NMR shows substantial amounts of $W(O)Cl_2(PMePh_2)_3$, and other uncharacterized impurities.

$W(N$-*p*-tolyl$)[{=}C(CH_2)_4]Cl_2(PMePh_2)_2$ (6a). *N*-Cyclopentylidene-*p*-toluidine (0.080 mL) was added to a suspension of **1** (0.51 g) in 12 mL of benzene and the resultant mixture stirred for 2 days. More imine (0.060 mL) was added and stirring was continued with heating to 40 °C for 20 h. Volatiles were pumped away and the resulting solids dissolved in 10 mL of Et_2O. The mixture was concentrated to 1 mL, and 10 mL of pentane was added. The solids were filtered and dried in vacuo for 3 h, yielding 0.18 g (45%) of yellow powder. Anal. Calcd for $C_{38}H_{41}Cl_2NP_2W$: C, 55.09; H, 4.99; N, 1.69. Found: C, 54.92; H, 4.98; N, 1.47. IR: 1349, 1309 (w), 1281 (w), 1191 (w), 1098, 1028 (w), 1016 (w), 1000 (w), 891 (vs), 816, 742 (s), 694 (vs), 517, 505 (s), 485, 441.

$W(N$-*p*-tolyl$)({=}CMe_2)Cl_2(PMePh_2)_2$ (6g). *N*-Isopropylidene-*p*-toluidine (0.075 mL) was added to a suspension of **1** (0.30 g) in 10 mL of benzene and the resultant mixture heated to reflux for 3 h. The mixture was concentrated to 1 mL, and 10 mL of heptane was added. The solids were filtered, yielding 0.135 g of green-grey solids, mostly **6g** by ^1H NMR.

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Synthesis and Structure of the Cationic *tert*-Butoxide Complexes $Y_3(OR)_7Cl(THF)_3{}^+$, $Y_2(OR)_4Cl(THF)_4{}^+$, and $Y(OR)Cl(THF)_5{}^+$: Representatives of a New Class of Yttrium Alkoxides[1]

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Abstract: $Y_3(OR)_7Cl_2(THF)_2$ (**1**) ($R = CMe_3$) reacts with $AgBPh_4$ to form a mixture of $[Y_3(\mu_3\text{-}OR)(\mu_3\text{-}Cl)(\mu\text{-}OR)_3(OR)_3(THF)_3][BPh_4]$ (**2**) and $[Y_2(\mu\text{-}Cl)(\mu\text{-}OR)_2(OR)_2(THF)_4][BPh_4]$ (**3**). At 0 °C the reaction favors **2**, which can be isolated by crystallization from toluene at −37 °C. **2** forms crystals in space group $P\bar{1}$ (C_i^1; No. 2) with a = 14.131 (3) Å, b = 15.035 (3) Å, c = 18.712 (5) Å, α = 85.01 (2)°, β = 85.02 (2)°, γ = 81.75 (2)°, V = 3908 (2) Å^3, and D_{calcd} = 1.23 g cm^{-3} for Z = 2. Least-squares refinement of the model based on 4692 reflections converged to a final R_F = 9.1%. The three yttrium atoms in **2** form an equilateral triangle with doubly bridging alkoxide groups along the edges and triply bridging alkoxide and chloride ligands above and below the plane of metals. The three terminal alkoxide groups are all on the μ_3-alkoxide side of the plane. At room temperature, the reaction of **1** with $AgBPh_4$ favors **3**, which can be isolated in 74% yield by reaction of the product mixture with $NaBPh_4$. **3** crystallizes from THF/toluene/hexane at −37 °C in space group $P4_2/n$ with a = 18.424 (5) Å, c = 17.738 (9) Å, V = 6021 (4) Å^3, and D_{calcd} = 1.23 g cm^{-3} for Z = 4. Least-squares refinement of the model based on 1099 reflections converged to a final R_F = 9.9%. In **3**, two $Y(OR)(THF)_2$ units are connected by two alkoxide bridges and one chloride bridge to form a distorted face-shared bioctahedron. The six ligands around each yttrium atom are arranged such that the terminal alkoxide ligand is trans to the bridging chloride ion. **1** reacts with $NaBPh_4$ to form $[Y(OR)(Cl)(THF)_5][BPh_4]$ (**4**), which can be prepared in higher yield (85%) from the reaction of YCl_3 with NaOR and $NaBPh_4$. **4** crystallizes from THF/hexane at −37 °C in space group $P2_1/n$ with a = 13.675 (3) Å, b = 12.418 (3) Å, c = 32.803 (8) Å, β = 90.43 (2)°, V = 5570 (2) Å^3, and D_{calcd} = 1.22 g cm^{-3} for Z = 4. Least-squares refinement of the model based on 6073 reflections converged to a final R_F = 8.1%. The OR and Cl ligands in **4** are located at the axial positions of a pentagonal bipyramid. The five THF ligands occupy the equatorial sites. **1** can be regenerated from **2** and **3** by reaction with NaCl.

Recent studies of the utility of simple alkoxide ligands as replacements for the $C_5H_5^-$ ion in organometallic complexes of yttrium and the lanthanides have shown that the *tert*-butoxide ligand can provide alkoxide analogues of cyclopentadienylyttrium complexes.[2-4] In addition, a very rich polymetallic chemistry has been revealed, which suggests that these complexes may be interesting vis-à-vis metal oxides. For example, the facile conversion of $Y_3(OR)_7Cl_2(THF)_2$ (**1**) ($R = CMe_3$) to the extended alkoxide oxide $Y_{14}(OR)_{28}Cl_{10}O_2(THF)_4$[4] provides an interesting contrast to traditional ideas of how metal alkoxides transform into metal oxides via sol–gel processes.[5] The chemistry of **1** is of interest not only because of this reaction but also because its terminal chloride ligand is a site of potential reactivity.

We report here the utility of **1** to generate a new class of yttrium alkoxide complexes: cationic yttrium alkoxides. Given the recent interest in the chemistry of yttrium, barium, and copper alkoxides as precursors to mixed-metal oxides such as the superconducting $YBa_2Cu_3O_{7-x}$,[6,7] the existence of this class of cationic complexes provides a new set of alternatives for the synthesis of heteropolymetallic alkoxide compounds. We also describe our observations on the structure and reactivity of these cations, which suggest that this class of alkoxides follows a broader set of generalizations than those developed so far for neutral yttrium alkoxides.[3,4,7b]

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Table I. Crystallographic Data for **2**–**4**

	2	**3**	**4**
formula	$[C_{40}H_{87}O_{10}ClY_3]^+[B(C_6H_5)_4]^-\cdot C_7H_8$	$[C_{32}H_{68}O_8ClY_2]^+[B(C_6H_5)_4]^-$	$[C_{24}H_{49}O_6ClY]^+[B(C_6H_5)_4]^-\cdot 2C_4H_8O$
mol wt	1441.9	1113.3	1021.4
space group	$P\bar{1}$	$P4_2/n$	$P2_1/n$
cell constants			
a, Å	14.131 (3)	18.424 (5)	13.675 (3)
b, Å	15.035 (3)		12.418 (3)
c, Å	18.712 (5)	17.738 (9)	32.803 (8)
α, deg	85.01 (2)		
β, deg	85.02 (2)		90.43 (2)
γ, deg	81.75 (2)		
V, Å^3	3908 (2)	6021 (4)	5570 (2)
Z	2	4	4
D_{calcd}, g cm^{-3}	1.225	1.228	1.218
temp, K	296	296	213
μ_{calcd}, cm^{-1}	23.0	20.19	11.5
radiation	Mo Kα; λ = 0.71073 Å	Mo Kα; λ = 0.71073 Å	Mo Kα; λ = 0.71073 Å
monochromator	highly oriented graphite	highly oriented graphite	highly oriented graphite
data collected	$+h,\pm k,\pm l$	$+h,+k,+l$	$+h,+k,\pm l$
scan type	coupled θ(crystal)–2θ(counter)	ω	coupled θ(crystal)–2θ(counter)
scan range	1.2° plus Kα separation	1.00°	1.0° plus Kα separation
scan speed, deg min^{-1} (in ω)	2.0	2.0	3.0
$2\theta_{max}$, deg	45.0	40.0	50.0
total reflcns	10279	3062	10289
obsd data	4692 reflcns with $\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$	1099 reflcns with $\lvert F_o\rvert > 5.0\sigma(\lvert F_o\rvert)$	6073 reflcns with $\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$
no. of variables	365	122	555
transmissn coeff: min–max	0.18–0.22	0.417–1.00	0.3982–0.4714
R, %	9.1	9.9	8.1
R_w, %	9.4	11.4	9.2
GOF	1.79	1.68	1.82

Experimental Section

Manipulations of the complexes described below were conducted with the rigorous exclusion of air and water with Schlenk, vacuum line, and glovebox (Vacuum Atmospheres HE-553 Dri Lab) techniques. Reagents were purified, and physical measurements were obtained as previously described.[8] $AgBPh_4$[9] was prepared as previously described. $NaOCMe_3$ was prepared by reacting dry, degassed $HOCMe_3$ with excess NaH in THF. This reaction mixture was filtered, the solvent was removed by rotary evaporation, and the sample was dried at 3 × 10^{-5} Torr. $NaBPh_4$ (Aldrich) was placed under high vacuum (3 × 10^{-5} Torr) before use. Complexometric titrations were conducted as previously described.[10] In the ^1H NMR spectra of the complexes in this paper, coordinated THF is typically observed as broad resonances at δ 3.60 and 1.74.

$[Y_3(OCMe_3)_7Cl(THF)_3][BPh_4]$ (2). In the glovebox, **1** (200 mg, 0.20 mmol), $AgBPh_4$ (172 mg, 0.42 mmol), and a stir bar were placed in a Schlenk flask that was wrapped in aluminum foil. An addition funnel containing 18 mL of THF was attached to the flask, which was removed from the glovebox and cooled to 0 °C. The THF was added, and the reaction was stirred in the dark for 6 h. The solvent was removed on the Schlenk line, and the resulting brownish powder was brought into the glovebox and extracted with toluene. The solution was centrifuged, and the toluene was removed to give a pale yellow powder (120 mg) that contained **1**, **2**, and **3** in an approximate ratio of 27:50:23. Crystallization of a concentrated toluene solution of this mixture at −37 °C gave X-ray-quality crystals of **2**: 111 mg, 37%; ^1H NMR (THF-d_8) δ 7.31 (br s, 8 H, BPh_4), 6.88 (t, 8 H, BPh_4), 6.73 (t, 4 H, BPh_4), 1.92 (s, 9 H, μ_3-$OCMe_3$), 1.46 (s, 27 H, μ-$OCMe_3$), 1.34 (s, 27 H, $OCMe_3$). Anal. Calcd for $Y_3C_{64}H_{107}BClO_{10}$: Y, 19.76. Found: Y, 19.5.

X-ray Data Collection, Structure Determination, and Refinement for 2. A colorless crystal of approximate dimensions 0.20 × 0.24 × 0.40 mm was mounted in a thin-walled glass capillary under a nitrogen atmosphere and aligned on a Syntex $P2_1$ automated four-circle diffractometer. Determination of Laue symmetry, crystal class, unit cell parameters, and crystal orientation matrix was carried out by previously described techniques similar to those of Churchill.[11] Unfortunately, the crystal exhibited very weak diffraction, and highly accurate bond distance and angle data were not anticipated. However, the gross structural information on the complex was deemed important enough to proceed with the structural determination despite the quality of the crystals. This crystal was the best of many examined from many different crystallization attempts. Room-temperature (21 °C) intensity data were collected with the θ–2θ scan technique with Mo Kα radiation under the conditions given in Table I. All 10279 data were corrected for decay (10%), absorption, and Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. A careful survey of a preliminary data set revealed no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The crystal, therefore, belongs to the triclinic system. Possible space groups are the noncentrosymmetric $P1$ [C_1^1; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. With $Z = 2$ and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable[12] and was later confirmed as the correct choice by successful solution of the structure.

All crystallographic calculations were carried out with either our locally modified version of the UCLA Crystallographic Computing Package[13] or the SHELXTL PLUS program set.[14] The analytical scattering factors for neutral atoms were used throughout the analysis;[15] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[16] were included. The quantity minimized during least-squares analysis was $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ where $1/w = \sigma^2(\lvert F_o\rvert) + 0.0010(\lvert F_o\rvert)^2$.

The structure was solved by direct methods (SHELXTL PLUS); the three yttrium atoms were located from an "E-map". Subsequent difference-Fourier maps revealed the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for yttrium and chlorine only) led to convergence with $R_F = 9.1\%$, $R_{wF} = 9.4\%$, and GOF = 1.79 for 365 variables against those 4692 data with $\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$. Hydrogen atom contributions were included with a riding model with d(C–H) = 0.96 Å and U(iso) = 0.12 Å^2. A final difference-Fourier synthesis showed no significant features.

$[Y_2(\mu\text{-}Cl)(\mu\text{-}OCMe_3)_2(OCMe_3)_2(THF)_4][BPh_4]$ (3). In the glovebox, a solution of **1** (200 mg, 0.20 mmol) in THF (7 mL) was added to $AgBPh_4$ (83 mg, 0.20 mmol) suspended in THF (7 mL) in a flask that was wrapped in aluminum foil. After the suspension was stirred for 34 h, the mixture was centrifuged. The solution was decanted, and the solvent was removed by rotary evaporation. The resultant oily yellow

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Table II. Composition of the AgBPh$_4$/Y$_3$(OR)$_7$Cl$_2$(THF)$_2$ Reaction Mixture as a Function of Time

	rel amt of ea complex in mixture		
reactn time	**1**	**2**	**3**
10 min	56	4	39
20 min	55	5	40
30 min	37	8	55
40 min	36	8	56
50 min	32	6	62
60 min	28	8	64
70 min	27	7	66
100 min	25	8	67
43 days	26	7	67
132 days	31	6	63

powder was washed with hexane and extracted with toluene. Upon removal of the toluene by rotary evaporation, a light yellow powder was isolated (226 mg), which by ^{1}H NMR spectroscopy was a mixture containing primarily **3** with small amounts of **1** and **2**. **3** was isolated in pure form by treating this mixture with NaBPh$_4$ (45 mg, 0.14 mmol) in THF (15 mL) for 72 h. The resulting yellowish mixture was centrifuged, and the solvent was removed by rotary evaporation. Extraction of the resulting powder with toluene and removal of the solvent left pure **3** as a white microcrystalline powder: 171 mg, 74% yield; ^{1}H NMR (THF-d_8) δ 7.28 (br s, 8 H, BPh$_4$), 6.86 (t, 8 H, BPh$_4$), 6.71 (t, 4 H, BPh$_4$), 1.50 (s, 18 H, μ-OCMe$_3$), 1.32 (s, 18 H, OCMe$_3$); ^{13}C NMR (THF-d_8) δ 138.4, 126.8, 122.9 (s, C_6H$_5$), 166.4 (q, $J_{^{13}\mathrm{C}-^{11}\mathrm{B}}$ = 49 Hz, C_6H$_5$), 74.5, 74.2 (s, OCMe$_3$), 35.9, 35.2 (s, OC(CH$_3$)$_3$), 69.4, 27.6 (s, THF); IR (KBr) 3020 m, 2970 s, 1580 w, 1460 m br, 1430 w, 1360 s, 1200 s, 1000 s, 950 s, 870 m, 735 s, 705 s, 610 m cm^{-1}. Anal. Calcd for Y$_2$C$_{56}$H$_{88}$BClO$_8$: Y, 15.97. Found: Y, 16.0. Colorless crystals of **3** suitable for X-ray diffraction were grown out of a mixture of THF/toluene/hexane at −37 °C. When toluene was removed from a solution of **3**, the resulting solid was no longer soluble in toluene. However, it was very soluble in THF. Upon removal of the THF by rotary evaporation, the sample was again soluble in toluene. This cycle of insolubility in toluene upon removal of the toluene and restoration of solubility in toluene after extraction with THF was repeated several times. Integration of the C$_6$D$_6$ ^{1}H NMR spectrum of the material obtained from THF showed more than four THF molecules per **BPh$_4$**. Apparently, the arene-soluble material has additional THF molecules of solvation.

X-ray Data Collection, Structure Determination, and Refinement for 3. A colorless crystal of approximate dimensions 0.17 × 0.55 × 0.58 mm was mounted in a thin-walled glass capillary under a nitrogen atmosphere, accurately aligned on a Nicolet P3 automated four-circle diffractometer, and indexed as described above for **2**. As in the case of **2**, this crystal of **3** exhibited weak diffraction. The best crystal available was examined to get gross structural information. Room-temperature (296 K) intensity data were collected with an ω-scan technique with Mo Kα radiation under the conditions given in Table I. All 3062 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. The systematic extinctions observed were $hk0$ for $h + k = 2n + 1$ and $00l$ for $l = 2n + 1$; the diffraction symmetry was $4/m$. The centrosymmetric tetragonal space group $P4_2/n$ [C_{4h}^4; No. 86] is uniquely defined.

The crystallographic calculations were carried out as described above for **2**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.002(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Refinement of positional and thermal parameters (anisotropic for yttrium and chlorine) led to convergence with R_F = 9.9%, R_{wF} = 11.4%, and GOF = 1.68 for 122 variables refined against those 1099 data with $|F_o| > 5.0\sigma(|F_o|)$. The phenyl carbon atoms of the tetraphenylborate anion were refined as rigid groups with d(C–C) = 1.395 Å. Hydrogen atom contributions were included with a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. A final difference-Fourier map was "clean" with ρ(max) = 0.65 e Å^{-3}.

^{1}H NMR Study of the Reaction of 1 with AgBPh$_4$. **1** (25 mg, 0.025 mmol) and AgBPh$_4$ (11 mg, 0.026 mmol) were mixed together in the drybox and placed in an NMR tube. This tube was attached to a high-vacuum line and evacuated to 5 × 10^{-5} Torr. THF-d_8 (0.75 mL) was vacuum transferred into the NMR tube with a liquid nitrogen bath. The sample tube was sealed under vacuum, wrapped in aluminum foil, and kept in the liquid nitrogen bath until the NMR experiment was conducted. At the start of the NMR experiment, the sample was quickly thawed, shaken, and placed in the GN 500 NMR spectrometer. A spectrum was taken every 10 min for 100 min. Every 20 min the sample was removed from the probe and shaken. The composition of the mixture as a function of time is given in Table II.

[Y(OCMe$_3$)Cl(THF)$_5$][BPh$_4$] (4) from 1. In the glovebox, a solution of **1** (200 mg, 0.20 mmol) in THF (7 mL) was added to a solution of NaBPh$_4$ (71 mg, 0.22 mmol) in THF (8 mL). This clear solution was stirred and became cloudy after 10 min. After the solution was stirred for 72 h and centrifuged, the clear solution was decanted from a white precipitate. Removal of solvent left an oily white powder, which was extracted with toluene to remove any **1** and toluene-soluble cationic products, e.g., **2** and **3** (111 mg). The toluene-insoluble powder was extracted with THF and centrifuged. Solvent was removed from the decanted solution, and the solids were washed with hexane to give a white powder (115 mg). ^{1}H NMR spectroscopy showed what appeared to be a mixture of products. Single crystals of **4** were grown at −37 °C from a mixture of THF/hexane.

X-ray Data Collection, Structure Determination, and Refinement of 4. A colorless crystal of approximate dimensions 0.37 × 0.47 × 0.61 mm was immersed in Paratone-N, mounted on a glass fiber, and transferred to the Syntex P2$_1$ diffractometer that was equipped with a modified LT-1 apparatus. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (213 K) intensity data were carried out as described above for **2**. As in the case of **2**, this crystal of **4** exhibited weak diffraction. The best crystal available was examined to get gross structural information. Final cell parameters are based on least-squares analysis of 27 reflections in well-separated regions of reciprocal space, all having 25° < 2θ < 30°. Details are given in Table I.

All 10 289 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale by means of a Wilson plot. A careful survey of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ [C_{2h}^5; No. 14], is thus uniquely defined.

The crystallographic calculations were carried out as described above for **2**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0003(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atom contributions were included with a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and thermal parameters (isotropic for the solvent molecules) led to convergence with R_F = 8.1%, R_{wF} = 9.2%, and GOF = 1.82 for 555 variables refined against those 6073 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map was "clean" with ρ(max) = 1.2 e Å^{-3} at a distance of 0.72 Å from C(31).

[Y(OCMe$_3$)Cl(THF)$_5$][BPh$_4$] (4) from YCl$_3$. In the glovebox, YCl$_3$ (200 mg, 1.02 mmol) was added to a solution of NaOCMe$_3$ (98 mg, 1.02 mmol) and NaBPh$_4$ (332 mg, 1.02 mmol) in THF (15 mL). This mixture was stirred for 15 h. The resultant cloudy solution was centrifuged to give a white precipitate (118 mg) and a clear colorless solution. Removal of solvent left an oily white solid that was washed with toluene and extracted with THF. This solution was centrifuged and decanted and the solvent removed to give **4** as a white microcrystalline solid: 771 mg, 88% yield; ^{1}H NMR (THF-d_8) δ 7.29 (br s, 8 H, BPh$_4$), 6.87 (t, 8 H, BPh$_4$), 6.71 (t, 4 H, BPh$_4$), 1.23 (s, 9 H, OCMe$_3$); IR (KBr) 3020 m, 2970 s, 2880 s, 1585 w, 1480 m, 1460 m, 1430 m, 1360 w, 1225 w, 1200 s, 1020 s, 1000 s, 920 w, 870 s, 735 m, 705 s, 610 m cm^{-1}. Anal. Calcd for YC$_{48}$H$_{69}$BClO$_6$: Y, 10.14. Found: Y, 9.9. Crystals suitable for X-ray diffraction were grown from a concentrated THF solution at −37 °C, and the unit cell parameters were determined to be the same as those of the crystals described above. After several months in the drybox, the solid sample lost three coordinated THF molecules to give [Y(OCMe$_3$)Cl(THF)$_2$][BPh$_4$], as evidenced by elemental analysis. Anal. Calcd for the disolvate YC$_{36}$H$_{45}$BClO$_3$: Y, 13.45. Found: Y, 13.5. Crystals suitable for X-ray diffraction were grown from a concentrated THF solution at −37 °C and were indexed to ensure that these crystals were the same as those described above.

Results

Y$_3$(OR)$_7$Cl$_2$(THF)$_2$ (**1**) (R = CMe$_3$) reacts with AgBPh$_4$ and NaBPh$_4$ in THF to form mixtures of cationic yttrium alkoxide complexes and AgCl and NaCl, respectively. The composition of the mixtures is variable depending upon many factors, and frequently the mixture contains some of the starting material, **1**. Specific synthetic routes to pure samples of each of the cations will be described first followed by an evaluation of why the mixtures occur.

Synthesis of [Y$_3$(OR)$_7$Cl(THF)$_3$][BPh$_4$] (2). When the reaction

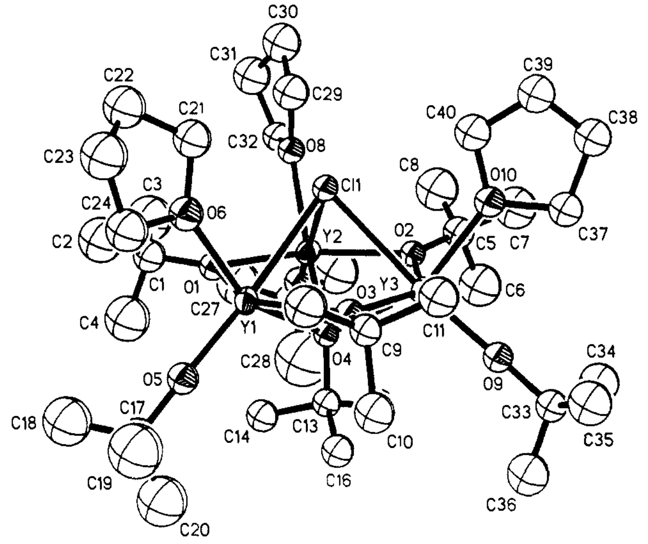
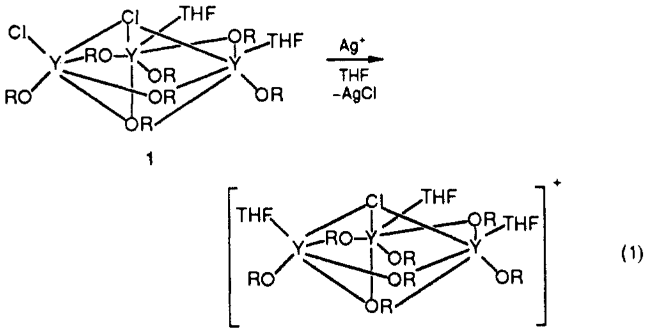


Figure 1. ORTEP diagram of the cation in $[Y_3(OCMe_3)_7Cl(THF)_3][BPh_4]$ (**2**) with the probability ellipsoids drawn at the 30% level.

of **1** with $AgBPh_4$ was carried out at 0 °C in the dark, the major cationic product was **2** (eq 1). The other components of the product mixture were **1** and a second cationic alkoxide complex, **3**, described below. Under these synthetic conditions, **2** could be selectively crystallized in the presence of **1** and **3** to give a 37% yield of crystals.



1

2

(1)

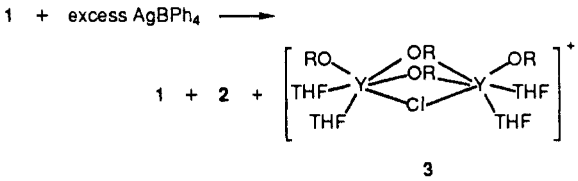
The ^1H NMR spectrum of **2** contained resonances characteristic of BPh_4 and *tert*-butoxide ligands in a ratio of one BPh_4 to seven $OCMe_3$ groups. The alkoxide region contained one resonance in the triply bridging range[3,4,17] (δ 1.92), one resonance in the doubly bridging range (δ 1.46), and one resonance assignable to terminal alkoxide ligands (δ 1.34) in a ratio of 1:3:3, respectively. The simplest expected product consistent with these data was the symmetrical trimeric cationic species $[Y_3(\mu_3\text{-}Cl)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_3(THF)_3]^+$ resulting from the removal of the terminal chloride ligand of **1** and its replacement by a solvent molecule (THF). The structure predicted on the basis of NMR data was confirmed by X-ray crystallography.

Structure of 2. The overall structure of the cation in **2**, shown in Figure 1, is much like that of **1** and its monochloride analogue $Y_3(\mu_3\text{-}Cl)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_4(THF)_2$ (**5**).[3] Each of these structures is comprised of a triangle of six-coordinate yttrium atoms with doubly bridging alkoxides along the edges, a triply bridging chloride above the trimetallic plane, and a triply bridging alkoxide below. Each yttrium ion also has a terminal alkoxide ligand on the triply bridging alkoxide side of the Y_3 plane. **1**, **2**, and **5** differ in the composition of the three terminal ligands on the chloride side of the Y_3 plane. **5** has two THF ligands and an alkoxide ligand, **1** has two THF ligands and a chloride, and **2** has three THF ligands. The quality of the crystal of **2** limited the accuracy of the bond distance and angle data on this complex (Table III). The data obtained are very similar to that found for **1**, **5**, $Y_4(OR)_{10}OCl_2^{2-}$ (**6**)[3], and $Y_{14}(OR)_{28}Cl_{10}O_2(THF)_4$ (**7**).[4]

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Y_3(OCMe_3)_7Cl(THF)_3][BPh_4]$ (**2**)

	Distances		
	Terminal $OCMe_3$		
Y(1)-O(5)	2.02 (1)	O(5)-C(17)	1.43 (2)
Y(2)-O(7)	2.00 (1)	O(7)-C(25)	1.45 (2)
Y(3)-O(9)	2.02 (1)	O(9)-C(33)	1.43 (2)
	μ_2-$OCMe_3$		
Y(1)-O(1)	2.31 (1)	O(1)-C(1)	1.45 (2)
Y(2)-O(1)	2.28 (1)	O(2)-C(5)	1.44 (2)
Y(2)-O(2)	2.27 (1)	O(3)-C(9)	1.44 (2)
Y(3)-O(2)	2.29 (1)		
Y(3)-O(3)	2.27 (1)		
Y(1)-O(3)	2.28 (1)		
	μ_3-$OCMe_3$		
Y(1)-O(4)	2.38 (1)	O(4)-C(13)	1.50 (2)
Y(2)-O(4)	2.36 (1)		
Y(3)-O(4)	2.37 (1)		
	THF		
Y(1)-O(6)	2.37 (1)		
Y(2)-O(8)	2.36 (1)		
Y(3)-O(10)	2.35 (1)		
	Cl		
Y(1)-Cl(1)	2.834 (4)		
Y(2)-Cl(1)	2.829 (4)		
Y(3)-Cl(1)	2.834 (4)		
	Angles		
Y(1)-O(5)-C(17)		178 (1)	
Y(2)-O(7)-C(25)		179 (1)	
Y(3)-O(9)-C(33)		177 (1)	

Synthesis of $[Y_2(OR)_4Cl(THF)_4][BPh_4]$ (3). When the reaction of **1** and $AgBPh_4$ was conducted at room temperature in the dark, **2** was only a minor component in the product mixture, **1** was still present in the product mixture, and the major product, **3**, had a ^1H NMR spectrum that lacked a resonance in the μ_3-$OCMe_3$ region. The ^1H NMR spectrum of **3** contained resonances characteristic of BPh_4, one type of doubly bridging alkoxide, and one type of terminal alkoxide ligand. The simplest structure consistent with these data was a cationic dimer containing two bridging and two terminal alkoxide ligands and a symmetrically bridging chloride ligand. To achieve the normal six-coordination found for yttrium in *tert*-butoxide complexes,[3,4] each yttrium atom would need two THF molecules of solvation. This structural prediction was confirmed by X-ray crystallography as described in a later section. Reaction 2 summarizes this synthetic result. Attempts to drive the reaction to completion with the use of excess $AgBPh_4$ gave similar product mixtures containing unreacted **1**.



3

(2)

A useful synthetic route to **3** was found by examining $NaBPh_4$ as an alternative halide abstraction reagent for **1**. A replacement for $AgBPh_4$ was desirable because of its expense and because side reactions occurred that diminished the yields of **2** and **3** when the reactions were carried out in the light. $NaBPh_4$ does react with **1** to form **2** and **3**, but the reaction is much slower and the composition of the product mixture changes with time. Long reaction times eliminated the trimetallic species **1** and **2** from the reaction mixture and formed yet another cationic product (see below). However, since this latter product was toluene insoluble, it could be readily separated from toluene-soluble **3**. Hence, treatment of a mixture of **1**–**3** with $NaBPh_4$ provided a route to pure **3** (reaction 3). The best overall yield of **3** is obtained by reaction

$$1 + 2 + 3 + NaBPh_4 \rightarrow 3 + \text{toluene-insoluble products} \quad (3)$$

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[17] Brown, L. M.; Mazdiyasni, K. S. *Inorg. Chem.* **1970**, *9*, 2783–2786.

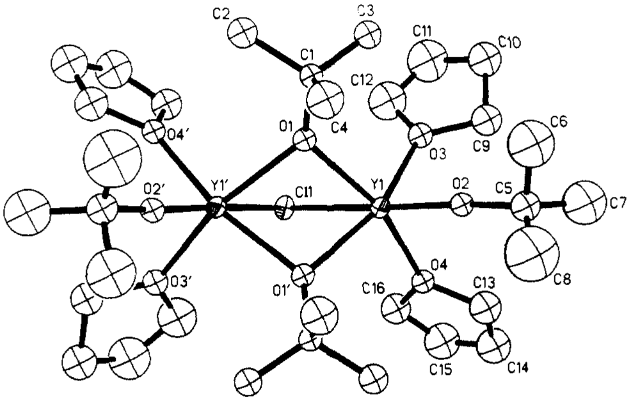

Figure 2. ORTEP diagram of the cation in $[Y_2(OCMe_3)_4Cl(THF)_4][BPh_4]$ (**3**) with the probability ellipsoids drawn at the 20% level. The cation contains a C_2 axis that goes through Cl(1) and the center of the Y(1)–Y(1′) vector.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[Y_2(OCMe_3)_4Cl(THF)_4][BPh_4]$ (**3**)

	Distances		
	Terminal $OCMe_3$		
Y(1)–O(2)	1.97 (2)	O(2)–C(5)	1.47 (4)
	μ_2-$OCMe_3$		
Y(1)–O(1)	2.24 (2)	O(1)–C(1)	1.49 (3)
Y(1)–O(1′)	2.26 (2)		
	Y–Cl		
Y(1)–Cl(1)	2.781 (9)		
	THF		
Y(1)–O(3)	2.37 (2)	O(3)–C(9)	1.47 (4)
Y(1)–O(4)	2.36 (2)	O(3)–C(12)	1.39 (5)
		O(4)–C(13)	1.44 (4)
		O(4)–C(16)	1.40 (4)
	Angles		
Y(1)–O(2)–C(5)		176 (2)	

of **1** with $AgBPh_4$ in the dark followed by treatment of the mixture of **1**–**3** with $NaBPh_4$. Pure **3** can be obtained from the toluene extract of this reaction in approximately 75% yield by this route.

Structure of 3. The structure of the cation in **3**, shown in Figure 2, is the first crystallographically characterized bimetallic yttrium *tert*-butoxide complex. The complex is comprised of two $Y(OR)(THF)_2$ units that are connected by two alkoxide bridges and one chloride bridge. Each metal center is six-coordinate as is common for yttrium *tert*-butoxides. The ligands around each metal describe a distorted octahedron with an 89.3° average angle between cis ligands and a 74.8°–110.3° range. The two octahedra are faced fused such that the bridging chloride ligand is trans to the terminal alkoxide ligand attached to each metal.

Although the bimetallic nature of **3** is unusual, the overall structure is not so strange if one considers it as a fragment of the $Y_3(\mu_3\text{-}OR)(\mu_3\text{-}X)(\mu\text{-}OR)_3$ unit common to the yttrium *tert*-butoxides **1**, **2** and **5**–**7**. The similarity of the bond distances and angles in **3** (Table IV) to those in **1**, **2** and **5**–**7** is consistent with this close relationship.

Synthesis of $[Y(OR)Cl(THF)_5][BPh_4]$ (4). The THF-soluble product obtained from reacting **1** with excess $NaBPh_4$ or with 1 equiv of $NaBPh_4$ with long reaction times could be recrystallized to give a product, **4**, that had an unusually simple ^1H NMR spectrum. The spectrum contained only one alkoxide resonance, which was located in the terminal region and which integrated for one alkoxide per BPh_4. X-ray crystallography revealed that **4** was the highly solvated monometallic species $[Y(OR)Cl(THF)_5][BPh_4]$, Figure 3. **4** is unusual in that despite the presence of only two anionic ligands it forms a monometallic rather than a polymetallic complex. Moreover, it retains a chloride ligand despite the halide abstraction conditions under which it was formed.

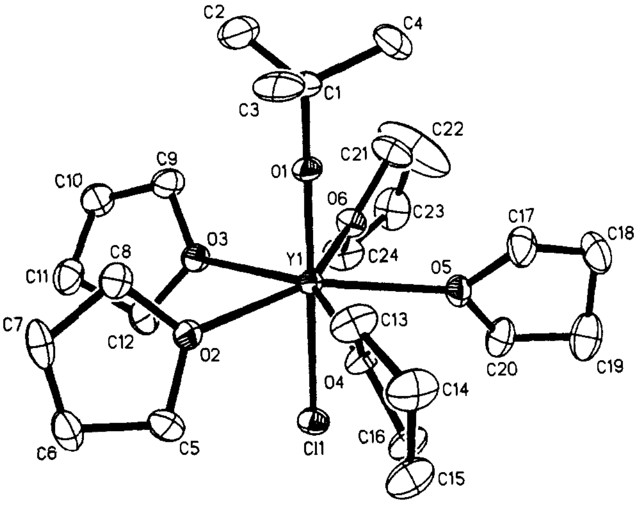

Figure 3. ORTEP diagram of the cation in $[Y(OCMe_3)Cl(THF)_5][BPh_4]$ (**4**) with the probability ellipsoids drawn at the 30% level.

Table V. Bond Distances (Å) and Angles (deg) for $[Y(OCMe_3)Cl(THF)_5][BPh_4]$, **4**

	Distances		
Y(1)–O(1)	2.026 (4)	Y(1)–O(5)	2.422 (5)
Y(1)–O(2)	2.405 (5)	Y(1)–O(6)	2.408 (5)
Y(1)–O(3)	2.411 (5)	Y(1)–O(THF), av	2.41 (1)
Y(1)–O(4)	2.391 (5)	Y(1)–Cl(1)	2.660 (2)
	Angles		
Y(1)–O(1)–C(1)	179.5 (4)	Cl(1)–Y(1)–O(1)	179.0 (1)

Since complex **4** was a simple monometallic yttrium species, attempts were made to prepare it directly from YCl_3. Indeed, **4** can be prepared in high yield by reacting YCl_3 with NaOR and $NaBPh_4$ (eq 4). Because of the high THF content of the product,

$$YCl_3 + NaOR + NaBPh_4 \rightarrow [Y(OR)(Cl)(THF)_5][BPh_4] + 2NaCl \quad (4)$$

this reaction is an interesting case in which the weight of the solid products exceeds the weight of the solid reactants. Trace amounts of **3** were also observed in this reaction.

Structure of 4. The structure of the cation in **4** is similar to that of the pentagonal-bipyramidal $SmI_2(THF)_5^+$ (**8**).[18] Both structures have the anions at axial positions with THF molecules at the five equatorial sites. The Cl(1)–Y(1)–O(1) angle of 179.0 (1)° (Table V) is essentially linear, and the 10 (axial ligand)–Y(1)–O(THF) angles cluster around the 90° angle of a regular pentagonal bipyramid with a range of 84.2 (1)–93.0 (2)°. The 71.9 (7)° average of the O–Y–O angles for adjacent THF molecules matches the 72° idealized angle, and the 71.1 (2)–73.1 (2)° range of values is narrow. As in $SmI_2(THF)_5^+$, the five THF molecules in **4** are canted in a propellor-like fashion around the metal center although the arrangement is not as regular as in **4**.[19]

The 2.41 (1) Å average Y–O(THF) distance (Table V) in **4** is close to that expected when compared to the 2.46 (1) Å average in **8** given that seven-coordinate Y^{3+} is 0.06 Å smaller than seven-coordinate Sm^{3+}.[20] The Y–O(THF) distance is longer than that in the cations **2** and **3** (Tables III and IV) as expected since seven-coordinate Y^{3+} is 0.06 Å larger than six-coordinate Y^{3+}.[20] The $Y–O(OCMe_3)$ distance in **4** is comparable to the terminal alkoxide distances in **1**–**3** and **5**–**7**. Given that the latter complexes all contain six-coordinate yttrium, one might have expected a

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(18) Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620–4623.

(19) The dihedral angles between the plane defined by the five THF oxygen atoms and yttrium and the "average planes" of the five atoms of each THF are 67.7°, 55.9°, 75.2°, 75.6°, and 67.6°.

(20) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

longer Y–O distance in seven-coordinate **4**. On the other hand, the 2.660 (2) Å Y–Cl distance in **4** is unusually long. The terminal Y–Cl distances in eight-coordinate $(C_5Me_5)_2YCl(THF)$[21] and $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$[22] are 2.578 (3) and 2.579 (6) Å, respectively. The distance in seven-coordinate **4** might have been expected to be smaller. In this regard, **4** differs from **8**. The Sm–I distances in **8** are smaller than the terminal Sm–I distance in $(C_5Me_5)_2SmI(THF)$[21] as expected.

Interconversion and Derivatization Reactions Involving 1–4. Since the reaction of **1** with $AgBPh_4$ at 0 °C forms primarily **2** and the same reaction at room temperature forms primarily **3**, it was conceivable that this system followed a **1** → **2** → **3** reaction pathway. Indeed, a **2** to **3** reaction pathway was observed by examining a mixture of **1–3** isolated from a 0 °C reaction. Over a period of days at room temperature, the amount of **2** decreased as **3** increased and **1** remained approximately constant.

NMR studies of this system at room temperature suggest that the system is more complicated, however. The reaction of **1** with $AgBPh_4$ in the absence of light was monitored by NMR over a period of hours, and the results are shown in Table II. Both **2** and **3** are formed within 10 min of mixing **1** and $AgBPh_4$. The amount of **2** does not change greatly after that. **3** forms at the expense of **1** until it comprises about two-thirds of the mixture. The 25:8:67 ratio of **1**:**2**:**3** formed after 70 min remains relatively constant for weeks. A minor product with an alkoxide resonance at δ 1.95 was also observed. This may be due to the μ_3-$OCMe_3$ ligand of an isomer of **1**. Since the rate of formation of **3** from **1** at room temperature is significantly faster than the independently observed **2** to **3** conversion described above, a separate pathway for the formation of **3** from **1** and $AgBPh_4$ appears to exist.

Since unreacted **1** remained at the end of the reaction and since a separate pathway from **1** to **3** was likely, it was possible that the formation of **3** required more than 1 equiv of $AgBPh_4$. Hence, the reaction of **1** with excess $AgBPh_4$ was examined by NMR. However, again a mixture of **1–3** was formed, and the relative ratio of products after 100 min was approximately 30:30:40. The fact that excess $AgBPh_4$ did not eliminate **1** from the mixture suggested that an equilibrium might exist between **1–3** and AgCl. Indeed, independent reactions showed that **2** and **3** react with chloride sources to form **1**. Hence, when a mixture of **2** and **3** was treated with NaCl in THF over a period of days, a mixture containing **1**, as well as **2** and **3**, resulted. The reaction of pure **3** with NaCl in THF formed **1** and **2**, as well as other products that exhibit ^1H NMR alkoxide resonances in the μ_3-OR region (i.e., trimetallic species). Hence, complexes **2** and **3** apparently are also effective halide abstractors.

Studies of the effect of temperature on possible equilibria in the **1**/$AgBPh_4$ product mixture were not definitive. Heating the mixture to 59 °C caused irreversible changes: the amount of **1** increased, the amount of **2** and **3** decreased, and a new NMR peak at δ 1.37 appeared. Reversal of eq 5 would account for the increase

$$Y_3(OR)_7Cl_2(THF)_2 + Ag^+ \rightleftarrows Y_3(OR)_7Cl(THF)_3^+ + AgCl \qquad (5)$$

in **1** and decrease in **2**. The δ 1.37 product could correspond to a symmetrical dimer of the type $[Y(OR)_2(\mu\text{-}Cl)(THF)_2]_2$, which would form from addition of chloride to **3**, e.g., from the abstraction of chloride from AgCl by **3**. Since a pure sample of the δ 1.37 material has not been obtainable so far, this remains unconfirmed. Cooling an NMR sample of a mixture of **1–3**, AgCl, and $AgBPh_4$ generated from **1** and 2 equiv of $AgBPh_4$ at room temperature for 100 min caused little change in the **1**:**2**:**3** ratio. Examination of this sample for prolonged periods at −2 °C and at room temperature caused little change.

When reactions were run in the light, the chemistry became even more complicated. The reaction mixtures changed from light tan to dark brown, *tert*-butyl alcohol was formed, and the δ 1.37 product appeared. Given the photosensitivity of silver salts,[23] this is not unusual.

The abstraction of chloride from AgCl and NaCl by **2** and **3** suggested that these yttrium *tert*-butoxide complexes could have a significant "halophilicity". As a further test of the halophilicity of these cations, the reaction of **4** with $NaOCMe_3$ was attempted to see if the terminal chloride could be replaced by alkoxide. No evidence for $Y(OCMe_3)_2(THF)_5^+$ was observed. Instead, the formation of trimetallic complexes (as evidenced by new NMR peaks in the μ_3-OR region) was observed.

Discussion

Previous studies of the reactivity of the neutral trimetallic yttrium *tert*-butoxide complexes $Y_3(\mu_3\text{-}Cl)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_3Cl(THF)_2$ (**1**) and $Y_3(\mu_3\text{-}Cl)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_4(THF)_2$ (**5**) with NaOR (R = CMe_3) showed that (a) the trimetallic units maintain their structural integrity during reactions (to the extent that **1** reacts with NaOR to form a single isomer of **5**) and (b) the terminal chloride ligand in **1** is more reactive than the triply bridging chloride ligands in **1** and **5**.[4] Consistent with this, $AgBPh_4$ does not react readily with **5**, whereas it abstracts chloride from **1** to generate **2** (reaction 1). Hence, the formation of the trimetallic cation **2** is the result expected from this reaction. The structure of **2**, which is just that of **1** with THF in the place of the terminal chloride ligand, is the most likely if the reaction involves direct abstraction of the terminal chloride ion. It is possible that the triply bridging chloride ligand is abstracted and rearrangement subsequently occurs, but this seems less likely in view of the reactivity of **1** with NaOR.[4]

The formation of $Y_2(OR)_4Cl(THF)_4^+$ from **1** and $AgBPh_4$ was unexpected. All previously known neutral yttrium *tert*-butoxide complexes had displayed at least a trimetallic nuclearity and the $Y_3(\mu_3\text{-}OR)(\mu_3\text{-}X)(\mu\text{-}OR)_3$ unit appeared to be a prevalent, stable, building block for this class of compounds.[3,4] Apparently, the chemistry of the cations is different. The fact that the structure of $Y_2(OR)_4Cl(THF)_4^+$ is similar to a two-yttrium fragment of **1** or **2** provides a formal connection between the complexes. Indeed, schemes for the formation of trimetallic species such as **1** and **5** from bimetallic precursors such as **2** have been discussed.[3,24] The facile formation of **3** from **1** and the reversibility of this reaction with NaCl suggest that these $Y_2L_a + YL_b \rightleftharpoons Y_3L_c$ conversions are quite reasonable under the appropriate conditions.

^1H NMR studies of the reaction of **1** with $AgBPh_4$ show that this is a complicated reaction system and that secondary reactions occur due to heat and light (as is common for silver-containing systems) and due to the presence of halide-containing byproducts. A detailed analysis of this reaction is not available at this time. Although it has been shown that **3** will form directly from **2**, the data on the composition of the **1**/$AgBPh_4$ reaction mixture suggest that there also is a direct **1** to **3** pathway. Hence, the initial chloride abstraction from **1** could form a reactive species, such as $Y_3(OR)_7Cl(THF)_2^+$, which could react in more than one way. This sterically unsaturated intermediate could add THF to form **2**, or it could fragment to form **3** and other products. The reformation of **1** from **3** and NaCl must be a more complicated reaction.

The formation of bimetallic **3** from trimetallic **1** and **2** suggested that some monometallic species could be generated in this system. Despite this, the formation of **4** was surprising. One might have expected that monometallic $Y(OR)_aCl_b(THF)_c$ units would oligomerize to insoluble material rather than to form a pentasolvated cation such as $Y(OR)Cl(THF)_5^+$. The cationic nature of this species may be responsible for its stability. In fact, complex **4** and the cation $SmI_2(THF)_5^+$ may be part of a general class of stable $LnX_2(THF)_5^+$ species.

The fact that both **3** and **4** retain halide ligands under halide abstraction conditions is another unusual aspect of this chemistry.

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[21] Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614–3619.

[22] Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554–559.

[23] For example, see: Baggett, N. In *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*; Barton, D., Ollis, W. D., Eds.; Pergamon: New York, 1979; Chapter 4.3.

[24] Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4454–4460.

Indeed, taken with the fact that the $Y_3(OR)_7Cl_2(THF)_2$ to $Y_{14}(OR)_{28}Cl_{10}O_2(THF)_4$ conversion is quantitative in retaining chloride, one could begin to develop an argument that halophilicity is an important factor in yttrium *tert*-butoxide systems. The formation of $Y_3(OR)_8Cl(THF)_2$ instead of $Y_3(OR)_9(THF)_2$ (analogous to $La_3(OR)_9(THF)_2$[3]) from the reaction of YCl_3 with 3NaOR can be explained in terms of steric factors. The formation of $Y(OR)Cl(THF)_5^+$ instead of $Y(OR)_2(THF)_5^+$ cannot be explained in this way. Neither can steric arguments explain the reluctance of **4** to react with NaOR to form $Y(OR)_2(THF)_5^+$.

The importance of halophilicity is likely to be part of a more general set of principles for yttrium and lanthanide alkoxide chemistry that will be revealed as more chemistry is developed. These undoubtedly will help explain the complicated reaction chemistry observed in this system.

Conclusion

The synthesis of the cationic *tert*-butoxide complexes **2–4** has considerably broadened the scope of known yttrium alkoxide chemistry in terms of structural types and reactivity patterns. The identification of bimetallic and highly solvated monometallic complexes in an area previously dominated by trimetallic species demonstrates the importance of the net charge on yttrium alkoxide complexes in governing the chemistry. More generally, this suggests that the amount of ligand electron density that is delivered to the metal will significantly influence which complexes are formed and how they will react.

In terms of reactivity, these studies have reinforced the idea that a terminal chloride ligand can be a reactive entry point to chemical derivatization. In addition, these reactions have demonstrated that monometallic and bimetallic intermediates are available and can be isolated for use as starting materials in subsequent synthesis. The utility of these cationic complexes in the synthesis of heteropolymetallic complexes is under study.

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Supplementary Material Available: Tables of crystal data, ORTEP diagrams, atomic positional parameters, bond distances and angles, thermal parameters, and hydrogen atom coordinates for the yttrium complexes (37 pages); listing of structure factor amplitudes (72 pages). Ordering information is given on any current masthead page.

Reactivity of $(C_5Me_5)_2Sm$ and Related Species with Alkenes: Synthesis and Structural Characterization of a Series of Organosamarium Allyl Complexes[1]

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Abstract: The reactivity of $(C_5Me_5)_2Sm$ (**1**) with alkenes has been examined and compared with that of $(C_5Me_5)_2Sm(THF)_2$ (**2**) and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (**3**). **1** reacted rapidly with a variety of alkenes in hexane or toluene to form allyl complexes and alkane byproducts. Reactions with propene, butene, and allylbenzene formed $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**4**), $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (**5**), and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)$ (**6**), respectively, in 85–95% yield. Complexes **4–6** were also prepared in similar yield from **3** and the appropriate alkene in hexane. The corresponding alkane was again the byproduct. Reactions of **3** with these alkenes in toluene formed $(C_5Me_5)_2Sm(CH_2C_6H_5)$ exclusively. **1** reacted with 1,3-butadiene and 1,5-hexadiene to form the bis-allyl complexes $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (**7**) and $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH\text{-})]_2$ (**8**). In contrast, **3** reacted with butadiene to form **5**. **2** reacts like **1** with allylbenzene and 1,3-butadiene to form **6** and **7**. **2** is not very reactive with propene and forms complex mixtures of products with butene and 1,5-hexadiene. Complex **4** crystallizes from hexane in the tetragonal space group $I\bar{4}$ (no. 82; S_4^2) with unit cell parameters a = 23.1043 (36) Å, c = 8.4586 (12) Å, V = 4515 (1) Å^3, and Z = 8 for D_{calcd} = 1.36 g cm^{-3}. Least-squares refinement of the model based on 1894 observed reflections converged to R_F = 4.7%. Complex **5** crystallizes from hexane in the monoclinic space group $P2_1/n$ with unit cell parameters a = 15.9367 (41) Å, b = 17.7780 (32) Å, c = 16.7024 (48) Å, β = 101.381 (20)°, V = 4639 (2) Å^3, and Z = 8 for D_{calcd} = 1.36 g cm^{-3}. Least-squares refinement of the two crystallographically independent molecules based on 4688 observed reflections converged to R_F = 7.5%. Complex **6** was crystallized from hexane at −34 °C as the 1,3-dihydroisobenzofuran adduct $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)(OC_8H_8)$, **6′**, in the monoclinic space group $P2_1/c$ with unit cell parameters a = 10.3851 (16) Å, b = 17.357 (3) Å, c = 17.703 (2) Å, β = 95.785 (12)°, and V = 3174.9 (8) Å^3 with Z = 4 for D_{calcd} = 1.38 g cm^{-3}. Least-squares refinement of the model based on 6964 observed reflections converged to R_F = 3.1%. Complex **7** crystallizes from toluene/hexane in the orthorhombic space group *Pbca* (no. 61; D_{2h}^{15}) with unit cell parameters a = 16.5911 (26) Å, b = 29.8565 (49) Å, c = 18.0130 (25) Å, V = 8923 (2) Å^3, and Z = 8 for D_{calcd} = 1.41 g cm^{-3}. Least-squares refinement of the model based on 4134 observed reflections converged to R_F = 6.9%. Complex **8** crystallizes from hexane in the monoclinic space group $P2_1/c$ with unit cell parameters a = 13.953 (12) Å, b = 8.445 (4) Å, c = 18.635 (10) Å, β = 102.85 (5)° and V = 2143 (2) Å^3 with Z = 2 for D_{calcd} = 1.43 g cm^{-3}.

The reduction, oligomerization, and polymerization of alkenes is an important area of chemistry and efforts are continually being made to develop better methods to manipulate these unsaturated hydrocarbon substrates.[2] Recently, we initiated a study[1,3] of the reactivity of $(C_5Me_5)_2Sm$ (**1**)[4] with alkenes both to determine if

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(1) Reported in part at the 193rd ACS National Meeting, Denver, CO, April 1987, INOR 315, the 2nd International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements, Lisbon, Portugal, April 1987, L(II) 1, the 194th ACS National Meeting, New Orleans, LA, INOR 262, and the 196th ACS National Meeting, Los Angeles, CA, Sept. 1988, INOR 377.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; and references therein.

(3) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292–4297.

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