Allyl complexes of the heavy alkaline-earth metals: molecular structure and catalytic behavior†‡

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Reaction of two equivalents of K[1,3-$(SiMe_3)_2C_3H_3$] (= KA′) with SrI_2 in thf produces the allyl complex $SrA'_2(thf)_2$. In the solid state, the monomeric complex is isostructural with its calcium counterpart; the allyl ligands are bound in a symmetrical trihapto manner to the metals, with an average Sr–C distance of 2.801(5) Å. The reaction of KA′ and BaI_2 does not result in the expected bis(allyl)barium complex, but rather in a heterometallic barium/potassium species, K(thf)$Ba_2A'_5$. The allyls are in fast exchange in solution, and in the solid state, the complex forms a polymeric chiral chain. Each barium center is coordinated by one terminal and two bridging allyl ligands; the potassium center is coordinated by two bridging allyl ligands and one thf molecule. On reaction with iodine, C–C coupling occurs with $CaA'_2(thf)_2$, $SrA'_2(thf)_2$ and K(thf)$Ba_2A'_5$ to give the 1,5-hexadiene, $[(SiMe_3)_2C_3H_3]_2$. $CaA'_2(thf)_2$, $SrA'_2(thf)_2$ and K(thf)$Ba_2A'_5$ are initiators for methyl methacrylate polymerization; the analogous magnesium complex is not active.

Introduction

The past quarter century has witnessed a revival of interest in the organometallic chemistry of the heavy alkaline-earth elements calcium, strontium, and barium.[1,2] Initially focused on cyclopentadienyl complexes,[3] more recent activity has examined non-cyclopentadienyl species, both those with π-delocalized ligands (*e.g.*, fluorenyl,[4] indenyl,[5] butadienyl[6] and pentadienyl[7]), and others with sigma-bonded groups (*e.g.*, aryls,[2,8,9] benzyls,[9,10] alkyls[11]). The allyl anion, $C_3H_5^-$, and its substituted derivatives occupy a special location among these ligands, as it can adopt both π-bound (η^3) and σ-bound (η^1) conformations. With the lighter alkaline-earth metal magnesium, both bonding modes are found in the unsolvated $\{MgA'_2\}_2$ dimer (A′ = $[1,3\text{-}(SiMe_3)_2C_3H_3]^-$), yet in the thf-solvated $MgA'_2(thf)_2$ complex, the allyl ligands are σ-bound; the shift in coordination modes has been modelled computationally.[12] Despite the presence of coordinated bases, the metal has π-bound ligands in the solid state structures of the heavier allyl complexes $Ca(C_3H_5)_2$(triglyme)[13] and $CaA'_2(thf)_2$.[14] This may reflect the more electropositive nature of calcium[15] and/or its larger metal radius, which can accommodate two π-ligands in its coordination sphere.[16]

Di(allyl)strontium and di(allyl)barium have been mentioned in the patent literature as polymerization initiators,[17] and several allylbarium compounds have been synthesized for use in synthetic organic reactions, but not separately characterized.[18] The use of the sterically bulky A′ allyl proved to be useful in the isolation of $CaA'_2(thf)_2$,[14] and we used the same ligand in our exploration of its heavier metal counterparts.

Several Group 1 (*e.g.*, KA′,[19] CsA′(thf)[20]) and many f-element allyl complexes (*e.g.*, $YbA'_2(thf)_2$, CeA'_3(thf), NdA'_3(thf), $[Li(thf)_4][CeA'_3I]$)[19] have been found to be initiators for methyl methacrylate polymerization, and given the parallels between the heavy alkaline-earth and divalent f-elements,[21] it seems reasonable that related activity could be expected with the heavier Group 2 elements. Because the ionic radii of Ca^{2+} and Yb^{2+} are almost identical (1.00 and 1.02 Å, respectively, for CN 6),[22] organometallic complexes containing these metals tend to have similar bond distances and angles.[21] It has recently been found, however, that the average M–C bond distances in the $MA'_2(thf)_2$ complexes of calcium and ytterbium differ by 0.086 Å.[19] To explore the possible consequences of this structural change, the catalytic activity of $CaA'_2(thf)_2$ and its heavier counterparts was examined.

Results and discussion

Metathesis reactions are often employed to make organometallic complexes of the heavy Group 2 metals, and the addition of two equivalents of KA′ to one equivalent of CaI_2 in thf forms $CaA'_2(thf)_2$.[14] It was expected that the trimethylsilyl-substituted allylstrontium and allylbarium could be formed analogously (Scheme 1).

Work-up of the reaction involving strontium iodide produced an air-sensitive powder in good yield. Like the calcium counterpart, the complex is soluble in both ethers

$$2\ KA' + MI_2\ (M = Sr, Ba) \rightarrow MA'_2(thf)_x + 2\ KI\downarrow$$

Scheme 1 Proposed formation of allylstrontium and -barium complexes.

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$$5\,KA' + 2\,BaI_2 \rightarrow K(thf)Ba_2A'_5 + 4\,KI\downarrow$$

Scheme 2 Synthesis of a heterometallic barium/potassium allyl complex.

and hydrocarbon solvents. Proton NMR data show a characteristic singlet, doublet, triplet pattern of *syn*, *syn* trimethylsilyl arrangements on the allyl ligands, consistent with π-bound allyl ligands.[23] Elemental analysis and a subsequent crystal structure determination (below) confirmed the expected $SrA'_2(thf)_2$ composition.

Analysis of the barium-containing product, however, indicated that the product should be formulated not as a monometallic barium complex but as the polymetallic species $K(thf)Ba_2A'_5$. The synthesis of the product can be rationalized as in Scheme 2.

In NMR spectra, there is only one set of resonances corresponding to allyl protons, and the proton resonances on the C_3 portion of the allyl (δ 2.59 (d); 6.53 (t)) are slightly upfield relative to those of KA′ alone (δ 2.75 (d); 6.60 (t)). This observation suggests that fast exchange is occurring between the allyls, and that they interact to some extent with the barium centers in solution.

To determine whether related mixed metal species could be deliberatively formed with calcium or strontium (*i.e.*, $K[MA'_3]$), CaI_2 and SrI_2 were each treated with three equivalents of KA′ in thf at −78 °C. Evaporation of the solvent, followed by extraction with toluene, yielded solid products whose NMR spectra indicated the presence of the di(allyl) complex $MA'_2(thf)_2$ and KA′, rather than the intended tri(allyl) anions. This indicates that the large size of barium, which can accommodate three allyl ligands in its coordination sphere (see below), is critical to the formation of $K(thf)Ba_2A'_5$. The similar size of the K^+ (1.35 Å) and Ba^{2+} (1.38 Å) ions[22] may contribute as well.

Reaction of $CaA'_2(thf)_2$, $SrA'_2(thf)_2$ and $K(thf)Ba_2A'_5$ with I_2 in thf results in oxidative C–C coupling to form the 1,3,4,6-tetrakis(trimethylsilyl)-1,5-hexadiene, $[(SiMe_3)_2C_3H_3]_2$.[23] Similar coupling reactions are known in transition metal chemistry,[24] but only recently have Okuda *et al.* reported the first example with a d^0 metal complex, in the unsubstituted calcium allyl complex $Ca(C_3H_5)_2(triglyme)$.[13] Evidently bulky trimethylsilyl groups do not interfere in the coupling reaction.

Solid state structures

$SrA'_2(thf)_2$

A single crystal of $SrA'_2(thf)_2$ was used to determine its structure by X-ray diffraction (Table 1). Like its calcium analogue,[14] the allylstrontium complex crystallizes in a tetragonal space group ($P4_2/n$), and as the Sr atom lies on a crystallographic two-fold axis, only half of the molecule is unique. $SrA'_2(thf)_2$ features two η^3-bound allyl ligands and two thf molecules in the coordination sphere of the metal (Fig. 1). The Sr–C bond distance range is 2.797(3)–2.805(3) Å, which is similar to the six-coordinate Sr–C bond lengths in $Sr(1,2,4\text{-}(SiMe_3)_3C_5H_2)_2$ (2.773(4)–2.850(4) Å)[25] and $Sr(1,2,4\text{-}(tBu)_3C_5H_2)_2$ (2.773(5)–2.832(5) Å).[26] It should be noted that the average Sr–C bond length of 2.801 Å is 0.15 Å longer than the 2.654 Å average Ca–C length in $CaA'_2(thf)_2$,[14] which approximately matches the 0.18 Å difference in the radii of 6-coordinate Ca^{2+} and Sr^{2+}.[22] This is in line with previous observations that when bonded to electropositive metals, the allyl ligand has a nearly constant "radius"; *i.e.*, changes in M–C distances can be estimated from differences in the metal radii alone.[27]

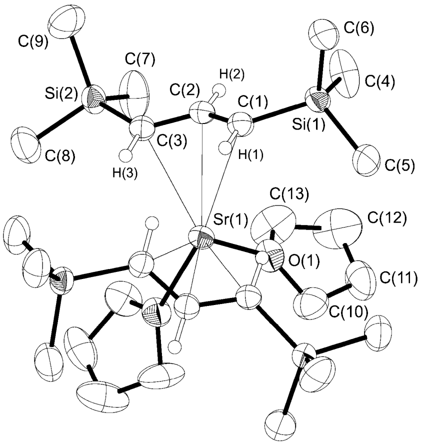

Fig. 1 A thermal ellipsoid representation of $SrA'_2(thf)_2$. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms not on the C3 framework of the allyl have been omitted for clarity. The trimethylsilyl group based on Si(1) and the thf ligand are disordered, and only the major conformations are depicted.

Even with the M–C bond length variation, the angle between the allyl planes for $SrA'_2(thf)_2$ (115.1°) and $CaA'_2(thf)_2$ (115.5°) is nearly identical. The angle may be controlled by the steric bulk of the trimethylsilyl substituents. The Sr–O distance of 2.514(10) Å is typical for thf-coordinated organostrontium complexes.[5,28]

The C–C–C angle within the allyl carbon ligand (129.4(3)°) is within the range found in other organometallic allyl complexes,[14,19,20] and the narrow C–C(allyl) bond range of 1.398(5)–1.406(5) Å reflects fully delocalized π-bonds. The terminal hydrogens on the allyl carbon backbone are displaced from the allyl plane by 10.2° for C1–C2–C3–H3 and 2.4° for C3–C2–C1–H1. These angles are noticeably smaller than the nearly equal torsion values for $CaA'_2(thf)_2$ (16.9° and 16.2°). Some of the variation may reflect different refinements for the hydrogens (riding model in $SrA'_2(thf)_2$, isotropic refinement in $CaA'_2(thf)_2$), but some may indicate changes in the rehybridization of the allyl carbon atoms. This effect is thought to improve metal–ligand bonding,[14] and may become less as the M–C distance increases. Longer bond lengths would also lessen interligand steric interactions and any accompanying pressure for ligand deformation.

$K(thf)Ba_2A'_5$

A crystal of $K(thf)Ba_2A'_5$ was isolated from a saturated thf solution and used to determine its structure by X-ray diffraction. The compound forms a coordination polymer parallel to the *c*-axis, in which the repeating unit contains one K^+ and two Ba^{2+} cations. Each barium center is coordinated by one terminal and two bridging allyl ligands; the potassium metal center is coordinated by two bridging allyl ligands and one thf molecule (Fig. 2 and 3).

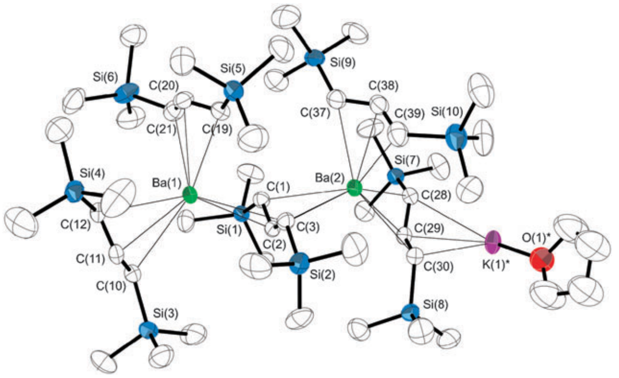

Fig. 2 Diagram of the unique non-hydrogen atoms in polymeric $\{K(thf)Ba_2A'_5\}_\infty$. Thermal ellipsoids are shown at the 50% probability level. Atoms flagged with an asterisk (*) are at equivalent position ($\frac{1}{2} - x$, $1 - y$, $-\frac{1}{2} + z$). The trimethylsilyl group based on Si(6) is disordered, and only the major conformation is depicted.

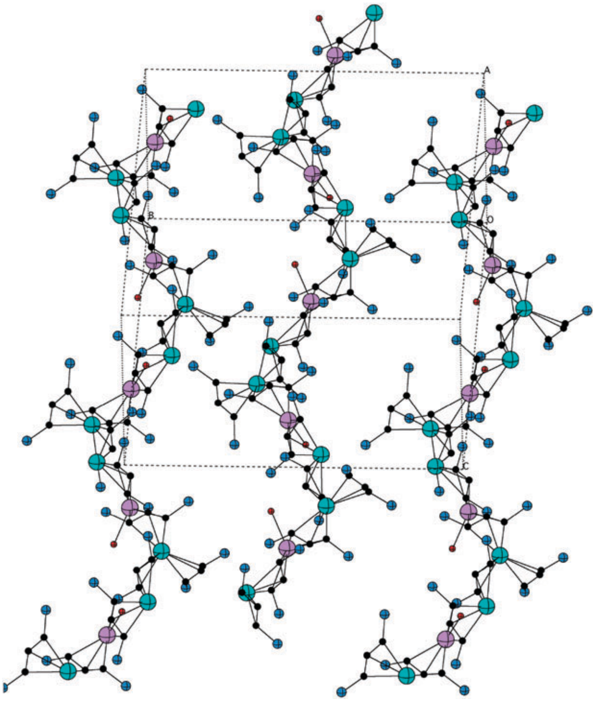

Fig. 3 Coordination polymer chains of $\{K(thf)Ba_2A'_5\}_\infty$. Barium atoms are in teal; potassium are purple. For clarity, methyl groups have been removed from silicon, and only the oxygen atoms of the thf ligands are shown. The K···K′ repeat distance is 15.2 Å.

The Ba–C$_{(terminal)}$ bond lengths (2.876(4)–2.969(4) Å; avg = 2.918 Å) are slightly shorter than the M–C$_{(bridging)}$ values (2.998(3)–3.141(4) Å, avg = 3.046 Å for Ba–C; 2.980(4)–3.157(4) Å, avg = 3.062 Å for K–C). The allyl carbons form angles within the range of 128.7(3)°–131.0(4)°, which is typical for organometallic allyl complexes.[14,19] The K–O bond length (2.681(4) Å) is similar to that found for the five-coordinate K^+ in $\{KA'(thf)_{3/2}\}_\infty$ (2.657 Å).[20]

The K–C bond range is typical for π-bound allyl ligands; for example, bond distances of 2.87–3.15 Å and 2.93–3.10 Å are observed in $\{KA'\}_\infty$[29] and $\{KA'(thf)_{3/2}\}_\infty$,[20] respectively. In general, the M–C distances in $K(thf)Ba_2A'_5$ are similar to those found in potassium and barium cyclopentadienyl complexes, a structural feature observed in $SrA'_2(thf)_2$ and previously documented in calcium[14] and caesium[20] compounds. The K–C bond range in $\{K[C_5(SiMe_3)_3H_2]\}_\infty$ (2.93–3.10 Å)[30] and $\{K[C_5(SiMe_3)H_4]\}_\infty$ (2.99–3.10 Å)[31] is comparable to those found in $K(thf)Ba_2A'_5$. In addition, average Ba–C distances of 2.94(1) Å and 2.99(2) Å are found for $Ba[C_5(C_3H_7)_4H]_2$[32] and $Ba(C_5Me_5)_2$.[33] Even in the more sterically crowded $Ba[C_5(C_6H_5)_2]_2$, the average Ba–C distance is 2.928(6) Å.[34] These overlap with the ranges in $K(thf)Ba_2A'_5$.

Table 1 Crystal data and structure refinement details

Compound	$SrA'_2(thf)_2$	$\{K(thf)Ba_2A'_5\}_\infty$
Empirical formula	$C_{26}H_{58}O_2Si_4Sr$	$C_{49}H_{113}Ba_2KOSi_{10}$
Formula weight	602.70	1313.07
Crystal system	Tetragonal	Orthorhombic
Space group	$P4_2/n$	$P2_12_12_1$
a/Å	14.9010(8)	11.4705(14)
b/Å	14.9010(8)	21.891(3)
c/Å	16.825(2)	30.387(4)
V/Å^3	3735.7(5)	7630.2(16)
Z	4	4
$D_{calc.}$/g cm^{-3}	1.072	1.143
T/K	173(2)	173(2)
F(000) (calculated)	1296	2744
μ/mm^{-1}	1.589	1.264
Reflections collected	36 801	91 768
Independent reflections	3303 $R_{int} = 0.057$	17 485 $R_{int} = 0.046$
Observed reflections	2380	15 246
R indices (all data)	$R_1 = 0.0660$ $wR_2 = 0.1243$	$R_1 = 0.0450$ $wR_2 = 0.0882$
Flack parameter	—	−0.005(10)

There is a considerable variation of trimethylsilyl torsion angles in the complex. The Ba–K bridging allyl ligands exhibit the largest range at 1.73°–9.61°. The angle spread on the Ba–Ba bridging allyls is smaller at 1.71°–5.82°, and the ranges on the terminal allyls on Ba1 and Ba2 are similar at 1.36°–5.69° and 3.01°–6.38°, respectively. These values are within expected parameters for allyl complexes.[14,35]

Polymerization reactions

Heterometallic trimethylsilyl-substituted allyl complexes of lanthanide/alkali metals are effective initiators of methyl methacrylate (MMA) polymerization.[36,37] Furthermore, KA′ polymerizes methyl methacrylate more effectively when used as the sole catalyst rather than as part of a mixed metal species.[38] To determine whether Group 2 allyl complexes exhibit similar catalytic activity, methyl methacrylate polymerization reactions were conducted with the $SrA'_2(thf)_2$ and $K(thf)Ba_2A'_5$ complexes, and with the previously known $MgA'_2(thf)_2$ and $CaA'_2(thf)_2$. Typical experiments were run in ∼20 mL toluene at 0 °C (Table 2). The microstructures of the polymers were analyzed with ^1H NMR spectroscopy.[39]

With the exception of $MgA'_2(thf)_2$, which did not initiate polymerization, the other Group 2 complexes displayed at least some activity with MMA. The behavior of the calcium complex was examined under several conditions, with largely expected variations. For example, higher activity was observed at 0 °C (trial 2) than at room temperature (25 °C, trial 4). Greater activity at lower temperatures has been observed in

Table 2 Results of MMA polymerization (except where noted, in ~20 mL toluene, 0.5 min) with allyl complexes. TOF = (mol monomer consumed) (mol catalyst)$^{-1}$ h^{-1}

				Tacticity (%)		
Complex	Trial	Convn (%)	TOF	rr	mr	mm
$\mathrm{MgA'_2(thf)_2}$	1	Not active				
$\mathrm{CaA'_2(thf)_2}$	2	76.8	19 000	14	28	58
$\mathrm{CaA'_2(thf)_2}^a$	3	18.4	11 000	42	42	16
$\mathrm{CaA'_2(thf)_2}^b$	4	24.3	8100	10	30	59
$\mathrm{SrA'_2(thf)_2}$	5	36.4	8100	12	34	54
$\mathrm{K(thf)Ba_2A'_5}$	6	44.3	20 600	19	40	41
$\mathrm{YbA'_2(thf)_2}^c$		41.4	100	26	51	23
$\mathrm{SmA'_2(thf)_2}^d$		5.3	1200	31	30	39

[a] In thf as solvent. [b] At 25 °C. [c] 35 min reaction time; data taken from ref. 38. [d] Data taken from ref. 38.

previous studies of MMA polymerization;[40–42] at room temperature the heat released from the highly exothermic polymerization reaction may cause catalyst decomposition or side reactions.[42,43] In addition, lower activity and decreased stereoselectivity was observed when a reaction was conducted in thf (trial 3). Polar solvents are known to depress activity and selectivity in polymerization reactions, owing to ion solvation effects.[44]

Other results are not as readily interpreted. The calcium and strontium complexes' TOF values are significantly higher than those for the corresponding divalent lanthanide complexes, despite their similar radii ($\mathrm{Ca^{2+}} \approx \mathrm{Yb^{2+}}$; $\mathrm{Sr^{2+}} \approx \mathrm{Sm^{2+}}$).[22] In addition, $\mathrm{CaA'_2(thf)_2}$ and $\mathrm{SrA'_2(thf)_2}$ give slightly isotactic PMMA (58 and 54% mm, respectively, in toluene), whereas as previously reported,[19] the lanthanide complexes $\mathrm{(Sm,Yb)A'_2(thf)_2}$ display no stereocontrol, and yield atactic PMMA. Polymer tacticity is not an easily predicted property with these metals; for example, MMA polymerization with $\mathrm{Ca(C_5Me_5)_2(thf)_2}$ in toluene yields atactic PMMA,[40] but the use of $\mathrm{Yb(C_5Me_5)_2(thf)_2}$ gives syndiotactic PMMA (84% rr).[45] Yet styrene polymerization with the chiral catalyst $\mathrm{M[1\text{-}(NMe_2)\text{-}2\text{-}(\mu\text{-}CHSiMe_3)C_6H_4][9\text{-}(SiMe_3)fluorenyl](thf)}$ (M = Ca, Yb) yields syndiotactic polymer with both metals, although not to the same extent (86 and 67% rr, respectively).[21,46] It is evident that the propagation mechanisms in these polymerizations differ for calcium and ytterbium catalysts.

In the heterometallic species $\mathrm{[\{K(thf)_2\}\{SmA'_3\}]_2}$,[37] there exist multiple centers of reactivity, which may explain the elevated TOF values found for this complex (83 100 h^{-1}), substantially higher than $\mathrm{SmA'_2(thf)_2}$ alone, although lower than the value for KA′ (104 000 h^{-1}).[19] All three complexes produce atactic PMMA. As $\mathrm{CaA'_2(thf)_2}$ and $\mathrm{SrA'_2(thf)_2}$ produce slightly isotactic PMMA, attempts were made to synthesize mixed metal complexes with potassium (*i.e.*, $\mathrm{K[MA'_3]}$) that might display heightened activity. As noted above, such attempts were not successful, but the $\mathrm{K(thf)Ba_2A'_5}$ complex was used in polymerization experiments (trial 6), and proved to be reasonably active, giving slightly isotactic polymer. The partial stereocontrol suggests that some initiation stems from the presence of the barium centers, although the potassium undoubtedly boosts the general activity.

Conclusions

Considering that the lanthanide complex $\mathrm{SmA_2(thf)_2}$ is a stable species, it is not too surprising that the analogous complex with the similarly sized $\mathrm{Sr^{2+}}$ could also be formed. As samarium centers are found in both monometallic and heterometallic allyl complexes (*i.e.*, $\mathrm{SmA_2(thf)_2}$ and $\mathrm{[\{K(thf)_2\}\{SmA'_3\}]_2}$), the isolation of the barium complex as the heterometallic $\mathrm{K(thf)Ba_2A'_5}$ species does not rule out eventual synthesis of a monometallic barium complex. The allyl ligands on the calcium, strontium, and barium complexes undergo coupling with iodine, and display activity as initiators of methyl methacrylate polymerization; the calcium and strontium species are substantially more active than the corresponding $\mathrm{Yb^{2+}}$ and $\mathrm{Sm^{2+}}$ counterparts. This suggests that the inexpensive alkaline-earth metals might serve as the basis for new versions of allyl-based polymerization initiators.

Experimental section

General considerations

All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or glovebox techniques. Proton and carbon (^{13}C) NMR spectra were obtained on a Bruker DPX-300 spectrometer at 300 and 75.5 MHz, respectively, and were referenced to the residual proton and ^{13}C resonances of $\mathrm{C_6D_6}$ or thf-d_8. Melting points were determined on a Laboratory Devices Mel-Temp apparatus in sealed capillaries. Metal and combustion analyses were performed by Desert Analytics, Tuscon, AZ.

Materials

Strontium and barium iodides were purchased from Aldrich; KA′[19] and $\mathrm{CaA'_2(thf)_2}$[14] were prepared as previously described. Anhydrous tetrahydrofuran (thf) was purchased from Aldrich and used as received. Toluene and hexanes were distilled under nitrogen from potassium benzophenone ketyl.[47] Deuterated solvents were vacuum distilled from Na/K (22/78) alloy prior to use. Purification of methyl methacrylate involved stirring over $\mathrm{CaH_2}$, followed by vacuum distillation and degassing using the freeze–pump–thaw method. Other reagents were obtained from commercial sources and used as received.

Polymerization reaction conditions

In typical reactions, MMA (4–5.4 mL, 37.4–50.5 mmol) was added *via* syringe to a solution of catalyst (~1000 mol MMA: 1 mol catalyst) in toluene (approx. 20 mL) at 0 °C. Polymerization reactions were allowed to run 30 s and then quenched with methanol. The precipitates were filtered and dried prior to analysis at ambient temperatures. The tacticity of PMMA samples was determined by integration of the methyl regions in ^{1}H NMR spectra of the polymers.[48]

$\mathrm{SrA'_2(thf)_2}$

A 125 mL Schlenk flask containing a magnetic stirring bar and fitted with an addition funnel was charged with $\mathrm{SrI_2}$ (0.775 g; 2.27 mmol) in 10 mL of thf. KA′ (1.017 g; 4.53 mmol) dissolved in 15 mL of thf was added to the addition funnel. The apparatus was cooled to −78 °C with a dry ice/acetone bath. The solution of KA' was added dropwise with stirring over the course of 30 min. The solution was allowed to warm to room temperature overnight, after which the solvent was removed under vacuum, and the residue extracted with hexanes. The extract was filtered over a medium porosity glass frit, and the hexanes were removed from the yellow filtrate under vacuum to afford a pale yellow powder (0.828 g, 61% yield), mp 128–129 °C. Recrystallization from hexanes resulted in the growth of transparent blocks over a period of days. $C_{26}H_{58}O_2Si_4Sr$ (602.71): calc.: C, 51.81; H, 9.70; Sr, 14.54%. Found: C, 49.71; H, 8.46; Sr 14.21%. ^{1}H NMR (300 MHz, thf-d_8, 298 K): δ −0.032 ppm (s, 36H, $Si(CH_3)_3$); 1.77 (mult, 8H, thf(β-CH_2)); 2.83 (d, J = 16.0 Hz, 4H, $C_{(1,3)}$–H); 3.62 (mult, 8H, thf(α-CH_2)); 6.75 (t, J = 16.0 Hz, 2H, $C_{(2)}$–H). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ −0.30 ppm (s, 36H, $Si(CH_3)_3$); 1.30 (mult, 8H, thf(β-CH_2)); 3.19 (d, J = 16.0 Hz, 4H, $C_{(1,3)}$–H); 3.49 (mult, 8H, thf(α-CH_2)); 7.13 (t, J = 16.0 Hz, 2H, $C_{(2)}$–H). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 2.12 ppm ($Si(CH_3)_3$); 25.22 (thf(β-CH_2)); 69.11 (thf(α-CH_2)); 78.40 ($C_{(1,3)}$); 158.88 ($C_{(2)}$).

$K(thf)Ba_2A'_5$

Prepared as above, using BaI_2 (0.847 g; 2.24 mmol) in 20 mL of thf, and KA' (1.010 g; 4.50 mmol) in 15 mL of thf. Workup from hexanes afforded a yellow powder (1.091 g; 92% yield), mp 190 °C (dec.). Recrystallization from hexanes resulted in the growth of yellow blocks over a period of days. $C_{49}H_{113}Ba_2KOSi_{10}$ (1313.04): calc. C, 44.82; H, 8.67; Ba, 20.92%. Found: C, 45.03; H, 9.01; Ba 20.70%. ^{1}H NMR (300 MHz, thf-d_8, 298 K): δ −0.026 ppm (s, 90H, $Si(CH_3)_3$); 1.78 (mult, 4H, thf(β-CH_2)); 2.59 (d, J = 15.9 Hz, 10H, $C_{(1,3)}$–H); 3.61 (mult, 4H, thf(α-CH_2)); 6.53 (t, J = 15.9 Hz, 5H, $C_{(2)}$–H). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.30 ppm (s, 90H, $Si(CH_3)_3$); 1.34 (mult, 4H, thf(β-CH_2)); 2.86 (d, J = 16.0 Hz, 10H, $C_{(1,3)}$–H); 3.48 (mult, 4H, thf(α-CH_2)); 6.80 (t, J = 16.0 Hz, 5H, $C_{(2)}$–H). ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 1.86 ppm ($Si(CH_3)_3$); 25.33 (thf(β-CH_2)); 68.76 (thf(α-CH_2)); 83.69 ($C_{(1,3)}$); 156.10 ($C_{(2)}$).

Reaction of $CaA'_2(thf)_2$ and I_2

$CaA'_2(thf)_2$ (0.161 g, 0.29 mmol) was dissolved in thf (40 mL) in a 125 mL Erlenmeyer flask. Iodine (74 mg, 0.29 mmol) was added to the solution with stirring. The solution turned purple and then quickly became colorless. THF was removed under vacuum, the residue was reconstituted in hexanes, and the extract was filtered. Hexanes was removed, leaving a yellow oil that was characterized from its ^{1}H NMR spectrum as 1,3,4,6-tetrakis(trimethylsilyl)-1,5-hexadiene, $[(SiMe_3)_2C_3H_3]_2$.[23] Analogous reactions with $SrA'_2(thf)_2$ (1 equiv. I_2) and $K(thf)Ba_2A'_5$ (2 equiv. I_2) also yielded the hexadiene.

Procedures for X-ray crystallography

A suitable crystal of each sample was located, attached to a glass fiber, and mounted on a Siemens SMART system for data collection at 173(2) K. Data collection and structure solution for all molecules were conducted at the X-ray Crystallographic Laboratory at the University of Minnesota. All calculations were performed by using the current SHELXTL suite of programs. Final cell constants were calculated from a set of strong reflections measured during the actual data collection. Relevant crystal and data collection parameters for each of the compounds are given in Table 1.

The structures were solved using SIR97[49] and refined using SHELXTL-97.[50] The space groups were determined based on systematic absences and intensity statistics. A direct-method was calculated that provided most of the non-hydrogen atoms from the E-map. Several full-matrix least squares/difference Fourier cycles were performed that located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. In the case of $SrA'_2(thf)_2$, one $SiMe_3$ group and the coordinated thf solvent molecule were modeled as disordered over two positions each (62 : 38 and 51 : 49, respectively). In the case of $K(thf)Ba_2A'_5$, one $SiMe_3$ group was modeled as disordered over three positions (53 : 26 : 21) as an approximation for the full distribution of electron density. Corresponding bond lengths and angles between the various orientations of the disorder of each ligand or group were restrained to be similar (*e.g.*, a $SiMe_3$ group was assigned the same internal geometry no matter how it was oriented). Thermal constraints were applied to corresponding atoms of the different orientations because the individual thermal parameters could not be distinguished due to resolution limitations.

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