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Approaches to Alkaline Earth Metal−Organic Chemical Vapor Deposition Precursors. Synthesis and Characterization of Barium Fluoro-*β*-ketoiminate Complexes Having Appended Polyether "Lariats"

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The synthesis and characterization of a family of *β*-ketoimines derived from 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) and the corresponding volatile barium *β*-ketoiminate−polyether complexes having the general formula $Ba[CF_3COCHC(NR)CF_3]_2$ where R = $(CH_2CH_2O)_2CH_3$, $(CH_2CH_2O)_2CH_2CH_3$, and $(CH_2CH_2O)_3CH_2CH_3$ is reported. These complexes can be transported in the vapor phase at 160 °C/0.05 Torr without decomposition. The *β*-ketoiminate ligands are synthesized by condensation of the appropriate amine-terminated poly(ethylene oxide)s with the trimethylsilyl enol ether derivative of hfa and converted to barium *β*-ketoiminate−polyether complexes by reaction with BaH_2. The poly(ethylene oxide) amines are in turn synthesized by triphenylphosphine-mediated reduction of the corresponding poly(ethylene oxide) azides (synthesized via the tosylates) to afford the amines in good yields and analytical purity. The amines, *β*-ketoimines, and barium complexes were characterized by elemental analysis, ^1H, ^{19}F, and ^{13}C NMR spectroscopy, mass spectroscopy, and thermogravimetric analysis. The eight- and ten-coordinate Ba^{2+} complexes having the formula $Ba[CF_3COCHC(NR)CF_3]_2$ where R = $(CH_2CH_2O)_2CH_2CH_3$ [$C_{22}H_{28}N_2F_{12}O_6Ba$; space group = monoclinic, $P2_1$; $a = 12.1175(2)$ Å, $b = 14.9238(2)$ Å, $c = 16.9767(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 90.0840(10)°$, $Z = 4$] and R = $(CH_2CH_2O)_3CH_2CH_3$ [$C_{26}H_{36}N_2F_{12}O_8Ba$; space group = triclinic, $P\bar{1}$ (#2); $a = 10.971(2)$ Å, $b = 12.134(2)$ Å, $c = 15.280(4)$ Å, $\alpha = 89.94(2)°$, $\beta = 110.00(2)°$, $\gamma = 116.75(2)°$, $Z = 2$] were characterized by single-crystal X-ray diffraction. Both analyses reveal monomeric structures with the *β*-ketoiminate ligands coordinated to the Ba^{2+} center through all available oxygen and nitrogen atoms. These complexes are substantially more volatile than $Ba(2,2,6,6\text{,-tetramethyl-3,5-heptanedionate})_2$ but less so than the most volatile $Ba(1,1,1,5,5,5\text{-hexafluoro-2,4-pentanedionate})_2\cdot$polyether complexes.

Introduction

Recently, considerable effort has been devoted to the synthesis of precursors for the metal−organic chemical vapor deposition (MOCVD) of alkaline earth-containing metal oxide ceramics. Successful MOCVD of these ceramics relies on the availability of precursors having high vapor pressures, long-term vapor pressure stability, appropriate reactivity with respect to film growth, ease of handling and synthesis, and low cost.[1] Considering these factors, film growth employing alkaline earth organic precursors as exemplified by neutral Lewis base adducts (polyethers, polyamines, or crown ethers) of metal *β*-diketonates of ligands, such as 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (hfa),[1c,d,2,6a] 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedionate,[3] and 2,2,6,6,-tetramethyl-3,5-heptanedionate (thd),[4] has been achieved with some success. However, simpler *homoleptic*

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(4) Although successfully implemented as MOCVD precursors, $M(thd)_2$-(Lewis base) (M = Ba, Sr, Ca) complexes are not ideal, suffering from low thermal stability, low volatility, and requiring high vapor transport temperatures (typically greater than 200 °C). (a) Hanninen, T.; Mutikainen, I.; Saanila, V.; Ritala, M.; Leskela, M.; Hanson, J. C. *Chem. Mater.* **1997**, *9*, 1234. (b) Van Buskirk, P. C.; Bilodeau, S. M.; Roeder, J. F.; Kirlin, P. S. *Jpn. J. Appl. Phys.* **1996**, *4B*, 2520. (c) Kimura, T.; Yamauchi, H.; Machida, H.; Kokubun, H.; Yamada, M. *Jpn. J. Appl. Phys.* **1994**, *33*, 5119. (d) Gardiner, R. A.; Gordon, D. C.; Stauf, G. T.; Vaartstra, B. A.; Ostrander, R. L.; Rheingold, A. L. *Chem. Mater.* **1994**, *6*, 1967. (e) Van Buskirk, P. C.; Gardiner, R.; Kirlin, P. S.; Nutt, S. *J. Mater. Res.* **1992**, *7*, 542.

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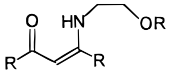
alkaline earth MOCVD precursors utilizing β-diketonate ligands have proven to be problematic, plagued by low volatilities, poor thermal stabilities, and unreliable syntheses.[5] These difficulties reflect, among other factors, the lability and small charge-to-radius ratios of the heavier group II metal ions. Therefore, the rational synthesis of sufficiently volatile and stable homoleptic alkaline earth sources has presented a significant chemical challenge, and the paucity of appropriate precursors is particularly significant given the importance of these elements in emerging technologies such as those requiring high-temperature superconductor (HTS)[1c,d,6] and ferroelectric (e.g., (Ba,Sr)TiO$_3$) thin films.[7] The potential advantages of homoleptic alkaline earth MOCVD precursors in such applications include more straightforward synthesis and reduced possibility of ligand scrambling during vapor transport.

Strategies for the design of volatile, thermally stable MOCVD precursors include metal center encapsulation in sterically saturating, nonpolar environments and/or ligand fluorination (to reduce intermolecular van der Waals interactions). β-Ketoiminate ligands offer a potential means to address the aforementioned issues and also offer the possibility of homoleptic complexes. For example, volatile zirconium[8] and copper β-ketoiminate complexes[9] have been synthesized, and several shown to be useful MOCVD precursors.[8a,10] In addition, nonfluorinated barium β-ketoiminates with appended polyether "lariat" arms have been implemented as Ba MOCVD precursors (**I**).[11] A related complex with a polyether fragment spanning two β-ketoiminate ligands has also been recently synthesized and used as a Ba MOCVD precursor (**II**).[12]



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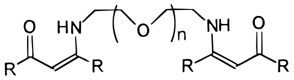
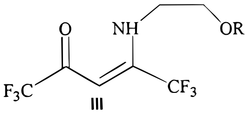
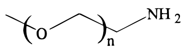


II

The ability to functionalize the imino residue of the β-ketoiminate ligand with various polyfunctional Lewis base moieties offers the attractive potential of tailoring coordinative saturation, thermal stability, volatility, and melting characteristics of the resultant metal complexes. We report here the synthesis and characterization of a series of β-ketoimines (**III**) and their corresponding Ba^{2+} complexes having the general formula Ba[CF$_3$COCHC(NR)CF$_3$]$_2$ (R = (CH$_2$CH$_2$O)$_2$CH$_3$, (CH$_2$CH$_2$O)$_2$CH$_2$CH$_3$, and (CH$_2$CH$_2$O)$_3$CH$_2$CH$_3$). We also report an efficient synthetic route to amine-terminated poly(ethylene oxide)s (PEA) (**IV**) used to prepare the β-ketoimine ligands by triphenylphosphine-mediated reduction of the corresponding poly(ethylene oxide) azides (synthesized via the tosylates). This procedure affords the amines in good yields and analytical purity.



III



IV

Experimental Section

Materials and Methods. Standard Schlenk techniques and a Vacuum Atmospheres N$_2$-filled glovebox were used in the isolation and handling of the β-ketoimines and barium β-ketoiminate complexes. Diethyl ether, tetrahydrofuran (THF), pentane, and heptane were distilled from NaK/benzophenone ketyl prior to use. Pyridine was dried and distilled from KOH. DMF, benzene, triphenylphosphine, tosyl chloride, chlorotrimethylsilane, hexamethyldisilane, and sodium azide were purchased from Aldrich and used as received. The β-diketone, H(hfa) (1,1,1,5,5,5-hexafluoro-2,4-pentanedione; Genzyme) was distilled before use and handled under N$_2$. BaH$_2$ (Strem) was used as received and handled under N$_2$. Glassware used in the synthesis and reactions of the silyl enol ether was passivated by treating the hot glassware with hexamethyldisilane followed by heat gun warming to remove the residue in vacuo. The tosylates of 2-(2-methoxyethoxyethanol) (1,4,7-trioxaoctyltosylate), 2-(2-ethoxyethoxyethanol) (1,4,7-trioxanonyltosylate), and 2-(2-(2-ethoxyethoxyethoxyethanol)) (1,4,7,10-tetraoxatosylate) were synthesized using a standard procedure.[2a−c,11,13]

Analytical Methods. Elemental analyses were performed by G. D. Searle, Inc. (Skokie, IL) or Midwest Microlabs (Indianapolis, IN). NMR spectra were recorded on a Varian Gemini 300 or XL-400 spectrometer with shifts for ^{1}H and ^{13}C NMR referenced to the solvent signal (CDCl$_3$). The ^{19}F chemical shifts are reported relative to CFCl$_3$ in CDCl$_3$. Electron impact mass spectra were obtained on a VG 70−250 SE spectrometer at 70 eV using a temperature ramp rate of 20°/s to 200 °C and referenced to Perfluorokerosene 755. Melting points were determined in sealed capillary tubes with a Mel-Temp apparatus. Vacuum TGA data were collected on a TA Instruments SDT 2960 instrument at a pressure of 5.00 ($\pm$0.05) Torr, an N$_2$ flow of $\sim$100 sccm, and a temperature ramp of 1.5 °C/min. Data were analyzed using a previously reported method.[6a,14]

General Synthetic Procedure for the Azides (1−3). A 500 mL round-bottom flask was charged with 35.0 g (0.128 mol) of 1,4,7-trioxaoctyltosylate, 200 mL of DMF, and 20.75 g (2.5 equiv, 0.319 mol) of sodium azide, placed under N$_2$, and immediately lowered into an oil bath preheated to 65−68 °C. The reaction solution was rapidly stirred for 10 h, removed from the oil bath, and diluted with 200 mL of distilled H$_2$O. The mixture was then stirred for an additional 30 min and poured into a 1 L Erlenmeyer flask containing $\sim$200 mL of ice. The aqueous phase was next transferred to a 1 L separatory funnel and extracted with 3 × 150 mL of diethyl ether. The combined organics were then washed by back extraction with 2 × 75 mL of water, dried overnight with Na$_2$SO$_4$, and the solvent was removed in vacuo at 0 °C, yielding the organic azides as colorless oils (*DANGER: THESE*

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MATERIALS ARE POTENTIALLY EXPLOSIVE AND SHOULD BE HANDLED WITH APPROPRIATE PRECAUTIONS).[15]

General Synthetic Procedure for the Amines (4−6). Under N_2, a 500 mL round-bottom flask was charged with 14.2 g (0.979 mol) of **1** and 200 mL of diethyl ether and cooled to 0 °C using an ice bath. To the chilled and stirring mixture was added 28.2 g (1.10 equiv, 0.108 mol) of triphenylphosphine in one portion. After 1 h, the vessel was removed from the cold bath and warmed to ambient temperature over a period of 1.5 h. At this point, the N_2 inlet was removed and 20 mL of distilled H_2O was added via syringe. The biphasic mixture was stirred for an additional 4 h, 100 mL of benzene was added, and stirring was continued overnight. The contents of the flask were subsequently poured into a separatory funnel, *the aqueous layer was isolated*, and it was washed again with 100 mL of benzene. The water (from the aqueous layer) was removed in vacuo (10^{-2} Torr at ambient temperature) to afford the product amines as colorless oils of satisfactory purity to be used in the next step.

1-Amino-3,6-dioxaheptane (4). Yield: 77%. ^{1}H NMR (DMSO-d_6): δ 2.10−1.20 (br, 2H), 2.64 (t, 2H, $J = 7.0$ Hz), 3.25 (s, 3H), 3.36 (t, 2H, $J = 6.5$ Hz), 3.45 (m, 4H). ^{13}C NMR (DMSO-d_6): δ 41.34, 58.03, 69.35, 71.25, 73.08. Anal. Calcd for $C_5H_{13}O_2N$: C, 50.42; H, 10.92; N, 11.76. Found: C, 49.66; H, 11.01, N,11.56.

1-Amino-3,6-dioxaoctane (5). Yield: 63%. ^{1}H NMR (DMSO-d_6): δ 1.10 (t, 3H, $J = 11.0$ Hz), 1.50−1.30 (br, 2H), 2.63 (t, 2H, $J = 7.0$ Hz), 3.35 (t, 2H, $J = 8.0$ Hz), 3.42 (q, 2H, $J = 5.5$ Hz), 3.49 (m, 4H). ^{13}C NMR (DMSO-d_6): δ 15.0, 41.3, 65.5, 69.2, 69.6, 73.2. Anal. Calcd for $C_6H_{15}O_2N$: C, 54.11; H, 11.35; N, 10.52. Found: C, 53.85; H, 11.17; N, 10.36.

1-Amino-3,6,9-trioxadecane (6). Yield: 76%. ^{1}H NMR (DMSO-d_6): δ 2.00−1.60 (br, 2H), 2.62 (t, 2H, $J = 6.0$ Hz), 3.22 (s, 3H), 3.32 (t, 2H, $J = 6.5$ Hz), 3.42 (m, 2H), 3.48 (m, 6H). ^{13}C NMR (DMSO-d_6): δ 41.4, 58.1, 69.6, 69.8, 69.9, 71.4, 73.2. Anal. Calcd for $C_7H_{15}O_3N$: C, 51.53; H, 10.42; N, 8.58. Found: C, 51.53; H, 10.64; N, 8.71.

Synthesis of 3-Ene-1,1,1,5,5,5-hexafluoro-4-(trimethylsiloxy)-2-pentanone (7). This synthesis utilized a modified literature procedure.[9] Under nitrogen, 12.7 g (0.530 mol) of NaH was suspended with stirring in 400 mL of diethyl ether in a silated 1 L Schlenk flask. The mixture was cooled to 0 °C with an ice bath. Freshly distilled hfa (94 g, 0.45 mol) was then added dropwise (2 drops/s) over 2 h with stirring. After an additional 2 h of stirring, the ice bath was removed and 57.7 g (0.530 mol) of chlorotrimethylsilane was added dropwise over 1 h. After refluxing overnight, the reaction mixture was filtered through Celite into a 500 mL silated flask. The diethyl ether was removed in vacuo at 0 °C, yielding 86.0 g (68% yield) of a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.34 (s, 9H, Si(CH_3)$_3$), 1.09 (s, 18H), 6.33 (s, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.80 (q, 36.08 Hz, *C*O), 155.62 (q, 35.25 Hz, *C*N), 118.57 (q, 276.98 Hz, CO*C*F_3), 115.52 (q, 289.35 Hz, CN*C*F_3), 100.05 (*C*H), 0.03 (COSi(*C*H_3)$_3$). Anal. Calcd for $C_8H_{10}F_6O_2Si$: C, 34.29; H, 3.57. Found: C, 34.69; H, 4.26.

General Synthesis of β-Ketoimine Ligands. This synthesis followed a modified literature procedure for β-ketoimines.[9] Under nitrogen with stirring, 14.6 g (0.120 mol) of **4** was added to 33.6 g (0.120 mol) of **7** at 0 °C. The solution immediately turned orange and was allowed to warm to room temperature overnight with stirring. The reaction mixture was then fractionally distilled, yielding 14.8 g of a colorless liquid.

1,1,1,5,5,5-Hexafluoro-2-*N*-(2-(2-methoxy)ethoxyethylimino)-4-pentanone (Hfadiki) (8). Yield: 44%; bp 78−82 °C/0.2 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (s, 3H, OC*H*$_3$), 3.52 (m, 2H, NC*H*$_2$), 3.58 (m, 2H, OC*H*$_2$), 3.64 (s, 4H, OC*H*$_2$), 5.79 (s, 1H, C*H*), 10.68 (br s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.70 (q, 35.7 Hz, *C*O), 153.17 (q, 32.32 Hz, *C*N), 118.71 (q, 276.75 Hz, CO*C*F_3), 116.21, (q, 286.28 Hz, CN*C*F_3), 85.13 (*C*H), 71.40 (O*C*H_2), 70.12 (O*C*H_2), 69.54 (O*C*H_2), 68.05 (O*C*H_2), 58.15 (O*C*H_3), 44.41 (N*C*H_2). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.76 (s, C*F*$_3$CN), −77.78 (s, C*F*$_3$CO) ppm. Anal. Calcd for $C_{10}H_{13}NF_6O_3$: C, 38.84; H, 4.24; N, 4.53. Found: C, 38.87; H, 4.66; N, 4.75. MS (EI, 70 eV, *m*/*e*$^+$; (fragment); HL = $C_{10}H_{12}NF_6O_3$): 309 (HL), 240 (HL−CF_3), 233), HL−$C_3H_7O_2$), 220 (HL−$C_4H_9O_2$), 196 (HL−CF_3−C_2H_5O), 164 (HL−CF_3−$C_3H_7O_2$), 102 ($C_5H_{11}O_2$), 89 (C_4H_9O), 69 (CF_3), 59 (C_3H_7O), 45 (C_2H_5O).

1,1,1,5,5,5-Hexafluoro-2-*N*-(2-(2-ethoxy)ethoxyethylimino)-4-pentanone (Hfaethyldiki) (9). Yield: 69%; bp 58−62 °C/0.4 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, 3H, C*H*$_3$), 3.58 (q, 2H, C*H*$_2$CH$_3$), 3.70 (m, 8H, C*H*$_2$), 5.83 (s, 1H, C*H*), 10.70 (br, 1H, N*H*). ^{19}F NMR: δ −67.8, −77.8. ^{13}C NMR ($CDCl_3$): δ 15.0, 44.9, 66.8, 68.7, 69.8, 70.8, 85.9, 116.6 (q, $J = 285$ Hz), 119.2 (q, $J = 277$), 153.6 (q, $J = 30$ Hz), 179.5 (q, $J = 35$ Hz). Anal. Calcd for $C_{11}H_{15}O_3NF_6$: C, 40.87; H, 4.68; N, 4.33. Found: C, 40.97; H, 4.86; N, 4.34.

1,1,1,5,5,5-Hexafluoro-2-*N*-(2-(2-(2-ethoxy)ethoxy)ethoxyethylimino)-4-pentanone (Hfaethyltriki) (10). Yield: 68%; bp 95−105 °C/0.2 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (t, 3H, C*H*$_3$), 3.50 (q, 2H, C*H*$_2$CH$_3$), 3.56 (m, 2H, NC*H*$_2$), 3.65 (m, 10H, OC*H*$_2$), 5.81 (s, 1H, C*H*), 10.68 (br s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.33 (q, 34.72 Hz, *C*O), 153.47 (q, 32.17 Hz, *C*N), 119.04 (q, 276.82 Hz, CO*C*F_3), 116.54, (q, 286.95 Hz, CN*C*F3), 85.76 (*C*H), 70.81 (O*C*H_2), 70.72 (O*C*H_2), 70.59 (O*C*H_2), 69.72 (O*C*H_2), 68.75 (O*C*H_2), 66.53 (O*C*H_2), 44.81 (N*C*H_2), 15.02 (*C*H_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ − 66.57 (s, C*F*$_3$CN), −77.62 (s, C*F*$_3$CO) ppm. Anal. Calcd for $C_{13}H_{19}NF_6O_4$: C, 42.51; H, 5.18; N, 3.81. Found: C, 42.19; H, 5.67; N, 4.20. MS (EI, 70 eV, *m*/*e*$^+$; (fragment); HL = $C_{13}H_{19}NF_6O_4$): 367 (HL), 298 (HL−CF_3), 308 (HL−$C_3H_7O_2$), 234 (HL−$C_6H_{13}O_3$), 220 (HL−$C_7H_{15}O_3$), 195 (HL−CF_3−$C_5H_{11}O_2$), 164 (HL−CF_3−$C_6H_{13}O_3$), 138 (HL−CF_3−$C_8H_{17}O_3$), 103 ($C_5H_{11}O_2$), 89 (C_4H_9O), 69 (CF_3), 59 (C_3H_7O), 45 (C_2H_5O).

General Synthesis of Barium β-Ketoiminates. Under nitrogen, 8.9 g (0.029 mol) of **8** was added to 2.0 g (0.014 mol) of BaH_2 in a Schlenk frit assembly. Vigorous bubbling was observed as **8** was added. The reaction mixture was stirred and heated at 50−60 °C for 2 h, at which time a yellow solid formed. Heptane (50 mL) and THF (20 mL) were then added, and the mixture refluxed overnight. The resulting solution was filtered hot and allowed to slowly cool to room temperature, at which time a colorless, crystalline precipitate formed. The solvent was then removed in vacuo, and the precipitate recrystallized from hot heptane, yielding 6.29 g of a colorless solid.

Bis[1,1,1,5,5,5-hexafluoro-2-*N*-(2-(2-methoxy)ethoxyethylimino)-4-pentanonato]barium(II) (Ba(hfadiki)$_2$) (11). Yield: 30%; mp 110−113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.32 (s, 3H, OC*H*$_3$), 3.64 (s, 2H, NC*H*$_2$), 3.71 (s, 4H, OC*H*$_2$), 3.85 (s, 2H, OC*H*$_2$), 5.44 (s, 1H, C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ {*C*O, *C*N *C*F_3 not observed; limited sample solubility} 84.32 (s, *C*H), 72.93 (O*C*H_2), 69.85 (O*C*H_2), 69.08 (O*C*H_2), 68.76 (O*C*H_2), 68.07 (O*C*H_2), 66.51 (O*C*H_2CH$_3$), 50.81 (N*C*H_2), 14.18 (*C*H_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.80 (s, COC*F*$_3$), −64.25 (s, CNC*F*$_3$). Anal. Calcd for $C_{20}H_{24}N_2F_{12}O_4Ba$: C, 31.87; H, 3.21; N, 3.72. Found: C, 31.86; H, 3.32; N, 3.80. MS (EI, 70 eV, *m*/*e*$^+$; L = $C_{10}H_{12}NF_6O_3$): 753 (BaL_2), 734 (BaL_2−F), 711 (BaL_2−NC_2H_4), 695 (BaL_2−C_3H_7O), 635 (BaL_2−$NC_5H_{11}O_2$), 445 (BaL), 426 (BaL−F), 395 (BaL−CF_2), 376 (BaL−CF_3), 233 (L−$C_3H_7O_2$), 220 (L−$C_4H_9O_2$), 156 (BaF), 102 ($NC_4H_8O_2$), 69 (CF_3), 59 (C_3H_7O), 58 (NC_2H_4O), 45 (C_2H_5O).

Bis[1,1,1,5,5,5-hexafluoro-2-*N*-(2-(2-methoxy)ethoxyethylimino)-4-pentanonato]barium(II) (Ba(hfaethyldiki)$_2$) (12). Yield, 63%; mp 117−120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, 3H, $J = 7.2$ Hz, C*H*$_3$), 3.58 (q, 2H, $J = 6.9$ Hz, OC*H*$_2$), 3.73 (m, 6H), 3.87 (br, 2H), 5.34 (s, 1H, C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ {*C*O, *C*N *C*F_3 not observed; limited sample solubility} 84.64 (s, *C*H), 72.54 (O*C*H_2), 69.62 (O*C*H_2), 68.61 (O*C*H_2), 66.89 (O*C*H_2CH$_3$), 50.60 (N*C*H_2), 14.08 (*C*H_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ −75.29 (s, COC*F*$_3$), −64.74 (s, CNC*F*$_3$). Anal. Calcd for $C_{22}H_{28}N_2F_{12}O_6Ba$: C, 33.80; H, 3.61; N, 3.58. Found: C, 33.01; H, 3.66; N, 3.52.

Bis[1,1,1,5,5,5-hexafluoro-2-*N*-(2-(2-(2-ethoxy)ethoxy)ethoxyethylimino)-4-pentanonato]barium(II) (Ba(hfatriki)$_2$) (13). Yield: 46%; mp 153−155 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (s, 3H, C*H*$_3$), 3.02 (m, 2H, OC*H*$_2$), 3.06 (t, 2H, OC*H*$_2$), 3.22 (s, 6H, OC*H*$_2$), 3.41 (q, 2H, OC*H*$_2$), 3.82 (s, 2H, NC*H*$_2$), 5.40 (s, 1H, C*H*). ^{13}C NMR (75 MHz, C_6D_6): δ {*C*O, *C*N *C*F_3 not observed; limited sample solubility} 84.32 (s, *C*H), 72.93 (O*C*H_2), 69.85 (O*C*H_2), 69.08 (O*C*H_2), 68.76 (O*C*H_2), 68.07 (O*C*H_2), 66.51 (O*C*H_2CH$_3$), 50.81 (N*C*H_2), 14.18 (*C*H_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ −75.37 (s, C*F*$_3$), −64.42 (s, C*F*$_3$). Anal.

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Table 1. Summary of Crystallographic Data and Experimental Details for Complexes **12** and **13**

	12	**13**
chem formula	$C_{22}H_{28}N_2F_{12}O_6Ba$	$C_{26}H_{36}N_2F_{12}O_8Ba$
fw	781.80	869.89
temp, °C	−50	−120 ± 1
space group	$P2_1$	$P\bar{1}$ (No. 2)
a, Å	12.1175(2)	10.971(2)
b, Å	14.9238(2)	12.134(2)
c, Å	16.9767(3)	15.280(4)
α, deg	90.00	89.94(2)
β, deg	90.0840(10)	110.00(2)
γ, deg	90.00	116.75(2)
V, Å^3	3070	1678
Z	4	2
d_{calc}, g/cm^3	1.691	1.721
μ(Mo Kα_1), cm^{-1}	14.04	12.9
radiation (Mo Kα), Å	0.710 73	0.710 69
R^a	0.0380	0.059
$R_w{}^b$	0.0803	0.081

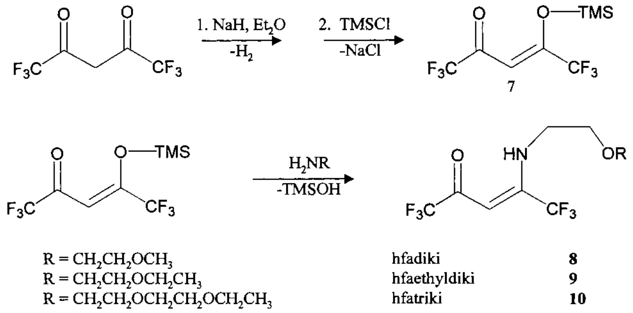
$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b\ R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$.

Calcd for $C_{26}H_{36}N_2F_{12}O_8Ba$: C, 35.90; H, 4.17; N, 3.22. Found: C, 35.59; H, 4.30; N, 3.09. After sublimation found: C, 36.14: H, 4.17; N, 3.15. MS (EI, 70 eV, m/e^+; L = $C_{13}H_{19}NF_6O_4$): 870 (BaL_2), 851 (BaL_2-F), 830 ($BaL_2-NC_2H_4$), 810 ($BaL_2-C_3H_7O$), 504 (BaL (485 (BaL−F), 308 ($L-C_3H_7O$), 298 ($L-CF_3$), 234 ($L-C_6H_{13}O_3$), 220 ($L-C_7H_{15}O_3$), 157 (BaF), 146 ($NC_6H_{12}O_3$), 117 ($C_6H_{13}O_2$), 103 ($C_5H_{11}O_2$), 75 ($C_3H_7O_2$), 72 (NC_3H_6O), 69 (CF_3), 59 (C_3H_7O), 58 (NC_2H_4O), 45 (C_2H_5O).

Single-Crystal Structure Determinations. Single crystals of complexes **12** and **13** were grown by slow evaporation of heptane solutions. A summary of crystallographic data, data collection, refinement parameters, and intensity data options is given in Table 1. Suitable crystals of **12** were selected and mounted in thin-walled, nitrogen-flushed glass capillaries. The crystal structure of **12** was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. An empirical absorption correction was applied, based on a Fourier series in the polar angles of the incident and diffracted beam paths, and was used to model an absorption surface for the difference between the observed and calculated structure factors.[16] There are two crystallographically independent, chemically similar molecules in the asymmetric unit. The absolute configuration of the structure was determined (Flack parameter = 0.05(2)). All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scatterings factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

The cell constants and orientation matrix for **13** were obtained by least-squares refinement using setting angles of 25 carefully centered reflections in the range 23.0° < 2θ < 23.9°. The intensity data were collected according to the options listed in Table 1. The intensities of three representative reflections, which were measured after every 90 min of X-ray exposure time, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.86 to 1.14. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.11363 × 10^{-5}). The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in idealized positions with thermal parameters 1.2 times those of the attached carbon atom. Neutral atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_{calc};[18] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[19] All calculations were performed using the TEXSAN[20] crystallographic software package of Molecular Structure Corporation.

Scheme 1. Synthesis of Ether-Appended Fluoro-β-ketoimines Based upon Hexafluoropentanedione



Results and Discussion

Precursor Synthesis and Characterization. In the design of metal−organic chemical vapor deposition (MOCVD) precursors for group II-containing ceramics,[1c,d,6,12] amine-terminated poly(ethylene oxide)s (PEAs) (**IV**) are versatile ligand building blocks as a consequence of their ability to readily undergo Schiff-base condensations with β-diketonates.[8−11] The resulting multidentate β-ketoimines (Scheme 1; ligands **8**, **9**, and **10**) are then configured to fully saturate small charge-to-radius ratio metal ions (e.g., alkaline earths), yielding monomeric coordination complexes which serve as volatile, thermally stable MOCVD precursors. However, efficient routes to unsymmetrical, "designer" PEAs are limited. In this work and that of other groups, a variety of approaches have been employed to construct PEA synthons. The common precursor for many synthetic pathways is typically a poly(ethylene glycol) (PEG) mono- or ditosylate (terminal halogens have also been employed as leaving groups), which undergoes nucleophilic displacement by either the alkoxide of ethanolamine[2a−c,11,13,21] or an amine synthetic equivalent (e.g., a nitrile[22] or pthalamide[23]). Although these routes afford the desired PEAs in low to modest overall yields, purification often involves laborious vacuum distillations (<10^{-3} Torr) due to the high boiling points. In this contribution, we developed a synthesis of PEAs that proceeds in good yields, does not require repeated vacuum distillations to achieve analytical purity, and is amenable to preparative scales.

The overall route and yields for monoamine PEAs are shown in Scheme 2. Although azide amine equivalents[24] have previously been employed, the corresponding reductions were accomplished using either heterogeneous catalytic hydrogenation[25] or LAH.[22] These methods require expensive equipment or potentially hazardous reagents and necessitate more involved

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(16) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(18) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(19) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

(20) *TEXSAN*, Texray Structural Analysis Package; Molecular Structure Corp: The Woodlands, TX, 1985, 1992.

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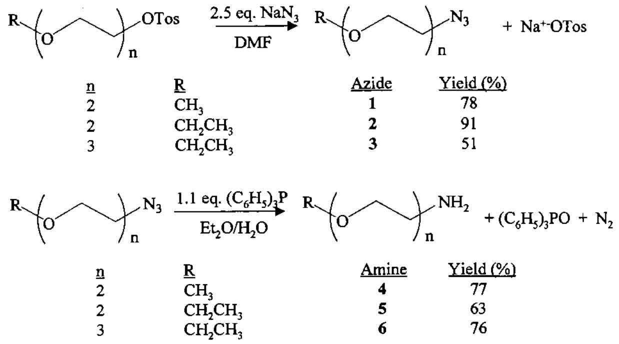
(22) Krakowiak, K. E.; Bradshaw, J. S.; Dalley, N. K.; Zhu, C.; Yi, G.; Curtis, J. C.; Li, D.; Izatt, R. M. *J. Org. Chem.* **1992**, *57*, 3166.

(23) Dietrich, B.; Lehn, J. M.; Sauvage, J. P.; Blanzat, J. *Tetrahedron* **1973**, *29*, 1623.

(24) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 351.

(25) (a) Gatto, V. J.; Arnold, K. A.; Viscariello, A. M.; Miller, S. R.; Morgan, C. R.; Gokel, G. W. *J. Org. Chem.* **1986**, *51*, 5373. (b) Gehrhardt, H.; Mutter, M. *Polym. Bull.* **1987**, *18*, 487.

Scheme 2. Staudinger Reaction for the Synthesis of Amine-Terminated Poly(ethylene oxide)s



product purification. In contrast, the biphasic Staudinger reaction[26] is ideally suited to accomplishing this transformation given the complete aqueous solubility of the PEA final products and complete aqueous insolubility of triphenylphosphine oxide, the sole reaction byproduct (neglecting liberated N_2). Hence, PEA purification is simplified to benzene extraction and removal of the aqueous phase in vacuo or by ambient pressure azeotrope (benzene). The overall yields for this process are high (Scheme 2). The readily isolated amines are formed in analytical purity and can be used directly in the next step.

The fluorinated β-ketoimine ligands **8**, **9**, and **10** are prepared by condensing the corresponding PEA, **4**, **5**, or **6**, with the trimethylsilyl enol ether derivative of hfa, **7**, following the general procedure of Hampden-Smith et al. (Scheme 1).[9,10] Barium β-ketoiminate complexes **11**, **12**, and **13** were synthesized by reaction of the corresponding β-ketoimines with BaH_2 under inert atmosphere (eq 1) and purified by repeated recrystallization from heptane. Fluorinated barium β-ketoiminates **11**, **12**, and **13** are slightly hygroscopic, colorless solids that can be handled in air and slowly vapor transported (distilled) without decomposition at 160 °C/0.05 Torr. They are soluble in ether solvents, slightly soluble in halogenated solvents, and sparingly soluble in boiling hydrocarbons. The melting points of the compounds increase as the molecular weights increase, i.e., **11**(110−113 °C) < **12**(117−120 °C) < **13**(153−155 °C).

$$2HL + BaH_2 \xrightarrow{\Delta} BaL_2 + 2H_2 \qquad (1)$$

hfadiki	**8**	Ba(hfadiki)$_2$	**11**
hfaethyldiki	**9**	Ba(hfaethyldiki)$_2$	**12**
hfatriki	**10**	Ba(hfatriki)$_2$	**13**

Mass Spectral Data. Mass spectral data for the free β-ketoimine ligands and the corresponding barium complexes prepared in this study are compiled in the Experimental Section. The electron impact mass spectroscopic data for **11** and **13** exhibit similar behavior and are consistent with the monomeric nature of these complexes. The major fragment observed is the BaL^+ ion, which occurs with loss of one ligand. Other fragments of lower abundance can be attributed to fragmentation of the polyether lariat and loss of CF_3 from the hfa β-ketoiminate backbone in **11** and **13**. Also present at lower m/e^+ values are free ligand fragments. Polynuclear fragments have been reported in electron impact studies of some barium β-diketonate complexes;[27] however, no fragments with $m/e^+ >$ parent ions were observed for any of the present β-ketoiminate complexes.

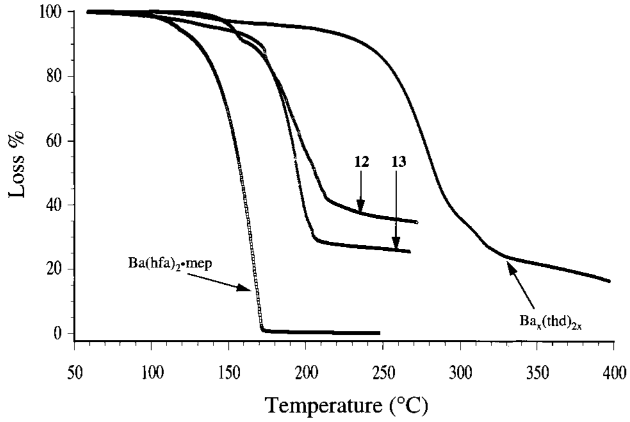


Figure 1. Vacuum thermogravimetric analysis data for complexes **12** and **13** compared with those for Ba(thd)$_2$ and Ba(hfa)$_2$•(pentaethylene glycol methyl ethyl ether). Data were recorded at a temperature ramp rate of 1.5 °C/min and at 5.00 (±0.05) Torr of N_2.

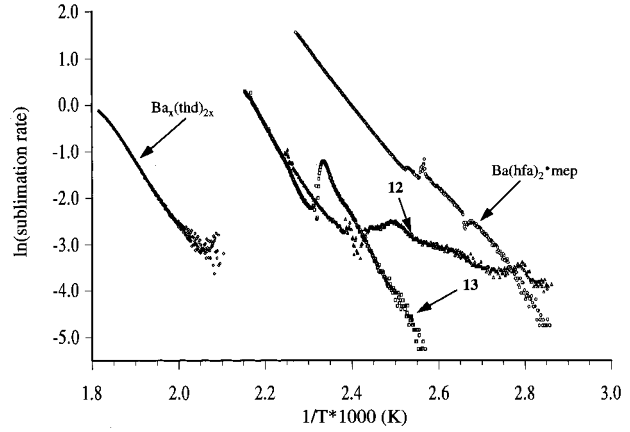


Figure 2. Volatilization data presented in an Arrhenius format comparing the volatilities of complexes **12** and **13** with those of Ba(thd)$_2$ and Ba(hfa)$_2$•(pentaethylene glycol methyl ethyl ether). Data were recorded at a temperature ramp rate of 1.5 °C/min and at 5.00 (±0.05) Torr of N_2.

This presumably is due to the coordinately saturated and generally monomeric structure of these complexes.

NMR Studies. NMR data for the free β-ketoimine ligands and corresponding barium complexes prepared in this study are compiled in the Experimental Section. The spectra are consistent with the proposed ligand structures and molecular connectivities. The ^1H, ^{19}F, and ^{13}C NMR spectra of barium complexes **11**, **12**, and **13** at room temperature in $CDCl_3$ are consistent with a single molecular stereoisomer and/or type of β-ketoiminate. For example, the ^{19}F NMR spectra of barium complexes **11**, **12**, and **13** exhibit only a single $COCF_3$ and a single $CNCF_3$ signal. Although the solid-state structure of **12** reveals a low-symmetry chiral complex with two enantiomers in the unit cell, this is not obvious from the NMR data and implies that **11**, **12**, and **13** are stereochemically nonrigid in solution at room temperature on the NMR time scale.[11]

Volatility Studies. Figures1 and 2 show raw TGA-derived weight loss data and volatilization Arrhenius plots (ln of the sublimation rate vs 1/T), corrected for diffusion distance[6a,14] at 5.00 (±0.05) Torr N_2, respectively. From analysis of these curves, it is apparent that the fluorinated barium β-ketoiminates **12** and **13** are substantially more volatile than Ba(thd)$_2$ but less volatile than Ba(hfa)$_2$•(pentaethyleneglycol methylethyl ether).[2a−c] As observed for the fluorine-free barium β-ketoiminates,[11] the present complexes exhibit residues in the TGA curves (Figure

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[26] Taber, D. F.; Hoerrner, R. S. *J. Org. Chem.* **1992**, *57*, 441.

[27] (a) Turpinseed, S. B.; Barkley, R. M.; Sievers, R. E. *Inorg. Chem.* **1991**, *30*, 1164. (b) Purdy, A. P.; Berry, A. D.; Holm, R. T.; Fatemi, M.; Gaskill, D. K. *Inorg. Chem.* **1989**, *28*, 2799.

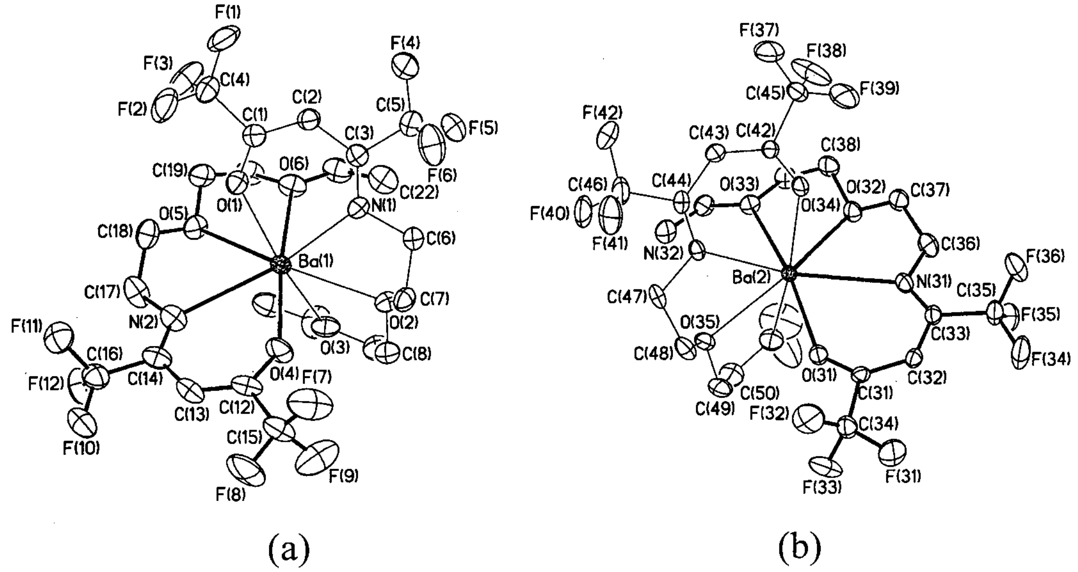
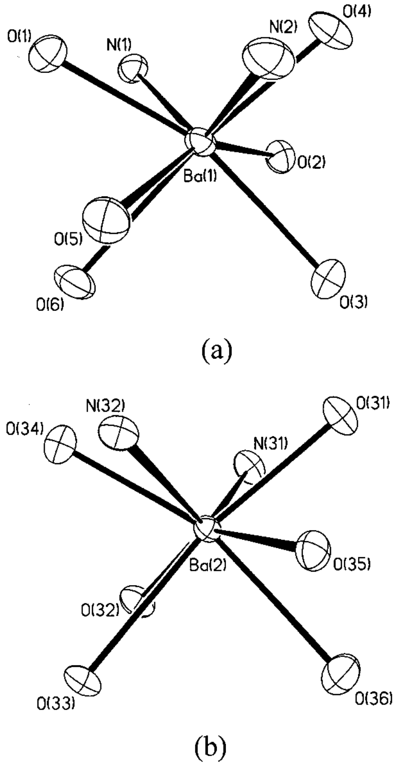


Figure 3. Perspective view of the molecular structure of complex **12** showing the two independent molecules (denoted as a and b) in the unit cell. Thermal ellipsoids are drawn at 50% probability, and H atoms have been omitted for clarity.

1) at 5 Torr and a slight decrease in percent residue as the polyether lariat is lengthened. The relative volatility of the barium *β*-ketoiminates was independently confirmed by preparative vapor transport experiments. Fluorinated barium *β*-ketoiminates **11**, **12**, and **13** distill slowly *without decomposition* at 160 °C/0.05 Torr overnight. As detailed in the Experimental Section, no change in the spectral properties or elemental analysis was observed before and after distillation at 0.05 Torr overnight. In fact the compounds may be purified by vaporization onto a coldfinger. The fluorinated barium *β*-ketoiminates **11**, **12**, and **13** are substantially more volatile than the analogous fluorine-free barium *β*-ketoiminates reported previously, which sublime slowly at 150−200 °C/10^{-3} Torr and with appreciable thermal decomposition.[11] In contrast to these results, Ba(hfa)$_2$•(pentaethyleneglycol methylethyl ether) sublimes rapidly and quantitatively at 120 °C/0.05 Torr.[2a−c]

Molecular Structure Studies. The diffraction-derived molecular structures of Ba(hfaethyldiki)$_2$ (**12**) (Figures 3 and 4) and Ba(hfatriki)$_2$ (**13**) (Figures 5 and 6) reveal that the *β*-ketoiminate ligands completely encircle the Ba^{2+} center and are coordinated through all available oxygen and nitrogen atoms, resulting in eight-coordination for complex **12** and ten-coordination for complex **13**. This coordination mode resembles other Ba(*β*-diketonate)$_2$•(polyether) and •(polyamine) complexes which feature meridional coordination of the coordinately saturated Ba^{2+} ion by the polyether ligands.[2a−d,3−5,28,29]

Metrical parameters are compiled in Table 2. The Ba−N(ketoiminate) distances range from 2.954(5) to 3.033(7) Å and from 2.945(8) to 2.956(8) Å for **12** and **13**, respectively, and are slightly longer than Ba−N(ketoiminate) distances in other structurally characterized, fluorine-free, Ba^{2+} *β*-ketoiminates, which range from 2.787(6) to 2.857(5) Å.[11] The present distances are comparable to the related ten-coordinate fluorinated Ba *β*-ketoiminate having a bridging triethylene glycol linkage between two hfa ligands Ba(hfa)$_2$CAP-4•2DMSO {1,1,1,24,-24,24-hexafluoro-4,21-(ditrifluoromethyl)-8,11,14,17-tetraoxa-3,21-diene-5,20-diimino-2,23-tetracosandionato bisdimethyl sulfoxide barium(II)} (ligand **II**), which has a Ba−N(ketoiminate) bond distance of 3.026(3) Å.[11] The present Ba−O(ketoiminate) bond distances, which range from 2.591(4) to 2.634(5) and from 2.617(6) to 2.623(6) Å for **12** and **13**, respectively**,** are comparable to Ba^{2+}−O(ketoiminate) distances in other structurally characterized Ba^{2+} *β*-ketoiminates, which range from 2.540(6) to 2.647(2) Å,[11,12] and are shorter than the corresponding



(a)

(b)

Figure 4. Immediate Ba^{2+} coordination geometry of complex **12** around (a) molecule 1 and (b) molecule 2 illustrating the approximate trigonal dodecahedral geometry.

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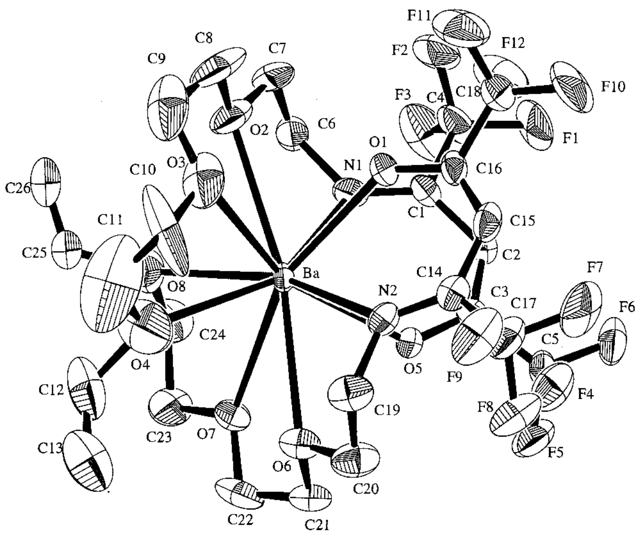

Figure 5. Perspective view of the molecular structure of complex **13**. Thermal ellipsoids are drawn at 50% probability, and H atoms have been omitted for clarity.

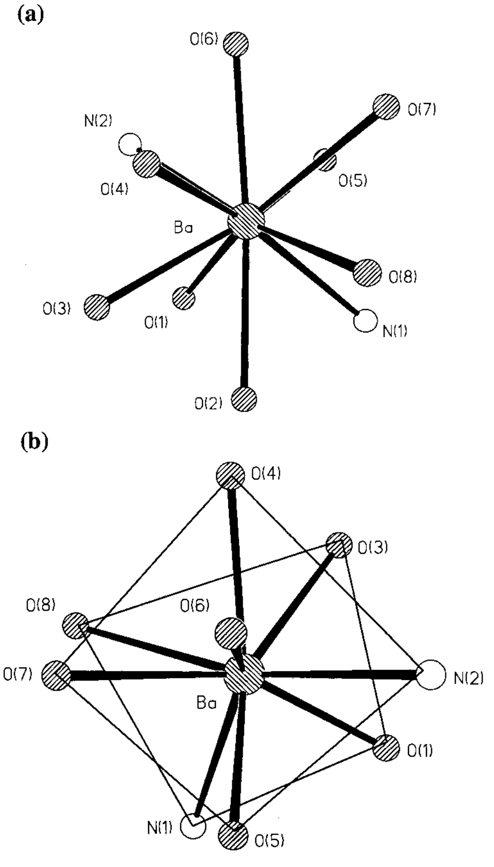

Figure 6. (a) Immediate Ba^{2+} coordination geometry of complex **13**. (b) Immediate Ba^{2+} coordination geometry of complex **13** viewed along the 4-fold axis defined by the capping oxygen atoms and Ba of the bicapped square antiprism geometry illustrating the approximate square antiprismatic geometry.

Table 2. Selected Bond Distances (Å) for Complexes **12** and **13**

	13	**12**		**12**
Ba1−O1	2.623(6)	2.634(5)	Ba2−O31	2.591(4)
Ba1−O2	2.905(7)	2.827(5)	Ba2−O32	2.817(4)
Ba1−O3	2.887(8)	2.932(6)	Ba2−O33	2.874(5)
Ba1−O4	2.892(9)	2.601(5)	Ba2−O34	2.607(4)
Ba1−O5	2.617(6)	2.849(5)	Ba2−O35	2.817(4)
Ba1−O6	2.922(6)	2.868(5)	Ba2−O36	2.855(6)
Ba1−O7	2.995(6)	n/a		
Ba1−O8	2.920(8)	n/a		
Ba1−N1	2.956(8)	2.954(5)	Ba2−N31	2.995(6)
Ba1−N2	2.945(8)	3.033(7)	Ba2−N32	3.005(6)

Table 3. Selected Bond Angles (deg) for Complexes **12** and **13**

	12		**13**
O1−Ba1−O2	126.69(14)	O1−Ba1−O2	66.7(2)
O1−Ba1−O3	163.9(2)	O1−Ba1−O3	71.8(2)
O1−Ba1−O4	108.3(2)	O1−Ba1−O4	123.0(3)
O1−Ba1−O5	71.3(2)	O1−Ba1−O5	84.0(2)
O1−Ba1−O6	79.5(2)	O1−Ba1−O6	121.3(2)
O1−Ba1−N1	65.46(14)	O1−Ba1−O7	153.8(2)
O1−Ba1−N2	85.3(2)	O1−Ba1−O8	132.2(2)
O2−Ba1−O3	58.6(2)	O1−Ba1−N1	70.0(2)
O2−Ba1−O4	71.9(2)	O1−Ba1−N2	63.2(2)
O2−Ba1−O5	153.4(2)	O2−Ba1−O3	58.0(3)
O2−Ba1−O6	101.8(2)	O2−Ba1−O4	98.1(3)
O2−Ba1−N1	61.23(14)	O2−Ba1−O5	123.3(2)
O2−Ba1−N2	131.8(2)	O2−Ba1−O6	167.8(2)
O3−Ba1−O4	87.8(2)	O2−Ba1−O7	121.9(2)
O3−Ba1−O5	98.8(2)	O2−Ba1−O8	67.3(2)
O3−Ba1−O6	84.5(2)	O2−Ba1−N1	60.1(2)
O3−Ba1−N1	117.0(2)	O2−Ba1−N2	123.2(2)
O3−Ba1−N2	101.4(2)	O3−Ba1−O4	55.4(3)
O4−Ba1−O5	125.0(2)	O3−Ba1−O5	152.8(2)
O4−Ba1−O6	171.9(2)	O3−Ba1−O6	113.9(3)
O4−Ba1−N1	90.4(2)	O3−Ba1−O7	134.3(2)
O4−Ba1−N2	63.4(2)	O3−Ba1−O8	94.2(2)
O5−Ba1−O6	59.0(2)	O3−Ba1−N1	115.8(3)
O5−Ba1−N1	131.1(2)	O3−Ba1−N2	82.0(3)
O5−Ba1−N2	61.8(2)	O4−Ba1−O5	137.9(3)
O6−Ba1−N1	90.9(2)	O4−Ba1−O6	69.9(3)
O6−Ba1−N2	120.7(2)	O4−Ba1−O7	81.9(3)
N1−Ba1−N2	132.7(2)	O4−Ba1−O8	75.8(3)
O31−Ba2−O32	125.24(15)	O4−Ba1−N1	150.0(3)
O31−Ba2−O35	74.01(14)	O4−Ba1−N2	87.8(3)
O31−Ba2−O33	168.72(15)	O5−Ba1−O6	68.3(2)
O31−Ba2−O36	87.8(2)	O5−Ba1−O7	70.8(2)
O31−Ba2−N32	92.7(2)	O5−Ba1−O8	111.5(2)
O31−Ba2−N31	64.37(14)	O5−Ba1−N1	64.6(2)
O32−Ba2−O35	148.49(14)	O5−Ba1−N2	76.1(2)
O32−Ba2−O33	59.75(14)	O6−Ba1−O7	55.7(2)
O32−Ba2−O36	94.5(2)	O6−Ba1−O8	106.3(2)
O32−Ba2−N32	132.55(14)	O6−Ba1−N1	129.9(2)
O32−Ba2−N31	61.84(15)	O6−Ba1−N2	60.4(2)
O33−Ba2−O36	81.5(2)	O7−Ba1−O8	56.4(2)
O33−Ba2−N32	88.8(2)	O7−Ba1−N1	92.4(2)
O33−Ba2−N31	121.59(14)	O7−Ba1−N2	114.9(2)
O34−Ba2−O32	74.42(14)	O8−Ba1−N1	76.6(2)
O34−Ba2−O35	126.60(13)	O8−Ba1−N2	162.1(2)
O34−Ba2−O33	81.7(2)	N1−Ba1−N2	120.8(2)
O34−Ba2−O36	162.9(2)		
O34−Ba2−N32	65.95(13)		
O34−Ba2−N31	83.5(2)		
O35−Ba2−O33	97.15(13)		
O35−Ba2−O36	58.8(2)		
O35−Ba2−N32	60.65(13)		
O35−Ba2−N31	135.43(14)		
O36−Ba2−N32	116.5(2)		
O36−Ba2−N31	103.0(2)		
N32−Ba2−N31	133.6(2)		

Ba−O(hfa) distances in structurally characterized $Ba(hfa)_2$·(polyether) complexes, which range from 2.698(3) to 2.929(4) Å.[2a−d,28] The shorter Ba−O(ketoiminate) bond distances as compared to typical Ba−O(hfa) bond distances may reflect, among other factors, greater oxygen donor basicity of the β-ketoiminate ligand.[10] The Ba−O(lariat ether) distances, which range from 2.817(4) to 2.932(6) and from 2.887(8) to 2.995(6) Å for **12** and **13**, respectively, are similar to the Ba−O(lariat ether) distances in other Ba β-ketoiminates, which range from 2.790(3) to 3.061(2) Å,[11,12] and are similar to reported Ba−O(polyether) distances in various Ba(β-diketonate)$_2$·polyether complexes, which range from 2.763(3) to 2.96(3) Å.[2a−d,3−5,28,29]

Chiral complex **12** contains both enantiomers in the unit cell. The coordinated nitrogen and oxygen atoms of each β-ketoiminate ligand in **12** form a meridional plane with an approximately normal dihedral angle between the planes. In the Ba1 molecule, the meridional planes formed by O1, O2, O3, N1 and by O4, O5, O6, N2 are planar to within 0.1524 and 0.0021 Å, with Ba^{2+} displaced from the mean-square planes by −0.3569 and 0.1609 Å, respectively, and with a dihedral angle between the planes of 92.9°. In the Ba1 molecule of **12**, the β-ketoiminate portions of the ligands defined by O1−N1−C1−C2−C3 and O4−N2−C12−C13−C14 are planar to within 0.0105 and 0.0121 Å, respectively, with the Ba1 atom displaced from the mean-square planes by 0.7928 and 0.2953 Å, respectively. In the Ba1 molecule of **12**, the O1−Ba1−N1 and O4−Ba1−N2 planes are tilted from the O1−N1−C1−C2−C3 and O4−N2−C12−C13−C14 planes by 19.7° and 7.2°, respectively. In the Ba1 molecule of **12**, the dihedral angle between planes O1−Ba1−N1 and O4−Ba1−N2 is 105.2°. In the Ba2 molecule, the meridional planes formed by O31, O32, O33, N31 and by O34, O35, O36, N32 are planar to within 0.0619 and 0.1496 Å, with Ba^{2+} displaced from the mean-square planes by 0.2227 and 0.3738 Å, respectively, and with a dihedral angle between the planes of 88.4°. In the Ba2 molecule of **12**, the β-ketoiminate portions of the ligands defined by O34−N32−C42−C43−C44 and O31−N31−C31−C32−C33 are planar to within 0.0134 and 0.0278 Å, respectively, with the Ba^{2+} ion displaced by −0.7482 and 0.3467 Å, respectively, from the mean-square planes. In the Ba2 molecule of **12**, the O31−Ba2−N31 and O34−Ba2−N32 planes are tilted from the O31−N31−C31−C32−C33 and O34−N32−C42−C43−C44 planes by 8.5° and 18.7°, respectively. In the Ba2 molecule of **12**, the dihedral angle between planes O31−Ba2−N31 and O34−Ba2−N32 is 73.7°.

The polyether portions of the β-ketoiminate ligands define partial regular hexagons in molecules 1 and 2 of **12**. Three of six vertexes are defined by N1, O2, O3 and N2, O5, O6, and by N31, O32, O33 and N32, O33, O34, for each ligand in molecules 1 and 2 of **12**, respectively. Typically, a planar regular hexagon defined by a polyether or crown ether is defined by a pseudo-D_{3d} configuration with an $a(g\pm)a$ $\{a =$ anti, $g =$ gauche; the O−C−C−O(N) torsion angles are in parentheses$\}$ torsion angle sequence, with the gauche angles strictly alternating in sign.[30] The planes of the partial hexagons defined by N1, O2, O3 and N2, O5, O6, and N31, O32, O33 and N32, O33, O34, for each ligand in molecule 1 and 2 of **12**, respectively, are perfectly planar by definition. The sequence of the torsion angles agrees with the ideal $a(g\pm)a$ of a planar hexagonal configuration with the sign of the gauche angles strictly alternating. The only deviation is observed in the other β-ketoiminate ligand of molecule 2, where the sequence of torsion angles from N32−C47−C48−O35 to C50−O36−C51−C52 is $(g-)aa(g+)a{\sim}g$. The terminal C_2H_5 of the β-ketoiminate ligand is bent out of the partial hexagonal plane defined by N32, O33, O34, forcing the C50−O36−C51−C52 torsion angle toward gauche (−46.2°).

The immediate Ba^{2+} coordination geometry of **12** (Figure 4) is distorted from an ideal trigonal dodecahedron, distinguished by having two trapezoidal planes intersecting with a dihedral angle of 90°.[31] In molecule 1 of **12**, the trapezoid planes are defined by Ba1, N1, N2, O2, O5 and Ba1, O1, O3, O4, O6 with mean-square deviations of 0.7833 and 0.0398 Å, respectively, and a dihedral angle between the planes of 86.2°. In molecule 2 of **12**, the trapezoidal planes are Ba2, N31, N32, O32, O35 and Ba2, O31, O33, O34, O36, with mean-square deviations of 0.8039 and 0.0574 Å, respectively, and a dihedral angle between the planes of 85.0°.

In complex **13**, the β-ketoiminate ligands encircle the Ba^{2+} center with all oxygen and nitrogen atoms coordinated. The coordinated nitrogen and oxygen atoms of each β-ketoiminate ligand in **13** define a meridional plane with an approximately normal dihedral angle between the planes. The meridional planes defined by Ba, N2, O1, O2, O3, O4 and Ba, N1, O5, O6, O7, 08 are planar to within 0.4437 and 0.3540 Å, respectively, with Ba^{2+} displaced from the mean-squares planes by −0.0116 and −0.1000 Å, respectively, and with a dihedral angle between the planes of 91.7°. The β-ketoiminate backbones of **13**, defined by hfa chelates O1, N2, C1, C2, C3 and N1, O5, C14, C15, C16 are planar to within 0.1734 and 0.0075 Å, respectively, with Ba^{2+} displaced −0.2199 and 0.8731 Å from the mean-square planes, respectively. The planes O1−Ba−N2 and O5−Ba−N1 are tilted from the O1, N2, C14, C15, C16 and O5, N1, C1, C2, C3 planes by 12.0° and 21.8°, respectively. The dihedral angle between planes O1−Ba−N2 and O5−Ba−N1 is 80.4°.

As for complex **12**, partial regular hexagons are defined by the polyether portion of the β-ketoiminate ligands of **13** with N1, O2, O3, O4 and N2, O6, O7, O8 defining four of six vertexes for each ligand, respectively. However, the planes of the partial hexagons defined by N1, O2, O3, O4 and N2, O6, O7, O8 are not perfectly planar, with deviations of 0.4029 and 0.2623 Å, respectively. To accommodate a helical twisting of the poly(ethylene oxide) portion of the β-ketoiminate ligand, the sequence of the torsion angles differs from the ideal $a(g\pm)a$ of a planar hexagon. The sequence of torsion angles from N1−C6−C7−O2 to C11−04-C12−C13 is $(g-)aa(g+)a{\sim}g(g+)a(\sim g)$. The O2−C8−C9−03 torsion angle (59(1)°) has the same sign as the O3−C10−C11−O4 torsion angle (51(3)°) forming a “pseudocorner” in the poly(ethylene oxide) portion of the ligand.[30] This forces the C9−O3−C10−C11 and C11−O4−C12−C13 torsion angles of 89(2)° and −86(2)°, respectively, toward gauche. In the other β-ketoiminate ligand, the sequence of torsion angles from N2−C19−C20−O6 to C24−O8−C25−C26 is $(g-)aa(g+)aa(g-){\sim}ga$, which is closer to the ideal $a(g\pm)a$. However, the terminal ethyl group of the ligand is bent out of the hexagonal plane defined by N2, O6, O7, O8, forcing the C23−C24−O8−C25 torsion angle toward gauche (−96(1)°).

The immediate coordination geometry of **13** (Figure 5) is a distorted bicapped square antiprism. The two capping atoms are O2 and O6, and the two square planes are defined by N1, O1, O3, O8 and N2, O4, O5, O7. The planes defined by N2, O4, O5, O7 and by N1, O1, O3, O8 are planar to within 0.2946 and 0.2090 Å, respectively, with Ba^{2+} displaced −1.2726 and 1.2954 Å, respectively, from the mean-square planes. In an undistorted bicapped square antiprism, the O(capping)−M−O(antiprism) angles would all be equal at 65.5°.[31] In complex **13**, the coordination polyhedron is distorted by unequal O(capping)−Ba−O(antiprism) angles ranging from 55.7° to 69.9° and averaging 63(7)°. This distortion from an ideal bicapped square antiprism is due to the geometric constraints imposed by the unsymmetrical β-ketoiminate ligation. The capping oxygens O2 and O6 are the innermost oxygens of the respective polyether lariats. In an electrostratic analysis of the bicapped square antiprismatic coordination, the capping atoms experience greater

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overall repulsive energy than the eight noncapping antiprismatic atoms due to the presence of four close neighbors.[32] The noncapping antiprismatic ligand atoms have only three close neighbors. A bicapped square antiprismatic coordination geometry has been previously assigned for ten-coordinate $Ba(hfa)_2\cdot$(hexaethylene glycol methyl butyl ether).[2b,c]

Conclusions

This report presents the synthesis and characterization of a series of homoleptic volatile barium fluoro-β-ketoiminates having covalently appended polyethers and which relies on an efficient and convenient synthetic route to amine-terminated poly(ethylene oxide)s. These complexes can be transported in the vapor phase at 160 °C/0.05 Torr *without decomposition*. Fluorinated barium β-ketoiminate complexes **11**, **12**, and **13** are substantially more volatile than $Ba(thd)_2$ but somewhat less volatile than heteroleptic $Ba(hfa)_2\cdot$(pentaethyleneglycol methylethyl ether).[2a−c] The results of two X-ray structural analyses demonstrate the flexibility of the β-ketoiminate ligand and coordination of the polyether portion in a meridional plane about the Ba^{2+} center. This coordination mode resembles those of most Ba(β-diketonate)$_2\cdot$(polyether) and $\cdot$polyamine complexes characterized to date which also feature meridional coordination by the polyether ligand.[2a−d,3−5,28,29]

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Supporting Information Available: An X-ray crystallographic file in CIF format for $Ba(hfaethyldiki)_2$ (**12**) and $Ba(hfatriki)_2$ (**13**) is available on the Internet only. Access information is given on any current masthead page.

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