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Oxygen or Nitrogen Chelates Stabilizing Barium and Yttrium β-Diketonates

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In the last 5 years, homo- and heterometallic alkoxides and β-diketonates have found extensive applications as polymerization catalysts[2] and as molecular precursors for high-purity electroceramic metal oxides, e.g. $YBa_2Cu_3O_{7-x}$, $BaMg_{0.33}Ta_{0.66}O_3$, $BaTiO_3$, and $K_{0.4}Ba_{0.6}BiO_3$.[3] The use of metal alkoxides or alternatively β-diketonates as organometallic chemical vapor deposition (OMCVD) precursors for metal oxides is a field of intense current interest, due to their potential applications in the area of electroceramics. Previous work has centered on the use of either tetramethylheptane-2,4-dionato or hexafluoropentane-2,4-dionato alkaline earth salts, but the character and properties of *such materials have been found to be highly dependent not only on their synthesis but also on their "later history"*. Suitable examples include the following: "$[Ba(thd)_2]_\infty$" prepared by an aqueous route was found to be $[Ba_5(OH)(thd)_9(H_2O)_n]$,[4] while the hexafluoropentane-2,4-dionato salts available commercially are hydrated species, e.g. $[Ba(hfa)_2(H_2O)]_\infty$.[5] Recent studies have used more rigorous procedures and produced the Lewis base stabilized barium β-diketonates, e.g. $[Ba_2(thd)_4(NH_3)_2]$[6] and $[Ba_2(thd)_4(Et_2O)_2]$,[7] while the use of closed or open chain polyethers has yielded the monomeric species, i.e. $[Ba(hfa)_2(18\text{-crown-}6)]$[8] and $[Ba(hfa)_2(tetraglyme)]$.[9]

We,[19] and others, have shown that the group IIA β-diketonates may be sufficiently acidic[8,9] and react in a manner akin to the highly studied group IIA organometallics.[10] The molecular architecture of these complexes can be modified by adding a "multipronged" Lewis base, such as a glyme or an amine, thereby plugging possible vacant coordination sites.[8,9,19] Such a strategy has been previously demonstrated for group IIA metal halides and pseudohalides with crowns ethers and glymes.[11,12] This has also been applied to other metal salts, e.g. mercury salts by Iwamoto $[HgCl_2(tetraglyme)]$,[14] and bismuth salts by Rogers et al., $[Bi(NO_3)_2(OCH_2CH_2OCH_2CH_2OCH_2CH_2OH)]_2$.[13]

The majority of the above materials suffer from poor thermal stability and mass transport properties; to overcome these difficulties, a wide range of synthetic strategies have been adopted. Earlier research utilized bifunctional alcohols, such as $MeOCH_2CH_2OH$ (in an attempt to saturate the high coordination numbers demanded by the large metal centers); the reaction of this ligand with barium metal yielded the volatile hexanuclear aggregate $[H_4Ba_6(O)(OCH_2CH_2OMe)_{14}]$,[15] while Rees et al. have used the higher alkoxy alcohols, containing several ether linkages, to synthesize "liquid barium" complexes.[16] More recently Rees,[17] and also Marks and co-workers,[18] have used a strategy of combining a pendant Lewis base chain onto a diketonate group in an attempt to obtain more volatile materials.

Our current studies are directed toward single-source anhydrous volatile molecular barium CVD precursors. To this end, we have utilized the crystalline, hydrocarbon-soluble metal ethoxide $[Ba(OEt)_2(HOEt)_4]_\infty$.[19,20] We have observed a facile reaction with this alkoxide and a variety of β-diketonate ligands in *n*-hexane at R.T. (room temperature) to yield a range of barium complexes, $[Ba(\beta\text{-diket})_2]_\infty$ [where β-diket = acac ($CH_3COCHCOCH_3$), Ph_2acac (PhCOCHCOPh), tfa ($CF_3COCHCOCH_3$), hfa ($CF_3COCHCOCF_3$), and thd ($^tBuCOHCOBu^t$)],[21] analogous to the reactions of transition metal alkoxides.[22]

Developments in the related area of lanthanide alkoxide and β-diketonate chemistry have also been exceptionally productive. Notable contributions include the use of bulky aryloxides or siloxides to synthesize molecular complexes, e.g. $[Y(OAr')_3(thf)_2]$[23] and $[Y(OSiPh_3)_3]_2$.[24] When simple alcohols are used, a wide range of oligomeric compounds are obtained, e.g. $[Ln_5(O)(OPr^i)_{13}]$[25] and $[La_3(OBu^t)_9(Bu^tOH)_2]$.[26] Given the equally high Lewis acidity of these metals, polyfunctionalized ligands have also been extensively used, e.g. $[Y(OCH_2CH_2OMe)_3]_{10}$,[27] $Y_3(OCH_2CH_2OMe)_5(acac)_4$,[28] and $[Y_4(OH)_2(acac)_{10}]$.[29] In contrast to the alkaline earth metal complexes, there has been far

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less success at controlling the resulting degree of oligomerization of lanthanide molecular precursors.

We report here a synthetic route to complexes of the type [M(diket)$_n$(L-L)] {M = Ba, diket is tfa, and L-L is Hmteta (**1**); M = Y, diket is thd, and L-L is triglyme (**2**)}.

Experimental Section

General Methods. The manipulations of all reactants and products were carried out under a nitrogen atmosphere (Schlenk line), under an argon atmosphere (glovebox), or *in vacuo*, with rigorous exclusion of moisture and air. The solvent *n*-hexane was predried over 4A molecular sieves, distilled prior to use over sodium metal, and then stored under an atmosphere of nitrogen in a glass storage vessel fitted with a J. Youngs high-vacuum PTFE stopcock.

Physical Techniques. Infrared spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer as either Nujol or hexachlorobutadiene mulls, in the region 4000–400 cm^{-1}. The NMR spectra were recorded on a Jeol GS 270 at 270 MHz in dry and oxygen-free d_6-benzene and d_6-dmso using the protio impurities of the deuterated solvents as reference for ^{1}H NMR and the ^{13}C NMR resonances of the solvent as a reference for ^{13}C NMR. Elemental analyses were performed by Imperial College and Butterworth Laboratories; both compounds were handled in an inert atmosphere. Mass spectroscopic data were obtained on a Kratos MS30 by the Royal School of Pharmacy Mass Spectrometry service, University of London. The melting points recorded are uncorrected values.

Controlled thermal analysis of complex **2** was investigated using a Polymer Laboratories 1500H simultaneous thermal analyzer, controlled by a Omni Pro 486DX-33 PC connected to a Ricoh 1200 laser printer. The weight of the sample investigated was 11 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (25 mL/min) nitrogen gas, using a heating rate of 5 °C/min.

Synthesis. All reactions were performed using standard Schlenk techniques with dry, oxygen-free solvents, stored over 4A molecular sieves. Trifluoroacetylacetonate, hmteta [$Me_2NCH_2CH_2N(Me)CH_2CH_2N(Me)CH_2CH_2NMe_2$], and triglyme [$Me(OCH_2CH_2O)_3OMe$] were purchased from Aldrich and predried over 4A molecular sieves. 2,2,6,6-Tetramethyl-3,5-heptanedione was obtained from Inorgtech of Mildenhall, Suffolk, U.K. The tetraethanol-solvated barium ethoxide [$Ba(OEt)_2(EtOH)_4$]$_\infty$ and yttrium β-diketonate hydrate [$Y(thd)_3(H_2O)$]$_\infty$ were prepared according to literature procedures.[19,30]

Preparation of [Ba(tfa)$_2$(hmteta)] (1). [$Ba(OEt)_2(EtOH)_4$]$_\infty$ (1.92 g, 4.92 mmol) was dissolved in *n*-hexane (25 mL) in a Schlenk tube. Tfa-H (1.12 mL, 9.84 mmol) was added to the clear solution and the reaction stirred for 5 min; hmteta (1.1 mL, 4.90 mmol) was then added, and the mildly exothermic reaction mixture was stirred for 10 min. The solvent and liberated ethanol were then removed under vacuum to yield a white solid, which was redissolved in hot *n*-hexane (20 mL) and left to crystallize at –25 °C. Yield: 2.0 g, 86% based on barium ethoxide. Anal. Calcd for $C_{22}H_{32}O_4N_4F_6Ba$: C, 39.80; H, 4.82; N, 7.84. Found: C, 40.03; H, 5.14; N, 7.96. Mp: 143–147 °C. ^{1}H NMR (270 MHz, 20 °C, d_6-dmso): δ 1.84 (3H, s, Me), 2.65 (s, 6H, NMe), 2.93 (s, 12H, NMe$_2$, 3.15 (m, 4H, CH$_2$), 3.22 (m, 8H, CH$_2$), 5.77 (4H, s, CH). ^{13}C{^{1}H} NMR (67.94 MHz, 20 °C, d_6-dmso): δ 29.87 (s, Me), 42.17 (s, NMe), 44.16 (s, NMe$_2$), 52.41 (s, CH$_2$), 54.13 (s, CH$_2$), 54.71 (s, CH$_2$), 93.07 (s, CH), 118.63 (q, CF$_3$, ^1J = 302 Hz), 175.72 (q, CO, ^2J = 31 Hz), 193.58 (s, CO). MS (electron impact positive ion) (*m/e*): 591 [Ba(tfa)$_2$(hmteta)] (38%); 517, [Ba(tfa)(F$_3$COCH)(hmteta)] (19%); 406, [Ba(tfa)(hmteta)] (11%); 271, [Ba(tfa)] (27%).

Preparation of [{(thd)$_3$Y}$_2$(triglyme)] (2). [$Y(thd)_3(H_2O)$]$_\infty$ (1.00 g, 1.50 mmol) was added to a Schlenk tube containing *n*-hexane (10 mL). To the resulting clear solution was added triglyme (0.27 mL, 1.50 mmol), and the reaction mixture was stirred for a further 1 h. The solvent and liberated water were then removed under vacuum to yield a colorless oil, which was allowed to stand for several days during which time a large crop of colorless crystalline blocks formed at 20 °C. Yield: 1.25 g, 98%. Anal. Calcd for $C_{74}H_{132}O_{16}Y_2$: C, 61.07; H, 9.08. Found: C, 60.81; H, 9.20. Mp: 77–80 °C. ^{1}H NMR (270 MHz, C$_6$D$_6$, 20 °C): δ 1.20 (54H, s, Me), 3.26 (3H, s, OCH$_3$, -a), 3.33 (2H, S, OCH$_2$-b), 3.60 (2 H, m, OCH$_2$-c), 3.74 (2H, s, OCH$_2$-d), 5.85 (3H, s, CH). ^{13}C{^{1}H} NMR (67.94 MHz, C$_6$D$_6$, 20 °C): δ 28.21 (s, Me), 40.33 (s, CMe$_3$), 59.05 (s, OMe), 70.21 (s, OCH$_2$–b), 71.16 (s, OCH$_2$–c), 71.68 (s, OCH$_2$–d), 90.64 (s, CH), 199.19 (s, CO). MS (electron impact positive ion) (*m/e*): 1148, [Y$_2$(thd)$_4$(Me$_2$CHOH)(triglyme)] (100%); 1088, [Y$_2$(thd)$_4$(triglyme)] (8%); 910, [Y$_2$(thd)$_4$] (2.4%); 682, [Y(thd)$_3$(Me$_2$CH$_2$)] (6%); 611, [Y(thd)$_2$(Bu^{t}COCHCOCH$_2$Me)] (8%).

Table I. Crystallographic Data for Complexes **1** and **2**

	complex	
	1	**2**
formula	$C_{22}H_{38}F_6O_4N_4Ba$	$C_{74}H_{132}O_{16}Y_2$
fw	673.89	1455.66
cryst system	orthorhombic	monoclinic
space group	*Pbca*	*P*2$_1$/*c*
unit cell params at 150 K		
a/Å	14.607(7)	20.018(3)
b/Å	17.155(6)	20.078(4)
c/Å	25.507(9)	20.668(5)
β/deg		94.90(1)
Z	8	4
d_{calc}/g cm^{-3}	1.520	1.168
V/Å^3	5890.46	8276.55
F(000)	2720	3128
λ(Mo Kα) Å	0.710 69	0.710 69
μ(Mo Kα)/cm^{-1}	14.1	14.6
no. of unique obsd data	3608	19 923
no. of obsd reflcns $F_o > 3\sigma(F_o)$	2208	6365
R^a	0.0384	0.0469
R_w^b	0.0417	0.0557

[a] $R = \Sigma(\Delta F)/\Sigma(F_o)$. [b] $R_w = [\Sigma\{w(\Delta F)^2\}/\Sigma\{w(F_o)^2\}]^{1/2}$.

Table II. Fractional Atomic Coordinates (×10 000) and Equivalent Isotropic Temperature Factors (Å^2 × 1000) for [$Ba(C_5H_4F_3O_2)_2(C_{12}H_{30}N_4)$] (**1**)

atom	x	y	z	U_{eq}
Ba	1752.1(3)	1835.1(2)	1547.6(3)	23.4(3)
F(1)	1154(5)	3004(4)	3603(3)	75(3)
F(2)	2032(5)	2280(4)	4103(3)	64(3)
F(3)	2596(4)	3096(4)	3526(3)	52(2)
F(4)	1907(7)	644(5)	–571(3)	100(4)
F(5)	1418(7)	–250(5)	–61(4)	99(4)
F(6)	2732(7)	–350(6)	–387(4)	142(5)
O(1)	1911(4)	688(3)	2320(3)	32(2)
O(2)	1875(5)	2318(3)	2624(3)	36(3)
O(3)	3423(4)	1308(4)	1304(3)	40(3)
O(4)	1874(5)	882(4)	644(3)	39(2)
N(1)	–69(5)	1073(4)	1639(4)	35(3)
N(2)	296(6)	2329(5)	740(4)	37(3)
N(3)	940(5)	3452(4)	1623(4)	33(3)
N(4)	2963(5)	3193(5)	1344(3)	35(3)
C(1)	2000(7)	–222(6)	3069(5)	38(4)
C(2)	1946(6)	610(5)	2844(4)	28(4)
C(3)	1926(6)	1221(5)	3245(4)	27(3)
C(4)	1906(6)	1990(5)	3103(4)	29(3)
C(5)	1915(7)	2588(6)	3587(4)	40(4)
C(6)	4876(7)	940(7)	961(6)	56(4)
C(7)	3860(7)	959(5)	921(5)	35(4)
C(8)	3425(7)	578(6)	458(5)	40(4)
C(9)	2513(9)	584(6)	356(4)	35(3)
C(10)	2157(9)	164(7)	–174(5)	50(4)
C(11)	–407(7)	1083(7)	2226(5)	47(4)
C(12)	115(7)	262(5)	1465(5)	43(4)
C(13)	–742(6)	1402(6)	1254(5)	37(4)
C(14)	–365(6)	1689(6)	693(4)	40(4)
C(15)	779(7)	2413(7)	194(5)	47(4)
C(16)	–171(7)	3056(7)	880(4)	38(4)
C(17)	462(7)	3676(6)	1105(5)	40(4)
C(18)	308(8)	3454(6)	2114(5)	49(5)
C(19)	1699(7)	4000(6)	1755(5)	47(4)
C(20)	2481(7)	3952(5)	1356(5)	41(4)
C(21)	3526(7)	3136(8)	829(5)	50(4)
C(22)	3573(7)	3139(7)	1843(5)	42(3)

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Table III. Fractional Atomic Coordinates (×10 000) and Equivalent Isotropic Temperature Factors ($Å^2$ × 1000) for [{(thd)$_3$Y}$_2$(triglyme)] (**2**)

atom[a]	x	y	z	U_{eq}	atom[a]	x	y	z	U_{eq}
Y(1)	7745.1(3)	7673.3(3)	1401.9(3)	32.8(2)	Y(2)	7008.0(3)	3842.9(3)	1293.6(3)	30.3(2)
O(1)	6768(2)	7530(2)	1858(2)	40(2)	O(7)	8094(2)	3897(2)	1718(2)	44(2)
O(2)	7047(2)	8550(2)	1043(2)	41(2)	O(8)	7602(2)	3007(2)	803(2)	43(2)
O(3)	7971(2)	8431(2)	2216(2)	43(2)	O(9)	6052(2)	4479(2)	1168(2)	39(2)
O(4)	8452(2)	8420(2)	1007(2)	37(2)	O(10)	6880(2)	4304(2)	2308(2)	39(2)
O(5)	8235(2)	7051(2)	2223(2)	40(2)	O(11)	6855(3)	2986(3)	1947(3)	50(2)
O(6)	8587(2)	7051(2)	957(2)	41(2)	O(12)	6223(2)	3209(2)	700(3)	49(2)
C(1)	5826(4)	7599(4)	2473(3)	43(3)	C(34)	9148(4)	3709(4)	2309(4)	54(3)
C(2)	6272(4)	7889(3)	1971(3)	38(3)	C(35)	8590(4)	3498(4)	1786(4)	47(3)
C(3)	6128(4)	8507(4)	1683(4)	42(3)	C(36)	8639(4)	2925(4)	1420(4)	59(3)
C(4)	6515(3)	8806(4)	1226(3)	39(2)	C(37)	8157(4)	2714(4)	928(4)	48(3)
C(5)	6312(4)	9480(4)	915(4)	51(3)	C(38)	8265(4)	2102(4)	508(5)	59(3)
C(6)	6264(4)	7521(5)	3111(4)	83(4)	C(39)	8820(5)	3816(6)	2944(5)	97(5)
C(7)	5579(4)	6914(4)	2232(4)	62(3)	C(40)	9415(5)	4378(5)	2098(5)	86(4)
C(8)	5208(4)	8021(4)	2583(4)	56(3)	C(41)	9701(5)	3211(5)	2421(6)	108(5)
C(9)	6897(5)	9893(5)	810(7)	139(7)	C(42)	7857(7)	1570(5)	688(9)	227(11)
C(10)	5904(8)	9899(6)	1335(7)	181(9)	C(43)	8043(6)	2285(6)	–211(5)	127(7)
C(11)	5907(9)	9360(6)	326(7)	233(11)	C(44)	8975(4)	1908(5)	478(5)	84(4)
C(12)	8141(4)	9386(4)	2897(4)	48(3)	C(1A)	4945(4)	4872(4)	1269(4)	42(3)
C(13)	8243(4)	9008(4)	2257(3)	40(3)	C(2A)*	5662(7)	4705(6)	1638(7)	36(5)
C(14)	8600(3)	9288(3)	1772(4)	40(2)	C(3A)*	5787(7)	4754(6)	2300(6)	35(5)
C(15)	8693(3)	8983(3)	1182(3)	36(3)	C(4A)*	6427(7)	4593(7)	2613(7)	36(5)
C(16)	9107(4)	9325(3)	688(4)	42(3)	C(5A)	6649(5)	4610(6)	3386(4)	84(5)
C(17)	8427(9)	9018(7)	3433(5)	214(11)	C(6A)	5073(4)	5506(4)	851(4)	52(3)
C(18)	8494(8)	10056(6)	2937(6)	161(8)	C(7A)*	4652(8)	4319(8)	901(7)	47(5)
C(19)	7437(5)	9509(9)	2925(7)	215(11)	C(8A)*	4479(8)	5161(8)	1813(8)	54(6)
C(20)	8614(4)	9593(4)	136(4)	60(3)	C(9A)	6045(5)	4315(5)	3680(4)	72(4)
C(21)	9576(4)	8815(4)	417(5)	74(4)	C(10A)	7308(6)	4486(6)	3769(7)	130(6)
C(22)	9536(4)	9909(4)	967(4)	62(3)	C(11A)*	6748(11)	5238(9)	3200(9)	69(9)
C(23)	8962(4)	6557(4)	3055(4)	48(3)	C(12A)	6884(5)	2048(4)	2634(5)	65(4)
C(24)	8791(4)	6749(3)	2342(3)	40(3)	C(13A)*	6622(7)	2429(8)	1970(8)	45(6)
C(25)	9230(4)	6589(4)	1871(4)	47(3)	C(14A)*	6210(8)	2198(7)	1427(7)	49(6)
C(26)	9097(4)	6741(4)	1196(4)	43(3)	C(15A)*	6007(7)	2592(8)	877(7)	46(5)
C(27)	9624(4)	6519(4)	735(4)	52(3)	C(16A)	5230(18)	2046(11)	611(9)	300(20)
C(28)	9654(5)	6252(6)	3184(5)	97(5)	C(17A)	7635(5)	1976(5)	2788(7)	113(6)
C(29)	8460(6)	6057(5)	3234(4)	106(5)	C(18A)	6536(7)	2139(9)	3221(6)	151(8)
C(30)	8928(5)	7171(4)	3466(4)	76(4)	C(19A)*	6649(13)	1647(10)	2124(10)	93(11)
C(31)	9382(5)	6689(5)	44(5)	94(5)	C(20A)*	5791(13)	1692(15)	85(14)	161(16)
C(32)	10285(5)	6885(5)	925(5)	86(4)	C(2B)*	6821(7)	4004(7)	2840(7)	37(5)
C(33)	9764(5)	5767(4)	803(5)	82(4)	C(3B)*	6845(8)	3310(8)	2966(7)	53(6)
O(13)	7277(3)	7452(2)	272(2)	48(2)	C(4B)*	6869(7)	2844(7)	2490(8)	39(5)
O(14)	7290(3)	6478(2)	1169(2)	45(2)	C(6B)*	6444(11)	5474(9)	3497(8)	67(8)
O(15)	7445(2)	5034(2)	1145(2)	40(2)	C(10B)*	6561(14)	1273(11)	2476(12)	125(12)
O(16)	7260(3)	4203(2)	180(2)	53(2)	C(12B)	5412(6)	2457(9)	232(8)	173(9)
C(45)	7513(5)	7830(5)	–251(4)	80(4)	C(13B)*	5604(6)	3204(6)	527(6)	27(4)
C(46)	7077(5)	6789(4)	71(4)	66(4)	C(14B)*	5186(7)	3699(6)	754(6)	29(4)
C(47)	6785(4)	6475(4)	644(4)	60(3)	C(15B)*	5421(7)	4307(6)	1018(6)	30(4)
C(48)	7161(4)	6037(3)	1695(4)	48(3)	C(17B)*	5633(7)	2527(7)	–415(6)	38(5)
C(49)	7623(4)	5455(4)	1706(4)	45(3)	C(18B)*	4570(8)	2605(8)	48(8)	55(6)
C(50)	7910(4)	5074(4)	660(4)	57(3)	C(21B)*	4190(7)	4634(9)	1088(10)	68(8)
C(51)	7550(5)	4829(4)	37(4)	62(3)	C(22B)*	5094(8)	4951(7)	1974(7)	49(6)
C(52)	7029(5)	3849(4)	–400(4)	73(4)					

[a] All the carbon atoms with A or B in the labeling belong to the two disordered thd ligands bonded to Y(2). The best refinement was achieved by assigning full occupancy to the oxygens O(9), O(10), O(11), and O(12) and the carbons C(5A), C(6A), C(9A), C(12A), C(16A), C(17A), C(18A), and C(12B); the remaining carbons in these ligands (marked with an asterisk) were each assigned an occupancy of 0.5.

X-ray Crystal Structure Determinations of 1 and 2. A summary of the crystallographic data for compounds **1** and **2** is given in Table I. The X-ray measurements for complex **1** were made on a colorless crystal of approximate dimensions 0.30 × 0.20 × 0.18 mm^3, which was mounted onto a fiber using silicon oil and transferred to the goniostat. The unit cell parameters and intensity data were obtained at 150 K using a Delft-Instruments FAST TV area detector diffractometer and graphite-monochromated Mo Kα radiation = 0.710 69 Å, following previously described procedures.[31]

The total of 9140 intensities measured within a θ range 2.0–24.8°, corresponding to slightly more than one hemisphere, yielded 3608 unique and 2208 observed [$F_o > 3\sigma(F)$] reflections (merging R = 0.040). The data were corrected for Lorentz and polarization effects, and also for absorption using the program DIFABS,[32] adapted for FAST geometry.[33] The structure was solved via the Patterson and Fourier methods and refined (on F) by full-matrix least squares (SHELX-80)[34] to give a final R-value of 0.0384 for 2208 observed data and 334 parameters. All non-hydrogen atoms were treated anisotropically. The hydrogens atoms were all located from difference maps; these were not refined but included in the calculation of F_c with a common U_{iso} assigned to all (0.05 $Å^2$).

For complex **2** measurements were made on a colorless crystal of approximate dimensions 0.40 × 0.25 × 0.20 mm^3, which was mounted using silicon oil and transferred to the goniostat. The total of 42295 intensities measured within θ range 2.2–28.3° yielded 19 923 unique and 6365 observed [$F_o > 3\sigma(F)$] reflections (merging R = 0.045). The data were corrected for Lorentz and polarization effects, and also for absorption using the program DIFABS,[32] adapted for FAST geometry.[33] The structure was solved as for **1** to give a final R-value of 0.0469 for 6365 observed data and 334 parameters. All of the hydrogens atoms belonging to the regular thd groups were allowed to ride on the parents in calculated

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(31) Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 1855.

(32) Walker, N. P. C.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 1980.

(33) Karaulov, A. University of Wales College of Cardiff, 1991.

(34) Sheldrick, G. M. University of Gottingen, 1980. Scattering factor data as included in the SHELX-S program (Sheldrick, G. M. University of Gottingen, FRG, 1986).

positions (C–H = 0.96 Å), and a common U_{iso} was refined for all; other hydrogens on the methyl groups of the disordered thd ligands were ignored.

All calculations were performed on a T800 transputer hosted by an IBM/AT personal computer. Final atomic parameters are given in Tables II and III; selected bond lengths and angles are found in Tables IV and V. The structures of single molecules of complex **1** and **2** are shown in Figures 1 and 3.

Results and Discussion

Our synthetic strategy for both alkaline- and rare-earth organics has some notable features. First, this approach aims to coordinatively saturate the metal centers with the combined use of both a chelating chain type ligand, i.e. glymes or amines, and a chelating metalated group, e.g. a diketonate, functionalized alcohol, diolate, or acetate (A–R–BH, where A is generally a pendant b-chelating site, R is the hydrocarbon chain linker, and B–H is the predominate site of metalation).[35] The general synthetic strategy is outlined as follows:

$$[\mathrm{M(OR)}_x]_\infty + 2\mathrm{A{-}R{-}BH} + \mathrm{L{-}L} \rightarrow [\mathrm{M(A{-}R{-}B)}_x(\mathrm{L{-}L})] + x\mathrm{ROH} \quad (1)$$

This point is of importance and presumably gives rise to their exceptional stability in the atmosphere, since the chelating ligands are less readily hydrolyzed than would be monodentate alkoxides.[8,9,15–18] Second, the application of multidentate ligands (L–L) has previously been shown to force oligomeric complexes into a more strictly molecular regime, generally reducing the possibility of interactions between monomeric units (although there will always be exceptions to this, e.g. the yttrium complex **2** and also in the well-known situation of β-diketonate bridging). Third, this technique of using a preformed metal β-diketonate (either anhydrous or a hydrate) leads to water-free products. Thus hard Lewis bases (either O- or N-based) can utilize the entropic advantages of the chelate effect and facilitate the preparation of anhydrous metal β-diketonates via a low cost route, e.g. by the use of simple hydrated complexes prepared via metathesis in aqueous/alcohol media. This latter point is of possible importance if such materials are going to have real applications as either sol-gel or CVD precursors, where low-cost chemicals that may be manipulated on the open laboratory bench are an important objective.[1–3]

The reaction of $[\mathrm{Ba(OEt)_2(EtOH)_4}]_\infty$ with 2 equiv of tfa-H in the presence of hmteta, in hexane at ambient temperature, yields colorless crystals of the product [Ba(tfa)$_2$(hmteta)] (**1**) in 86% yield. Our synthesis may be compared with a previous published route to barium β-diketonates stabilized by glyme ligands, which gave low yields of products (25–42%).[9] This substantial difference in the yields of the products compared with those from our route (and the necessity of subliming the raw product to obtain a pure material,[9] which is not required when utilizing the ethoxide route) is because our starting material is a pure, crystalline, hydrocarbon-soluble solid, unlike the $\mathrm{BaH_2}$ used by previous workers which suffers from variable metalation behavior (and in the worst instances, commercial samples are completely unreactive). We also note that our route uses a stoichiometric amount of amine, since the ligand is only required as a Lewis base in our synthesis; previous researchers have used it as both a solvent and Lewis base.[9]

The IR spectrum of **1** (Nujol mull) reveals only one set of broad $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretches, possibly indicative of only one tfa ligand environment in the complex. This result may be contrasted with the parent complex $[\mathrm{Ba(tfa)_2}]_\infty$, which has multiple bands in its IR spectrum, and is most likely due to its polymeric nature, since it contains several different coordination modes for the tfa ligand.[21] On exposure to air for several days, the IR spectrum remains essentially unchanged.

Table IV. Bond Lengths (Å) and Angles (deg) for [Ba(C$_5$H$_4$F$_3$O$_2$)$_2$(C$_{12}$H$_{30}$N$_4$)] (**1**)

O(1)–Ba	2.687(9)	O(2)–Ba	2.669(10)
O(3)–Ba	2.665(9)	O(4)–Ba	2.688(10)
N(1)–Ba	2.972(10)	N(2)–Ba	2.975(11)
N(3)–Ba	3.022(10)	N(4)–Ba	2.963(11)
C(5)–F(1)	1.323(12)	C(5)–F(2)	1.334(13)
C(5)–F(3)	1.330(13)	C(10)–F(4)	1.296(14)
C(10)–F(5)	1.319(15)	C(10)–F(6)	1.316(14)
C(2)–O(1)	1.242(12)	C(4)–O(2)	1.258(12)
C(7)–O(3)	1.256(12)	C(9)–O(4)	1.261(13)
C(11)–N(1)	1.465(15)	C(12)–N(1)	1.476(13)
C(13)–N(1)	1.451(13)	C(14)–N(2)	1.466(13)
C(15)–N(2)	1.474(13)	C(16)–N(2)	1.459(14)
C(17)–N(3)	1.455(14)	C(18)–N(3)	1.478(14)
C(19)–N(3)	1.487(13)	C(20)–N(4)	1.481(13)
C(21)–N(4)	1.467(13)	C(22)–N(4)	1.476(13)
C(2)–C(1)	1.524(15)	C(3)–C(2)	1.411(14)
C(4)–C(3)	1.362(14)	C(5)–C(4)	1.532(15)
C(7)–C(6)	1.488(15)	C(8)–C(7)	1.419(15)
C(9)–C(8)	1.353(16)	C(10)–C(9)	1.532(17)
C(14)–C(13)	1.512(16)	C(17)–C(16)	1.505(16)
C(20)–C(19)	1.479(16)		
O(2)–Ba–O(1)	65.2(3)	O(3)–Ba–O(1)	79.5(3)
O(3)–Ba–O(2)	104.4(3)	O(4)–Ba–O(1)	94.7(3)
O(4)–Ba–O(2)	159.1(2)	O(4)–Ba–O(3)	64.1(3)
N(1)–Ba–O(1)	72.9(3)	N(1)–Ba–O(2)	97.3(3)
N(1)–Ba–O(3)	133.3(2)	N(1)–Ba–O(4)	81.3(3)
N(2)–Ba–O(1)	134.5(2)	N(2)–Ba–O(2)	124.4(3)
N(2)–Ba–O(3)	127.9(3)	N(2)–Ba–O(4)	73.5(3)
N(2)–Ba–N(1)	62.1(3)	N(3)–Ba–O(1)	131.8(2)
N(3)–Ba–O(2)	71.7(3)	N(3)–Ba–O(3)	133.1(2)
N(3)–Ba–O(4)	129.1(3)	N(3)–Ba–N(1)	92.8(3)
N(3)–Ba–N(2)	59.7(3)	N(4)–Ba–O(1)	129.3(3)
N(4)–Ba–O(2)	82.5(3)	N(4)–Ba–O(3)	71.7(3)
N(4)–Ba–O(4)	108.1(3)	N(4)–Ba–N(1)	153.1(2)
N(4)–Ba–N(2)	95.7(3)	N(4)–Ba–N(3)	61.4(3)
C(2)–O(1)–Ba	138.9(6)	C(4)–O(2)–Ba	135.4(5)
C(7)–O(3)–Ba	141.4(7)	C(9)–O(4)–Ba	136.0(6)
C(11)–N(1)–Ba	111.4(7)	C(12)–N(1)–Ba	103.4(6)
C(12)–N(1)–C(11)	109.5(9)	C(13)–N(1)–Ba	113.0(6)
C(13)–N(1)–C(11)	110.8(9)	C(13)–N(1)–C(12)	108.5(9)
C(14)–N(2)–Ba	107.8(7)	C(15)–N(2)–Ba	104.0(7)
C(15)–N(2)–C(14)	108.8(9)	C(16)–N(2)–Ba	115.7(7)
C(16)–N(2)–C(14)	110.5(9)	C(16)–N(2)–C(15)	109.7(9)
C(17)–N(3)–Ba	112.5(7)	C(18)–N(3)–Ba	107.0(7)
C(18)–N(3)–C(17)	110.7(9)	C(19)–N(3)–Ba	107.5(6)
C(19)–N(3)–C(17)	111.5(9)	C(19)–N(3)–C(18)	107.5(9)
C(20)–N(4)–Ba	113.9(6)	C(21)–N(4)–Ba	114.6(7)
C(21)–N(4)–C(20)	109.9(9)	C(22)–N(4)–Ba	100.5(7)
C(22)–N(4)–C(20)	109.1(9)	C(22)–N(4)–C(21)	108.2(8)
C(1)–C(2)–O(1)	116.6(10)	C(3)–C(2)–O(1)	125.6(10)
C(3)–C(2)–C(1)	117.8(10)	C(4)–C(3)–C(2)	123.8(10)
C(3)–C(4)–O(2)	130.8(9)	C(5)–C(4)–O(2)	111.5(9)
C(5)–C(4)–C(3)	117.7(10)	F(2)–C(5)–F(1)	107.2(10)
F(3)–C(5)–F(1)	106.1(9)	F(3)–C(5)–F(2)	105.2(9)
C(4)–C(5)–F(1)	112.0(9)	C(4)–C(5)–F(2)	114.4(9)
C(4)–C(5)–F(3)	111.4(9)	C(6)–C(7)–O(3)	118.1(12)
C(8)–C(7)–O(3)	122.8(10)	C(8)–C(7)–C(6)	119.1(11)
C(9)–C(8)–C(7)	124.9(10)	C(8)–C(9)–O(4)	129.7(11)
C(10)–C(9)–O(4)	112.0(11)	C(10)–C(9)–C(8)	118.3(11)
F(5)–C(10)–F(4)	104.9(11)	F(6)–C(10)–F(4)	109.4(13)
F(6)–C(10)–F(5)	103.8(11)	C(9)–C(10)–F(4)	112.5(11)
C(9)–C(10)–F(5)	111.6(11)	C(9)–C(10)–F(6)	114.0(11)
C(14)–C(13)–N(1)	115.1(9)	C(13)–C(14)–N(2)	114.7(9)
C(17)–C(16)–N(2)	113.4(9)	C(16)–C(17)–N(3)	113.7(9)
C(20)–C(19)–N(3)	114.1(9)	C(19)–C(20)–N(4)	115.3(9)

The ^{1}H and ^{13}C NMR spectra in d_6-dmso at room temperature for complex **1** show only one tfa and hmteta ligand environment. These data are not in accord with our solid-state structure, which has two inequivalent tfa ligands, and thus therefore suggests either that a rapid fluxional process is occurring which is time averaging the tfa and amine ligand or, as an alternative explanation, that the dmso is coordinating to the metal coordination sphere, i.e.

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Table V. Bond Lengths (Å) and Angles (deg) for [{(thd)$_3$Y}$_2$(triglyme)] (**2**)

O(1)–Y(1)	2.262(7)	O(2)–Y(1)	2.329(7)	C(15B)–O(9)	1.321(15)	C(4A)–O(10)	1.287(16)
O(3)–Y(1)	2.285(7)	O(4)–Y(1)	2.261(7)	C(2B)–O(10)	1.268(15)	C(13A)–O(11)	1.214(17)
O(5)–Y(1)	2.262(7)	O(6)–Y(1)	2.348(7)	C(4B)–O(11)	1.155(18)	C(15A)–O(12)	1.371(17)
O(13)–Y(1)	2.481(6)	O(14)–Y(1)	2.597(8)	C(13B)–O(12)	1.259(14)	C(35)–C(34)	1.545(13)
O(7)–Y(2)	2.275(6)	O(8)–Y(2)	2.337(7)	C(39)–C(34)	1.533(15)	C(40)–C(34)	1.523(14)
O(9)–Y(2)	2.298(7)	O(10)–Y(2)	2.326(7)	C(41)–C(34)	1.497(13)	C(36)–C(35)	1.384(12)
O(11)–Y(2)	2.224(7)	O(12)–Y(2)	2.295(7)	C(37)–C(36)	1.407(12)	C(38)–C(37)	1.530(14)
O(15)–Y(2)	2.574(8)	O(16)–Y(2)	2.504(8)	C(42)–C(38)	1.415(16)	C(43)–C(38)	1.557(16)
C(2)–O(1)	1.264(9)	C(4)–O(2)	1.268(9)	C(44)–C(38)	1.480(13)	C(2A)–C(1A)	1.603(17)
C(13)–O(3)	1.279(9)	C(15)–O(4)	1.269(9)	C(6A)–C(1A)	1.571(12)	C(7A)–C(1A)	1.443(18)
C(24)–O(5)	1.273(10)	C(26)–O(6)	1.260(10)	C(8A)–C(1A)	1.629(20)	C(15B)–C(1A)	1.597(17)
C(2)–C(1)	1.539(12)	C(6)–C(1)	1.527(12)	C(21B)–C(1A)	1.598(18)	C(22B)–C(1A)	1.471(17)
C(7)–C(1)	1.532(13)	C(8)–C(1)	1.534(13)	C(3A)–C(2A)	1.373(20)	C(15B)–C(2A)	1.551(20)
C(3)–C(2)	1.397(11)	C(4)–C(3)	1.407(11)	C(22B)–C(2A)	1.469(22)	C(4A)–C(3A)	1.422(19)
C(5)–C(4)	1.538(12)	C(9)–C(5)	1.465(14)	C(22B)–C(3A)	1.541(22)	C(5A)–C(4A)	1.620(18)
C(10)–C(5)	1.500(19)	C(11)–C(5)	1.425(18)	C(11A)–C(4A)	1.851(25)	C(2B)–C(4A)	1.476(20)
C(13)–C(12)	1.553(12)	C(17)–C(12)	1.411(15)	C(9A)–C(5A)	1.519(16)	C(10A)–C(5A)	1.501(17)
C(18)–C(12)	1.519(17)	C(19)–C(12)	1.438(14)	C(11A)–C(5A)	1.338(23)	C(2B)–C(5A)	1.713(19)
C(14)–C(13)	1.400(11)	C(15)–C(14)	1.391(11)	C(6B)–C(5A)	1.801(23)	C(14B)–C(7A)	1.685(22)
C(16)–C(15)	1.532(12)	C(20)–C(16)	1.541(12)	C(15B)–C(7A)	1.538(22)	C(21B)–C(7A)	1.210(24)
C(21)–C(16)	1.528(13)	C(22)–C(16)	1.536(12)	C(21B)–C(8A)	1.886(26)	C(22B)–C(8A)	1.316(23)
C(24)–C(23)	1.534(12)	C(28)–C(23)	1.516(15)	C(6B)–C(11A)	1.017(30)	C(13A)–C(12A)	1.617(20)
C(29)–C(23)	1.490(14)	C(30)–C(23)	1.501(13)	C(17A)–C(12A)	1.519(16)	C(18A)–C(12A)	1.461(18)
C(25)–C(24)	1.403(12)	C(26)–C(25)	1.430(12)	C(19A)–C(12A)	1.377(24)	C(4B)–C(12A)	1.626(18)
C(27)–C(26)	1.546(14)	C(31)–C(27)	1.507(14)	C(10B)–C(12A)	1.705(26)	C(14A)–C(13A)	1.413(22)
C(32)–C(27)	1.536(14)	C(33)–C(27)	1.540(13)	C(19A)–C(13A)	1.602(27)	C(4B)–C(13A)	1.414(22)
C(45)–O(13)	1.435(11)	C(46)–O(13)	1.440(10)	C(15A)–C(14A)	1.417(22)	C(12B)–C(15A)	1.731(21)
C(47)–O(14)	1.418(10)	C(48)–O(14)	1.443(10)	C(13B)–C(15A)	1.607(21)	C(20A)–C(16A)	1.775(43)
C(49)–O(15)	1.453(9)	C(50)–O(15)	1.427(11)	C(12B)–C(16A)	1.215(30)	C(10B)–C(19A)	1.071(33)
C(51)–O(16)	1.426(11)	C(52)–O(16)	1.437(10)	C(12B)–C(20A)	1.750(36)	C(3B)–C(2B)	1.418(21)
C(47)–C(46)	1.504(14)	C(49)–C(48)	1.488(11)	C(4B)–C(3B)	1.362(22)	C(13B)–C(12B)	1.652(23)
C(51)–C(50)	1.504(13)	C(35)–O(7)	1.275(9)	C(17B)–C(12B)	1.451(21)	C(18B)–C(12B)	1.722(21)
C(37)–O(8)	1.264(9)	C(2A)–O(9)	1.374(16)	C(14B)–C(13B)	1.405(19)	C(15B)–C(14B)	1.403(18)
O(2)–Y(1)–O(1)	73.3(3)	O(3)–Y(1)–O(1)	84.3(3)	C(10)–C(5)–C(4)	113.0(9)	C(10)–C(5)–C(9)	104.5(9)
O(3)–Y(1)–O(2)	78.9(3)	O(4)–Y(1)–O(1)	145.6(2)	C(11)–C(5)–C(4)	108.6(8)	C(11)–C(5)–C(9)	111.9(11)
O(4)–Y(1)–O(2)	76.2(3)	O(4)–Y(1)–O(3)	74.6(3)	C(11)–C(5)–C(10)	106.8(11)	C(17)–C(12)–C(13)	109.8(9)
O(5)–Y(1)–O(1)	87.2(3)	O(5)–Y(1)–O(2)	150.0(2)	C(18)–C(12)–C(13)	112.7(9)	C(18)–C(12)–C(17)	105.4(10)
O(5)–Y(1)–O(3)	76.7(3)	O(5)–Y(1)–O(4)	113.1(3)	C(19)–C(12)–C(13)	108.6(9)	C(19)–C(12)–C(17)	113.0(12)
O(6)–Y(1)–O(1)	140.4(2)	O(6)–Y(1)–O(2)	135.1(2)	C(19)–C(12)–C(18)	107.4(11)	C(12)–C(13)–O(3)	114.4(7)
O(6)–Y(1)–O(3)	122.7(3)	O(6)–Y(1)–O(4)	73.7(3)	C(14)–C(13)–O(3)	123.8(7)	C(14)–C(13)–C(12)	121.8(7)
O(6)–Y(1)–O(5)	73.8(3)	O(13)–Y(1)–O(1)	95.7(3)	C(15)–C(14)–C(13)	124.4(7)	C(14)–C(15)–O(4)	124.5(7)
O(13)–Y(1)–O(2)	70.6(3)	O(13)–Y(1)–O(3)	148.0(2)	C(16)–C(15)–O(4)	115.1(7)	C(16)–C(15)–C(14)	120.4(7)
O(13)–Y(1)–O(4)	88.7(3)	O(13)–Y(1)–O(5)	135.3(2)	C(20)–C(16)–C(15)	107.5(7)	C(21)–C(16)–C(15)	109.1(7)
O(13)–Y(1)–O(6)	76.2(3)	O(14)–Y(1)–O(1)	69.9(3)	C(21)–C(16)–C(20)	109.7(7)	C(22)–C(16)–C(15)	114.2(7)
O(14)–Y(1)–O(2)	116.6(3)	O(14)–Y(1)–O(3)	142.7(2)	C(22)–C(16)–C(20)	108.3(7)	C(22)–C(16)–C(21)	108.0(7)
O(14)–Y(1)–O(4)	140.0(2)	O(14)–Y(1)–O(5)	75.6(3)	C(28)–C(23)–C(24)	113.3(8)	C(29)–C(23)–C(24)	107.9(7)
O(14)–Y(1)–O(6)	71.8(3)	O(14)–Y(1)–O(13)	64.0(3)	C(29)–C(23)–C(28)	108.0(8)	C(30)–C(23)–C(24)	108.6(7)
C(2)–O(1)–Y(1)	136.5(4)	C(4)–O(2)–Y(1)	135.0(4)	C(30)–C(23)–C(28)	108.6(8)	C(30)–C(23)–C(29)	110.3(8)
C(13)–O(3)–Y(1)	135.1(4)	C(15)–O(4)–Y(1)	136.2(4)	C(23)–C(24)–O(5)	115.2(7)	C(25)–C(24)–O(5)	124.3(7)
C(24)–O(5)–Y(1)	136.4(4)	C(26)–O(6)–Y(1)	133.9(5)	C(25)–C(24)–C(23)	120.5(7)	C(26)–C(25)–C(24)	123.5(8)
C(45)–O(13)–Y(1)	119.5(5)	C(46)–O(13)–Y(1)	120.8(5)	C(25)–C(26)–O(6)	124.5(8)	C(27)–C(26)–O(6)	118.2(8)
C(47)–O(14)–Y(1)	111.2(5)	C(48)–O(14)–Y(1)	120.7(5)	C(27)–C(26)–C(25)	117.4(7)	C(31)–C(27)–C(26)	109.8(8)
O(16)–Y(2)–O(15)	61.7(3)	O(7)–Y(2)–O(15)	71.2(3)	C(32)–C(27)–C(26)	108.8(8)	C(32)–C(27)–C(31)	109.5(8)
O(7)–Y(2)–O(16)	94.6(3)	O(8)–Y(2)–O(15)	115.2(3)	C(33)–C(27)–C(26)	110.8(8)	C(33)–C(27)–C(31)	110.5(8)
O(8)–Y(2)–O(16)	70.1(3)	O(8)–Y(2)–O(7)	72.4(3)	C(33)–C(27)–C(32)	107.5(8)	C(46)–O(13)–C(45)	111.8(7)
O(9)–Y(2)–O(15)	76.0(3)	O(9)–Y(2)–O(16)	88.1(3)	C(48)–O(14)–C(47)	114.4(7)	C(50)–O(15)–C(49)	113.4(6)
O(9)–Y(2)–O(7)	140.9(2)	O(9)–Y(2)–O(8)	143.1(2)	C(47)–C(46)–O(13)	106.0(7)	C(46)–C(47)–O(14)	107.5(8)
O(10)–Y(2)–O(15)	78.6(3)	O(10)–Y(2)–O(16)	139.5(2)	C(49)–C(48)–O(14)	110.0(7)	C(48)–C(49)–O(15)	109.6(7)
O(10)–Y(2)–O(7)	79.0(3)	O(10)–Y(2)–O(8)	140.9(2)	C(51)–C(50)–O(15)	106.8(7)	C(50)–C(51)–O(16)	106.5(7)
O(10)–Y(2)–O(9)	74.1(3)	O(11)–Y(2)–O(15)	149.0(2)	C(15B)–O(9)–C(2A)	70.3(9)	C(2B)–O(10)–C(4A)	70.6(10)
O(11)–Y(2)–O(16)	146.1(2)	O(11)–Y(2)–O(7)	88.9(3)	C(4B)–O(11)–C(13A)	73.2(11)		
O(11)–Y(2)–O(8)	79.0(3)	O(11)–Y(2)–O(9)	110.0(3)	C(13B)–O(12)–C(15A)	75.2(9)	C(39)–C(34)–C(35)	107.5(7)
O(11)–Y(2)–O(10)	74.3(3)	O(12)–Y(2)–O(15)	132.5(2)	C(40)–C(34)–C(35)	107.1(8)	C(40)–C(34)–C(39)	108.0(9)
O(12)–Y(2)–O(16)	81.4(3)	O(12)–Y(2)–O(7)	145.2(2)	C(41)–C(34)–C(35)	114.0(8)	C(41)–C(34)–C(39)	109.0(9)
O(12)–Y(2)–O(8)	73.8(3)	O(12)–Y(2)–O(9)	73.8(3)	C(41)–C(34)–C(40)	111.1(8)	C(34)–C(35)–O(7)	114.5(7)
O(12)–Y(2)–O(10)	125.4(3)	O(12)–Y(2)–O(11)	76.8(3)	C(36)–C(35)–O(7)	123.5(8)	C(36)–C(35)–C(34)	122.0(7)
C(35)–O(7)–Y(2)	136.2(4)	C(37)–O(8)–Y(2)	135.8(5)	C(37)–C(36)–C(35)	124.8(8)	C(36)–C(37)–O(8)	122.9(8)
C(2A)–O(9)–Y(2)	128.5(7)	C(15B)–O(9)–Y(2)	130.7(6)	C(38)–C(37)–O(8)	115.0(7)	C(38)–C(37)–C(36)	122.1(8)
C(4A)–O(10)–Y(2)	139.3(6)	C(2B)–O(10)–Y(2)	128.2(8)	C(42)–C(38)–C(37)	110.2(10)	C(43)–C(38)–C(37)	108.0(8)
C(13A)–O(11)–Y(2)	144.1(8)	C(4B)–O(11)–Y(2)	141.9(8)	C(43)–C(38)–C(42)	107.8(11)	C(44)–C(38)–C(37)	114.7(8)
C(15A)–O(12)–Y(2)	125.1(8)	C(13B)–O(12)–Y(2)	140.2(6)	C(44)–C(38)–C(42)	113.0(9)	C(44)–C(38)–C(43)	102.7(9)
C(6)–C(1)–C(2)	107.4(7)	C(7)–C(1)–C(2)	108.1(7)	C(6A)–C(1A)–C(2A)	104.4(8)	C(7A)–C(1A)–C(2A)	113.4(10)
C(7)–C(1)–C(6)	109.5(8)	C(8)–C(1)–C(2)	114.4(7)	C(7A)–C(1A)–C(6A)	114.4(9)	C(8A)–C(1A)–C(2A)	106.8(9)
C(8)–C(1)–C(6)	109.8(7)	C(8)–C(1)–C(7)	107.5(7)	C(8A)–C(1A)–C(6A)	102.8(8)	C(8A)–C(1A)–C(7A)	114.1(10)
C(1)–C(2)–O(1)	114.7(7)	C(3)–C(2)–O(1)	124.5(7)	C(15B)–C(1A)–C(2A)	58.0(8)	C(15B)–C(1A)–C(6A)	105.6(8)
C(3)–C(2)–C(1)	120.8(7)	C(4)–C(3)–C(2)	124.0(8)	C(15B)–C(1A)–C(7A)	60.5(9)	C(15B)–C(1A)–C(8A)	150.5(9)
C(3)–C(4)–O(2)	123.6(7)	C(5)–C(4)–O(2)	115.5(7)	C(21B)–C(1A)–C(2A)	147.0(9)	C(21B)–C(1A)–C(6A)	108.1(9)
C(5)–C(4)–C(3)	120.9(7)	C(9)–C(5)–C(4)	111.9(8)	C(21B)–C(1A)–C(7A)	46.6(9)	C(21B)–C(1A)–C(8A)	71.5(10)

Table V (Continued)

C(21B)–C(1A)–C(15B)	106.8(10)	C(22B)–C(1A)–C(2A)	56.9(9)	C(19A)–C(13A)–C(12A)	50.6(10)	C(19A)–C(13A)–C(14A)	81.0(13)
C(22B)–C(1A)–C(6A)	115.4(9)	C(22B)–C(1A)–C(7A)	130.1(10)	C(4B)–C(13A)–O(11)	51.5(10)	C(4B)–C(13A)–C(12A)	64.5(10)
C(22B)–C(1A)–C(8A)	49.9(9)	C(22B)–C(1A)–C(15B)	108.7(10)	C(4B)–C(13A)–C(14A)	159.8(14)	C(4B)–C(13A)–C(19A)	115.1(15)
C(22B)–C(1A)–C(21B)	111.8(12)	C(1A)–C(2A)–O(9)	105.8(10)	C(15A)–C(14A)–C(13A)	124.3(14)	C(14A)–C(15A)–O(12)	130.0(13)
C(3A)–C(2A)–O(9)	131.4(12)	C(3A)–C(2A)–C(1A)	122.6(12)	C(12B)–C(15A)–O(12)	98.5(11)	C(12B)–C(15A)–C(14A)	131.5(13)
C(15B)–C(2A)–O(9)	53.3(8)	C(15B)–C(2A)–C(1A)	60.8(8)	C(13B)–C(15A)–O(12)	49.2(7)	C(13B)–C(15A)–C(14A)	152.5(14)
C(15B)–C(2A)–C(3A)	151.3(12)	C(22B)–C(2A)–O(9)	162.8(12)	C(13B)–C(15A)–C(12B)	59.2(10)	C(12B)–C(16A)–C(20A)	68.7(19)
C(22B)–C(2A)–C(1A)	57.0(9)	C(22B)–C(2A)–C(3A)	65.6(11)	C(13A)–C(19A)–C(12A)	65.3(12)	C(10B)–C(19A)–C(12A)	87.4(20)
C(22B)–C(2A)–C(15B)	111.4(12)	C(4A)–C(3A)–C(2A)	121.2(14)	C(10B)–C(19A)–C(13A)	144.8(24)	C(12B)–C(20A)–C(16A)	40.3(11)
C(22B)–C(3A)–C(2A)	60.2(10)	C(22B)–C(3A)–C(4A)	178.1(13)	C(4A)–C(2B)–O(10)	55.3(9)	C(5A)–C(2B)–O(10)	105.8(10)
C(3A)–C(4A)–O(10)	121.6(12)	C(5A)–C(4A)–O(10)	110.3(11)	C(5A)–C(2B)–C(4A)	60.5(9)	C(3B)–C(2B)–O(10)	128.4(13)
C(5A)–C(4A)–C(3A)	127.2(13)	C(11A)–C(4A)–O(10)	114.6(12)	C(3B)–C(2B)–C(4A)	148.6(13)	C(3B)–C(2B)–C(5A)	125.6(13)
C(11A)–C(4A)–C(3A)	112.8(12)	C(11A)–C(4A)–C(5A)	44.7(8)	C(4B)–C(3B)–C(2B)	123.1(15)	C(12A)–C(4B)–O(11)	114.8(12)
C(2B)–C(4A)–O(10)	54.1(9)	C(2B)–C(4A)–C(3A)	139.8(12)	C(13A)–C(4B)–O(11)	55.3(10)	C(13A)–C(4B)–C(12A)	63.9(10)
C(2B)–C(4A)–C(5A)	67.0(9)	C(2B)–C(4A)–C(11A)	101.9(12)	C(3B)–C(4B)–O(11)	122.2(14)	C(3B)–C(4B)–C(12A)	122.9(14)
C(9A)–C(5A)–C(4A)	103.1(9)	C(10A)–C(5A)–C(4A)	132.2(10)	C(3B)–C(4B)–C(13A)	157.1(14)	C(11A)–C(6B)–C(5A)	47.2(13)
C(10A)–C(5A)–C(9A)	114.7(9)	C(11A)–C(5A)–C(4A)	76.8(11)	C(19A)–C(10B)–C(12A)	53.8(16)	C(16A)–C(12B)–C(15A)	80.5(18)
C(11A)–C(5A)–C(9A)	128.7(14)	C(11A)–C(5A)–C(10A)	99.3(13)	C(20A)–C(12B)–C(15A)	89.5(13)	C(20A)–C(12B)–C(16A)	71.0(19)
C(2B)–C(5A)–C(4A)	52.5(8)	C(2B)–C(5A)–C(9A)	101.5(9)	C(13B)–C(12B)–C(15A)	56.7(9)	C(13B)–C(12B)–C(16A)	116.9(17)
C(2B)–C(5A)–C(10A)	90.7(10)	C(2B)–C(5A)–C(11A)	115.9(12)	C(13B)–C(12B)–C(20A)	140.4(12)	C(17B)–C(12B)–C(15A)	116.8(11)
C(6B)–C(5A)–C(4A)	95.7(10)	C(6B)–C(5A)–C(9A)	97.3(11)	C(17B)–C(12B)–C(16A)	142.4(18)	C(17B)–C(12B)–C(20A)	75.8(14)
C(6B)–C(5A)–C(10A)	106.9(11)	C(6B)–C(5A)–C(11A)	33.9(11)	C(17B)–C(12B)–C(13B)	99.9(13)	C(18B)–C(12B)–C(15A)	137.6(12)
C(6B)–C(5A)–C(2B)	145.9(9)	C(14B)–C(7A)–C(1A)	115.4(12)	C(18B)–C(12B)–C(16A)	85.2(20)	C(18B)–C(12B)–C(20A)	122.9(14)
C(15B)–C(7A)–C(1A)	64.7(9)	C(15B)–C(7A)–C(14B)	51.3(9)	C(18B)–C(12B)–C(13B)	96.8(11)	C(18B)–C(12B)–C(17B)	98.6(12)
C(21B)–C(7A)–C(1A)	73.5(13)	C(21B)–C(7A)–C(14B)	163.1(16)	C(15A)–C(13B)–O(12)	55.6(8)	C(12B)–C(13B)–O(12)	107.7(10)
C(21B)–C(7A)–C(15B)	137.6(15)	C(21B)–C(8A)–C(1A)	53.5(8)	C(12B)–C(13B)–C(15A)	64.1(9)	C(14B)–C(13B)–O(12)	120.0(11)
C(22B)–C(8A)–C(1A)	58.8(10)	C(22B)–C(8A)–C(21B)	103.7(13)	C(14B)–C(13B)–C(15A)	132.9(110	C(14B)–C(13B)–C(12B)	129.6(12)
C(5A)–C(11a)–C(4A)	58.5(10)	C(6B)–C(11A)–C(4A)	121.9(21)	C(13B)–C(14B)–C(7A)	170.9(11)	C(15B)–C(14B)–C(7A)	58.9(10)
C(6B)–C(11A)–C(5A)	98.9(20)	C(17A)–C(12A)–C(13A)	117.8(11)	C(15B)–C(14B)–C(13B)	123.7(13)	C(1A)–C(15B)–O(9)	108.8(9)
C(18A)–C(12A)–C(13A)	120.2(11)	C(18A)–C(12A)–C(17A)	111.8(10)	C(2A)–C(15B)–O(9)	56.5(8)	C(2A)–C(15B)–C(1A)	61.2(8)
C(19A)–C(12A)–C(13A)	64.1(12)	C(19A)–C(12A)–C(17A)	111.9(14)	C(7A)–C(15B)–O(9)	163.2(11)	C(7A)–C(15B)–C(1A)	54.8(9)
C(19A)–C(12A)–C(18A)	123.6(15	C(4B)–C(12A)–C(13A)	51.7(9)	C(7A)–C(15B)–C(2A)	111.0(12)	C(14B)–C(15B)–O(9)	127.0(12)
C(4B)–C(12A)–C(17A)	97.7(9)	C(4B)–C(12A0–C(18A)	91.6(11)	C(14B)–C(15B)–C(1A)	123.7(12)	C(14B)–C(15B)–C(2A)	147.3(12)
C(4B)–C(12A)–C(19A)	115.8(13)	C(10B)–C(12A)–C(13A)	100.4(12)	C(14B)–C(15B)–C(7A)	69.8(110	C(7A)–C(21B)–C(1A)	59.9(11)
C(10B)–C(12A)–C(17A)	107.8(12)	C(10B)–C(12A)–C(18A)	94.2(13)	C(8A)–C(21B)–C(1A)	55.0(9)	C(8A)–C(21B)–C(7A)	110.9(14)
C(10B)–C(12A)–C(19A)	38.8(12)	C(10B)–C(12A)–C(4B)	149.5(11)	C(2A)–C(22B)–C(1A)	66.1(10)	C(3A)–C(22B)–C(1A)	120.2(13)
C(12A)–C(13A)–O(11)	111.9(12)	C(14A)–C(13A)–O(11)	118.0(14)	C(3A)–C(22B)–C(2A)	54.2(10)	C(8A)–C(22B)–C(1A)	71.3(11)
C(14A)–C(13A)–C(12A)	130.0(13)	C(19A)–C(13A)–O(11)	154.8(15)	C(8A)–C(22B)–C(2A)	137.2(14)	C(8A)–C(22B)–C(3A)	168.5(14)

[Ba(tfa)$_2$(hmteta)(dmso)$_x$], and creating a barium coordination environment different from that of the parent complex (**1**).

The mass spectroscopic data reveal the highest mass ion to be a monomeric species [Ba(tfa)$_2$(hmteta)] with *m/z* 591. The complex decomposes under high-vacuum sublimation at 105 °C and 10^{-3} Torr; the crystalline sublimate was found to be [Ba(tfa)$_2$]$_\infty$ (in 35% yield). This is an important observation since we are thus subliming the complex at approximately 100 °C lower than the parent complex. Similar observations have been made by other workers that complexation of barium β-diketonates with Lewis bases results in a marked decrease of the melting point and sublimation conditions are considerably improved.[9,17]

The single-crystal X-ray structure is in agreement with the spectroscopic data. The molecular structure of **1** is shown in Figure 1. The barium ion is eight-coordinated, with a distorted square prismatic geometry. The tetradendate amine ligand lies in one plane, while the tfa β-diketonate ligands are located in separate planes to give overall a twisted propellane type structure. The average Ba–O$_{\text{tfa}}$ distance of 2.677(9) Å and the O–Ba–O chelate angle of 64.6(3)° are slightly different from those for the recently reported dimeric complex [Ba(thd)$_2$(Et$_2$O)]$_2$ [2.578(5) Å and 66.7(2)°],[7] for [Ba(hfa)$_2$(18-crown-6)] with a chelating Ba–O$_{\text{hfa}}$ distance of 2.83 Å and O–Ba–O angle of 61.2(3)°,[8] and for [Ba(tfa)$_2$(tetraglyme)] with a Ba–O$_{\text{tfa}}$ distance of 2.691(3) Å and the O–Ba–O angle of 64.4(1)°.[9] The small differences in both Ba–O bond lengths and O–Ba–O angles may in these three structures be attributed to the steric hindrance from both the tfa Me and CF$_3$ groups and the methylated amines on the multidendate nitrogen Lewis base for **1** and that of the hfa CF$_3$ moieties and the 18-crown-6 ligand of [Ba(hfa)$_2$(18-crown-6)].[8]

The amine ligand chelates to the barium atom in a four-pronged coordination mode, with Ba–N(1), Ba–N(2), Ba–N(3) and Ba–N(4) distances of 2.972(1), 2.975(1), 3.022(1), and 2.963(1) Å, respectively, with an average Ba–N$_{\text{amine}}$ distance of 2.983(1) Å. The two terminal chelating NMe$_2$ groups N(1) and N(9) bind marginally closer to the barium center, and this effect may primarily be due to steric reasons. The binding mode of the amine ligand is very similar to that of the tetraglyme ligand in [Ba(tfa)$_2$(tetraglyme)].[9]

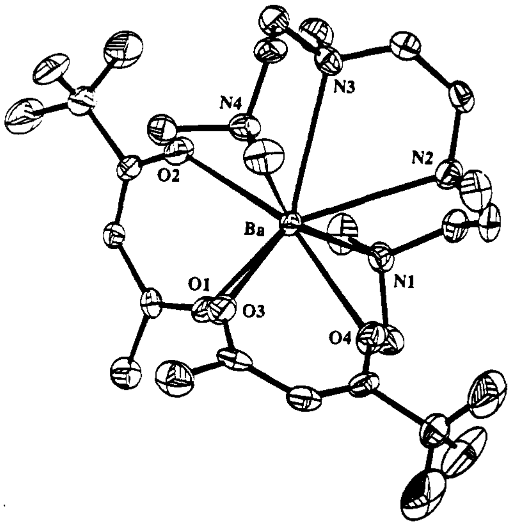

Figure 1. Molecular structure of [Ba(tfa)$_2$(hmteta)] (**1**), showing the atom-numbering scheme. H-atoms have been omitted for clarity.

Using the same synthetic strategy as for **1**, we can switch not only β-diketonates, i.e. tfa to thd (where thd is Bu^{t}COCHCOBu^t), but also chelating ligands, from N-centered to O-centered, and use triglyme (where triglyme is Me(OCH$_2$CH$_2$)$_3$OMe). We have thus explored the potential of using a lanthanide β-diketonate as a starting material.[36] Such materials have several pertinent properties, namely that they are readily obtainable as crystalline solids of known stoichiometry, soluble in hydrocarbons (both aliphatic or aromatic), stable in the atmosphere, and sufficiently

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(36) Mehrotra, R. C.; Singh, A.; Tripathi, U.M. *Chem. Rev.* **1991**, *91*, 1287.

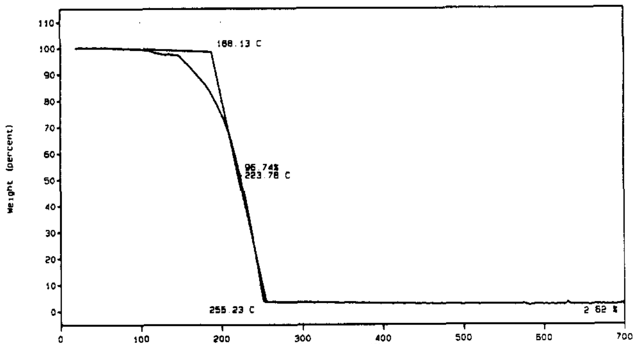

Figure 2. Thermal gravimetric analysis curve of [{(thd)$_3$Y}$_2$(triglyme)] (**2**).

reactive that most reactions will occur at, or slightly above, room temperature.

We have found that reaction of the yttrium hydrated compound $[Y(thd)_3(H_2O)]_\infty$[30] with 1 equiv of triglyme at R.T. yields a triglyme-bridged dimeric yttrium complex, {[(thd)$_3$Y]$_2$(triglyme)} (**2**), with *elimination of the coordinated water* (see eq 2).[37]

$$[Y(thd)_3(H_2O)]_\infty + Me(OCH_2CH_2)_3OCH_3 \xrightarrow{\text{hexane, R.T.}} \{[(thd)_3Y]_2(triglyme)\} + H_2O \quad (2)$$

The ^{1}H and ^{13}C NMR spectroscopic data for complex **2** reveal the presence of only one thd and glyme time-averaged ligand environments in a ratio of 6:1 in C_6D_6 at room temperature. An extensive variable-temperature study (−70° to +70 °C in C_7D_8) reveals no substantial changes in the NMR behavior of this material. These data therefore suggest that in solution the molecule is highly fluxional with rapid exchange between thd and triglyme coordination sites.

The mass spectroscopic data reveal that the highest mass ion observed is a dimeric species [Y$_2$(thd)$_4$(Me$_2$CHOH)(triglyme)] at *m/e* 1148, and fragment ions are observed at *m/e* 1088 for [Y$_2$(thf)$_4$(triglyme)] and *m/e* 910 for [Y$_2$(thd)$_4$]. The complex has a low melting point of 77-80 °C with respect to the starting complex, which melts over the range 146–149 °C. This material sublimes intact over the range 90–130 °C at 10^{-3} Torr attesting to its remarkable thermal stability. More importantly, this complex displays excellent stability to both moisture and oxygen, with negligible decomposition over a period of months in the open laboratory.

The thermal behavior of this complex was studied by simultaneous thermal analysis (STA) over the temperature range 20–700 °C under a carrier gas of nitrogen. The TGA plot (Figure 2) shows a single step with an onset temperature of 110 °C and completion by 250 °C. Over the temperature range studied, 96 ± 2% of the yttrium complex volatilizes into the gas phase, leaving a very small (ca. 2%) carbonaceous residue, with a $T_{50\%} = 223$ °C. This data suggests that complex **2** has mass transport properties and thermal characteristics at least as good or if not better than those of conventional yttrium CVD precursors. Associated with this is the added advantage of the excellent air/moisture stability of this complex, making it amenable to use in the open laboratory.

The X-ray structure of **2** is shown in Figure 3, with important bond distances and angles in Table V. The molecular structure consists of a pair of Y(thd)$_3$ moieties linked by a triglyme involving an unusual bonding mode. There is a 50/50 disorder in the orientation of the thd ligands around one of the yttrium atoms. Although the two yttrium metal centers are formally related by a 2-fold axis, due to severe disorder of the thd ligands around Y(2), this is in fact not the case.

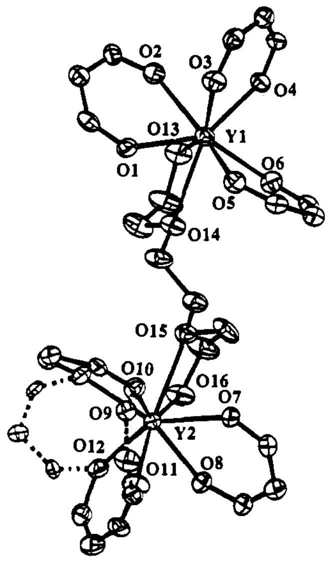

Figure 3. Molecular structure of [{(thd)$_3$Y}$_2$(triglyme)] (**2**), showing the atom-numbering scheme. The terminal methyl groups of the triglyme, the *tert*-butyl groups of the thd ligands, and the H-atoms are omitted for clarity. The alternative orientations of the two disordered thd ligands on Y(2) are indicated by atoms with broken bonds.

Both yttrium metal centers are found to be eight coordinate, with the overall coordination polyhedron being a distorted square antiprism. This high coordination number is common for lanthanides and other yttrium alkoxides or β-diketonates, e.g. $Y_3(OCH_2CH_2OMe)_5(acac)_4$[28] and $Y_2(OAc)_2(acac)_4(H_2O)_2$.[38] One of the most interesting features of **2** is the triglyme acting as both a chelate *and* as a bridging ligand via the central ethylene bridge [C(48) and C(49)]. To the best of our knowledge, this coordination mode of a glyme ligand is quite unique; such ligands are normally found either chelating or acting as η^1-terminally bound.

The Y–O bond lengths [2.481(6)–2.597(8) Å] of the glyme binding to the metal center are an interesting example of the subtle steric factors involved in this unusual structural motif. The Y(1)–O(13) bond length of 2.481(6) Å is ca. 0.1 Å shorter than that of Y(1)–O(14) bond of 2.597(8) Å, and this is most likely due to O(13) carrying the pendant methyl group, which can swing in and bind very tightly to the metal center. In striking contrast to this, O(14) must bend back and snap into place to create the chelate, with a fairly acute angle in the O(13)–Y–O(14) plane of 64.0(3)°. Similar bonding is also observed in the other end of the glyme to Y(2), with Y(2)–O(15) and Y(2)–O(16) bond lengths of 2.574(8) and 2.504(8) Å, respectively, and an O(15)–Y(2)–O(16) angle of 61.7(3)°. This mode of binding may be contrasted with the use of functionalized alcohols with yttrium such as methoxyethanol, which has yielded the crownlike decameric complex $[Y_{10}(OCH_2CH_2OMe)_{30}]$[27] or $Y_3(OCH_2CH_2OMe)_5(acac)_4$.[28]

The Y–O$_{thd}$ bond lengths [2.224(7)–2.348(7) Å] are, as expected, much shorter than the Y–O$_{glyme}$ distances, given that the β-diketonates are observed to be here in classical, nearly symmetrical mode. These values are comparable with the Y–O distances in the recently characterized yttrium dimer $Y_2(OAc)_2(acac)_4(H_2O)_2$,[38] although it should be noted that compound **2** is an anhydrous dimer, and also with the M–O distances in other lanthanide acac derivatives.[27,28,38,39]

The observation that the water is removed from the hydrated yttrium β-diketonate $[Y(thd)_3(H_2O]_\infty$ is an important one, given that only 1 equiv of glyme ligand is needed and not an excess.

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(37) This route has been successfully extended to a range of other lanthanides, e.g. Eu, Tb, and La, to yield [{Ln(thd)$_3$}$_2$(triglyme)]: Drake, S. R.; Otway, D. J.; Williams, D. J.; Slawin, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2379.

(38) Poncelet, O.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1990**, *9*, 1305.

Analysis of the remaining liquid from the [{Y(thd)$_3$}$_2$(triglyme)] reaction shows it to be rich in H_2O/excess triglyme. This observation suggests that the triglyme ligand in this particular case is acting as a partioning agent for the water. This is also consistent with the observed reaction stoichiometry which requires 1 molar equiv of glyme O-donor ligand, rather than the expected 0.5 equiv incorporated into complex **2**. It should be noted, however, that glyme and glycol ligands have previously been used as dehydrating agents for metal chloride hydrates; e.g., 2,2-dimethoxypropane (a *gem*-diol) reacts with metal hydrates producing acetone and methanol.[40] Unfortunately, these byproducts are often found complexed to the metal halide; in contrast to long-chain glymes (i.e. tri- or tetraglyme) and yttrium β-diketonates no ligand cleavage is observed (from IR and ^{1}H NMR spectroscopic data).

The design of such precursors should reap great benefit to the metal–oxygen based chemistry of these metals, and in addition, one can also envisage the use of these complexes to prepare mixed-metal β-diketonates suitable for CVD applications. Studies are currently in progress along these lines.

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Supplementary Material Available: Complete listings of crystallographic data, fractional atomic coordinates for the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for complexes **1** and **2** (9 pages). Ordering information is given on any current masthead page.

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