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The Role of Alkali Metal Cations in MMA Polymerization Initiated by Neutral and Anionic Allyl Lanthanide Complexes

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Reaction of 2 or 3 equiv of potassium 1,3-bis(trimethylsilyl)allyl (K[1,3-$(SiMe_3)_2C_3H_3$] = K[A′]) with the triflate salts of Ce, Nd, Eu, Tb, and Yb gives the corresponding neutral bis-(Yb, Eu) and tris-(Ce, Nd, Tb) allyl lanthanide complexes in yields ranging from 40 to 80%. These complexes, which have been crystallographically characterized, initiate the polymerization of methyl methacrylate (MMA), but with poor turnover frequencies when compared with the corresponding salt complexes of the type K[LnA'_3]. K[A′] itself initiates MMA polymerization, however, and its presence as an ion-pair in the salt complexes may contribute to the activity of heterometallic lanthanide catalysts.

Introduction

Allyl lanthanide complexes are promising candidates for materials precursors and polymerization catalysts. The neodymium compound $Nd(C_3H_5)_3$, for instance, is a stereospecific initiator for the polymerization of butadiene,[1] and the analogous lanthanum species is only slightly less selective.[2] Owing to the large radii of the lanthanide ions[3] and the sterically compact nature of the allyl anion, however, neutral $Ln(C_3H_5)_3$ species remain comparatively rare. Typically, treatment of 3 or 4 equiv of M[allyl] (M = Li, Na, K) reagents with LnX_3 (X = Cl, Br, I) produces salts of composition M[Ln(allyl)$_3$X] and M[Ln(allyl)$_4$].[4] In the case of lanthanum and neodymium, Taube has reported the use of BEt_3 to abstract Li[C_3H_5] from Li[$Ln(C_3H_5)_4$] to produce the neutral species $Ln(C_3H_5)_3$.[2]

A broader variety of neutral complexes is potentially available with the use of substituted allyl ligands, such as the bulky 1,3-bis(trimethylsilyl)allyl anion (A′). The latter has been used to stabilize chromium, iron, cobalt, and nickel complexes whose corresponding monomeric parent allyl $M(C_3H_5)_2$ complexes are unknown or thermally unstable.[5−7] Yasuda has reported the formation of the neutral complex $SmA'_2(thf)_2$ from the reaction of SmI_2 and 2 equiv of K[A′] (**1**) and its subsequent reaction with MMA.[8] However, the samarium complex was poorly characterized and had limited catalytic activity (see below). More recently, the salt $[\{K(thf)_2\}\{SmA'_3\}]_2$ has been reported from the reaction of $SmI_2(thf)_2$ and 3 equiv of K[A′]; it crystallizes with a cyclic structure, comprising two samarium and two potassium centers.[9] We have shown previously that reaction of 3 or 4 equiv of K[A′] with other lanthanide(III) iodides affords salt complexes of the general type $[K(thf)_4][LnA'_3I]$.[10] Bochmann has reported that salt complexes containing bulky allyl ligands of the general types K[LnA'_3][9] and $[Ln\{(C_3H_3\text{-}SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(thf)\}(thf)_x]_\infty$[11] show higher than expected activity relative to $SmA'_2(thf)_2$[8] as initiators in MMA polymerization.

We have been interested in determining the relative importance of various features of these complexes in their catalytic behavior. For example, are either neutral or charged complexes consistently the more active? What is the exact role of the metals in these systems, and in particular, is polymerization aided by the pres-

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(1) Maiwald, S.; Weissenborn, H.; Sommer, C.; Müller, G.; Taube, R. *J. Organomet. Chem.* **2001**, *640*, 1−9.

(2) Taube, R.; Windisch, H.; Maiwald, S.; Hemling, H.; Schumann, H. *J. Organomet. Chem.* **1996**, *513*, 49−61.

(3) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

(4) Bursten, B. E.; Casarin, M.; Ellis, D. E. A.; Fragala, I. L.; Marks, T. J. *Inorg. Chem.* **1986**, *25*, 1257−1261.

(5) Smith, J. D.; Hanusa, T. P.; Young, V. G., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6455−6456.

(6) Smith, J. D.; Quisenberry, K. T.; Hanusa, T. P.; Brennessel, W. W. *Acta Crystallogr., Sect. C* **2004**, *60*, m507−m508.

(7) Quisenberry, K. T.; Smith, J. D.; Voehler, M.; Stec, D. F.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc.* **2005**, *127*, 4376−4387.

(8) Ihara, E.; Koyama, K.; Yasuda, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1999**, *574*, 40−49.

(9) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2003**, *22*, 3028−3030.

(10) Kuehl, C. J.; Simpson, C. K.; John, K. D.; Sattelberger, A. P.; Carlson, C. N.; Hanusa, T. P. *J. Organomet. Chem.* **2003**, *683*, 149−154.

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ence of two metal-containing fragments in the salt complexes? If so, does each fragment act as an independent catalytic site? Answers to such questions will provide a foundation for the rational expansion of catalytic lanthanide allyl chemistry.

We describe here some initial answers to these questions through the synthesis and crystallographic characterization of **1**, coupled with a generalized route to neutral lanthanide allyl complexes formed by reactions of **1** with divalent and trivalent lanthanide triflates. We also report the results of polymerization experiments with methyl methacrylate, using lanthanide complexes, **1** itself, and various mixtures of **1** and $SmA'_2(thf)_2$ as catalytic initiators.

Experimental Section

General Considerations. All syntheses and manipulations were performed under an inert atmosphere using standard glovebox or Schlenk techniques. NMR spectra were recorded at ambient temperature on a Bruker DPX-300 MHz or Avance 400 MHz spectrometer; PMMA samples were studied at either ambient temperature or, when necessary, 50 °C. Assignment of the tacticity of each PMMA sample was made by integrating the methyl region in the ^1H NMR spectra.[12] Magnetic moments (μ_{eff}) were determined via the Evans method in toluene-d_8.[13,14] Chemical shifts are referenced to tetramethylsilane using the residual ^1H or natural abundance ^{13}C resonances of the solvent. Elemental analyses (C, H) were performed either by Desert Analytics (Tucson, AZ) or by Midwest Microlabs (Indianapolis, IN); complexometric methods were used for metals.[15]

Materials. Bis(1,3-trimethylsilyl)propene was prepared as described by Fraenkel.[16] Nominally anhydrous lanthanide triflates (Aldrich) were dried under vacuum for 12 h at 100−120 °C prior to use. Anhydrous samarium diiodide was purchased from Aldrich and used as received. The triflate starting materials $Ce(OSO_2CF_3)_3$[17−19] and $Yb(OSO_2CF_3)_2(thf)_3$[20] were prepared according to literature procedures; as details were not given for $Yb(OSO_2CF_3)_2(thf)_3$, we include its synthesis below. The syntheses of $NdA'_3(thf)$ (**5**) and $[K(thf)_4][CeA'_3I]$ have been reported previously.[10] Methyl methacrylate (MMA) was stirred over CaH_2, vacuum transferred, and stored in a glovebox freezer at −30 °C prior to use. HPLC-grade solvents, stored under argon in stainless steel cylinders, were purified by passing them under argon pressure through a stainless steel system consisting of either two 4.5 in. × 24 in. (1 gal) columns of activated A2 alumina (diethyl ether and THF) or one column of activated A2 alumina and one column of activated BASF R3-11 catalyst (toluene and hexanes).[21] Anhydrous pentane (Aldrich) was sparged with argon and stored over activated molecular sieves (Type 4). Deuterated solvents (C_6D_6, THF-d_8, toluene-d_8) used for NMR experiments were sparged with argon and stirred over Na/K (1:2) alloy, from which they were transferred under vacuum; $CDCl_3$ (Acros) was used as received. All other reagents were obtained from commercial sources and used as received.

Synthesis of $Yb(OSO_2CF_3)_2(thf)_3$. In a 250 mL round-bottom flask, $Yb(OSO_2CF_3)_3$ (15.26 g, 24.6 mmol) was suspended in 100 mL of THF. Ethylmagnesium bromide (24.6 mL, 1 M in THF) was then added slowly; the initial white suspension became a yellow solution with generation of heat. When the addition was complete, a yellow precipitate formed after about 1 min, and the mixture was allowed to stir for 1.5 h. Filtration and subsequent washing of the yellow precipitate with THF and drying under vacuum gave a quantitative yield of $Yb(OSO_2CF_3)_2$ with three molecules of coordinated thf as determined by elemental analysis. Anal. Calcd for $C_{14}H_{24}F_6O_9S_2Yb$: C, 24.46; H, 3.52. Found: C, 23.80; H, 3.24.

Synthesis of K[A′] (1). In a 250 mL Schlenk flask equipped with a stirring bar, 1,3-$(SiMe_3)_2C_3H_4$ (10.02 g, 53.7 mmol) was degassed, and hexanes (100 mL) was added. After cooling the solution to 0 °C in an ice bath, *n*-BuLi (21.5 mL, 53.7 mmol) was added dropwise over 15 min. After the solution was stirred for 6 h while allowing it to warm to room temperature, KO*t*-Bu (6.09 g, 54.3 mmol) was slowly added, and the solution was stirred for 10 h. A pale peach colored solid was produced that was filtered over a medium-porosity glass frit. The solid was washed with hexanes until the filtrate was colorless. The solid was then dried to yield 9.90 g of off-white product (44.1 mmol, 82% yield). ^1H NMR (25 °C, 300 MHz, C_6D_6): δ 6.69 (t, J = 15.9 Hz, CHC*H*CH, 1H), 2.78 (d, J = 15.9 Hz, C*H*CHC*H*, 2H), 0.23 (s, Si*Me*$_3$, 18H). ^{13}C NMR (25 °C, 75 MHz, C_6D_6): δ 155.74 (CH*C*HCH), 68.68 (*C*HCH*C*H), 2.52 (Si*Me*$_3$). Anal. Calcd for $C_9H_{21}KSi_2$: C, 48.14; H, 9.43. Found: C, 47.63; H, 9.42. Redissolution of the powder in dimethoxyethane (dme) followed by slow evaporation at room temperature produced colorless crystals of **1**·dme.

Synthesis of $EuA'_2(thf)_2$ (2). From $Eu(OSO_2CF_3)_3$. In a 100 mL flask, $Eu(OSO_2CF_3)_3$ (1.30 g, 2.17 mmol) was suspended in 20 mL of THF. A solution of **1** (1.50 g, 6.68 mmol) in 10 mL of diethyl ether at ambient temperature was added dropwise. The resulting mixture was stirred overnight to give a red solution. The solvent was then removed under vacuum and the residue dried for 0.5 h, after which hexanes (20 mL) was added and the resulting solution was filtered through Celite to remove all insoluble material. The red hexanes solution was reduced to dryness, and diethyl ether (10 mL) was added. Concentration and subsequent cooling of the **2**/diethyl ether solution at −30 °C resulted in the formation of red crystals of **2** (0.70 g, 1.05 mmol) in 48% yield. Anal. Calcd for $C_{26}H_{58}EuO_2Si_4$: Eu, 22.78. Found: Eu, 22.65. Solution magnetic moment (μ_{eff}) calcd for $4f^7$: 7.94 μ_B. Found: 7.44 μ_B.

Synthesis of $YbA'_2(thf)_2$ (3). From $Yb(OSO_2CF_3)_2(thf)_3$. Inside an inert atmosphere glovebox, $Yb(OSO_2CF_3)_2(thf)_3$ (0.76 g, 1.10 mmol) was placed in a flask equipped with a stirring bar and suspended in 5 mL of THF. Solid **1** (0.50 g, 2.2 mmol) was placed in a scintillation vial and was dissolved in THF (15 mL). This **1**/THF solution was added dropwise to the $Yb(OSO_2CF_3)_2$ slurry with stirring at room temperature. The reaction mixture turned purple upon addition, and stirring was continued overnight at ambient temperature. The solvent was removed under vacuum, and the resulting residue was dried for 0.5 h, also under vacuum. Hexanes (10 mL) was used to dissolve the residue; filtration through Celite yielded a purple filtrate. Concentration and cooling of the resulting solution at −30 °C produced blue crystals of **3** (0.560 g, 0.814 mmol, 74% yield). Anal. Calcd for $C_{26}H_{58}O_2Si_4Yb$: C, 45.38; H, 8.50. Found: C, 45.20; H, 8.95. ^1H NMR (25 °C, 400 MHz, C_6D_6): δ 7.07 (t, CHC*H*CH, 2H), 3.57 (bs, thf, 8H), 3.50 (d, C*H*CHC*H*, 4H), 1.30 (bs, thf, 8H), 0.30 (s, Si*Me*$_3$, 36H). ^{13}C NMR (25 °C, 100.6 MHz, C_6D_6): δ 159.4 (CH*C*HCH), 78.47 (*C*HCH*C*H), 70.26 (thf), 25.59 (thf), 2.32 (Si*Me*$_3$).

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(11) Woodman, T. J.; Schormann, M.; Bochmann, M. *Organometallics* **2003**, *22*, 2938−2943.

(12) Strauch, J. W.; Fauré, J.-L.; Bredeau, S.; Wang, C.; Kehr, G.; Fröhlich, R.; Luftmann, H.; Erker, G. *J. Am. Chem. Soc.* **2004**, *126*, 2089−2104.

(13) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005.

(14) Grant, D. H. *J. Chem. Educ.* **1995**, *72*, 39−40.

(15) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*, 2nd ed.; Methuen: London, 1969; pp 194−197.

(16) Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 1382−1386.

(17) Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. *J. Org. Chem.* **1987**, *52*, 1017−1021.

(18) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1986**, *24*, 243−250.

(19) Hahn, F. E.; Mohr, J. *Chem. Ber.* **1990**, *123*, 481−484.

(20) Hanamoto, T.; Sugimoto, Y.; Sugino, A.; Inanaga, J. *Synlett* **1994**, 377−378.

(21) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

Synthesis of YbA′$_2$(thf)$_2$ (3). From Yb(OSO$_2$CF$_3$)$_3$. Reactions of Yb(OSO$_2$CF$_3$)$_3$ with 3 equiv of **1** in THF led to isolated yields of **3** that were never greater than 50%. Blue crystals suitable for X-ray diffraction were grown by cooling a hot pentane solution of **3** obtained from one of these reactions to −30 °C overnight.

Synthesis of CeA′$_3$(thf) (4). Inside an inert atmosphere glovebox, Ce(OSO$_2$CF$_3$)$_3$ (1.36 g, 2.32 mmol) was placed in a scintillation vial equipped with a stirring bar. Addition of THF (5 mL) created a suspension to which a solution of **1** (1.6 g, 7.1 mmol) dissolved in 10 mL of THF was added dropwise. The reaction mixture turned brick red after about 1 min and was allowed to stir overnight. The solvent was then removed under vacuum, and 20 mL of hexanes was added to the residue. Filtration of the resulting mixture through Celite, concentration of the filtrate to ca. 5 mL, and subsequent storage at −30 °C gave 1.1 g of **4** (1.4 mmol, 80% yield). Red crystals suitable for X-ray diffraction were obtained after 3 weeks. Anal. Calcd for $C_{31}H_{71}CeOSi_6$: Ce, 18.23. Found: Ce, 18.67. Solution magnetic moment (μ_{eff}) calcd for 4f^1: 2.54 μ_B. Found: 2.01 μ_B.

Synthesis of TbA′$_3$(thf) (6). Inside an inert atmosphere glovebox, **1** (0.61 g, 2.72 mmol) was dissolved in 10 mL of THF in a scintillation vial. A suspension of Tb(OSO$_2$CF$_3$)$_3$ (0.55 g, 0.90 mmol) in 2 mL of THF was placed in a separate scintillation vial equipped with a stirring bar. Both vials were then placed in the glovebox freezer (−30 °C for 0.5 h). The **1**/THF solution was added dropwise to the Tb(OSO$_2$CF$_3$)$_3$ slurry with stirring, and the resulting reaction mixture was allowed to warm to room temperature overnight while stirring was maintained. Removal of the solvent under vacuum, addition of ca. 10 mL of hexanes to the residue, and filtration through Celite gave a bright orange solution that was concentrated to ca. 3 mL. Cooling of this solution to −30 °C yielded orange crystals of **6** (0.29 g, 0.37 mmol, 41%). Anal. Calcd for $C_{31}H_{71}OSi_6Tb$: Tb, 20.18. Found: Tb, 20.03. Solution magnetic moment (μ_{eff}) calcd for 4f^8: 9.72 μ_B. Found: 9.2 μ_B.

Synthesis of SmA′$_2$(thf)$_2$ (7). In a scintillation vial, SmI$_2$ (2.00 g, 4.95 mmol) was suspended in 10 mL of THF and cooled to −30 °C for 0.5 h. To this suspension was added a solution of **1** (2.23 g, 9.93 mmol) in 10 mL of THF. The resulting solution turned green immediately and was allowed to stir at room temperature overnight. The solvent was removed under vacuum, and hexanes (30 mL) was added to extract the soluble components. The resulting solution was filtered through Celite, the filtrate obtained was reduced to dryness under vacuum, and a minimum amount of diethyl ether was used to dissolve the remaining solid. This solution yielded, after two crops, 1.90 g (2.86 mmol, 58% yield) of **7** as dark green crystals upon cooling to −30 °C. ^{1}H NMR (25 °C, 400 MHz, THF-d_8): δ 16.35 (br s, CHC*H*CH, 2H), 3.64 (s, coordinated-thf), 1.78 (s, coordinated-thf), −0.180 (s, Si*Me*$_3$, 36H), −15.45 (br s, C*H*CHC*H*, 4H). Anal. Calcd for $C_{26}H_{58}O_2Si_4Sm$: Sm, 22.59. Found: Sm, 22.13.

General Polymerization Reaction and Polymer Work-up. MMA (4 mL, 37.4 mmol) was added via syringe to a solution of catalyst in toluene (approximately 20 mL) at 0 °C. Polymerization reactions were allowed to run for lengths of time between 30 s and 30 min, after which methanol was added to quench the reaction mixture. The resulting solids were filtered, concentrated to dryness, dissolved in chloroform, and precipitated with methanol to give white solids that were dried under vacuum prior to GPC analysis.

GPC Determinations. Molecular weights were determined in tetrahydrofuran (THF) or dimethylformamide (DMF; only the PMMA sample generated from **5** was measured in this solvent) by gel permeation chromatography (GPC). The GPC consisted of an Alliance 2690 pump equipped with a 2410 differential refractive index detector. The column set utilized for DMF consisted of two Polymer Labs PL Mixed B GPC columns held at 80 °C at a flow rate of 1.0 mL/min. The columns used for the THF analysis consisted of Shodex 806, 804, and 802.5 columns at 40 °C at a flow rate of 1.0 mL/min. The molecular weights were calculated relative to the retention times of narrow MW polystyrene standards or poly(ethylene oxide) standards using Waters Corporation's Millennium32 software. The shape of the MW distribution for the PMMA sample generated from **2** indicated that this polymer was uniform. However, the PMMA sample generated from **3** has a high molecular weight shoulder, and the PMMA sample generated from **5** is broad, with shoulders possessing high and low molecular weight components. For PMMA generated by **7**, the GPC chromatogram was very broad. Note that the PMMA sample from **5** did not completely dissolve in either DMF or THF. The cloudy solution was filtered through a 0.45 μm syringe filter. The PMMA samples generated from **4** and **7** were also filtered to remove undissolved solids prior to analysis. Other samples appeared to dissolve completely and were not filtered.

X-ray Crystallography of 1·dme. Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory at the University of Minnesota. All calculations were performed using the current SHELXTL[22] suite of programs. A suitable crystal was located and attached to the tip of a glass capillary and mounted on a CCD area detector diffractometer for data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. Data collection of a randomly oriented region of reciprocal space was carried out using Mo Kα radiation (graphite monochromator). The intensity data were corrected for absorption with SADABS.[23] Final cell constants were calculated from strong reflections from the actual data collection after integration (SAINT).[24] Relevant crystal and collection data parameters can be found in Table 1.

X-ray Crystallography of 2. Data collection of **2** was performed at the University of Chicago. The crystal was mounted and centered on a Bruker SMART[25] APEX system at 100 K. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters was done using SAINT[26] at Los Alamos National Laboratory. Absorption corrections were applied using SADABS[27] based on redundant diffractions. Direct methods were used to locate the Eu and Si atoms as well as most C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected Eu, Si, O, and C atoms. Following anisotropic refinement of all non-hydrogen atoms, ideal H atom positions were calculated. The final refinement was anisotropic for Eu, Si, O, and C atoms and isotropic-riding for H atoms. Relevant crystal and collection data parameters can be found in Table 1.

X-ray Crystallography of 3, 4, 6, and 7. Single-crystal X-ray diffraction experiments for complexes **3**, **4**, **6**, and **7** were performed on a Bruker P4/CCD/PC diffractometer at Los Alamos National Laboratory. Diffraction data were refined using SHELXTL PC.[28] Crystals were coated in mineral oil and mounted on a glass fiber at 203 K. Data collection and initial

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(22) Sheldrick, G. M. *SHELXTL*, Version 6.10; Bruker Analytical X-ray Systems, Inc: Madison, WI, 2000.

(23) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.

(24) *SAINT Software Users Guide*, Version 6.2; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.

(25) *SMART Software Users Guide*, Version 5.628; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

(26) *SAINT Software Users Guide*, version 4.05 ed.; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1996.

(27) Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 1996.

(28) Sheldrick, G. M. *SHELXTL*, Version 5.10; University of Göttingen: Germany, 1999.

Table 1. Crystal Data and Summary of X-ray Data Collection[a]

chemical formula	$C_{26}H_{62}O_4Si_4K_2$ (**1**)	$C_{26}H_{58}O_2Si_4Eu$ (**2**)	$C_{26}H_{58}O_2Si_4Yb$ (**3**)	$C_{31}H_{71}OSi_6Ce$ (**4**)	$C_{31}H_{71}OSi_6Tb$ (**6**)	$C_{26}H_{58}O_2Si_4Sm$ (**7**)
color of cryst	colorless	red	blue	orange	orange	dark green
fw	629.32	667.04	688.12	768.52	787.33	665.44
cryst syst	monoclinic	tetragonal	tetragonal	orthorhombic	monoclinic	tetragonal
space group	$P2_1/c$	$P4_2/n$	$P4_2/n$	$Pca2_1$	$P2_1/c$	$P4_2/n$
a, Å	10.7102(10)	14.8273(17)	15.227(6)	20.969(5)	10.622(4)	14.911(2)
b, Å	20.4087(19)	14.8273(17)	15.227(6)	10.579(2)	42.017(17)	14.911(2)
c, Å	18.6521(17)	16.60(3)	17.212(15)	20.325(5)	19.919(8)	16.907(5)
α, deg	90	90	90	90	90	90
β deg	93.045(2)	90	90	90	94.522(7)	90
γ, deg	90	90	90	90	90	90
V, Å^3	4071.2(7)	3673(8)	3991(4)	4508.8(17)	8862(6)	3759.1(13)
ρ_{calcd}, g cm^{-3}	1.027	1.206	1.145	1.132	1.171	1.176
Z	4	4	4	4	8	4
μ (mm^{-1})	0.374	1.856	2.480	1.188	1.777	1.707
F(000) (e$^-$)	1376	1396	1424	1628	3264	1392
T, K	173(2)	100	203	203	203	203
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
no. rflns collected	26 915	34 707	15 944	30 969	53 392	23 422
no. indep rflns	7209	3250	3142	9598	14 810	3442
no. data/restraints/ params	7209/98/413	3250/0/150	3142/0/150	9598/1/352	14 810/0/703	3442/0/150
GOF[b]	1.039	1.069	1.176	1.085	3.361	1.068
R_1 [$I > 2\sigma(I)$][c]	0.0394	0.0381	0.0577	0.0597	0.0905	0.0531
wR_2 [$I > 2\sigma(I)$][d]	0.0952	0.0965	0.1161	0.0916	0.1270	0.0979
R_1 (all data)[c]	0.0568	0.0434	0.0997	0.0948	0.1034	0.1127
wR_2 (all data)[d]	0.1067	0.0998	0.1349	0.1002	0.1280	0.1172
largest diff peak, e Å^{-3}	0.350	1.309	0.625	1.363	1.565	0.621

[a] See ref 10 for crystallographic data of complex **5**. [b] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; n = no. independent reflections; p = no. parameters refined. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

indexing and cell refinement was performed using SMART[29] software. Frame integration and final cell parameter calculations were carried out using SAINT[26] software. The data were corrected for absorption using the SADABS[27] program. The structures were solved using difference Fourier techniques. The initial solutions revealed the metal center and the majority of all other non-hydrogen positions. The remaining atomic positions were determined from subsequent Fourier syntheses. All hydrogen atoms were placed in ideal positions and refined using a riding model. The crystal and refinement parameters are listed in Table 1.

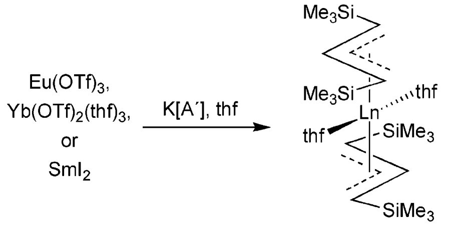
Results and Discussion

In 1990, Fraenkel described the synthesis and subsequent deprotonation of the substituted propene 1,3-$(SiMe_3)_2C_3H_4$ (HA′).[16] The originally reported lithium salt Li[A′] can be transmetalated with KO*t*Bu to yield K[A′] (**1**), which in turn has been treated with various metal halides and triflates to produce numerous metal allyl complexes.[8−11,30] In the present study, both divalent and trivalent lanthanide triflates were used to produce allyl compounds. Our need for substantial quantities of divalent Yb(II) triflate was met by the reduction of Yb(III) triflate by reaction with ethylmagnesium bromide in THF at room temperature (eq 1).[20] This reduction method produces $Yb(OTf)_2(thf)_3$ quantitatively.

$$Yb(OTf)_3 + EtMgBr \xrightarrow[THF]{25\ °C} Yb(OTf)_2(thf)_3 + MgBr(OTf) + 0.5\ C_4H_{10} \quad (1)$$

The lanthanide(II) complexes $[1,3\text{-}(SiMe_3)_2C_3H_3]_2Ln(thf)_2$ ($LnA'_2(thf)_2$; Ln = Eu (**2**), Yb (**3**), Sm (**7**)) can be readily prepared from the bis(triflate) precursors (Scheme 1). The corresponding lanthanide diiodides can be used as well, and we found no difference in yield when either precursor is used. If Yb(III) or Eu(III) triflate is treated with **1**, reduction to the lanthanide(II) product is observed, but the yield of the allyl complex is reduced (<50%). The samarium complex (**7**) has been previously reported but only marginally characterized.[8] For use in subsequent polymerization studies, we repeated its synthesis and obtained its crystal structure.

Scheme 1. Reaction Scheme for the Synthesis of $LnA'_2(thf)_2$, where Ln = Eu (2), Yb (3), Sm (7)



We have previously described the reaction of CeI_3, TbI_3, and NdI_3 with 3 or 4 equiv of **1** to give salt complexes of the general type $[K(thf)_4][LnA'_3I]$ in moderate to good yield.[10] In contrast, when the triflates of Ce(III), Nd(III), and Tb(III) are treated with 3 equiv of **1** in THF at room temperature or −30 °C, neutral lanthanide(III) allyl complexes $[1,3\text{-}(SiMe_3)_2C_3H_3]_3Ln(thf)$ ($LnA'_3(thf)$; Ln = Ce (**4**), Nd (**5**),[10] Tb (**6**)) can be isolated in 40−80% yield (Scheme 2). Both the salt and neutral complexes are highly colored (Ce: brick-red; Nd: green; Tb: orange) and extremely air- and moisture-sensitive. Under inert atmosphere and at ambient temperature, however, these complexes are stable for several days. They are stable indefinitely under an inert atmosphere at reduced temperature (<−25 °C).

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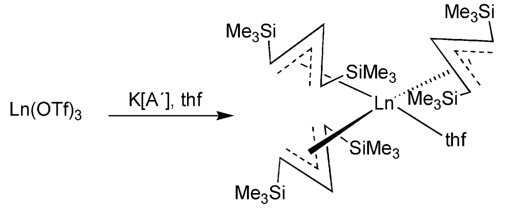
[29] *SMART Software Users Guide*, Version 4.210; Bruker Analytical X-ray Systems: Madison, WI, 1996.

[30] Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 217−219.

Scheme 2. Reaction Scheme for the Synthesis of $\mathrm{LnA'_3(thf)}$, where Ln = Ce (4), Nd (5), Tb (6)



Crystallographic Results

$[\mathrm{K(dme)}\{1,3\text{-}(\mathrm{SiMe_3})_2\mathrm{C_3H_3}\}]_\infty$ ((1)·dme). Owing to its extensive use as a starting material for these reactions, the solid state structure of **1** was of considerable interest. Crystals of **1**·dme were grown by dissolving solid **1** in dimethoxyethane and allowing the solution to evaporate at room temperature. Colorless needlelike crystals grew overnight, which were shown to be the oligomerized product of **1** with coordinated dme (Figure 1).

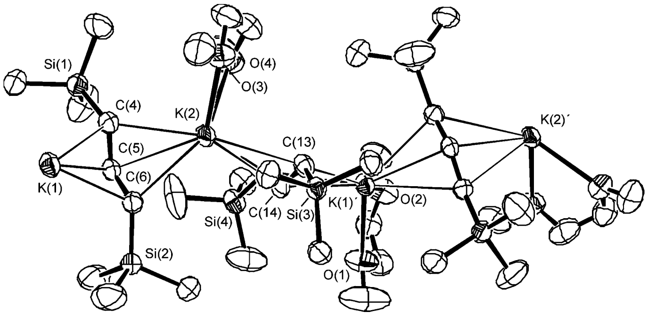


Figure 1. Thermal ellipsoid representation of **1**·dme shown at the 50% probability level. All hydrogen atoms were removed for clarity.

As is typical for organometallic coordination polymers of the heavy alkali metals, the potassium ions constitute a zigzag chain, with K(1)−K(2)−K(1) and K(2)−K(1)−K(2) angles of 153.3° and 141.9°, respectively (cf. the K−K′−K″ angle of 138.0° in $[\mathrm{K(C_5H_5)}]_\infty$[31] and the K−K′−K″ angle of 150.7° in $[\mathrm{K(C_5(SiMe_3)H_4)}]_\infty$[32]). The K−C distances of 2.98−3.10 Å are similar to those for potassium cyclopentadienides (cf. 2.988−3.079 Å in $[\mathrm{K(C_5(SiMe_3)H_4)}]_\infty$ and 2.933−3.101 Å in $[\mathrm{K(C_5(SiMe_3)_3H_2)}]_\infty$[33]), an indication of the comparably ionic bonding in the complexes.

Coordination of the allyl anion to potassium causes relatively little perturbation in its geometry, as suggested by the average C−C−C angle of 130.7(3)°, which is close to the 130.3° angle calculated for the free $[\mathrm{A'}]^-$ anion.[30] The $\mathrm{SiMe_3}$ groups in **1**·dme are arranged in a *syn,syn* configuration. As is generally found for such substituents,[5,34] the silicon atoms Si(1) and Si(2) are near the $\mathrm{C_3}$ plane; their average 0.10 Å displacements are reflected in the nearly linear C−C−C−Si torsion angles of 176.3° (av); the values for Si(3) and Si(4) are similar.

Table 2. Average Bond Distances (Å) and Angles (deg) for 1·dme and $\mathrm{LnA'_3(thf)}$ Complexes (where Ln = Ce (4), Tb (6))[a]

	1	4	6
	Bond Lengths		
$\mathrm{M{-}C_{methylene}}$	2.977[4]	2.730[7]	2.655[8]
$\mathrm{M{-}C_{methine}}$	3.097[6]	2.796[7]	2.684[8]
M−O	2.758[14]	2.522(5)	2.387(5)
	Bond Angles		
C−C−C	130.7[3]	128.0[8]	127.2[9]
C−M−C[b]	48.13[10]	54.5[2]	56.4[2]

[a] Standard deviations are given in parentheses. Values in square brackets are the errors of the averages. [b] This value represents the angle involving the methylene carbons on the same allyl.

Table 3. Average Bond Distances (Å) and Angles (deg) for $\mathrm{MA'_2(thf)_2}$ Complexes (where M = Sm (7), Eu (2), Yb (3), Ca)[a]

	7	2	3	$\mathrm{CaA'_2(thf)_2}$[30]
	Bond Lengths			
$\mathrm{M{-}C_{methylene}}$	2.770[6]	2.780[5]	2.741[9]	2.655[3]
$\mathrm{M{-}C_{methine}}$	2.796(6)	2.793(5)	2.748(9)	2.652(3)
M−O	2.530(6)	2.536(4)	2.452(8)	2.353(2)
	Bond Angles			
C−C−C	128.4[6]	128.8[4]	128.9[9]	129.8(3)
C−M−C[b]	54.5(19)	54.4(12)	56.5(3)	56.82(9)
C−M−C[c]	127.2(3)	128.3(2)	129.9(4)	131.01(14)
O−M−O	79.3(3)	79.6(2)	80.2(4)	80.44(13)

[a] Standard deviations are given in parentheses. Values in square brackets are the errors of the averages. [b] This value represents the angle involving the methylene carbons on the same allyl. [c] This value represents the angle involving the methylene carbons trans to each other.

$[1,3\text{-}(\mathrm{SiMe_3})_2\mathrm{C_3H_3}]_2\mathrm{Ln(thf)_2}$ (2, 3, 7). The divalent complexes **2**, **3**, and **7** crystallize as isostructural monomeric species with *trihapto* allyl ligands and *cis*-ligated thf molecules. Crystallographically imposed C_2 axes run through the metal atoms, so that only half of each molecule is unique. The average Ln−C bond distances for all three molecules (2.74−2.80 Å; Tables 2 and 3) are typical for η^3-coordinated allyl lanthanide complexes, and those for **3** reflect the smaller ionic radii of Yb(II) as compared to those of Sm(II) (in **7**) and Eu(II) (in **2**).[3,35] The structure of **2** is typical for the group, and a representation of it is given as Figure 2.

The two allyl ligands in **2** are in an *anti*-configuration, and the angle between the $\mathrm{C_3}$ planes is 118.3°. The average C−C−C angle (128.9°) has contracted slightly from that in **1**·dme, but the $\mathrm{SiMe_3}$ groups, which display a *syn,syn* arrangement, again lie close to the $\mathrm{C_3}$ plane (0.02 Å for Si(1), 0.27 Å for Si(2)).

Complexes **2**, **3**, and **7** are isomorphous with the previously reported calcium complex, $\mathrm{CaA'_2(thf)_2}$.[30] As the ionic radii of calcium and ytterbium differ only slightly (Ca(II) 1.00 Å; Yb(II) 1.02 Å for coordination number 6),[3] bond distances and angles of the ligands in their respective complexes are almost always similar (Table 3).[35] It is unusual, therefore, to find that this is not the case with $\mathrm{CaA'_2(thf)_2}$ and **3**; there is an approximate increase of 0.1 Å in the bond distances to the allyl carbons and thf oxygen atoms on moving from calcium to ytterbium. The general expansion of the ytterbium compound is also reflected in the unit cell constants and resulting volumes of the two com-

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(31) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855−3858.

(32) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem.* **1987**, *99*, 563−564.

(33) Harvey, M. J.; Hanusa, T. P.; Pink, M. *J. Chem. Soc., Dalton Trans.* **2001**, 1128−1130.

(34) Carlson, C. N.; Hanusa, T. P.; Brennessel, W. W. *J. Am. Chem. Soc.* **2004**, *126*, 10550−10551.

(35) Harder, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2714−2718.

Table 4. Polymerization of MMA by Allyl Complexes

entry	complex	amt of cat., mmol	yield, g (time, min)	convn, %	TOF[e]	M_w	M_n	M_w/M_n	tacticity rr	mr	mm
1	$EuA'_2(thf)_2$ (**2**)	0.01	0.92 (30)	24.6	2400	131 000	41 200	3.2	21	41	38
2	$YbA'_2(thf)_2$ (**3**)	0.15	0.779 (35)	20.8	89	378 400	98 100	3.9	26	51	23
3	$CeA'_3(thf)$ (**4**)	0.15	0.51 (30)	13.6	67	148 000	9070	16.3	23	30	47
4[a]	$NdA'_3(thf)$ (**5**)	0.20	0.63 (30)	16.8	63	272 400	87 200	3.1	23	27	50
5[b]	$SmA'_2(thf)_2$ (**7**)	0.20	0.20 (0.5)	5.3	1200	237 000	32 400	7.3	31	30	39
		0.04	*− (300)*	*12.3*		*63 200*	*13 600*	*4.65*			
6[a]	$[K(thf)_4][CeA'_3I]$	0.02	2.4 (30)	64.1	2400	613 600	70 600	8.7	25	28	47
7[c]	$[\{K(thf)_2\}\{SmA'_3\}]_2$	0.02	1.296 (0.5)	69.2	83 100	87 600	43 800	2.0	24	54	22
8[d]	$[La\{(\eta^3\text{-}C_3H_3\ SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(thf)\}(thf)_{0.5}]_\infty$	0.02	0.728 (1.5)	38.9	15 600	636 000	197 000	3.2	26	55	19
9[d]	$[Y\{(\eta^3\text{-}C_3H_3\text{-}SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(thf)\}(thf)]_\infty$	0.02	1.348 (0.5)	72.0	86 400	297 000	99 900	3.0	25	54	21
10[d]	$[Sc\{(\eta^3\text{-}C_3H_3\text{-}SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(thf)\}(thf)]_\infty$	0.02	1.331 (1)	71.1	42 700	207 000	88 600	2.3	24	51	25
11[d]	$[Nd\{(\eta^3\text{-}C_3H_3\text{-}SiMe_3)_2SiMe_2\}_2\{\mu\text{-}K(thf)\}(thf)\cdot(C_7H_8)]_\infty$	0.02	0.107 (10)	5.7	343	204 000	85 600	2.4	19	54	27
12	$K[A']$ (**1**)	0.04	3.09 (0.5)	82.5	104 000	215 000	110 000	1.95	23	54	23
13	2 $SmA'_2(thf)_2$ (**7**) + $K[A']$ (**1**)	0.20	0.766 (0.5)	24.4	4590	42 800	22 100	1.93	20	47	32
14	$SmA'_2(thf)_2$ (**7**) + $K[A']$ (**1**)	0.20	2.845 (0.5)	75.8	17 000	62 500	39 700	1.57	22	51	27
15	$SmA'_2(thf)_2$ (**7**) + 2 $K[A']$ (**1**)	0.20	3.133 (0.5)	83.3	18 800	46 500	29 400	1.58	22	54	23

[a] See ref 10. [b] Values italicized represent those for PMMA prepared by Yasuda; see ref 8. [c] See ref 9 for all data except tacticity. [d] See ref 11. [e] TOF = (mol monomer consumed) (mol catalyst)$^{-1}$ h^{-1}.

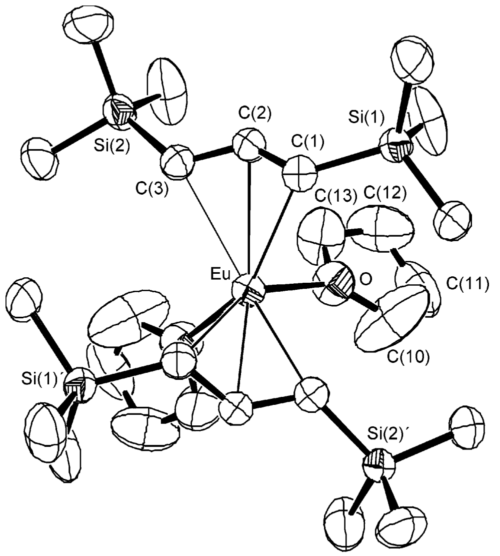

Figure 2. Thermal ellipsoid representation of **2** shown at the 50% probability level. All hydrogen atoms were omitted for clarity.

pounds: 3613 Å^3 for $CaA'_2(thf)_2$ and 3991 Å^3 for **3**, a 10.5% increase.

It may be that the ytterbium complex should be considered the more anomalous. The original report of the $CaA'_2(thf)_2$ complex noted that the average Ca−C distance of 2.654(5) Å in $CaA'_2(thf)_2$ is indistinguishable from that for cyclopentadienyl rings in complexes with formally six-coordinate Ca(II) centers (e.g., 2.64(1) Å in $Ca[C_5(i\text{-}Pr)_4H]_2$[36] or 2.677(4) Å in $Ca[C_5(t\text{-}Bu)_3H_2]I(thf)_2$).[37] In contrast, the Yb−C range of 2.741(9)−2.748(9) Å in **3** is noticeably longer than that for cyclopentadienyl rings in complexes with six-coordinate Yb(II) centers (e.g., 2.636(3)−2.690(3) Å in $Yb(C_5Me_5)_2$[38] and 2.63(2)−2.670(13) Å in $Yb(C_5Me_5)Si(SiMe_3)_3(thf)_2$).[39] Harder has recently proposed that Yb−L bonds may be weaker than analogous Ca−L bonds, even when of similar length, owing to repulsion from the filled f^{14} shell of Yb(II).[35] If so, compound **3** may represent a case in which the weakness is reflected in longer bonds.

$[1,3\text{-}(SiMe_3)_2C_3H_3]_3Ln(thf)$ (4, 6). The structures of complexes **4** and **6** are analogous to that of the previously reported complex **5**[10] and consist of three *trihapto* allyl ligands and a single thf ligand. As with the divalent lanthanide complexes, the average Ln−C bond distances in the Ce(III), Nd(III), and Tb(III) species (2.65−2.80 Å) are typical for η^3-coordinated allyl ligands and contract systematically upon moving across the lanthanide series. The structure of **4**, which is representative of the three compounds, is given in Figure 3. There is some evidence that steric crowding may be affecting the geometric parameters. For example, although the allyl ligands in all three complexes have *syn,syn* trimethylsilyl substituents, they are not always as close to their respective C_3 planes as in the bis(allyl) complexes; in **4**, the average $-SiMe_3$ displacement is 0.32 Å. Furthermore, the C−C−C angle in **4** varies somewhat between the ligands, from near the value expected for the free anion (C(4)−C(5)−C(6) = 130.5(9)°) to a moderately contracted 125.9(7)° (C(7)−C(8)−C(9)). In **6**, the range of C−C−C angles is slightly greater, from 129.1° to 123.4°.

Polymerization Results

Polymerization of methyl methacrylate (MMA) by complexes **2**−**5**, **7**, and $[K(thf)_4][CeA'_3I]$ gave, in all cases, atactic poly(methyl methacrylate) (PMMA). The polymerization data are compared with those of complexes of similar constitution[9−11] and displayed in Table 4. As a control, the lanthanide iodide and triflate salts of Ce(III), Nd(III), Eu(III), Yb(III), and Yb(II) were subjected to similar polymerization conditions; no PMMA was formed from these lanthanide iodides and triflates under the present nonradical conditions.[40]

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[36] Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843−4851.

[37] Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *J. Organomet. Chem.* **2001**, *626*, 43−48.

[38] Schultz, M.; Burns, C. J.; Schwartz, D. J.; Andersen, R. A. *Organometallics* **2000**, *19*, 781−789.

[39] Corradi, M. M.; Frankland, A. D.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A. *Chem. Commun.* **1996**, 2323−2324.

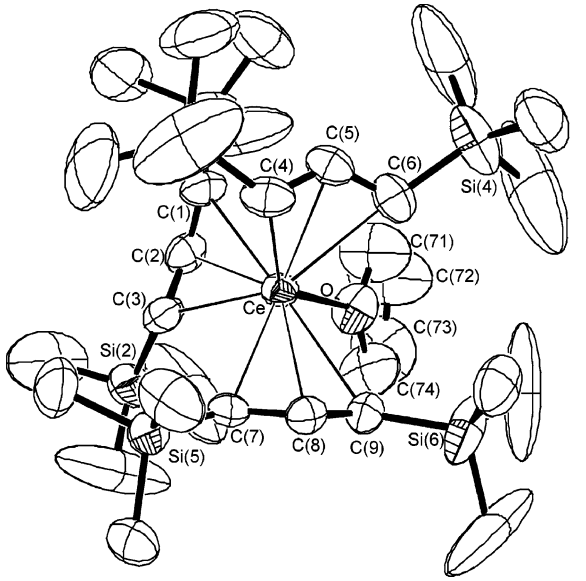

Figure 3. Thermal ellipsoid representation of **4** shown at the 50% probability level. All hydrogen atoms were omitted for clarity.

Among the neutral lanthanide allyl complexes, the polymerization activity appears to vary with the radius of the lanthanide metals and with the number of coordinated allyls; i.e., with the access of MMA to the metal centers (Table 4; entries 1−5). The divalent complexes **7** and **2**, for example, which contain the larger metals samarium and europium (Sm(II) ≈ Eu(II) 1.17 Å for coordination number 6),[3] have TOF values over 10 times higher than **3** (Yb(II) = 1.02 Å for coordination number 6). Furthermore, the complexes containing trivalent cerium (**4**) and neodymium (**5**) have lower activity than any of the divalent species. This result probably reflects their smaller radii (CeIII) 1.07 Å; Nd(III) 1.03 Å for coordination number 7) and the steric congestion from the three bulky allyl ligands. The tacticity data for complexes **2**−**5** and **7** (entries 1−5) are consistent with a metal center from which two or three independent polymer chains propagate without stereocontrol. The tacticity data of the PMMA generated by these complexes also compare well with those reported by Bochmann[9,11] (entries 7−11).

Interestingly, most of the salt complexes (entries 6−11) are more efficient catalysts than the neutral complexes (entries 1−5); they exhibit TOF values that are 10−100 times greater. Surprisingly, however, the potassium complex **1** displayed the highest TOF for MMA polymerization of all tested compounds (entry 12). Given its level of activity, it is possible that the increased effectiveness of the salt complexes stems from the presence of the alkali metal center. To test this hypothesis, catalyst mixtures of independently prepared **1** and **7** in varying ratios (entries 13−15) were subjected to MMA polymerization conditions similar to those described above. Various polymer yields were found, but higher TOFs consistently accompanied increased amounts of **1** in the catalyst mixtures.

The TOFs of the catalysts in entries 13−15 are still not nearly as high as when **1** is used alone. The ^{1}H NMR spectra of the mixtures of **1** and **7** are not simple superpositions of the spectra of the independent complexes, and the polydispersities of the combinations of **1** and **7** (M_w/M_n = 1.57−1.93) are lower than either **1** (1.95) or **7** (7.3) by itself, which also indicates that the two species are not functioning as separate initiators.

Although an interaction clearly exists between **1** and **7** when both initiators are dissolved in toluene, the mixtures do not behave exactly like the previously synthesized complex [{K(thf)$_2$}{SmA′$_3$}]$_2$, which is prepared by a halide metathesis reaction in THF.[9] The latter has substantially heightened polymerization activity compared with all of the combinations of **1** and **7**. To further confirm that the combinations of **1** and **7** do not produce the [{K(thf)$_2$}{SmA′$_3$}]$_2$ complex, a 1:1 ratio of **1** and **7** was allowed to stir in thf overnight. Upon removal of the solvent, the mixture was tested for MMA polymerization under the previously described conditions. The activity was similar to the 1:1 ratio (entry 14) and, hence, significantly lower than the activity of separately prepared [{K(thf)$_2$}{SmA′$_3$}]$_2$. Despite the fact that they consist of the same basic components, the polymerization activity of [{K(thf)$_2$}{SmA′$_3$}]$_2$ could not be reproduced with combinations of **1** and **7**.

Conclusions

We have demonstrated that a general route exists for the preparation of monomeric neutral lanthanide complexes containing sterically bulky allyl ligands. Such complexes initiate the polymerization of MMA to produce atatic PMMA. The divalent complexes, with their larger metal radii and less crowded coordination spheres, are generally more active than their trivalent counterparts. High MMA polymerization activity, however, depends critically on the presence of an auxiliary alkali metal-allyl fragment. It seems clear that aggregation of **1** with another metal center (e.g., one containing Sm(II)) suppresses the former's activity as an initiator for the polymerization of MMA. As **1** proves to be an effective initiator by itself, the presence of alkali metal ions clearly needs to be considered in studies of the activity of allyl lanthanide salt complexes in polymerization reactions.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**, **2**, **3**, **4**, **6**, and **7**. These are available free of charge via the Internet at http://pubs.acs.org.

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(40) White, D.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 286−287.