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Synthesis, Structure, and Reactivity of Dimeric Mono(cyclopentadienyl)yttrium Bis(*tert*-butoxide) Complexes: $[(C_5R_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ (C_5R_5 = C_5Me_5, C_5H_5, C_5H_4Me, $C_5H_4SiMe_3$, and C_9H_7)[1]

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The reaction of $Y_3(OR)_7Cl_2(THF)_2$ (R = CMe_3) with alkali metal cyclopentadienyl reagents, MC_5R_5 (M = Na or K), in toluene disrupts the trimetallic structure of the starting material and forms the halide-free bimetallic compounds $[(C_5R_5)Y(\mu\text{-}OR)(OR)]_2$ (C_5R_5 = C_5Me_5, **1**; C_5H_5, **2**; C_5H_4Me, **3**; $C_5H_4SiMe_3$, **4**). **1** and **4** were also obtained from the reaction of $YCl_3(THF)_x$ with 2 equiv of $NaOCMe_3$ and 1 equiv of MC_5R_5 in toluene at reflux. Also prepared in this manner was the indenyl analog, $[(C_9H_7)Y(\mu\text{-}OR)(OR)]_2$, **5**. X-ray crystallographic data on **1**, **2**, **4**, and **5** reveal that structurally analogous complexes are formed in these reactions despite the different substituents on the cyclopentadienyl rings. In each of these four complexes, the two cyclopentadienyl ligands are arranged in a *cis* orientation around a $(RO)Y(\mu\text{-}OR)_2Y(OR)$ central core which has similar metrical parameters in each compound. The ligand redistribution product $(C_5H_5)_2Y(\mu\text{-}OR)_2Y(C_5H_5)(OR)$, **6**, is also isolated as a minor component in the reaction between $Y_3(OR)_7Cl_2(THF)_2$ and NaC_5H_5. **2**–**5** react with $LiCH_2SiMe_3$ to unexpectedly lose LiC_5R_5 instead of LiOR. Crystallization of the **2**/$LiCH_2SiMe_3$ reaction product in the presence of dimethoxyethane (DME) yields the cyclopentadienyl-free complex $(RO)Y(\mu\text{-}OR)_3Li_5(\mu_3\text{-}OR)_2(THF)(\mu\text{-}OCH_2CH_2OMe)_2$, **7**. **7** can be viewed as a $(RO)Y(\mu\text{-}OR)[(\mu\text{-}OR)_2Li(THF)]$ unit connected to a Li_4O_4 cube which has oxygen donor atoms provided by bridging *tert*-butoxide ligands and two bidentate ligands formally derived from DME by loss of a methyl group. In the reaction of **4** with $LiCH_2SiMe_3$, the cyclopentadienyl component is recovered in a crystalline form as the polymeric, supersandwich metallocene, $[Li(\mu,\eta^5,\eta^5\text{-}C_5H_4SiMe_3)]_n$, **8**. **4** reacts with $LiN(SiMe_3)_2$ by a ligand redistribution pathway to form $(C_5H_4SiMe_3)_2Y(\mu\text{-}OR)_2Li(THF)_2$, **9**. **1** crystallized from hexanes at −35 °C in space group $P2_1/c$ with a = 12.657(3) Å, b = 17.412(5) Å, c = 18.532(5) Å, β = 99.16(2)°, V = 4032(2) Å^3, and D_{calcd} = 1.22 Mg/m^3 for Z = 4. Least squares refinement of the model based on 3296 reflections ($|F_o| > 6.0\sigma(|F_o|)$) converged to a final R_F = 8.8%. **2** crystallized from toluene or hexanes at −35 °C in space group $P\bar{4}2_1m$ with a = 9.7738(13) Å, c = 16.133(4) Å, V = 1541.1(5) Å^3, and D_{calcd} = 1.29 Mg/m^3 for Z = 2. Least squares refinement of the model based on 888 reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final R_F = 7.3%. **4** crystallized from toluene at −35 °C in space group $P2_1/c$ with a = 20.697(4) Å, b = 10.1222(14) Å, c = 21.264(4) Å, β = 114.328(13)°, V = 4059.2(12) Å^3, and D_{calcd} = 1.219 Mg/m^3 for Z = 4. Least squares refinement of the model based on 3724 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final R_F = 6.7%. **5** crystallized from hexanes at −35 °C in the space group $P2_1/c$ with a = 13.231(2) Å, b = 15.481(3) Å, c = 17.516(5) Å, β = 99.91(2)°, V = 3534.0(13) Å^3, and D_{calcd} = 1.317 Mg/m^3 for Z = 4. Least squares refinement of the model based on 3229 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final R_F = 6.8%. **9** crystallized from hexanes at −35 °C in space group $P2_1/c$ with a = 17.285(12) Å, b = 13.022(11) Å, c = 17.30(2) Å, β = 104.63(7)°, V = 3767(6) Å^3, and D_{calcd} = 1.165 Mg/m^3 for Z = 4. Least squares refinement of the model based on 2159 reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final R_F = 8.1%.

Introduction

Recent studies evaluating the utility of the *tert*-butoxide group as a robust coligand alternative to cyclopentadienyl ligands in yttrium and lanthanide complexes have revealed an extensive polymetallic chemistry for these elements.[2–9] Complexes with three to fourteen metals have been crystallographically characterized with the predominant structural unit being the trimetallic moiety "$Ln_3(OR)_3(\mu\text{-}OR)_3(\mu_3\text{-}OR)(\mu_3\text{-}Z)Z(L)_2$" (Ln = Y or lanthanide; R = CMe_3; Z = OR, O, or halide; L = THF, ROH).[3–7] The initial synthetic and structural studies on these *tert*-butoxide complexes suggested that this readily-formed

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trimetallic unit would be present whenever these metals were ligated with two or more *tert*-butoxide ligands.

However, we have recently found that trimethylaluminum disrupts these trimetallic structures forming monoyttrium species such as $Y[(\mu\text{-}OR)(\mu\text{-}Me)AlMe_2]_3$, $(RO)(THF)Y[(\mu\text{-}OR)(\mu\text{-}Me)AlMe_2]_2$, and $(RO)(Cl)(THF)_2Y(\mu\text{-}OR)_2AlMe_2$.[10] As part of an investigation of the basic organometallic chemistry of the trimetallic yttrium *tert*-butoxide complexes and to further test the stability of the trimetallic framework, a study of the reactivity of $Y_3(OR)_7Cl_2(THF)_2$ with alkali metal cyclopentadienyl complexes was undertaken.

Cyclopentadienyl reagents were chosen for two reasons. First, since the chemistry of cyclopentadienyl systems has been extensively studied,[11,12] the results of our investigation can be readily compared with data in the literature. Such comparisons are needed to evaluate the *tert*-butoxide group as a coligand for these metals vis-a-vis cyclopentadienyl groups.[3] Second, the polyhapto nature of cyclopentadienyl reagents had the potential to strain the trimetallic structure into fragmentation.

$Y_3(OR)_7Cl_2(THF)_2$ was chosen as the trimetallic reagent since it possesses a terminal chloride ligand and can be considered[4] the trimetallic *tert*-butoxide analog of the common cyclopentadienyl starting material $(C_5H_5)_2YCl(THF)$. Hence, in a sense this *tert*-butoxide reaction system is analogous to the conversion of $(C_5H_5)_2YCl(THF)$ to $(C_5H_5)_3Y(THF)$.[12] A further objective of this study was to test the tendency of these trimetallic *tert*-butoxide complexes to retain halide ligands, a trend which has been previously observed in several systems.[3,4,6,7]

We report here that the trimetallic structure of $Y_3(OR)_7Cl_2(THF)_2$ is not maintained in reactions with cyclopentadienyl reagents. Instead, a new series of bimetallic yttrium *tert*-butoxide products is formed which is unusual in both structure and reactivity. Each member of the series contains a central $(RO)Y(\mu\text{-}OR)_2Y(OR)$ core which is surprisingly structurally invariant despite the size of the attached cyclopentadienyl ligands. The $[(C_5R_5)Y(\mu\text{-}OR)(OR)]_2$ complexes react with alkyllithium reagents to unexpectedly lose cyclopentadienyl ligands rather than alkoxide ligands and the resulting products appear to be quite reactive.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were dried and physical measurements were obtained as previously described.[13] NMR spectra were obtained on General Electric GN and Omega 500-MHz spectrometers at ambient temperature. YCl_3[14] (Rhône-Poulenc), $Y_3(OR)_7Cl_2(THF)_2$ ($R = CMe_3$),[4] and $NaOCMe_3$,[3] were prepared as previously described. The MC_5R_5 reagents were prepared from the diene and the metal or the metal hydride by standard procedures.[15] $LiN(SiMe_3)_2$ was prepared from *n*-BuLi (Aldrich) and $HN(SiMe_3)_2$ (Aldrich) in hexanes.

$[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 1. Method A. In a glovebox, NaC_5Me_5 (0.36 g, 2.3 mmol) was added to $Y_3(OR)_7Cl_2(THF)_2$ (0.75 g, 0.76 mmol) in toluene (12 mL) in a 25-mL Schlenk flask fitted with a reflux condensor. The flask was attached to a Schlenk line, and the mixture was heated at reflux for 12–18 h. After cooling to room temperature, the solvent was removed by rotary evaporation and the resulting white powder was extracted with hexanes. The extract was concentrated and cooled to −35 °C for 4 h. Colorless crystals were formed which were acceptable for X-ray crystallographic studies (0.58 g, 70%). ^1H NMR: (C_6D_6) δ 2.19 (s, 15H, $C_5\mathit{Me}_5$), 1.32 (s, 18H, $OC\mathit{Me}_3$); (C_6D_{12}) δ 2.09 (s, 15H, $C_5\mathit{Me}_5$), 1.39 (s, 9H, $OC\mathit{Me}_3$), 1.13 (s, 9H, $OC\mathit{Me}_3$); (toluene-*d*$_8$) δ 2.17 (s, 15H, $C_5\mathit{Me}_5$), 1.33 (s, 9H, $OC\mathit{Me}_3$), 1.29 (s, 9H, $OC\mathit{Me}_3$). ^{13}C NMR: (C_6D_6) δ 117.5 (C_5Me_5), 72.0 ($O\mathit{C}Me_3$), 34.5 ($OC\mathit{Me}_3$), 33.5 ($OC\mathit{Me}_3$), 12.5 ($C_5\mathit{Me}_5$); (C_6D_{12}) δ 118.0 (C_5Me_5), 72.5 ($O\mathit{C}Me_3$), 34.6 ($OC\mathit{Me}_3$), 34.0 ($OC\mathit{Me}_3$), 12.6 ($C_5\mathit{Me}_5$). IR (KBr): 2875 (s), 2969 (s), 1457 (w), 1384 (w), 1374 (w), 1354 (m), 1281 (m), 1240 (m), 1205 (m), 1180 (s), 1098 (w), 1057 (s), 1010 (w), 934 (m), 913 (w), 802 (w) cm^{-1}. Anal. Calcd for $C_{36}H_{66}O_4Y_2$: C, 58.37; H, 8.98; Y, 24.00. Found: C, 58.17; H, 8.73; Y, 24.35.

Method B. In a glovebox, YCl_3 (0.85 g, 4.35 mmol) was stirred in 20 mL of THF in a Schlenk flask for 10 min and the solvent was removed by rotary evaporation. To a slurry of this material in toluene (50 mL) were slowly added $NaOCMe_3$ (0.82 g, 8.73 mmol) and KC_5Me_5 (0.76 g, 4.35 mmol) as solids. A condensor was attached to the flask, and the mixture was heated at reflux for 12 h. Removal of solvent and extraction with hexanes gave 1 (1.0 g, 65%).

$[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 2. The reaction of $Y_3(OR)_7Cl_2(THF)_2$ (0.20 g, 0.20 mmol) and NaC_5H_5 (0.053 g, 0.60 mmol) was run for 6 h as described above for 1 (method A) and produced a hexane extract of 2 in 80% yield (150 mg). This reaction was run for a shorter time than that of 1, since other products, which are yellow, form after 6 h. The formation of this yellow color is reproducible, and the observation of a yellow tinge in the white reaction mixture can be used as an end point indicator to signal that the reaction should be stopped. Crystallization of the hexane soluble fraction from a concentrated hexanes solution at −35 °C yields crystals which are unacceptable for X-ray studies; however, adequate crystals were grown from toluene at −35 °C (120 mg, 68%). This compound decomposes after several hours in toluene at ambient temperature. Decomposition in the solid state occurs after approximately 1 week in a glovebox. ^1H NMR (C_6D_6): δ 6.44 (s, 5H, $C_5\mathit{H}_5$), 1.24 (s, 9H, $OC\mathit{Me}_3$), 1.16 (s, 9H, $OC\mathit{Me}_3$). Anal. Calcd for $C_{26}H_{46}O_4Y_2$: C, 52.00; H, 7.72; Y, 29.61. Found: C, 51.80; H, 7.58; Y, 29.80.

$[(C_5H_4Me)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 3. 3 was prepared from $Y_3(OR)_7Cl_2(THF)_2$ (0.35 g, 0.35 mmol) and NaC_5H_4Me (0.18 g, 1.1 mmol) as described above for 1 (method A) except that the reaction was heated at reflux for only 6 h. This system also is more sensitive to the duration of heating time than 1, and the reaction mixture begins to turn yellow after approximately 7 h at reflux. 3 was isolated as a white powder after removal of solvent by rotary evaporation (235 mg, 70%). Crystals were grown from hexanes at −35 °C. 3 decomposes in solution within 12 h at room temperature. ^1H NMR: (C_6D_6) δ 6.33 (m, 2H, $C_5\mathit{H}_4Me$), 6.18 (m, 2H, $C_5\mathit{H}_4Me$), 2.37 (s, 3H, $C_5H_4\mathit{Me}$), 1.22 (s, 18H, $OC\mathit{Me}_3$); (C_6D_{12}) δ 6.18 (m, 2H, $C_5\mathit{H}_4Me$), 6.07 (m, 2H, $C_5\mathit{H}_4Me$), 1.39 (s, 3H, $C_5H_4\mathit{Me}$), 1.32 (s, 18H, $OC\mathit{Me}_3$). ^{13}C NMR (C_6D_6): δ 112.0 (C_5H_4Me), 111.2 (C_5H_4Me), 72.9 ($O\mathit{C}Me_3$), 34.2 ($OC\mathit{Me}_3$), 33.4 ($OC\mathit{Me}_3$), 15.5 ($C_5H_4\mathit{Me}$).

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[(C$_5$H$_4$SiMe$_3$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$, 4. Method A. 4 was prepared from Y$_3$(OR)$_7$Cl$_2$(THF)$_2$ (0.50 g, 0.50 mmol) and KC$_5$H$_4$SiMe$_3$ (0.27 g, 1.5 mmol) in 15 mL of toluene as described above for 1 except that the reaction was heated only 7 h. After approximately 8 h at reflux, the white solution becomes increasingly yellow and large amounts of hexane soluble impurities are present. 4 is initially isolated as an oil, but it can be obtained as a powder by drying the oil in vacuo for several hours (0.46 g, 80%). X-ray quality crystals were grown from toluene at −35 °C. ^{1}H NMR (C$_6$D$_6$): δ 6.66 (s, 4H, C$_5$*H*$_4$SiMe$_3$), 1.26 (s, 18H, OC*Me*$_3$), 0.42 (s, 9H, C$_5$H$_4$Si*Me*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 118.9 (*C*$_5$H$_4$SiMe$_3$), 115.5 (*C*$_5$H$_4$SiMe$_3$), 72.6 (*O*CMe$_3$), 71.7 (OCMe$_3$), 34.2 (OC*Me*$_3$), 33.0 (OC*Me*$_3$), 0.93 (C$_5$H$_4$Si*Me*$_3$). Anal. Calcd for $C_{32}H_{61}O_4Y_2$: C, 51.60; H, 8.39; Cl, 0.00; Si, 7.54; Y, 23.87. Found: C, 51.34; H, 8.33; Cl, <0.05; Si, 7.60; Y, 24.15.

Method B. In a glovebox, YCl$_3$ (0.30 g, 1.5 mmol) was stirred in 5–10 mL of THF in a Schlenk flask for 10 min and the solvent was removed by rotary evaporation. To a slurry of this material in toluene were slowly added, NaOCMe$_3$ (0.30 g, 3.1 mmol) and KC$_5$H$_4$SiMe$_3$ (0.27 g, 1.5 mmol) as solids. A condensor was attached to the flask, and the mixture was heated at reflux for 6 h. Removal of solvent and extraction gave a slightly lower yield of 4 than was obtained from method A (0.41 g, 72%), but this initially-obtained product is a solid which can be used without further purification.

[(C$_9$H$_7$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$, 5. 5 was isolated in 73% yield (0.88 g) from YCl$_3$ (0.67 g, 3.4 mmol), NaOCMe$_3$ (0.50 g, 6.8 mmol), and KC$_9$H$_7$ (0.53 g, 3.4 mmol) as described above for 1 (method B). ^{1}H NMR (THF-d_8): δ 7.50 (m, 2H, C$_9$*H*$_7$), 6.90 (m, 2H, C$_9$*H*$_7$), 6.40 (t, 2H, C$_9$*H*$_7$, *J* = 3 Hz), 5.92 (d, 1H, C$_9$*H*$_7$, J = 3 Hz), 1.070, 1.065 (s, s, 18H, OC*Me*$_3$). ^{13}C NMR (THF-d_8): δ 128.5 (C$_9$H$_7$), 123.3 (C$_9$H$_7$), 120.6 (C$_9$H$_7$), 119.8 (C$_9$H$_7$), 97.8 (C$_9$H$_7$), 73.3 (*O*CMe$_3$), 34.1 (OC*Me*$_3$). IR (KBr pellet): 2957 (s), 2960 (s), 1456 (w), 1365 (w), 1355 (w), 1329 (w), 1203 (s), 1012 (m), 992 (m), 931 (w), 921 (w), 768 (m) cm^{-1}. 5 was crystallized from hexanes at −35 °C. Anal. Calcd for $C_{34}H_{50}O_4Y$: Y, 25.38. Found: Y, 26.1.

(C$_5$H$_5$)$_2$Y(μ-OCMe$_3$)$_2$Y(C$_5$H$_5$)(OCMe$_3$), 6. 6 was fortuitously crystallized from hexane at −35 °C in low yield as a hexane soluble byproduct in the preparation of 2. ^{1}H NMR (C$_6$D$_6$): δ 6.41 (s, 5H, C$_5$*H*$_5$), 6.17 (s, 5H, C$_5$*H*$_5$), 6.15 (s, 5H, C$_5$*H*$_5$), 1.32 (s, 9H, OC*Me*$_3$), 1.13 (s, 18H, OC*Me*$_3$).

(Me$_3$CO)Y(μ-OCMe$_3$)$_3$Li$_5$(μ_3-OCMe$_3$)$_2$(THF)(μ-OCH$_2$CH$_2$OMe)$_2$, 7. In a glovebox, a solution of LiCH$_2$SiMe$_3$ in hexanes (0.39 mL of a 1.0 M solution (Aldrich), 0.39 mmol) was added by syringe to [(C$_5$H$_5$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$ (0.12 g, 0.20 mmol) dissolved in hexanes. A white precipitate formed immediately. After the reaction mixture was stirred for 12 h, the solvent was removed by rotary evaporation and the resulting oil (0.14 g) was extracted with hexanes. The solvent was removed, the resulting oil was dissolved in a minimum of hexanes, and the solution was cooled to −35 °C. When crystals failed to form, the solvent was removed and crystallization from approximately 2 mL of THF was tried unsuccessfully. To this mixture was added ten drops of dimethoxyethane (DME). After approximately 1 week at −35 °C, small crystals formed. One of these was identified by X-ray crystallography as 7.

(C$_5$H$_4$SiMe$_3$)$_2$Y(μ-OCMe$_3$)$_2$Li(THF)$_2$, 9. In a glovebox, [(C$_5$H$_4$SiMe$_3$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$ (0.32 g, 0.86 mmol) was added to LiN(SiMe$_3$)$_2$ (0.29 g, 1.7 mmol) dissolved in 5 mL of hexanes. The reaction mixture was stirred for 8–12 h, and a precipitate formed. The solvent was removed by rotary evaporation, and the resulting solid was extracted with hexanes. Removal of solvent gave a powder (0.43 g). A concentrated solution of this powder in hexanes at −35 °C yielded crystals of 9. ^{1}H NMR (C$_6$D$_6$): δ 6.70 (t, 2H, C$_5$*H*$_4$SiMe$_3$, *J* = 4 Hz), 6.51 (t, 2H, C$_5$*H*$_4$SiMe$_3$, *J* = 4 Hz), 3.56 (m, OC*Me*$_3$, *THF*), 1.24 (m, *THF*), 0.49 (s, 18H, C$_5$H$_4$Si*Me*$_3$), 0.37 (s, Y(N(Si*Me*$_3$)$_2$)$_3$).

X-ray Data Collection, Structure Determination, and Refinement. For [(C$_5$Me$_5$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$, 1. Under nitrogen, a pale yellow-gold crystal of approximate dimensions 0.40 × 0.43 × 0.47 mm was immersed in Paratone-D oil.[16] The oil-coated crystal was then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Siemens P3 diffractometer (R3m/V system) which is equipped with a modified LT-2 low-temperature system. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (173 K) intensity data were carried out using standard techniques similar to those of Churchill.[17] Details appear in Table I.

All 5841 data were corrected for absorption and for Lorentz and polarization effects, merged to yield a unique data set, and placed on an approximately absolute scale. The diffraction symmetry was 2/*m* with systematic absences for 0*k*0 where $k = 2n + 1$ and *h*0*l* for $l = 2n + 1$. The centrosymmetric space group $P2_1/c$[C^5_{2h}; No. 14] is therefore uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[18] or the SHELXTL PLUS program set.[19] The analytical scattering factors for neutral atoms were used throughout the analysis;[20a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[20b] were included. The quantity minimized during least squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0007(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL) and refined by full-matrix least squares techniques. Hydrogen atoms were included using 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 carbon atoms) led to convergence with R_F = 8.8%, R_{wF} = 11.3%, and GOF = 2.86 for 200 variables refined against those 3296 data with $|F_o| > 6.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 1.44 e Å^{-3} at a distance of 0.82 Å from C(2).

For [(C$_5$H$_5$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$, 2. A colorless crystal of approximate dimensions 0.20 × 0.24 × 0.33 mm was handled as described above for 1. Details appear in Table I. The 1649 data were handled as described for 1. Any reflection with I(net) < 0 was assigned the value of $|F_o| = 0$. Systematic absences revealed the space group to be the noncentrosymmetric tetragonal $P\bar{4}2_1m$ [D^3_{2d}; No. 113] or $P42_12$ [D^2_4; No. 90]. It was later determined that the structure is best described in space group $P\bar{4}2_1m$.

The structure was solved by direct methods (SHELXTL) and refined by full-matrix least squares techniques. The molecule is located on a *mm* symmetry site at (1/2,0, *z*). The C(7)–C(8) and C(7)–C(9) distances were fixed at 1.50 Å in order to model disorder which is probably caused by the location of the molecule on the mirror planes. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and thermal parameters led to convergence with R_F = 7.3%, R_{wF} = 8.5%, and GOF = 1.79 for 76 variables refined against those 888 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 1.39 e Å^{-3}.

For [(C$_5$H$_4$SiMe$_3$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$, 4. A colorless crystal of approximate dimensions 0.20 × 0.40 × 0.47 mm was handled as described for 1 and examined on a Syntex P2$_1$ automated four-circle diffractometer which is equipped with a modified LT-1 low-temperature system. Details appear in Table I. The 5874 data were handled as described for 1. The diffraction symmetry was 2/*m* with systematic absences 0*k*0 for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C^5_{2h}; No. 14] is therefore uniquely defined. Refinement of positional and thermal parameters led to convergence with R_F = 6.7%, R_{wF} = 7.3%, and GOF = 1.14 for 361 variables refined against those

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(16) Paratone-d oil is an Exxon lube oil additive.

(17) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, *16*, 265–271.

(18) (a) *UCLA Crystallographic Computing Package*; University of California, Los Angeles, 1981. (b) Strouse, C. Personal communication.

(19) *SHELXTL PLUS*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, (a) pp 99–101, (b) pp 149–150.

(21) Rogers, D. *Acta. Crystallogr.* 1981, *A37*, 734–741.

Table I. Experimental X-ray Data for $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 1, $[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 2, $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 4, $[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 5, and $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2$, 9

compd	1	2	4	5	9
formula	$C_{36}H_{66}O_4Y_2$	$C_{26}H_{46}O_4Y_2$	$C_{32}H_{62}O_4Si_2Y_2$	$C_{34}H_{50}O_4Y_2$	$C_{36}H_{60}LiO_4Si_2Y$
fw	740.7	600.4	744.8	700.6	660.8
temp (K)	173	168	168	163	173
cryst syst	monoclinic	tetragonal	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{4}2_1m$	$P2_1/c$	$P2_1/c$	$P2_1/c$
	$[C^5_{2h}$; No. 14]	$[D^3_{2d}$; No. 113]	$[C^5_{2h}$; No. 14]	$[C^5_{2h}$; No. 14]	$[C^5_{2h}$; No. 14]
α (Å)	12.657(3)	9.7738(13)	20.697(4)	13.231(2)	17.285(12)
β (Å)	17.412(5)	9.7738(13)	10.1222(14)	15.481(3)	13.022(11)
c (Å)	18.532(5)	16.133(4)	21.264(4)	17.516(5)	17.30(2)
β (deg)	99.16(2)		114.32(1)	99.91(2)	104.63(7)
V (Å^3)	4032(2)	1541.4(5)	4059.2(12)	3534.0(13)	3767(6)
Z	4	2	4	4	4
D_{calc} (Mg/m^3)	1.22	1.29	1.219	1.317	1.165
diffractometer	Siemens P3	Siemens P3	Syntex P2$_1$	Siemens P3	Siemens P3
(Mo Kα radiation) (Å)	0.710 730	0.710 730	0.710 730	0.710 730	0.710 730
monochromator	highly oriented graphite	highly oriented graphite	highly oriented graphite	highly oriented graphite	highly oriented graphite
data colled	$+h,+k,\pm l$	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
scan type	θ–2θ	θ–2θ	θ–2θ	θ–2θ	θ–2θ
scan width (deg)	1.20 (plus Kα separation)	1.20 (plus Kα separation)	1.20 (plus Kα separation)	1.20 (plus Kα separation)	1.20 (plus Kα separation)
scan speed (ω)	3.0	3.0	3.0	3.0	3.0
2θ range (deg)	4.0–45.0	4.0–55.0	4.0–45.0	4.0–45.0°	4.0–45.0
μ, (mm^{-1})	2.91	3.8	2.95	3.318	1.647
(Mo Kα) abs corr	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)
no. of reflns colld	5841	1649	5874	5102	3907
no. of reflns with ($\lvert F_o\rvert > X\sigma(\lvert F_o\rvert)$)	3296 ($X = 6$)	888 ($X = 4$)	3724 ($X = 3$)	3229 ($X = 3$)	2159 ($X = 4$)
no. of variables	200	76	361	361	356
R_F (%)	8.8	7.3	6.7	6.8	8.1
R_{wF} (%)	11.3	8.5	7.3	7.9	9.1
goodness of fit	2.86	1.79	1.14	1.23	1.42

3724 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.73$ e Å^{-3}.

For $[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 5. A colorless crystal of approximate dimensions 0.23 × 0.27 × 0.33 mm was handled as described for 1. Details appear in Table I. The 5102 data were handled as described for 1. Refinement of positional and thermal parameters led to convergence with $R_F = 6.8\%$, $R_{wF} = 7.9\%$, and GOF = 1.23 for 361 variables refined against 3229 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.91$ e Å^{-3}.

For $(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)(OCMe_3)$, 6. A colorless crystal of 6 was handled as described for 2. A data set (2θ range 4.0–36.0°) was collected at 173 K, but only the atomic connectivity of the compound could be unambiguously determined. 6 crystallizes from hexanes in space group $P2_1$ with $a = 9.209(3)$ Å, $b = 15.228(8)$ Å, $c = 12.213(4)$ Å, $\beta = 122.89(2)°$, $V = 1438.1(9)$ Å^3, and $D_{calcd} = 1.37$ Mg/m^3 for $Z = 2$. Of the 1237 reflections collected, a least squares refinement of the model based on 851 observed reflections ($|F_o| > 4.0\sigma|F_o|$) converged to a final $R_F = 11.1\%$.

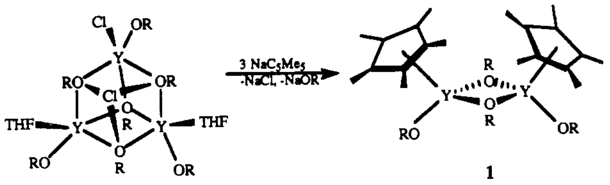
For $(OCMe_3)Y(\mu\text{-}OCMe_3)_3Li_5(\mu_3\text{-}OCMe_3)_2(THF)(\mu\text{-}OCH_2CH_2OMe)_2$, 7. A colorless crystal of approximate dimensions 0.15 × 0.17 × 0.22 mm was mounted under a stream of nitrogen onto a Syntex P2$_1$ diffractometer equipped with a modified LT-1 low-temperature system. A data set (2θ range 4.0–40.0°) was collected at 173 K, but only the atomic connectivity of the compound could be unambiguously determined. 7 crystallizes from a THF/hexane mixture in space group $P\bar{1}$ with $a = 9.575(9)$ Å, $b = 11.893(17)$ Å, $c = 21.388(24)$ Å, $\alpha = 77.60(10)°$, $\beta = 82.29(8)°$, $\gamma = 80.13(10)°$, $V = 2322(5)$ Å^3, and $D_{calcd} = 1.12$ Mg/m^3 for $Z = 2$. Of the 4681 reflections collected, a least squares refinement of the model based on 1548 observed reflections ($|F_o| > 6.0\sigma|F_o|$) converged to a final $R_F = 12.6\%$.

For $(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2$, 9. A colorless crystal of approximate dimensions 0.21 × 0.13 × 0.15 mm was handled as described for 1. Details appear in Table I. The 3907 data were handled as described for 1. Refinement of positional and thermal parameters led to convergence with $R_F = 8.1\%$, $R_{wF} = 9.1\%$, and GOF = 1.42 for 356 variables refined against those 2159 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 0.68$ e Å^{-3}.

Results

Synthesis. $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 1. NaC_5Me_5 reacts with $Y_3(OCMe_3)_7Cl_2(THF)_2$ in toluene over a 48-h period at ambient temperature to form a new hexane soluble product, 1, which has a ^{1}H NMR spectrum much simpler than that of the starting alkoxide complex.[4] Higher yields of 1 are obtained when the reaction stoichiometry is changed to 3 equiv of NaC_5Me_5 per trimetallic alkoxide, and the reaction time can be reduced to 12 h if the reaction is conducted at reflux.

The ^{1}H NMR spectrum of 1 indicated that the trimetallic structure of $Y_3(OR)_7Cl_2(THF)_2$ had been disrupted in this reaction: in C_6D_6, singlets attributable to C_5Me_5 and $OCMe_3$ were observed with a 1:2 C_5Me_5:$OCMe_3$ ratio. Elemental analysis was also consistent with a "$(C_5Me_5)Y(OCMe_3)_2$" empirical formula. X-ray crystallography identified the complex as $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 1 (Figure 1 and eq 1). Lanthanum and cerium analogs of 1 had previously been synthesized from the reaction of $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ (Ln = La, Ce) with *tert*-butanol.[22]



(1)

1

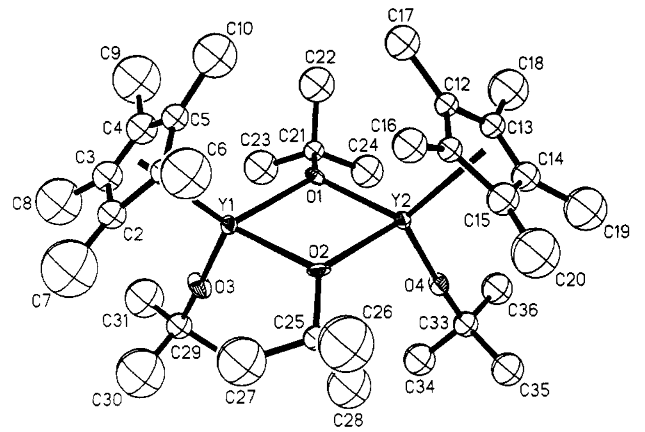


Figure 1. ORTEP diagram of $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **1**, with probability ellipsoids drawn at the 50% level.

Since the 500-MHz ^1H NMR spectrum of **1** in C_6D_6 did not display separate resonances for the two types of alkoxide observed in the crystal structure, the NMR spectrum was examined in C_6D_{12} and toluene-d_8. In both of these solvents, two separate *tert*-butoxide signals are observed, which is consistent with the existence of the dimeric structure in solution. The ^{13}C NMR spectrum of **1** in C_6D_6 and C_6D_{12} also contained separate resonances for the two $OCMe_3$ groups, but the two $OCMe_3$ resonances were not resolved. In contrast, in the ^1H and ^{13}C NMR spectra of $[(C_5Me_5)La(OCMe_3)_2]_2$ in C_6D_6, all of the expected resonances were resolved.[22]

Once the identity of **1** was established, its synthesis directly from YCl_3 was examined. Reaction of THF-solvated yttrium trichloride with 1 equiv of NaC_5Me_5 and 2 equiv of $NaOCMe_3$ in toluene forms **1** in 65% yield (eq 2, M = Na, K). Although the yield of reaction 2 is slightly lower than that of reaction 1, reaction 2 is the preferable route to **1** since it does not require the separate synthesis of $Y_3(OR)_7Cl_2(THF)_2$.

$$YCl_3(THF)_x + 2NaOCMe_3 + MC_5Me_5 \underset{-MCl}{\overset{-NaCl}{\rightarrow}} \underset{\textbf{1}}{[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2} \quad (2)$$

1 shows no signs of decomposition at ambient temperature in a glovebox over a 6-month period. It decomposes in air, but the decomposition is relatively slow for an organoyttrium complex. Solid samples require several minutes before a color change to yellow occurs. NMR samples of **1** in THF-d_8 slowly develop a yellow color over a 1-h period, but at the end of this time, the bulk of the sample (80–90%) is still predominantly **1**. Eventually, the solution reaction turns orange, a precipitate forms, and HC_5Me_5 and $HOCMe_3$ (identified by ^1H NMR spectroscopy) are produced. Reactions with dry oxygen produced an orange solid which was insoluble in THF.

$[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 2. As described below in the reactivity section, **1** proved to be a rather unreactive complex. To circumvent this problem, the synthesis of analogs ligated with smaller cyclopentadienyl groups was examined, since decreasing the steric bulk around the metal center should result in increased reactivity.[11,23] NaC_5H_5 reacts with $Y_3(OR)_7Cl_2(THF)_2$, and again a product with a simple ^1H NMR spectrum was obtained. However, this reaction product was not as stable as **1** and shorter heating times were required to prevent the formation of yellow decomposition products. The NaC_5H_5 reaction produces $[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **2**, which was identified by elemental analysis, NMR spectroscopy, and X-ray crystallography (Figure 2, eq 3). Although the C_5H_5 ligand is much smaller than C_5Me_5, **2** adopts a dimeric solid state structure analogous to that of **1** with an identical *cis* arrangement of cyclopentadienyl ligands around the central $(Me_3CO)Y(\mu\text{-}OCMe_3)_2Y(OCMe_3)$ core.

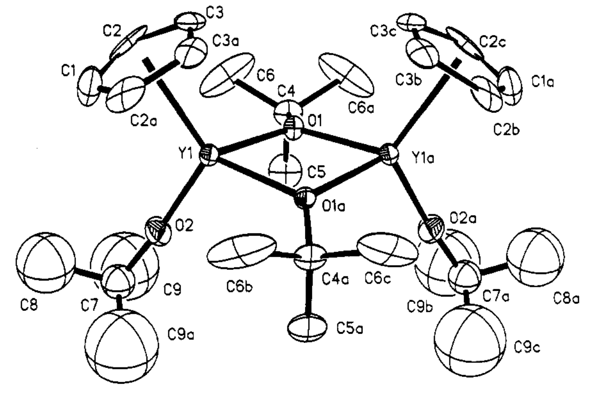


Figure 2. ORTEP diagram of $[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **2**, with probability ellipsoids drawn at the 50% level.

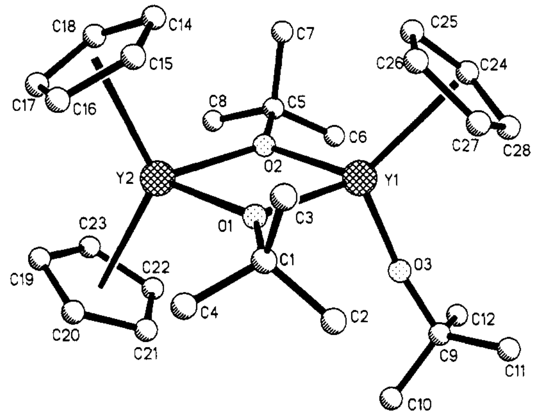


Figure 3. Ball and stick diagram of $[(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)(OCMe_3)]$, **6**.

$$Y_3(OCMe_3)_7Cl_2(THF)_2 + 3NaC_5H_5 \underset{-NaCl}{\overset{-NaOCMe_3}{\rightarrow}} \underset{\textbf{2}}{[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2} \quad (3)$$

The ^1H NMR spectrum of **2** in C_6D_6 contains one C_5H_5 resonance and two $OCMe_3$ resonances, which is consistent with the solid state structure. However in C_6D_{12}, the $OCMe_3$ peaks coincidentally overlap, which is opposite the situation with **1**. The less sterically saturated **2** is much less stable than **1** and decomposes in the glovebox overnight in toluene at ambient temperature and over the period of a week in the solid state.

$(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)(OCMe_3)$, 6. The $NaC_5H_5/Y_3(OR)_7Cl_2(THF)_2$ reaction (eq 3) produces a byproduct in low yield which was identified by X-ray crystallography as the ligand redistribution product $(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)(OCMe_3)$, **6** (Figure 3). This complex differs from **2** in that one C_5H_5 ligand has replaced

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[22] Heeres, H. J.; Teuben, J. H.; Rogers, R. D. *J. Organomet. Chem.* **1989**, *364*, 87–96.

[23] Evans, W. J. *Polyhedron* **1987**, *6*, 803–835.

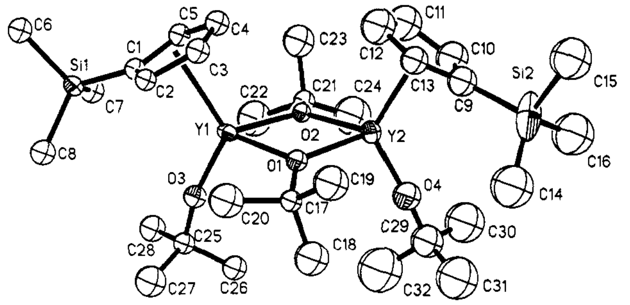


Figure 4. ORTEP diagram of $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **4**, with probability ellipsoids drawn at the 50% level.

one $OCMe_3$ ligand in **2**. This complex is unusual in that formation of a bimetallic compound with the two metals in disparate coordination environments occurred instead of formation of two different bimetallic complexes each containing a more uniform metal coordination sphere. The formation of more byproducts in the C_5H_5 reaction compared to the C_5Me_5 reaction is consistent with the expected greater reactivity of the C_5H_5 products versus the C_5Me_5 analogs.

$[(C_5H_4Me)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 3, and $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 4. To modulate the reactivity/stability of these dimeric mixed ligand cyclopentadienyl alkoxides, complexes containing cyclopentadienyl ligands intermediate in size between C_5H_5 and C_5Me_5 were sought. Given the similarity in structure of **1** and **2**, analogous bridged structures were anticipated. Both NaC_5H_4Me and $KC_5H_4SiMe_3$ react with $Y_3(OR)_7Cl_2(THF)_2$ to form analogs of **1** and **2**, namely $[(C_5H_4Me)Y(OCMe_3)(\mu\text{-}OCMe_3)]_2$, **3**, and $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **4**, eqs 4 and 5. The ^1H NMR spectra

$$Y_3(OCMe_3)_7Cl_2(THF)_2 + 3NaC_5H_4Me \xrightarrow[-NaCl]{-NaOCMe_3} \underset{\mathbf{3}}{[(C_5H_4Me)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2} \quad (4)$$

$$Y_3(OCMe_3)_7Cl_2(THF)_2 + 3KC_5H_4SiMe_3 \xrightarrow[-KCl]{-KOCMe_3} \underset{\mathbf{4}}{[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2} \quad (5)$$

of **3** and **4** in C_6D_6, like that of **1**, contain single $OCMe_3$ resonances. The spectrum of **4** has one resonance associated with the cyclopentadienyl ring protons whereas **3** has the expected two resonances. Complex **4** was characterized by X-ray crystallography and, as anticipated, it has a structure analogous to that of **1** and **2** (Figure 4).

3 is chemically similar to **2** in that it degrades both in solution and in the solid state in the glovebox at ambient temperature. **4** is more stable than **2** and **3** but more reactive than **1** and represents the best compromise in reactivity/stability in this series. When **4** is prepared from $Y_3(OR)_7Cl_2(THF)_2$, it is isolated as an oil. However, direct preparation of **4** from $YCl_3(THF)_x$ according to the method in eq 2 produces a solid material which is pure enough to be used directly in subsequent reactions.

$[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 5. An indenyl analog of **1**–**4** was also sought to determine how steric bulk localized on one side of the cyclopentadienyl ring would affect the structure of these mixed ligand species.

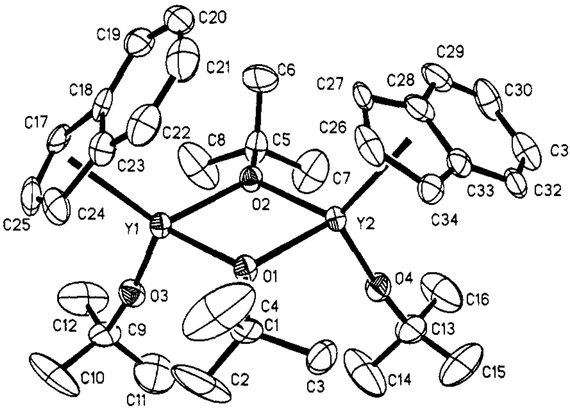


Figure 5. ORTEP diagram of $[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **5**, with probability ellipsoids drawn at the 50% level.

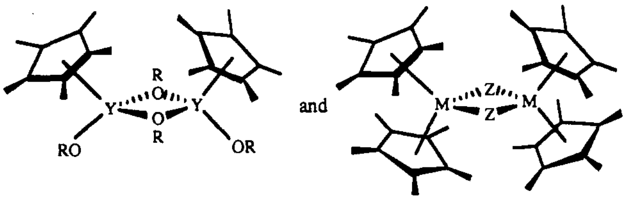
$[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **5**, was prepared from $YCl_3(THF)_x$ as shown in eq 6, and its structure, Figure 5,

$$YCl_3(THF)_x + 2NaOCMe_3 + KC_9H_7 \xrightarrow[-KCl]{-2NaCl} \underset{\mathbf{5}}{[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2} \quad (6)$$

is analogous to that of **1**, **2**, and **4**. The ^1H NMR spectrum of **5** in THF-d_8 shows the four resonances associated with the indenyl ligand and two closely shifted $OCMe_3$ resonances. The complex is very similar in stability to **4**. However, isolating pure samples is much more difficult and usually requires recrystallization.

Structural Studies of the $[(C_5R_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ Complexes. $[(C_5Me_5)Y(\mu\text{-}OR)(OR)]_2$, **1**, $[(C_5H_4SiMe_3)Y(\mu\text{-}OR)(OR)]_2$, **4**, and $[(C_9H_7)Y(\mu\text{-}OR)(OR)]_2$, **5**, all crystallize in the same space group, $P2_1/c$. $[(C_5H_5)Y(\mu\text{-}OR)(OR)]_2$, **2**, on the other hand, crystallizes in the higher symmetry space group $P\bar{4}2_1m$ and the molecule is located on a *mm* symmetry site.

In each complex, the cyclopentadienyl ring centroid, the terminal alkoxide, and the two bridging alkoxides form a distorted tetrahedron around yttrium. Each metal is formally six-coordinate, which is the coordination number most common for yttrium *tert*-butoxide complexes.[3-7] The overall structure of these complexes is reminiscent of bridged bent metallocenes of formula $[(C_5R_5)_2M(\mu\text{-}Z)]_2$ (Z = monoanionic ligand),[24] i.e.



The large bridging $OCMe_3$ ligand in **1**, **2**, **4**, and **5** may allow the terminal *tert*-butoxide ligands to become ef-

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(24) For example: (a) $\{[(C_5H_4Me)_2Ti(\mu\text{-}Z)]_2$ (Z = Cl, Br)$\}$ Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645–1655. (b) $\{[Cp_2Zr(\mu\text{-}I)]_2\}$ Wielstra, Y.; Gambarotta, S.; Meetsma, A.; de Boer, J. L. *Organometallics* **1990**, *8*, 250–251. (c) $\{[Cp_2Zr(\mu\text{-}PMe_2)]_2\}$ Chiang, M. Y.; Gambarotta, S.; Van Bolhuis, F. *Organometallics* **1988**, *7*, 1864–1865. (d) $\{[Cp_2Ti(\mu\text{-}PMe_2)]_2\}$ Payne, R.; Hachgenei, J.; Fritz, G.; Fenske, D. *Z. Naturforsch.* **1986**, *41B*, 1535–1540. (e) $\{[Cp_2Zr(\mu\text{-}S)]_2\}$ Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986**, *5*, 1620–1625. Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987**, 421–422. (f) $\{[Cp_2Ti(\mu\text{-}SiH_2)]_2\}$ Hencken, G.; Weiss, E. *Chem. Ber.* **1973**, *106*, 1747–1751.

Table II. Bond Distances and Angles for $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 1, $[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 2, $[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 4, $[(C_9H_7)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 5, and $[(C_5Me_5)Ce(\mu\text{-}OCMe_3)(OCMe_3)]_2$[a]

	1	2	4	5	$[(C_5Me_5)Ce(OR)_2]_2$
		Distances (Å)			
M–O(OR)	1.995(10), 2.018(9)	2.001(12)	2.023(6), 2.015(7)	2.005(6), 2.017(7)	2.116(6), 2.124(6)
M–O(μ–OR)	2.282(9), 2.259(9), 2.229(10), 2.256(10)	2.230(7)	2.233(7), 2.236(5), 2.231(5), 2.242(6)	2.241(6), 2.205(7), 2.247(7), 2.203(7)	2.401(6), 2.396(6), 2.380(6), 2.431(6)
Cn-M	2.415	2.389	2.411	2.416	2.55
$C(C_5R_5)$-M (av)	2.68(2)	2.66(2)	2.69(3)	2.70(4)	
M···M	3.570(2)	3.500(3)	3.524(2)	3.510(2)	
		Angles (deg)			
Cn–M–O(OR)	115.9, 114.8	120.1	124.6, 123.4	116.2, 119.4	119.5
O(μ–OR)–M–O(μ–OR)	74.9(3), 75.9(3)	76.0(1)	75.8(2), 75.7(2)	75.8(2), 75.7(2)	74.7(2), 74.4(2)
M–O(μ–OR)–M	103.7(4), 105.5(4)	103.4(1)	104.2(2), 103.8(2)	102.9(3), 105.6(3)	104.7(2), 106.1(2)

[a] R = CMe_3, Cn = Cyclopentadienyl ring centroid.

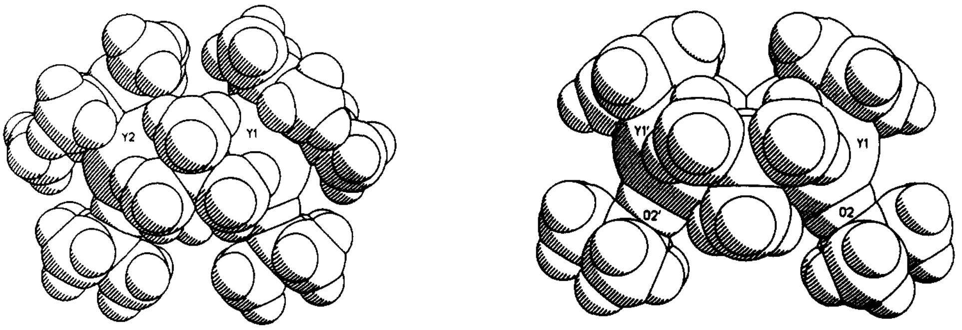

Figure 6. Space filling models of the side views of $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 1 (left), and $[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, 2 (right).

fectively equivalent to cyclopentadienyl ligands in these complexes. The structure of the cerium analog, $[(C_5Me_5)Ce(\mu\text{-}OR)(OR)]_2$, has previously been reported.[22] Yttrium and cerium aryloxide analogs have been synthesized, but these are monomers, $(C_5Me_5)Ln(OC_6H_3Bu^t_2\text{-}2,6)_2$ (Ln = Y, Ce).[25]

Table II shows a comparison of important bond distances and angles in 1, 2, 4, 5, and $[(C_5Me_5)Ce(\mu\text{-}OR)(OR)]_2$.[22] The Y–O(terminal OR) distances are very similar in 1, 2, 4, and 5, and the narrow 1.995(10)–2.023(6)-Å range is within the 1.97(2)–2.09(3)-Å range of terminal *tert*-butoxide yttrium distances in the literature.[3,4,6,7] As is typical, the Y–O(μ-OR) distances are longer than the Y–O(terminal OR) distances. The bridging distances are also very similar and again their narrow range, 2.203(7)–2.282(9)-Å, falls in the 2.19(2)–2.358(10)-Å range previously observed.[3,4,6,7] The similarity of the Y–O distances as well as the Y–O(μ-OR)–Y and O(μ-OR)–Y–O(μ-OR) angles and the Y···Y distances shows that the central (RO)Y(μ-OR)$_2$Y(OR) core is nearly invariant in these complexes. Even the Y–(ring centroid) distances are equivalent within experimental error despite the considerable differences in the size of the rings.

The major metrical difference in the structures of 1, 2, 4, and 5 is the (C_5R_5 ring centroid)–Y–O(OR) angle, which does not vary regularly: the complex with the largest C_5R_5 ring, 1, has the smallest angle, but the complex with the smallest ring, 2, does not have the largest angle. The variation of this angle in these structurally similar compounds may be one way in which the central core accommodates C_5R_5 ligands of different sizes.

The other major difference in these structures is the orientation of the methyl groups of the bridging *tert*-butoxide ligands. This is most easily seen by examining the space filling models[26] in Figure 6 (side views) and Figure 7 (top and bottom views) and considering the triangle defined by the three methyl groups of the bridging *tert*-butoxide ligand which faces out. The extremes in orientation are shown in the views of 1, which has a *vertex* of this triangle "up" near the C_5Me_5 groups, and 2, which has an *edge* of the triangle "up" near the cyclopentadienyl groups. It must be remembered that in 2, the methyl orientations are fixed by the *mm* site symmetry. The above orientations put a single methyl group near the large C_5Me_5 groups of 1 and two methyl groups near the smaller cyclopentadienyl ligands in 2; i.e. the orientation is adjusted to compensate for the size of the cyclopentadienyl ligand. The other μ-$OCMe_3$ ligand in 1 has its methyl groups in an intermediate orientation. Complexes 4 and 5 are similar to 1 in that they have one μ-$OCMe_3$ group with a single methyl pointing "up" and the other μ-$OCMe_3$ group with the methyl groups in an intermediate orientation (see supplementary material). Apparently, by varying the orientation of the methyl groups of the two bridging groups, the overall steric saturation of the molecules can be changed according to the different sizes of the cyclopentadienyl ligands.

The metrical parameters in 1, 2, 4, and 5 are quite normal compared to the cerium analog[22] when the 0.11-Å difference in the ionic radii[27] of the metals is considered. The Y–ring centroid distances are also similar to the 2.363(3)-Å distance found in the only other monocyclopentadienylyttrium complex in the Cambridge Crystallographic Data Base, $(C_5Me_5)Y(OC_6H_3Bu^t_2\text{-}2,6)_2$.[25] The 3.500(3)–3.570(2)-Å Y···Y separations in the central core are comparable to the 3.53- and 3.58(1)-Å Y···Y separations

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(25) Schaverien, C. J.; Frijns, J. H. G.; Heeres, H. J.; van den Hende, J. R.; Teuben, J. H.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 642–644. Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637–2646.

(26) Space filling model generated from Siemens Analytical X-ray Instruments-SHELX Graphics package.[19]

(27) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

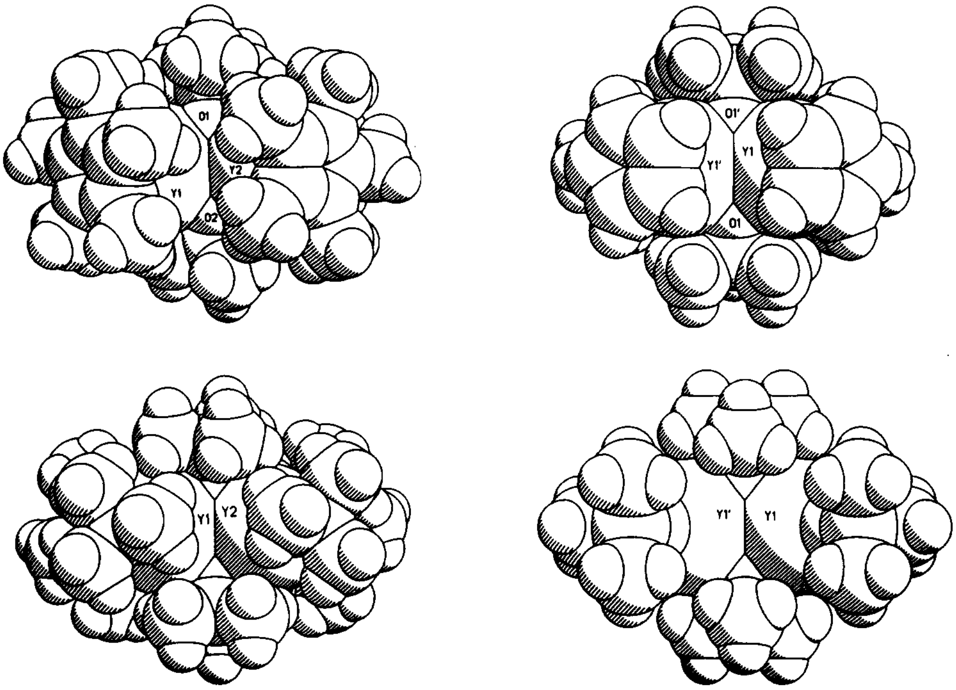

Figure 7. Space filling models of the top and bottom views of $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **1** (left), and $[(C_5H_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **2** (right).

in eight-coordinate $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$[28] and $[(C_5H_3Me_2)_2Y(\mu\text{-}Me)]_2$,[29] but they are shorter than the 3.66(1)- and 3.68(1)-Å distances in nine-coordinate $[(C_5H_4Me)_2(THF)Y(\mu\text{-}H)]_2$[30] and $[(C_5H_3Me_2)_2(THF)Y(\mu\text{-}H)]_2$,[29] respectively. In comparison the Y···Y distances in the trimetallic yttrium *tert*-butoxide complexes $Y_3(OCMe_3)_7Cl_2(THF)_2$[3] and $Y_3(OCMe_3)_8Cl(THF)_2$,[4] which contain six-coordinate yttrium, vary over a wide range: 3.50–3.63 and 3.52–3.78 Å, respectively.

Structure of $(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)(OCMe_3)$, 6. Although disorder problems and poor crystal quality preclude a detailed discussion of the metrical parameters of **6**, it is worth considering the overall structure especially in terms of evaluating the *tert*-butoxide group as a coligand alternative to cyclopentadienyl ligands. Complex **6** is even more similar to the bridged bent metallocenes of formula $Cp_2M(\mu\text{-}Z)_2MCp_2$[24] than **1**, **2**, **4**, and **5**, as mentioned above. Comparing **2** and **6**, a C_5H_5 for $OCMe_3$ substitution has formally occurred; i.e. in these two complexes an exact $C_5H_5/OCMe_3$ equivalence exists. Interestingly, the more symmetrical ligand distribution product $[(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)_2]$, which would be the product of yet another C_5H_5 for $OCMe_3$ substitution, is not isolated. Hence, it is possible that the *tert*-butoxide and C_5H_5 ligands can be equivalently substituted only when the size of the other ligands is just right for formation of a sterically saturated stable species.[23] Although **6**, $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)_2Y(C_5H_4SiMe_3)_2]$,[31] and $(C_5H_4SiMe_3)_2Y(OCMe_3)_2Li(THF)_2$, **9** (see below), are known to be crystallographically characterizable, it is possible that the combination $[(C_5H_5)_2Y(\mu\text{-}OCMe_3)_2Y(C_5H_5)_2]$ is not as sterically favored.

Reactivity of the $[(C_5R_5)Y(\mu\text{-}OR)(OR)]_2$ Complexes. The reactivity of the new series of yttrium alkoxide compounds composed of **1**–**5** was initially examined by studying reactions with alkyllithium reagents. Previously, the reaction of $(C_5Me_5)Y(OAr)_2$ ($Ar = C_6H_3Bu^t_2\text{-}2,6$) with $LiCH(SiMe_3)_2$ in toluene had been reported to cause removal of one aryloxide ligand and formation of $(C_5Me_5)Y[CH(SiMe_3)_2](OAr)$.[25] Similarly, $(C_5Me_5)Ce(OAr)_2$ was reported to react with 2 equiv of $LiCH(SiMe_3)_2$ in pentane to form $(C_5Me_5)Ce[CH(SiMe_3)_2]_2$.[25,32] In both systems, substitution occurred and LiOR was preferentially removed rather than LiC_5Me_5. However, when the reaction of $LiCH_2SiMe_3$ with $[(C_5Me_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$, **1**, was carried out, only starting materials were recovered. Reaction of **1** with $LiCH_2SiMe_3$ in toluene at reflux for 12 h also returned primarily unreacted **1**, although a complicated mixture of minor products was also observed. The limited reactivity of **1** suggests that the molecule is both sterically and electronically saturated, as is seen in the space filling diagrams, Figures 6 and 7.[26] Since **2**–**5** are less sterically saturated, these complexes proved to be better suited for reactivity studies.

Reactions of $[(C_5H_5)Y(\mu\text{-}OR)(OR)]_2$, 2. Complex **2** reacts immediately with $LiCH_2SiMe_3$ in hexanes to form a white precipitate. The hexane insoluble product of this reaction was subsequently identified as LiC_5H_5 by ^1H NMR spectroscopy in THF. The hexane soluble product of the reaction was an oil whose ^1H NMR spectrum contained several resonances for $OCMe_3$ and CH_2SiMe_3 groups but no evidence for cyclopentadienyl moieties. The alkyl resonances displayed couplings of 3 Hz consistent with $^2J_{YH}$ splitting.[33] Attempts to obtain crystals from this oil

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[32] Heeres, H. J.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 962–963.

[33] $^2J_{YH}$ coupling constants for yttrium alkyl complexes are typically 2–5 Hz.[28,29,34,35]

[34] Heeres, H. J.; Heeres, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 1508–1510 and references therein.

[35] den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682–683.

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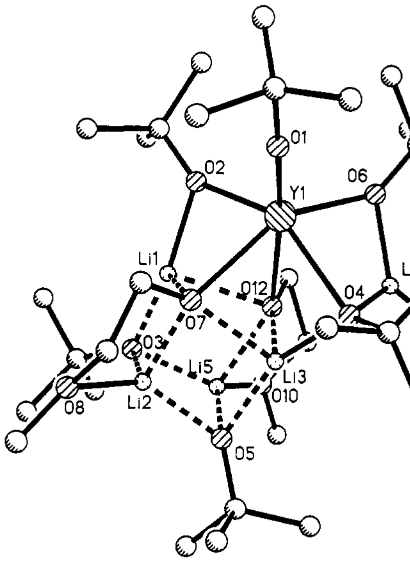

Figure 8. Ball and stick diagram of $(Me_3CO)Y(\mu\text{-}OCMe_3)_3Li_5(\mu_3\text{-}OCMe_3)_2(THF)(\mu\text{-}OCH_2CH_2OMe)_2$, **7**.

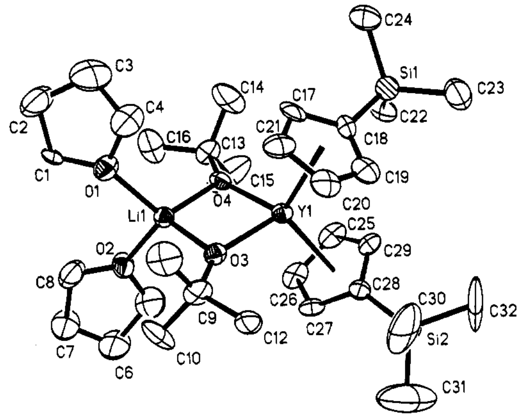

Figure 9. ORTEP diagram of $(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2$, **9**, with probability ellipsoids drawn at the 50% level.

using hexanes or THF were unsuccessful. However, from a mixture of ten drops of DME in approximately 2 mL of THF, crystals were isolated. Although the crystal chosen did not provide a strong diffraction pattern, the data were sufficient to establish unequivocally the composition of the compound as $(Me_3CO)Y(\mu\text{-}OCMe_3)_3Li_5(\mu_3\text{-}OCMe_3)_2(THF)(\mu\text{-}OCH_2CH_2OMe)_2$, **7**, Figure 8.

Structure of $(RO)Y(\mu\text{-}OR)_3Li_5(\mu_3\text{-}OR)_2(THF)(\mu\text{-}OCH_2CH_2OMe)_2$, 7. The description of this complex is facilitated by considering it as three subunits: a "$Y(OR)_3$" moiety, a "$(THF)Li(OR)$" moiety (involving Li(4), O(4), and O(9)), and a cube containing four oxygen atoms and four lithium atoms, i.e. "Li_4O_4". The yttrium in **7** is six-coordinate, as is typical for yttrium *tert*-butoxide complexes. Three of the coordination positions arise from the $Y(OR)_3$ unit, which has one terminal OR, one OR bridged to the $(THF)Li(OR)$ unit, and one OR bridged to the Li_4O_4 cube. Another coordination site is occupied by the bridging *tert*-butoxide ligand of the $(THF)Li(OR)$ unit, and the remaining two coordination positions arise from $MeOCH_2CH_2O$ oxygen atoms shared with the Li_4O_4 cube. In a sense, **7** is composed of the $Y(OCMe_3)_3$ unit, which has never been isolated in an unbridged form, coordinated with lithium alkoxide moieties.

The lithium atom in the $(THF)Li(OR)$ unit is three-coordinate with the third connection arising from a bridging OR group of the $Y(OR)_3$ moiety. The *tert*-butoxide oxygen atom of the $(THF)Li(OR)$ group, O(4), is linked to Li(4), yttrium, and a lithium in the Li_4O_4 cube. In the Li_4O_4 cube, two of the oxygen atoms arise from bridging *tert*-butoxide ligands. The other two oxygen atoms are the anionic parts of two OCH_2CH_2OMe groups formally related to the DME in the crystallization system by loss of a methyl group. Each of the lithium atoms in the cube is four coordinate due to one exopolyhedral attachment. For Li(2) and Li(5), this fourth donor oxygen atom arises from the ether group in OCH_2CH_2OMe. For Li(1), a connection is made to one of the bridging OR groups of the $Y(OR)_3$ unit and Li(3) is bridged to the bridging OR in $(THF)Li(OR)$.

Reactions with $[(C_5H_4SiMe_3)Y(\mu\text{-}OR)(OR)]_2$, 4. (a) $LiCH_2SiMe_3$. Complex **4** also reacts immediately with $LiCH_2SiMe_3$ and again oily products are formed. As described previously, the polymeric supersandwich metallocene, $[Li(\mu,\eta^5,\eta^5\text{-}C_5H_4SiMe_3)]_n$, **8** (eq 7),[36] can be

$$[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2 + 4LiCH_2SiMe_3 \xrightarrow{\text{hexanes}} \text{“}Y(OCMe_3)_x(CH_2SiMe_3)_y\text{”} + \underset{\mathbf{8}}{[Li(\mu,\eta^5,\eta^5\text{-}(C_5H_4SiMe_3)]_n} \quad (7)$$

crystallized from this reaction mixture and shows that again the cyclopentadienide ligand is lost in this alkyllithium reaction. **8** was the first nonsolvated lithium salt of a simple cyclopentadienyl ligand to be crystallographically characterized. No other single products have been isolated in pure form from the reaction of **4** with $LiCH_2SiMe_3$.

(b) $LiN(SiMe_3)_2$. In efforts to generate a cyclopentadienyl-free reaction product which would be more readily isolated, the reaction of **4** with $LiN(SiMe_3)_2$ was investigated. The larger size of this anionic reagent and the greater electronegativity of its donor atom offered the potential to generate well characterized "$Y(OR)_{3-x}[N(SiMe_3)_2]_x$" complexes if cyclopentadienyl cleavage again occurred. **4** reacts with $LiN(SiMe_3)_2$ in hexanes, but the reaction differs from the $LiCH_2SiMe_3$ reactions in that no precipitate was formed initially. However, after 8 h, a white powder was observed. The hexane soluble products of this reaction were isolated and identified as $Y[N(SiMe_3)_3]_3$[37] and $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2]$, **9** (Figure 9, eq 8). In this reaction, the formation of the

$$[(C_5H_4SiMe_3)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2 + 2LiN(SiMe_3)_2 \xrightarrow[\text{hexanes}]{} Y[N(SiMe_3)_2]_3 + \underset{\mathbf{9}}{(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2} \quad (8)$$

tris(amide) complex shows that the cyclopentadienyl ligand was again removed, but in this case, ligand redistribution was more extensive and the $(RO)Y(\mu\text{-}OR)_2Y(OR)$ unit was disrupted. The stability of $Y[N(SiMe_3)_3]_3$ may drive this reaction in this direction.

Structure of $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2]$, 9. Complex **9** is another example of a well-known class of complexes with general formula $(C_5R_5)_2Ln(\mu\text{-}Z)_2ML_2$, in which R is usually methyl but can be hydrogen, Z is a

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Table III. Bond Distances and Angles for $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OCMe_3)_2Li(THF)_2$, 9[a]

distance (Å)		angle (deg)	
Y–O(μ–OR)		O(3)–Y(1)–O(4)	81.8(4)
Y–O(3)	2.148(10)		
Y–O(4)	2.157(11)	Cn(1)–Y(1)–O(3)	108.5
Li-O(μ–OR)		Cn(2)–Y(1)–O(3)	113.1
Li(1)–O(3)	1.950(28)	Cn(1)–Y(1)–O(4)	112.6
Li(1)–O(4)	1.968(26)	Cn(2)–Y(1)–O(4)	109.8
Li–O(OR)			
Li(1)–O(1)	2.069(28)		
Li(1)–O(2)	2.014(25)		
Y···Li		O(3)–Li(1)–O(4)	92.0(12)
Y(1)···Li(1)	2.987(26)		
Others			
Cn–Y	2.458	Y(1)–O(3)–Li(1)	93.5(8)
$C(C_5R_5)$–Y (av)	2.74(4)	Y(1)–O(4)–Li(1)	92.7(9)

[a] R = CMe_3, Cn = Cyclopentadienyl ring centroid.

monoanionic ligand, M is an alkali metal, and L is a neutral donor ligand.[38] Although many complexes of this type have been reported,[38] **9** is the first crystallographically characterized yttrium complex in which Z is a simple alkoxide ligand. The bond distances and angles (Table III) around the formally eight-coordinate yttrium center and the four-coordinate lithium are quite normal when compared to related species. Hence, the O(μ-OR)—Y—O(μ-OR) angle of 81.8(4)° is in the range reported for $(C_5Me_5)_2Ln(\mu\text{-}Z)_2ML_2$ complexes, 82–87°,[38] and the Y–O(μ-OR) distances, 2.157(11) and 2.148(10) Å, are comparable to the 2.19(2)–2.358(10)-Å range found in yttrium *tert*-butoxide complexes.[3–7] However, these parameters are rather different from those of the symmetrical homometallic alkoxide bridged dimers $[(C_5H_4Me)_2Y(\mu\text{-}OCH{=}CH_2)]_2$[39] and $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OCH_3)]_2$,[31] which have O($\mu$-OR′)—Y—O($\mu$-OR′) angles of 73.1(1)–73.6° and Y—O(μ-OR′) distances of 2.217(3)–2.290(3) Å. The 2.04(3)-Å Li—O(THF) distance also differs from the 1.90(1)–1.93(3)-Å distances found in $(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2$[38] and $[C_5H_3(SiMe_3)_2]_2Nd(\mu\text{-}Cl)_2Li(THF)_2$.[40] These data are consistent with the larger size of $OCMe_3$ as a bridging ligand in $[(C_5R_5)_2Ln(\mu\text{-}Z)]_2$ complexes and their analogs.

The 2.74(4)-Å average Y–C($C_5H_4SiMe_3$) distance is equivalent within experimental error to the analogous 2.63(1)–2.67(1)-Å distances in $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OCH_3)]_2$ and $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$.[31] As in these last two examples, the $SiMe_3$ groups in **9** are in a *trans* orientation. The angle between the plane defined by Si(1), its ring centroid, and yttrium and the plane defined by Si(2), its ring centroid, and yttrium is 109.2°.

Reactions of $LiCH_2SiMe_3$ with $[(C_5H_4Me)Y(\mu\text{-}OR)(OR)]_2$, 3, and $[(C_9H_7)Y(\mu\text{-}OR)(OR)]_2$, 5. Reactions of **3** and **5** with $LiCH_2SiMe_3$ gave results similar to those found for **2** and **4**. In all of these reactions, hexane soluble products were formed which had ^1H NMR spectra which lacked cyclopentadienyl resonances and contained resonances for $OCMe_3$ and CH_2SiMe_3 ligands. Addition of $LiCH_2SiMe_3$ to **2–5** apparently generates a highly reactive system, since all of these reactions appear to be quite sensitive to specific reaction conditions including which cyclopentadienyl complex is used as the precursor. Hence, although the spectra of the cyclopentadienyl-free products (e.g. "$Y(OCMe_3)_{3-x}(CH_2SiMe_3)_x$") generated from **2–4** are similar, they are not identical.

Discussion

Implications in Yttrium *tert*-Butoxide Chemistry. The reaction of cyclopentadienyl reagents with $Y_3(OR)_7Cl_2(THF)_2$ to form the bimetallic complexes **1–5** is surprising in several respects in terms of yttrium *tert*-butoxide chemistry. First, these reactions provide another example of a reaction system in which the previously predominant trimetallic framework of yttrium *tert*-butoxide complexes is dismantled. Evidently, the trimethylaluminum reaction reported earlier[9] is not the only case in which the trimetallic yttrium *tert*-butoxide unit fragments. Obviously, reagents much different in reactivity from the Lewis acidic $AlMe_3$ can affect this fragmentation. In both of these systems, the isolated yttrium products contain the bridging and terminal *tert*-butoxide ligands necessary for formation of trimetallic species, but further oligomerization does not occur. These two reaction systems show that generalizations regarding a specific preferred polymetallic substructure cannot be made for *organometallic* yttrium *tert*-butoxide systems with currently available data. In addition, the generalization that halide is retained in yttrium *tert*-butoxide complexes[3,4,6,7] breaks down in both of these organometallic reaction systems. Clearly, yttrium *tert*-butoxide complexes have a more diverse chemistry than was indicated by initial studies.

It is also surprising that the series of $[(C_5R_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ bridged dimers which are generated in these reactions are structurally analogous despite the differences in the sizes of the cyclopentadienyl ligands. There are relatively few examples in the yttrium and lanthanide literature in which both C_5H_5 and C_5Me_5 ligands form complexes which are structurally analogous. For example, $(C_5Me_5)_3Sm$[41] differs from $(C_5H_5)_3Sm(py)$[42] and $[(C_5H_5)_3Sm]_n$,[43,44] $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$[45] differs from $[(C_5H_4Me)_2Yb(\mu\text{-}Cl)]$[46] and $\{[C_5H_3(SiMe_3)_2]_2Yb(\mu\text{-}Cl)\}_2$,[47] $[(C_5Me_5)_2MeLu(\mu\text{-}Me)Lu(C_5Me_5)_2$[48] differs from $[(C_5H_5)_2Ln(\mu\text{-}Me)]_2$ (Ln = Y, Yb),[28] etc. The pair $(C_5Me_5)_2LuCl(THF)$[49] and $(C_5H_5)_2LuCl(THF)$[50] is one of the rare examples in yttrium[51] and lanthanide chemistry in which crystallographically characterized C_5Me_5 and C_5H_5 complexes of analogous formula have the same structure.

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The similarity of **1**, **2**, **4**, and **5** suggests that the (RO)Y(μ-OR)$_2$Y(OR) inner core of these molecules may be quite flexible in accommodating two additional anionic organometallic ligands when R is CMe$_3$. The facile formation of the bridged cyclopentadienyl *tert*-butoxide dimers and the stability of the C$_5$Me$_5$ complex **1** under forcing reaction conditions suggests that these complexes are well balanced sterically and electronically. The (RO)Y(μ-OR)$_2$Y(OR) core is also formally present in a fused form in the trimetallic complexes such as Y$_3$(OR)$_7$Cl$_2$(THF)$_2$ and Y$_3$(OR)$_9$(THF)$_2$.[3-7] Hence, this bimetallic moiety may be the more fundamental structural unit in yttrium *tert*-butoxide chemistry. Although the steric and electronic stability limits of this [Y$_2$(OR)$_4$]$^{2+}$ unit have not been fully explored, it does appear from the reactions of LiCH$_2$SiMe$_3$ that this unit does not readily form stable complexes with monodentate alkyl anions of moderate size.

The visual similarity of **1**, **2**, **4** and **5** to bridged bis(cyclopentadienyl) complexes of formula [(C$_5$R$_5$)$_2$M(Z)]$_2$[24] (see above) is consistent with the idea that the *tert*-butoxide group can be an acceptable substitute for cyclopentadienide as a coligand in complexes of yttrium and the lanthanides. The direct substitution of C$_5$H$_5$ in **2** for OCMe$_3$ in **6** further supports the idea that *tert*-butoxide and cyclopentadienide ligands can be isostructurally interchanged in certain cases.

Structural Features. Each yttrium in **1**, **2**, **4**, and **5** is formally six-coordinate, which is the common coordination number in yttrium *tert*-butoxide complexes.[3-7] Since there are twice as many *tert*-butoxide ligands as cyclopentadienyl ligands in these complexes, it is reasonable that the observed coordination number is typical of *tert*-butoxide complexes rather than cyclopentadienylyttrium complexes which are typically eight-coordinate.[52] Interestingly, in (C$_5$H$_5$)$_2$Y(μ-OCMe$_3$)$_2$Y(OCMe$_3$)(C$_5$H$_5$), **6**, both eight-coordinate and six-coordinate yttrium centers are found. To our knowledge, this is the first polymetallic yttrium complex which has metals which differ in coordination number by 2. The closest example is a complex like (C$_5$Me$_5$)$_2$ClY(μ-Cl)Y(C$_5$Me$_5$)$_2$[45] which has yttrium centers which differ by 1 in formal coordination number.

Complex **7** provides another example of the complicated yttrium *tert*-butoxide structure which can result when lithium is present. A previous example involved the reaction of YCl$_3$ with 2 equiv of MOCMe$_3$:[4] with M = Na, Y$_3$(OR)$_7$Cl$_2$(THF)$_2$ is cleanly formed in 80% yield, but for M = Li, {[Y$_4$(OR)$_{10}$OCl$_2$][Li$_4$(OR)$_2$]}$_2$, which has a polylithium component composed of two [Li$_4$(OR)$_2$] units, is obtained. The formation of (RO)$_2$Sm(μ_4-OR)$_2$(μ_3-OR)$_4$Li$_5$ is another example of this phenomenon.[53] The Li$_4$O$_4$ cube in **7** is not a surprising arrangement when compared with the large number of Li$_4$O$_4$ moieties which have been crystallographically characterized.[53,54]

Complex **7** also constitutes another example of a structure which contains the Y(OCMe$_3$)$_3$ unit ligated by other metal–ligand groups. This has been previously seen in (RO)(THF)Y[(μ-OR)(μ-Me)AlMe$_2$]$_2$ and Y[(μ-OR)(μ-Me)AlMe$_2$]$_3$[9] as well as in all of the trimetallic yttrium *tert*-butoxide complexes, such as Y$_3$(OR)$_9$(THF)$_2$,[5] Y$_3$(OR)$_8$Cl(THF)$_2$,[3] Y$_3$(OR)$_7$Cl$_2$(THF)$_2$,[4] etc.[6,7] Apparently, the Y(OCMe$_3$)$_3$ unit is not sufficiently sterically saturated to exist on its own. This is a major difference from (C$_5$H$_5$)$_3$Y(THF).[55] Even simple solvated species such as Y(OCMe$_3$)$_3$L$_3$ analogous to the series Ln(OEPh$_3$)$_3$(THF)$_3$ (E = C, Si; Ln = La, Ce, Y)[56,57] and to Y[OCMe(CF$_3$)$_2$]$_3$(THF)$_3$[58] have not been isolated. The Y(OCMe$_3$)$_3$ unit clearly has a propensity to form polymetallic bridged complexes with yttrium and other metals, a result which is reasonable on the basis of its high electrophilicity and limited steric saturation.

Reactivity. Initial reactivity studies on **1**–**5** suggest that *tert*-butoxide coligand environments may provide complexes which display new patterns of yttrium and lanthanide chemistry alternative to cyclopentadienyl-based chemistry. For example, as discussed above, alkyllithium reagents typically react with the cyclopentadienyl alkoxide complexes, (C$_5$Me$_5$)Ln(OAr)$_2$ (Ln = Ce, Y), in pentane and toluene to substitute the alkoxide ligand rather than a cyclopentadienyl ligand.[25,32] Since the [(C$_5$R$_5$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$ complexes have *tert*-butoxide ligands in the terminal positions which are usually reactive,[23] similar reactivity was expected here. Furthermore, the aryloxide complexes Ln(OAr)$_3$ (OAr = OC$_6$H$_3$Bu$^t_2$-2,6; Ln = La, Ce) react with LiC$_5$Me$_5$ in toluene to *add* a cyclopentadienyl unit, displace an alkoxide, and form (C$_5$Me$_5$)Ln(OAr)$_2$ products.[59] However, with the *tert*-butoxide complexes, **2**, **4**, and **5**, the opposite reaction, i.e. *loss* of a cyclopentadienyl ligand, occurs in both pentane and toluene (eqs 6 and 7).

The removal of cyclopentadienyl ligands rather than alkoxide ligands suggests that the (Me$_3$CO)Y(μ-OCMe$_3$)$_2$Y(OCMe$_3$) inner core may have some special stability which may provide the basis for new yttrium reactivity. Data further supporting this idea include the limited reactivity of [(C$_5$Me$_5$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$ and the structural similarity of **1**, **2**, **4**, and **5**. The opportunity for new chemistry via these alkoxide ligands may be quite broadly available: since *tert*-butoxide and cyclopentadienyl ligands appear to be structurally equivalent coligands with certain combinations of ligands, a wide range of *tert*-butoxide complexes may be accessible.

The fact that a simple alkylalkoxide complex analogous to [(C$_5$R$_5$)$_2$LnR]$_2$ or (C$_5$R$_5$)$_2$LnR(THF) has not been readily isolated is consistent with the idea that alkoxide coligands may provide different types of reactivity to yttrium. Analogous complexes such as [(RO)$_2$LnR]$_2$ and (RO)$_2$LnR(THF) may be too sterically unsaturated to be isolable and even an alkyl derivative of the inner alkoxide core found in **1**–**5**, i.e. R′(RO)Y(μ-OR)$_2$Y(OR)R′ may be

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too sterically open to isolate. Since the low stability can translate into high reactivity, this provides opportunities for new reaction chemistry. The isolation of $MeOCH_2CH_2O$ ligands from the DME recrystallized complex **7** is consistent with this high reactivity.

Formation of $MeOCH_2CHO$ moieties from DME has been observed previously in systems containing silicon,[60] tungsten,[61,62] neodymium, and praseodymium[63] and a magnesium–mercury–silicon mixture,[64] but little is known about the mechanisms of these reactions. Crystallographic verification of a DME-derived $MeOCH_2CHO$ ligand has been obtained for $[Mg_4(OC_2H_4OMe)_6\cdot 2DME][Hg(SiMe_2Ph)_3]_2$,[64] and several examples of this ligand derived from $MeOCH_2CHOH$ are now in the literature.[65] Unfortunately, the reaction which led to **7** is too complicated to reveal the mechanistic origin of the $MeOCH_2CH_2O$ ligand.

Conclusion

Cyclopentadienyl reagents react with trimetallic yttrium *tert*-butoxide complexes to generate a new series of halide-free bimetallic mixed ligand complexes of formula $[(C_5R_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$. The similar structures of the several examples which were crystallographically characterized suggest that with the proper combination of ligands, the $(RO)Y(\mu\text{-}OR)_2Y(OR)$ core may be quite flexible to external substitution. For R = CMe_3, cyclopentadienyl ligands are the preferred extra two ligands. For other alkoxides a different set of external groups may be preferred. The reactivity of the $[(C_5R_5)Y(\mu\text{-}OCMe_3)(OCMe_3)]_2$ complexes with $LiCH_2SiMe_3$ suggests that the *tert*-butoxide coligand will generate chemistry different from that observed with the cyclopentadienyl-ligated systems and that highly reactive complexes may be accessible using a combination of alkyl and alkoxide ligands in this way.

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Supplementary Material Available: A complete set of space filling diagrams plus tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (79 pages). Ordering information is given on any current masthead page.

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