring CH_2SiMe_3 group from scandium to silicon.[51]

The ^{1}H–^{13}C and ^{1}H–^{29}Si HMBC NMR spectra provide further support the formation of a $CH_2SiMe_2CH_2SiMe_3$ ligand. For example, in the ^{1}H–^{13}C HMBC (Fig. S24†), the γ-*C*H$_2$ carbon signal couples to the proton signals of both the Si*Me*$_2$ and Si*Me*$_3$ groups, and the Si*Me*$_2$ proton signal couples to both the α-*C*H$_2$ and γ-*C*H$_2$ carbon signals. In the ^{1}H–^{29}Si HMBC (Fig. S27†), the



Scheme 3 Synthesis of dications **4** and **5** (Im = 1,3-diisopropylimidazol-2-ylidene). In the structures of **4** and **5**, the alkyl groups may be coordinated within or above the plane of the ligand backbone, and only one possibility is shown. The hapticity of toluene coordination in **5** is unknown (toluene coordination is proposed because attempted syntheses of **5** in the absence of toluene did not afford a stable product).

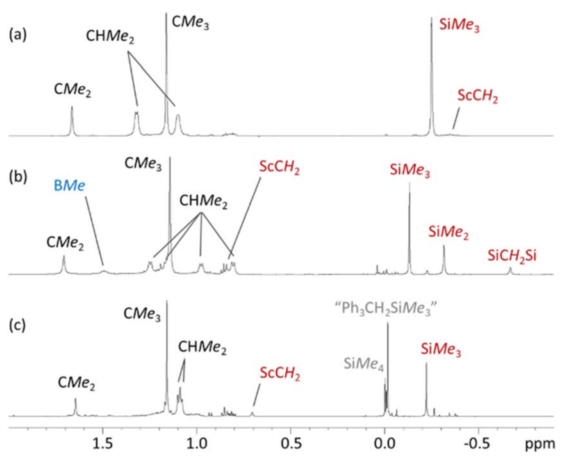


Fig. 4 Alkyl region of the ^{1}H NMR spectra of (a) [(XII$_2$)Sc(CH$_2$SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$] (**3**), (b) [(XII$_2$)Sc(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)][MeB(C$_6$F$_5$)$_3$][B(C$_6$F$_5$)$_4$] (**4**) generated *in situ*, and (c) [(XII$_2$)Sc(CH$_2$SiMe$_3$)(η^x-toluene)$_n$][B(C$_6$F$_5$)$_4$]$_2$ (**5**) generated *in situ* in the presence of 5 equiv. of toluene. All spectra are in C$_6$D$_5$Br. The spectra of **3** and **5** are at 298 K, whereas the spectrum of **4** is at 252 K.

α-C*H*$_2$ and Si*Me*$_2$ protons couple to just one silicon center (*Si*Me$_2$), the Si*Me*$_3$ protons couple to a different silicon center (*Si*Me$_3$), and the γ-CH$_2$ group appears to couple to both silicon centers, although this is harder to distinguish due to overlapping cross-peaks.

The ^{19}F and ^{11}B NMR spectra are also consistent with the proposed structure of **4**. For example, the ^{11}B NMR spectrum of **4** features two sharp signals corresponding to the B(C$_6$F$_5$)$_4$ (δ −16.2 ppm) and MeB(C$_6$F$_5$)$_3$ (δ −15.0 ppm) anions. The latter chemical shift is comparable to that in previously reported scandium contact ion pairs involving a MeB(C$_6$F$_5$)$_3$ anion.[51–53] The ^{19}F NMR spectrum shows the expected set of three signals for a free B(C$_6$F$_5$)$_4$ anion, accompanied by another set of signals for the MeB(C$_6$F$_5$)$_3$ anion {δ −133.27 (*o*-F), −157.57 (*p*-F), −162.09 (*m*-F)}. The large difference in the chemical shift between the *meta* and *para* fluorine signals {$\Delta\delta_{m,p}$} of the MeB(C$_6$F$_5$)$_3$ anion (4.52 ppm) is indicative of a contact ion pair where the borate interacts with the metal centre *via* the methyl group.[54] Contact ion pairing is also indicated by the high frequency chemical shift of the B*Me* methyl group in the ^{1}H NMR spectrum (1.51 ppm), relative to that of the free anion (1.13 ppm).[54]

Analogous reactivity (leading to a monocation rather than a dication) has previously been reported.[51,55,56] Piers *et al.* described the reaction of [(nacnac)Sc(CH$_2$SiMe$_3$)$_2$] {nacnac = ArNC(^{t}Bu)CHC(^{t}Bu)NAr; Ar = 2,6-C$_6$H$_3$^{i}Pr$_2$} with B(C$_6$F$_5$)$_3$ to afford the contact ion pair [(nacnac)Sc(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)][MeB(C$_6$F$_5$)$_3$],[51] and Gordon *et al.* reported the reaction of [(κ^3-L)Lu(CH$_2$SiMe$_3$)$_2$] {L = NC$_5$H$_3$(CMe=NAr)(CMe$_2$NAr)-2,6; Ar = 2,6-C$_6$H$_3$^{i}Pr$_2$} with B(C$_6$F$_5$)$_3$ in the presence of THF to form the solvent-separated ion pair [(κ^3-L)Lu(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)(THF)][MeB(C$_6$F$_5$)$_3$].[55] Notably, the ^{1}H NMR chemical shifts for the CH$_2$SiMe$_2$CH$_2$SiMe$_3$ ligand and MeB(C$_6$F$_5$)$_3$$^-$ anion in **4** are very similar to those in [(nacnac)Sc(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)][MeB(C$_6$F$_5$)$_3$]: 0.02 (Si*Me*$_3$), −0.20 (Si*Me*$_2$), 1.16 (α-C*H*$_2$), −0.73 (γ-C*H*$_2$) and 1.51 (B*Me*) ppm.[51]

The reaction of **3** with a slight excess of [CPh$_3$][B(C$_6$F$_5$)$_4$] in bromobenzene was also investigated, and with rapid stirring in the presence of 5 equiv. of toluene, the dicationic monoalkyl complex [(XII$_2$)Sc(CH$_2$SiMe$_3$)(η^x-toluene)$_n$][B(C$_6$F$_5$)$_4$]$_2$ (**5**; Scheme 3) was generated over the course of 2 hours. Compound **5** gave rise to a ScC*H*$_2$ signal at 0.70 ppm (2H) in the ^{1}H NMR spectrum (Fig. 4), and 63.9 ppm in the ^{13}C NMR spectrum. The expected $^3J_{C,H}$ correlations were observed between the ScC*H*$_2$ and Si*Me*$_3$ groups in the ^{1}H–^{13}C HMBC NMR spectrum, and ^{11}B and ^{19}F NMR spectra confirmed that the B(C$_6$F$_5$)$_4$ anions are intact, ruling out C$_6$F$_5$ transfer from boron to scandium. Compound **5** exhibits apparent C_{2v} symmetry in solution (between 25 and −33 °C; measurements at lower temperature were not possible due to the melting point of bromobenzene, insolubility of **5** in toluene, and decomposition of **5** in dichloromethane), indicating that the alkyl group migrates rapidly between positions above and below the plane of the ligand backbone, or less likely, is located within the plane of the ligand backbone.

Dicationic **5** is poorly soluble, so the reaction afforded a bright orange solution accompanied by a dark orange oil which precipitated over the course of the 2 hour reaction period. The formation of **5** was accompanied by previously described byproducts of trimethylsilylmethyl group abstraction by the trityl cation: Ph$_3$CH as well as a product attributed to "Ph$_3$CCH$_2$SiMe$_3$" (one of two typically observed isomers).‡[19,57]

Bromobenzene solutions of **5**, in the presence of five equivalents of toluene, were stable for hours at room temperature, with a substantial amount of the dication remaining after two days. However, in the absence of toluene, the 1 : 1 reaction of [CPh$_3$][B(C$_6$F$_5$)$_4$] with **3** in C$_6$D$_5$Br resulted in multiple unidentified products, as well as SiMe$_4$, indicative of decomposition. This strongly suggests that compound **5** is stabilized by toluene π-coordination (*i.e.* n = 1). Efforts to obtain crystals of **5** were unsuccessful, and ^{1}H NMR spectra at −33 °C did not show separate signals for free and coordinated toluene (consistent with the apparent C_{2v} symmetry of **5** at this temperature). However, arene π-coordination has frequently been observed for sterically similar monoalkyl monocations of the XA_2 ligand, such as $[(XA_2)ZrMe(\eta^6\text{-toluene})]^+$,[20] $[(XA_2)Th(CH_2SiMe_3)(\eta^6\text{-benzene})]^+$, $[(XA_2)Th(CH_2Ph)(\eta^6\text{-toluene})]^+$,[29] $[(XA_2)U(CH_2SiMe_3)(\eta^6\text{-benzene})]^+$, and $[(XA_2)U(CH_2SiMe_3)(\eta^3\text{-}C_6H_5R)]^+$ (R = Me or F).[30]

Dicationic **4** (a contact ion pair) showed negligible ethylene polymerization activity in fluorobenzene under 1 atm of ethylene at room temperature. By contrast, dicationic **5** proved to be a highly[3] active catalyst for ethylene polymerization: exposure of a 0.2 mM solution of **5** in toluene/*o*-difluorobenzene to 1 atm of ethylene at room temperature (with a water bath around the flask),§ followed by quenching with acidified methanol after 3 minutes, afforded a polymerization activity of 870 kg mol^{-1} h^{-1} atm^{-1} (Table 1). A similar activity of 740 kg mol^{-1} h^{-1} was obtained when the reaction was quenched after 2 minutes. However, a lower activity of 570 kg mol^{-1} h^{-1} atm^{-1} was achieved after 5 minutes, perhaps as a result of ineffective stirring due to precipitation of substantial amounts of polymer, catalyst entrapment within the precipitated polymer, and/or catalyst decomposition arising from the exothermic nature of the reaction. Attempted polymerization in neat *o*-difluorobenzene afforded (with quenching after 3 minutes) a lower polymerization activity of 170 kg mol^{-1} h^{-1} atm^{-1}, presumably due to significant catalyst decomposition in the absence of toluene.

The polydispersity of the polyethylene produced in these experiments was fairly narrow, with values of 1.40 and 1.41 when the reaction was carried out in toluene/*o*-difluorobenzene and quenched after 2 or 3 minutes, respectively (Table 1), indicative of single-site catalysis. The weight average molecular weight (M_w) of the polyethylene also increased with increasing reaction time; from 66 kg mol^{-1} when the reaction was quenched after 2 minutes, to 112 kg mol^{-1} after 3 minutes, and 202 kg mol^{-1} after 5 minutes, (although after 5 minutes, a higher polydispersity of 2.06 was observed).

The polymerization activity of **5** is comparable to that of $[Y(CH_2SiMe_3)_3(THF)_2]$ activated with 5 equiv. of $[HNMe_2Ph][B(C_6F_5)_4]$ in toluene to generate a dication *in situ* {activities between 272 and 1840 kg mol^{-1} h^{-1} atm^{-1} were obtained under 5 atm of ethylene in the presence of 200 equiv. of MAO or AlR_3; R = ^{i}Bu or CH_2SiMe_3}, although it is notable that under comparable conditions, the analogous reaction with $[Sc(CH_2SiMe_3)_3(THF)_2]$ exhibited negligible polymerization activity.[4]

Summary and conclusions

Palladium-catalysed coupling afforded the neutral XII_2 pincer ligand, 2,7-di-*tert*-butyl-4,5-bis(1,3-diisopropylimidazolin-2-imino)-9,9-dimethylxanthene (XII_2), and reaction with $YCl_3(THF)_{3.5}$ provided $[(XII_2)YCl_3]$ (**1**). However, compound **1** failed to react cleanly with 3 equiv. of $LiCH_2SiMe_3$, and the reaction of XII_2 with $[Y(CH_2SiMe_3)_3(THF)_2]$ afforded a complex mixture of products. To access group 3 alkyl complexes without the intermediacy of $[(XII_2)Y(CH_2SiMe_3)_3]$, the XII_2 ligand was protonated to form $[H(XII_2)][B(C_6F_5)_4]$, and subsequent reaction with $[M(CH_2SiMe_3)_3(THF)_2]$ (M = Y, Sc) directly afforded the cationic dialkyl complexes $[(XII_2)M(CH_2SiMe_3)_2][B(C_6F_5)_4]$ {M = Y (**2**) and Sc (**3**)}. Cations **2** and **3** feature substantially shorter M–C and M–N bond distances than in the isostructural neutral AII_2 complexes, $[(AII_2)M(CH_2SiMe_3)_2]$ (M = Y or Sc),[18] indicative of a much more electrophilic metal centre in **2** and **3**.

Compound **2** did not react cleanly with $B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$. By contrast, reaction of **3** with $B(C_6F_5)_3$ in C_6D_5Br afforded the dicationic contact ion pair $[(XII_2)Sc(CH_2SiMe_2CH_2SiMe_3)][MeB(C_6F_5)_3][B(C_6F_5)_4]$ (**4**), which features a $CH_2SiMe_2CH_2SiMe_3$ ligand, presumably resulting from methyl anion abstraction from silicon with concomitant migration of the neighbouring CH_2SiMe_3 group from scandium to silicon. This type of reactivity is uncommon, but has previously been observed in the synthesis of a scandium and a lutetium alkyl monocation. Alternatively, reaction of **3** with $[CPh_3][B(C_6F_5)_3]$ in C_6F_5Br/toluene or $o\text{-}C_6H_4F_2$/toluene afforded dicationic $[(XII_2)Sc(CH_2SiMe_3)(\eta^x\text{-toluene})_n][B(C_6F_5)_4]_2$ (**5**). Compounds **4** and **5** are extremely rare examples of monometallic rare earth alkyl dications, especially those free from ether solvent or crown-ether coordination. The reactivity of **3** with CPh_3^+ also contrasts that of $[(AII_2)Y(CH_2SiMe_3)_2]$ with CPh_3^+ which generated $[(AII_2\text{-}CH_2SiMe_3)Y(CH_2SiMe_3)_2][B(C_6F_5)_4]$ ($AII_2\text{-}CH_2SiMe_3$ is a neutral tridentate ligand with a central amine donor flanked by imidazolin-2-imine groups) in approx. 20% yield, accompanied by $HCPh_3$, an unidentified paramagnetic product, and a colourless precipitate, likely *via* a pathway involving initial oxidation of the acridanide ligand backbone.[18]

Table 1 Ethylene polymerization data for catalyst **5** (0.2 mM concentration)[a] under 1 atm of ethylene at room temperature

Solvent	Polymerization time (min)	Yield (g)	Activity (kg mol^{-1} h^{-1} atm^{-1})	M_w[b] (g mol^{-1})	M_w/M_n
Toluene/*o*-$C_6H_4F_2$	2	0.239	741	65 700	1.40
Toluene/*o*-$C_6H_4F_2$	3	0.420	868	111 880	1.41
Toluene/*o*-$C_6H_4F_2$	5	0.456	565	202 100	2.06
o-$C_6H_4F_2$	3	0.135	168	170 550	1.29

[a] The catalyst solution was generated *in situ* by stirring 15 mg of $[(XII_2)Sc(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) with 1 equiv. of $[CPh_3][B(C_6F_5)_4]$ in 3 mL of solvent (either a 1 : 2 mixture of toluene and *o*-$C_6H_4F_2$, or neat *o*-$C_6H_4F_2$) for 2 hours, followed by the addition of an additional 40 mL of solvent (either a 3 : 1 mixture of toluene and *o*-$C_6H_4F_2$, or neat *o*-$C_6H_4F_2$). [b] Values from GPC are relative to polyethylene standards. Additional data (M_p, M_z, M_v and M_p) is provided in the ESI.

Compounds **2–4** showed negligible ethylene polymerization activity. By contrast, dicationic **5** is a highly active catalyst (up to 870 kg mol^{-1} h^{-1} atm^{-1} in *o*-$C_6H_4F_2$/toluene under 1 atm of ethylene at room temperature). This illustrates the utility of highly electrophilic dicationic alkyl species for olefin polymerization, and highlights the ability of the neutral XII_2 pincer ligand to serve as a robust ancillary ligand, capable of stabilizing extremely reactive organometallic species. Ligand rigidity can be anticipated to be particularly important in the case of neutral ligands, to prevent dissociation of one or more neutral donor. The XII_2 ligand is sterically analogous to our dianionic XA_2 pincer ligand (4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene), which has been employed by our group and others for the synthesis of highly reactive organometallic complexes of the early transition metals and f-elements, as well as a range of reactive main group species.

Experimental

General experimental

An argon-filled M-Braun UNIlab glovebox equipped with a −29 °C freezer was employed for the manipulation and storage of all air sensitive compounds, and reactions were performed on a double manifold vacuum line (with all glass–glass connections, rather than connections *via* hose tubing) using standard techniques. A Fisher Scientific Ultrasonic FS-30 bath was used to sonicate reaction mixtures where indicated. The scandium and yttrium compounds reported in this article are very air and moisture sensitive, and the vacuum line operated at <5 mTorr. Argon (99.999%) and ethylene (99.999%) were purchased from Praxair, and both gases were further purified by passage through an Oxisorb-W scrubber from Matheson Gas Products.

Hexanes and THF were initially dried and distilled at atmospheric pressure from sodium/benzophenone, while toluene was dried and distilled at atmospheric pressure from sodium. These solvents were then stored over an appropriate drying agent (toluene, THF = Na/Ph_2CO; hexanes = Na/Ph_2CO/tetraglyme). Fluorobenzene, 1,2-difluorobenzene, C_6D_5Br, and CD_2Cl_2 were dried over 4 Å molecular sieves, and C_6D_6 was dried over sodium/benzophenone; these solvents were degassed *via* three freeze–pump–thaw cycles. All solvents were introduced to reactions or solvent storage flasks *via* room temperature vacuum transfer with condensation at −78 °C (except for C_6D_5Br which was distilled at elevated temperature *in vacuo*).

4,5-Dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene,[19] [$Y(CH_2SiMe_3)_3(THF)_2$],[58] [$Sc(CH_2SiMe_3)_3(THF)_2$],[59] $B(C_6F_5)_3$,[60,61] and 1,3-diisopropylimidazolin-2-imine[62] were synthesized using literature procedures. [$H(Et_2O)_2$][$B(C_6F_5)_4$] was prepared using a modification of the literature synthesis:[63] a 2.0 M solution of HCl in OEt_2 (100 mL) was added *via* canula to a −78 °C solution of K[$B(C_6F_5)_4$] (10.0 g) in OEt_2 (30 mL); the reaction was stirred for 4 h at −30 °C before removal of the cold bath, filtration to remove KCl, and evaporation of the filtrate to dryness; the resulting white solid was washed with 10 mL of OEt_2 and then dried *in vacuo* to afford 6.5–8.0 g of the product.

$LiCH_2SiMe_3$ (1.0 M in pentane), 1,3-diisopropylimidazolium chloride, HCl (2.0 M in OEt_2), anhydrous YCl_3, anhydrous $ScCl_3$, $Pd(OAc)_2$, NaO^tBu, and DPEPhos were purchased from Sigma Aldrich. [CPh_3][$B(C_6F_5)_4$] was purchased from Alfa Aesar. K[$B(C_6F_5)_4$] was purchased from Boulder Scientific. $YCl_3(THF)_{3.5}$ and $ScCl_3(THF)_3$ were obtained by refluxing anhydrous MCl_3 (M = Y, Sc) in dry THF for 24 hours, followed by removal of solvent under vacuum. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

Combustion elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, Indiana. NMR spectroscopy [^{1}H, ^{13}C{^{1}H}, DEPT-Q, COSY, HSQC, ^{1}H–^{13}C and ^{1}H–^{29}Si HMBC, ^{19}F, ^{11}B, ^{29}Si] was performed on a Bruker AV-600 or AV-500 Spectrometer. All ^{1}H NMR and ^{13}C NMR spectra were referenced relative to $SiMe_4$ using the resonance of the deuterated solvent (^{13}C NMR) or protio impurity in the deuterated solvent (^{1}H NMR); in ^{1}H NMR, 7.16 ppm for C_6D_6, 5.32 ppm for CD_2Cl_2, and 7.30, 7.02 and 6.94 ppm for C_6D_5Br; in ^{13}C NMR, 128.06 ppm for C_6D_6, 54.00 ppm for CD_2Cl_2, and 130.90, 129.41, 126.24 and 122.17 ppm for C_6D_5Br. All NMR spectra were obtained at 298 K unless otherwise specified.

X-ray crystallographic analyses were performed on crystals coated in Paratone oil and mounted on a Bruker SMART APEX II diffractometer with a 3 kW sealed-tube Mo generator and APEX II CCD detector in the McMaster Analytical X-Ray (MAX) Diffraction Facility. A semi-empirical absorption correction was applied using redundant and symmetry related data. Raw data was processed using XPREP (as part of the APEX v2.2.0 software), and solved by intrinsic (SHELXT)[64] methods. Structures were completed by difference Fourier synthesis and refined with full-matrix least-squares procedures based on F^2. In all cases, non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated in ideal positions and then updated with each cycle of refinement. Refinement was performed with SHELXL[65] in Olex2.[66] Two equivalents of disordered solvent (C_6H_5F or C_6H_{14}) were masked in the structures of **2** and **3** using the BYPASS method within Olex2.[67] Definitive identification of the masked solvent as either C_6H_5F or C_6H_{14} was not possible given the identical number of electrons in both solvents. For **2**, two equivalents of C_6H_{14} were masked, while for **3**, two equivalents of C_6H_5F were masked, because the difference map for the un-masked data contained maxima (in the void between molecular units) that roughly corresponded to a 6-membered ring.

Polyethylene molecular weights and molecular weight distributions were obtained using a Polymer Labs (now an Agilent company) PL-220 gel permeation chromatograph with 1,2,4-trichlorobenzene as the solvent at a flow rate of 1 mL min^{-1} and at 145 °C. 2,6-Di-*tert*-butyl-4-methylphenol (BHT) at a concentration of 0.5 g L^{-1} was used as a stabilizer in the solvent. An injection volume of 400 μL was used with a nominal polymer concentration of 1 g L^{-1}. Dissolution of the stabilized sample was carried out by heating at 150 °C for 5 h with occasional agitation. Three Waters HT-6E columns (7.8 × 300 mm) were used and calibrated with a broad linear polyethylene standard (Phillips Marlex® BHB 5003) whose molecular weight had previously been determined.

2,7-Di-*tert*-butyl-4,5-bis(1,3-diisopropylimidazolin-2-imino)-9,9-dimethylxanthene (XII_2)

A mixture of $Pd(OAc)_2$ (46.7 mg, 0.208 mmol), DPEPhos (156 mg, 0.29 mmol), NaO^tBu (479 mg, 2.49 mmol) was dissolved in approximately 20 mL of toluene in a 100 mL bomb, and stirred at room temperature for 10 minutes in the glovebox. A solution of 1,3-diisopropylimidazolin-2-imine (720 mg, 4.3 mmol) and 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (1.00 g; 2.08 mmol) in approximately 30 mL of toluene was added to the reaction mixture. The reaction mixture was sealed in the 100 mL bomb and placed in a room temperature oil bath which was heated slowly (over several hours) to 95 °C, and maintained at this temperature for 48 h {note: placing the flask directly into a 95 °C oil bath, or cooling and re-heating before the 48 h at 95 °C had elapsed, generated undesired byproducts}. The reaction solution was passed through a pad of Celite and volatiles were removed under reduced pressure to afford a dark brown oil. Under air, the product was extracted using approximately 60 mL of CH_2Cl_2 and was washed with 60 mL of water. The resulting aqueous layer was additionally extracted with 30 mL of CH_2Cl_2 and the organic layers were combined. The organic layer was dried over $MgSO_4$ and gravity filtered. Volatiles were removed from the filtrate under reduced pressure to afford a sticky dark brown solid. This solid was dissolved in approximately 50 mL of hexanes and was passed through a pad of Celite, yielding a dark orange filtrate. The filtrate was concentrated to approximately 10 mL and was placed at −18 °C overnight. The resulting beige powder was dried for 12 h at 80 °C under reduced pressure to yield 609 mg of XII_2 (45% yield). ^{1}H NMR (C_6D_6, 600 MHz, 298 K): δ 7.13 (s. 4H, $CH^{1,8}$ & $CH^{3,6}$), 5.92 (s, 4H, N-C*H*), 4.45 (sept, 4H, $^3J_{H,H}$ 7 Hz, C*H*Me$_2$), 1.82 (s, 6H, C*Me*$_2$), 1.38 (s, 18H, C*Me*$_3$) 1.00 (d, 24H, $^3J_{H,H}$ 7 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K): δ 144.64 (s, N*C*N), 144.47 (s, $C^{2,7}$), 142.77 (s, $C^{4,5}$), 140.09 (s, $C^{11,12}$) 130.46 (s, $C^{10,13}$), 118.00 (s, $CH^{1,8}$), 112.02 ($CH^{3,6}$), 107.73 (s, N-*C*H), 45.26 (s, *C*HMe$_2$), 35.57 (s, C^9). 34.58 (s, *C*Me$_3$), 32.03 (s, C*Me*$_2$ & C*Me*$_3$), 21.78 (s, CH*Me*$_2$) ppm. $C_{41}H_{60}N_6O_1$ (652.95 g mol^{-1}): calcd C 75.42, H 9.26, N 12.87%; found. C 75.63, H 9.47, N 12.51%.

[(XII_2)YCl_3] (1)

A solution of XII_2 (100 mg, 0.153 mmol) in 5 mL of THF was added dropwise to a solution of [$YCl_3(THF)_{3.5}$] (69 mg, 0.153 mmol) in THF (5 mL) at room temperature and the reaction was stirred for 1 hour. Approximately 40 mL of hexanes was added to the reaction, resulting in the precipitation of a white solid. The solution was decanted, and the white solid was further dried under vacuum for 1 hour. The solid was then washed with hexanes (3 × ∼5 mL) and dried under vacuum for 2 hours, yielding **1** as an air-sensitive white solid (106 mg, 82% yield). ^{1}H NMR (CD_2Cl_2, 600 MHz, 298 K): δ 7.07 (s, 4H, N-C*H*), 6.81 (s, 2H, $CH^{1,8}$), 5.65 (s, 2H, $CH^{3,6}$), 5.08 (sept, 4H, $^3J_{H,H}$ 7 Hz, C*H*Me$_2$), 1.73 (s, 6H, C*Me*$_2$), 1.54 (d, 12H, $^3J_{H,H}$ 7 Hz, C*H*Me$_2$), 1.29 (d, 12H, $^3J_{H,H}$ 7 Hz, C*H*Me$_2$), 1.20 (s, 18H, C*Me*$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz, 298 K): δ 148.39 (s, N*C*N), 147.12 (s, $C^{2,7}$), 141.66 (s, $C^{4,5}$), 137.89 ($C^{11,12}$), 129.23(s, $C^{10,13}$), 114.79 (s, N-*C*H), 112.94 (s, $CH^{1,8}$), 109.72 (s, $CH^{3,6}$), 48.81 (s, *C*HMe$_2$), 34.75 (s, *C*Me$_3$), 34.38 (s, C^9), 34.04 (s, C*Me*$_2$), 31.50 (s, C*Me*$_3$), 23.63, 23.33 (2 × s, CH*Me*$_2$) ppm. $C_{41}H_{60}N_6O_1Cl_3Y$ (848.22 g mol^{-1}): calcd C 58.06, H 7.13, N 9.91%; found. C 58.33, H 7.16, N 9.43%.

[H(XII_2)][B(C_6F_5)$_4$]·0.5hexane

A solution of [H(Et_2O)$_2$][B(C_6F_5)$_4$] (127 mg, 0.153 mmol) in approximately 10 mL of C_6H_5F was added dropwise to a solution of XII_2 (**1**) (100 mg, 0.153 mmol) in C_6H_5F (5 mL) at room temperature. The reaction was stirred for 1 hour and 40 mL of hexanes was added, which resulted in precipitation of a white solid. The solution was decanted, and the solid was dried under vacuum. The solid was further washed with hexanes (3 × ∼5 mL) and then dried under vacuum for 4 hours, yielding [H(XII_2)][B(C_6F_5)$_4$]·0.5 hexane as a white solid (182 mg, 86% yield). ^{1}H NMR (CD_2Cl_2, 600 MHz, 298 K): δ 7.03 (s, 2H, $CH^{1,8}$), 6.83 (br s, 4H, N-C*H*), 6.40 (br s, 2H, $CH^{3,6}$), 5.85 (br s, 1H, N*H*), 4.38 (sept, 4H, $^3J_{H,H}$ 7 Hz, C*H*Me$_2$), 1.67 (s, 6H, C*Me*$_2$), 1.29 (d, $^3J_{H,H}$ 7 Hz, 24H, CH*Me*$_2$), 1.26 (s, 18H, C*Me*$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz, 298 K): δ 146.76 (s, $C^{2,7}$), 142.3 (br s, N*C*N), 138.82 (s, $C^{11,12}$), 130.71 (s, $C^{10,13}$), 124.5 (br s, $C^{4,5}$), 115.62 (s, $CH^{1,8}$), 113.38 (br s, $CH^{3,6}$ & N*C*H), 35.52 (s, C^9), 35.02 (s, *C*Me$_3$), 32.61 (s, C*Me*$_2$), 31.73 (s, C*Me*$_3$), 22.40 (s, CH*Me*$_2$) ppm. $C_{68}H_{68}N_6O_1F_{20}B_1$ (1376.08 g mol^{-1}): calcd C 59.35, H 4.98, N 6.11%; found. C 59.75, H 5.48, N 5.55%.

[(XII_2)Y(CH_2SiMe_3)$_2$][B(C_6F_5)$_4$] (2)

A solution of [H(XII_2)][B(C_6F_5)$_4$]·0.5 hexane (300 mg, 0.218 mmol) in 10 mL of C_6H_5F was added dropwise to a solution of [Y(CH_2SiMe_3)$_3$(THF)$_2$] (108 mg, 0.218 mmol) in C_6H_5F (5 mL) at room temperature and the reaction was stirred for 1 hour. Approximately 40 mL of hexanes was added to the reaction resulting in the precipitation of a white solid. The solution was decanted, and the white solid was dried under vacuum for 1 hour. The solid was washed with hexanes (3 × ∼5 mL) and dried under vacuum for 2 hours, yielding **2** as a highly air-sensitive white solid (323 mg, 93% yield). X-ray quality crystals of **2** were grown by layering hexanes on top of a solution of **2** in C_6H_5F and cooling to −29 °C. ^{1}H NMR (C_6D_5Br, 600 MHz, 298 K): δ 7.01 (s, 2H, $CH^{1,8}$), 6.72 (s, 4H, N-C*H*), 5.64 (s, 2H, $CH^{3,6}$), 4.63 (sept, $^3J_{H,H}$ 7 Hz, 4H, C*H*Me$_2$), 1.68 (s, 6H, C*Me*$_2$), 1.32 (d, $^3J_{H,H}$ 7 Hz, 12H, CH*Me*$_2$), 1.16 (s, 18H, C*Me*$_3$), 1.10 (d, $^3J_{H,H}$ 7 Hz, 12H, CH*Me*$_2$), −0.19 (s, 18H, Si*Me*$_3$), −0.77 (appt s, 2H, YC*H*$_2$)-ppm. ^{13}C{^{1}H} NMR (C_6D_5Br, 151 MHz, 298 K): δ 148.49 (s, $C^{2,7}$), 147.47 (s, N*C*N), 140.49 (s, $C^{4,5}$), 138.01 ($C^{11,12}$), 130.23 (s, $C^{10,13}$), 114.68 (s, N-*C*H), 112.90 (s, $CH^{1,8}$), 109.28 (s, $CH^{3,6}$), 48.49 (s, *C*HMe$_2$), 37.69 (d, $^3J_{H,H}$ 42 Hz, Y*C*H$_2$), 34.57 (s, C^9), 34.49 (s, *C*Me$_3$), 32.14 (s, *C*Me$_2$), 31.19 (s, C*Me*$_3$), 23.06, 21.92 (2 × s, CH*Me*$_2$), 3.46 (s, Si*Me*$_3$) ppm. $C_{73}H_{82}N_6O_1F_{20}B_1Si_2Y$ (1595.32 g mol^{-1}): calcd C 54.96, H 5.18, N 5.27%; found. C 54.63, H 5.23, N 4.91%.

[(XII_2)Sc(CH_2SiMe_3)$_2$][B(C_6F_5)$_4$] (3)

A solution of [H(XII_2)][B(C_6F_5)$_4$]·0.5 hexane (300 mg, 0.218 mmol) in 10 mL of C_6H_5F was added dropwise to a solution of [Sc(CH_2SiMe_3)$_3$(THF)$_2$] (98 mg, 0.218 mmol) in C_6H_5F (5 mL) at room temperature and the reaction was stirred for 1 hour. Approximately 40 mL of hexanes was added to the reaction resulting in the precipitation of a white solid. The solution was decanted, and the white solid was dried under vacuum for 1 hour. The solid was further washed with hexanes (3 × ∼5 mL) and dried under vacuum for 2 hours, yielding **3** as a highly air-sensitive white solid (308 mg, 91% yield). X-ray quality crystals of **3** were grown by layering hexanes on top of a solution of **3** in C_6H_5F and cooling to −29 °C. ^1H NMR (C_6D_5Br, 600 MHz, 298 K): 6.94 (s, 2H, $CH^{1,8}$), 6.76 (s, 4H, N-C*H*), 5.62 (s, 2H, $CH^{3,6}$), 4.69 (br s, 4H, C*H*Me$_2$), 1.66 (s, 6H, C*Me$_2$*), 1.32 (d, 12H, $^3J_{H,H}$ 6 Hz, CH*Me$_2$*), 1.16 (s, 18H, C*Me$_3$*), 1.10 (d, $^3J_{H,H}$ 6 Hz, 12H, CH*Me$_2$*), −0.25 (s, 18H, Si*Me$_3$*), −0.35 (br s, 4H, ScC*H$_2$*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_5Br, 151 MHz, 298 K): 148.44 (s, N*C*N), 147.90 (s, $C^{2,7}$), 140.74 (s, $C^{4,5}$), 137.72 ($C^{11,12}$), 129.69 (s, $C^{10,13}$), 114.66 (s, N-*C*H), 112.14 (s, $CH^{1,8}$), 108.32 (s, $CH^{3,6}$), 48.34 (s, *C*HMe$_2$), 34.57 (s, C^9), 34.46 (s, *C*Me$_3$), 31.10 (s, C*Me$_3$* & C*Me$_2$*), 23.21, 21.54 (2 × s, CH*Me$_2$*), 2.87 (s, CH_2SiMe_3) ppm. Note: the ^{13}C NMR Sc*C*H$_2$ signal was not located from the ^1H–^{13}C HSQC NMR spectrum, but may be a very broad peak at 43.9 ppm. $C_{73}H_{82}N_6O_1F_{20}B_1Si_2Sc$ (1551.37 g mol^{-1}): calcd C 56.52, H 5.33, N 5.42%; found. C 56.21, H 5.46, N 5.08%.

In situ synthesis of $[(XII_2)Sc(CH_2SiMe_2CH_2SiMe_3)][MeB(C_6F_5)_3][B(C_6F_5)_4]$ (4)

A solution of $B(C_6F_5)_3$ (9 mg, 0.0176 mmol) in 0.4 mL of C_6D_5Br was added dropwise to a solution of $[(XII_2)Sc(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) (25 mg, 0.0161 mmol) in C_6D_5Br (0.4 mL) at room temperature and the reaction was stirred for 2 hours. ^1H NMR (C_6D_5Br, 500 MHz, 252 K): δ 7.09 (s, 2H, $C^{1,8}$), 6.79, 6.77 (2 × br s, 2H, N-C*H*), 5.46 (s, 2H, $C^{3,6}$), 4.91 (sept, 2H, $^3J_{H,H}$ 7 Hz, C*H*Me$_2$), 4.27 (sept, 2H, $^3J_{H,H}$ 7 Hz, C*H*Me$_2$), 1.72 (s, 6H, C*Me$_2$*), 1.51 (br s, 3H, *Me*B(C_6F_5)$_3$), 1.26 (d, 6H, $^3J_{H,H}$ 7 Hz, CH*Me$_2$*), 1.17 (d, 6H, $^3J_{H,H}$ 7 Hz, CH*Me$_2$*), 1.15 (s, 18H, C*Me$_3$*), 0.99 (d, 6H, $^3J_{H,H}$ 7 Hz, CH*Me$_2$*), 0.85 (s, 2H, ScC*H$_2$*), 0.82 (d, 6H, $^3J_{H,H}$ 7 Hz, CH*Me$_2$*), −0.12 (s, 9H, Si*Me$_3$*), −0.31 (s, 6H, Si*Me$_2$*), −0.66 (s, 2H, C*H$_2$*SiMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_5Br, 126 MHz, 252 K): δ 149.89 (s, $C^{2,7}$), 144.73 (s, N*C*N), 139.42 (s, $C^{4,5}$), 136.61 (s, $C^{11,12}$), 129.2 (s, $C^{10,13}$), 115.98, 115.38 (2 × s, N-*C*H), 114.87 (s, $CH^{1,8}$), 109.05 (s, $CH^{3,6}$), 65.7 (s, Sc*C*H$_2$), 49.31, 48.47 (2 × s, *C*HMe$_2$), 34.59 (s, *C*Me$_3$ & *C*Me$_2$), 34.30 (s, C^9), 30.85 (s, C*Me$_3$*), 31.4 (s, B*Me*), 30.02 (s, C*Me$_2$*), 23.32, 22.61, 21.59, 21.12 (4 × s, CH*Me$_2$*), 6.60 (s, *C*H$_2$SiMe$_3$), 2.46 (s, CH$_2$Si*Me$_2$*), 1.22 (s, CH$_2$Si*Me$_3$*) ppm. Note: the C,^{10,13} Sc*C*H$_2$ and B*Me* ^{13}C NMR signals were located *via* ^1H–^{13}C HSQC or HMBC NMR. ^{11}B NMR (C_6D_5Br, 161 MHz, 252 K): −15.02 (s, MeB(C_6F_5)$_3$), −16.20 (s, B(C_6F_5)$_4$) ppm. ^{19}F NMR (C_6D_5Br, 471 MHz, 252 K): −131.76 (br s, *o*-B(C_6F_5)$_4$), −133.27 (d, $^3J_{F,F}$ 22 Hz, *o*-MeB(C_6F_5)$_3$), −157.57 (br s, *p*-MeB(C_6F_5)$_3$), −161.76 (br s, *p*-B(C_6F_5)$_4$), −162.09 (br s, *m*-MeB(C_6F_5)$_3$), −165.58 (br s, *m*-B(C_6F_5)$_4$) ppm.

In situ synthesis of $[(XII_2)Sc(CH_2SiMe_3)\{\eta^x\text{-toluene}\}][B(C_6F_5)_4]_2$ (5)

A solution of $[CPh_3][B(C_6F_5)_4]$ (15.5 mg, 0.0168 mmol) in 0.4 mL of C_6D_5Br was added dropwise to a solution of $[(XII_2)Sc(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) (20 mg, 0.0129 mmol) and 5 equivalents of toluene (11.9 mg) in C_6D_5Br (0.4 mL) at room temperature. The reaction was stirred vigorously for 2 hours. ^1H NMR (C_6D_5Br, 600 MHz, 298 K): δ 7.11 (s, 2H, $CH^{1,8}$), 6.87 (s, 4H, N-C*H*), 5.63 (s, 2H, $CH^{3,6}$), 4.38 (br s, 4H, C*H*Me$_2$), 1.65 (s, 6H, C*Me$_2$*), 1.16 (s, 18H, C*Me$_3$*), 1.08 (appt t, $^3J_{H,H}$ 6 Hz, 24 H, CH*Me$_2$*), 0.70 (s, 2H, ScC*H$_2$*), −0.22 (s, 9H, Si*Me$_3$*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_5Br, 151 MHz, 298 K): δ 151.03 (s, $C^{2,7}$), 143.93 (s, N*C*N), 137.90 (s, $C^{4,5}$), 130.9 (s, $C^{10,13}$), 116.08 (s, N-*C*H), 115.10 (s, $CH^{1,8}$), 108.92 (s, $CH^{3,6}$), 63.9 (s, *C*H$_2$SiMe$_3$), 49.27 (s, *C*HMe$_2$), 35.05 (s, C^9), 34.73 (s, *C*Me$_3$), 30.86 (s, C*Me$_3$*), 30.4 (s, C*Me$_2$*), 22.72, 21.39 (2 × s, CH*Me$_2$*), 1.68 (s, Si*Me$_3$*) ppm. Note: the C,^{10,13} ScCH$_2$ and C*Me$_2$* ^{13}C NMR signals were located by ^1H–^{13}C HSQC or HMBC NMR. ^{11}B NMR (C_6D_5Br, 161 MHz, 298 K): δ −16.21 (s, B(C_6F_5)$_4$) ppm. ^{19}F NMR (C_6D_5Br, 471 MHz, 298 K): δ −131.50 (br s, *o*-B(C_6F_5)$_4$), −161.67 (br s, *p*-B(C_6F_5)$_4$), −165.44 (br s, *m*-B(C_6F_5)$_4$) ppm.

Ethylene polymerization

In the glovebox, 15 mg (9.7 μmol) of $[(XII_2)Sc(CH_2SiMe_3)_2][B(C_6F_5)_4]$ (**3**) was dissolved in approximately 1 mL of *o*-$C_6H_4F_2$ and 1 mL of toluene. To this was added a solution of 9 mg (9.8 μmol) of $[CPh_3][B(C_6F_5)_4]$ in 1 mL of *o*-$C_6H_4F_2$, and the solution was stirred vigorously for 2 hours at room temperature. The solution was diluted with 10 mL of *o*-$C_6H_4F_2$ and 30 mL of toluene, and the flask was affixed to a vacuum line. A room temperature water bath was placed around the flask, and with rapid stirring, the solution was briefly evacuated before placing the flask under dynamic ethylene (1 atm), causing an exothermic reaction, with the onset of polyethylene precipitation after approx. 1 minute. After 2, 3 or 5 minutes, the solution was opened to air and approximately 5 mL of acidified methanol (10 vol% 12 M $HCl_{(aq.)}$; 90 vol% MeOH) was added. The resulting solid was filtered, washed with methanol and acetone, and then dried at 50 °C under vacuum to afford dry polyethylene. This method was also carried out using the same masses and approximate solution volumes, but replacing toluene with *o*-$C_6H_4F_2$.

Data availability

All relevant data is in the ESI† or the CCDC.

Author contributions

DJHE conceptualized the project. AV performed the synthesis, characterization and polymerization experiments. JSP carried out the solution and refinement of X-ray data. All authors contributed to writing the manuscript and have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

D. J. H. E. thanks NSERC of Canada for a Discovery Grant. We are also grateful to Dr Carlos A. Cruz and Chevron Phillips Chemical Company for GPC analysis of polymer samples, and to

Dr Jim Britten of the McMaster Analytical X-ray Diffraction Facility for advice and support with X-ray diffraction.

Notes and references

‡ Two isomers of "$Ph_3CCH_2SiMe_3$" are frequently observed, giving rise to ^{1}H NMR signals at 2.36 and 2.06 ppm (CH_2), and −0.01 and −0.26 ppm ($SiMe_3$) in C_6D_5Br; see ref. 19 and 57. In the reaction to form **5**, only one of these isomers was formed (2.36, −0.02 ppm; relative integration 2 : 9). By contrast, in the reaction to form **B** in Fig. 1 (see ref. 15), only the other isomer (2.05, −0.26 ppm) was formed.

§ The polymerization reactions were exothermic, causing an increase in the solution temperature, despite the room temp. water bath around the flask.

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