Conclusions

The title compounds are Peierls distorted, pinned charge density wave systems with $4k_f$ superstructures. The mixed-valence chain structures were found to be dominated by electronic effects when disordered cations were present ($4k_f$ systems) but by crystal packing forces producing an additional distortion when ordered cations were present ($(TEA)Cu_2Br_4$). The presence of a strong intervalence charge-transfer band in the low-energy end of the visible region was demonstrated through absorption spectral data and EHMO band calculations. A picture utilizing localized magnetic orbitals offers the best description of the magnetic exchange. All of the experimental evidence presented in this work strongly indicate that the title compounds belong to Robin and Day class II.

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Registry No. $(TEM)Cu_2Br_4$, 141170-87-8; $(TEA)Cu_2Br_4$, 141170-88-9; $(DEM)Cu_2Br_4$, 141170-89-0; $(TEA)Cu_2Cl_4$, 110488-61-4.

Supplementary Material Available: Tables of X-ray data collection parameters, bond lengths and angles for the cations, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom positions and isotropic thermal parameters for all three structures (11 pages); structure factor tables for all three structures (26 pages). Ordering information is given on any current masthead page.

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Formation of Bimetallic, Trimetallic, and Pentametallic Yttrium Methoxide and Methoxide Oxide Complexes from Reactions of Alkali-Metal Methoxides with Bis(cyclopentadienyl)yttrium Chloride

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The superficially simple metathetical reaction of $(C_5H_5)_2YCl(THF)$ with alkali-metal methoxides has been found to form a variety of products and product mixtures depending on reaction conditions. $(C_5H_5)_2YCl(THF)$ reacts with NaOMe to form $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$ (**1**) in 80–95% yield depending on the method of isolation of the product. **1** can be generated analogously from KOMe in up to 75% yield depending on reaction conditions and the source of KOMe. The primary byproduct in KOMe reactions, which can be isolated in up to 20% yield, was identified as the trimetallic anion $\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_2[(C_5H_5)_2Y](\mu_3\text{-}O)\}^-$ (**2**). The yield of **2** can be increased to as high as 70% by varying the reaction conditions and the $(C_5H_5)_2YCl(THF)$ to KOMe stoichiometry. Me_2O has been isolated as a byproduct in this oxide-forming reaction. The previously characterized pentametallic complex $(C_5H_5)_5Y_5(\mu\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$ (**3**) is also formed in this reaction system. **3** can be obtained in high yield from the reaction of $(C_5H_5)YCl_2(THF)_3$, generated in situ, with 2 equiv of *Na*OMe in THF at reflux or from the reaction of $(C_5H_5)_2YCl(THF)$ and MeOH-solvated KOMe. Other cyclopentadienyl alkoxide products are also formed in these reactions, and the product mixtures are highly dependent upon the particular alkali-metal alkoxide used, its method of preparation, the reaction time and temperature, reagent concentrations, and workup procedure. The direct formation of the polymetallic products from **1** and methoxide reagents has been investigated and further shows the complexity of this system. Crystallographic data have been obtained on **1**–**3** as well as the (trimethylsilyl)cyclopentadienyl analogue of **1** $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$ (**4**) and its chloride precursor $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$ (**5**). Complexes **1**, **4**, and **5** are comprised of $(C_5H_4R)_2Y$ (R = H, $SiMe_3$) bent metallocene units bridged by methoxide or chloride ligands. In **2**, three $(C_5H_5)_2Y$ bent metallocene units define a triangle with two sides bridged by methoxide groups. Near the third side in the interior of the triangle and coplanar with the yttrium atoms is a μ_3-oxide ligand. **2** crystallized with the countercation $\{[(THF)_3Na]_2(\mu\text{-}C_5H_5)\}$ in which a bridging C_5H_5 group is sandwiched between two $Na(THF)_3$ moieties. $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$ crystallized from toluene in space group $P\bar{1}$ with unit cell dimensions $a = 16.747$ (11) Å, $b = 27.351$ (14) Å, $c = 8.404$ (4) Å, $\alpha = 90.00$ (4)°, $\beta = 109.49$ (4)°, $\gamma = 90.05$ (5)°, $V = 3629$ (3) Å^3, and $Z = 6$ for $D_{calcd} = 1.14$ g cm^{-3}. $\{[(C_5H_5)_2Y)]_3(OMe)_2O\}\{[(THF)_3Na]_2(C_5H_5)\}$ crystallized from THF in space group *Pnam* with unit cell dimensions $a = 18.854$ (6) Å, $b = 15.803$ (3) Å, $c = 22.355$ (8) Å, and $Z = 4$ for $D_{calcd} = 1.28$ g cm^{-3}. $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$ crystallized from benzene with two molecules of benzene in the lattice in space group $C2/c$ with unit cell dimensions $a = 24.930$ (3) Å, $b = 13.735$ (2) Å, $c = 14.764$ (2) Å, $\beta = 91.90$ (1)°, $V = 5052$ (1) Å^3, and $Z = 4$ for $D_{calcd} = 1.24$ g cm^{-3}. Least-squares refinement based on 3653 observed reflections led to a final R_F value of 5.3%. $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$ crystallized from benzene in space group $P\bar{1}$ with $a = 8.676$ (2) Å, $b = 9.763$ (2) Å, $c = 12.487$ (2) Å, $\alpha = 70.38$ (1)°, $\beta = 76.69$ (1)°, $\gamma = 88.67$ (1)°, $V = 967.7$ (3) Å^3, and $Z = 1$ for $D_{calcd} = 1.37$ g cm^{-3}. Least-squares refinement of the model based on 3285 reflections converged to a final $R_F = 4.3\%$.

Introduction

Recently, we have been studying the synthesis of oxygen-stabilized organoyttrium and organolanthanide complexes[1–8] in order to obtain more robust compounds with which to exploit the unusual chemistry of these metals.[9–12] In particular, we have been ex-

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ploring the use of simple alkoxide groups as coligands alternative to the oxidatively- and hydrolytically-sensitive cyclopentadienyl coligands so common in this area of organometallic chemistry. Traditionally in f element chemistry, the cyclopentadienyl group has been a valuable coligand which can make complicated and reactive systems more tractable for study. Indeed, our studies of cyclopentadienyl-free alkoxide yttrium compounds have revealed a synthetic and structural chemistry much more diverse and complicated than cyclopentadienyl chemistry.[1-8]

To aid us in understanding the myriad of polymetallic alkoxide and alkoxide oxide complexes accessible in the cyclopentadienyl-free systems, we have investigated the synthesis and structure of mixed-ligand complexes containing both cyclopentadienyl and alkoxide moieties. Since the η^5-C_5H_5 ligand can occupy several coordination sites, it was expected that fewer structural options would be available in these cyclopentadienyl-containing systems and a less complicated reaction chemistry would be observed. In this report, we present data on the reaction of bis(cyclopentadienyl)yttrium chloride complexes with alkali-metal methoxides (eq 1; R = H, Me_3Si; M = Na, K), which show that an unexpectedly diverse synthetic and structural chemistry is available even in cyclopentadienyl-containing alkoxide systems.

$$(C_5H_4R)_2YCl(THF) + MOCH_3 \rightarrow \text{products} \tag{1}$$

In 1963, the first synthesis of this type was reported for the paramagnetic ions Ln = Dy, Er, Yb (eq 2).[13] Retrospectively, the yields of 5, 52, and 60%, respectively, indicated that other products were formed in these reactions, but the paramagnetism of the metals and the lack of X-ray diffraction studies precluded definitive analysis of this system. By using NMR-accessible yttrium, which is similar in size and chemistry to erbium,[14] and by varying reaction conditions, we have been able to show that a variety of reaction pathways can be traversed in this system, leading to polymetallic as well as oxide-containing products.

$$(C_5H_5)_2LnCl + NaOCH_3 \xrightarrow[\text{reflux}]{\text{THF}} (C_5H_5)_2Ln(OCH_3) + NaCl \tag{2}$$

The formation of oxide ligands in lanthanide and yttrium alkoxide reactions has been frequently observed,[1-3,6,15-21] but the origin of the oxide is often ill-defined. Adventitious water is sometimes discussed as the source of oxides.[19,22] Reaction 1 seemed to provide a good opportunity to study oxide formation since the hydrolytically-sensitive cyclopentadienide ligands would form readily identifiable dicyclopentadiene if water were present. Accordingly, the synthesis, structure, and reaction chemistry of the complexes in this system were pursued.

Experimental Section

Manipulations of the complexes described below were conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Physical measurements were obtained as previously described.[23] NaOMe was prepared by slowly adding methanol (distilled from CaH_2, dried over sodium, and distilled into an additional funnel) to a Schlenk flask containing freshly-cut sodium in THF. After all of the alkali metal had reacted, the THF and any unreacted methanol were removed under vacuum to give a white powder which was dried at 65 °C at 10^{-5} Torr. KOMe prepared analogously gave samples which were not pure by elemental analysis. KOMe was obtained by syringing MeOH (1.45 mL, 35.9 mmol) into a Schlenk flask containing a colorless solution of freshly sublimed $KN(SiMe_3)_2$ (7.185 g, 35.9 mmol) in toluene (200 mL). The white precipitate which forms immediately was filtered, washed with THF, and dried by heating at 65 °C for 12 h at 10^{-5} Torr (2.496 g, 99%).

$(C_5H_5)_2YCl(THF)$ was formed by dissolving $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ in THF. $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ was prepared by a modification of the literature procedure.[24] Solvate-free NaC_5H_5 (857 mg, 9.73 mmol) was added to YCl_3 (1 g, 5.12 mmol) in THF in the glovebox, and the reaction mixture was stirred for 24–48 h. THF was removed by rotary evaporation, and the solids were extracted with toluene to give $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ (965 mg) in 74% yield. The remaining solids were extracted with THF, the THF was removed, and a second toluene extraction was carried out. Additional $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ (139 mg) was obtained for a total yield of 85%. The $Me_3SiC_5H_4$ analogue was prepared similarly. The following data were obtained for $[(Me_3SiC_5H_4)_2YCl]_2$. ^1H NMR (C_6D_6): δ 6.46 (m, 4 H, $C_5H_4SiMe_3$), 6.78 (m, 4 H, $C_5H_4SiMe_3$), 0.30 (s, 18 H, $C_5H_4SiMe_3$). ^{13}C NMR (C_6D_6): δ 121.03 ($C_5H_4SiMe_3$), 116.99 ($C_5H_4SiMe_3$), 0.28 ($C_5H_4SiMe_3$).

$[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$, 1, from NaOMe. In the glovebox, $(C_5H_5)_2YCl(THF)$ (500 mg, 1.53 mmol) was added to a suspension of NaOMe (83 mg, 1.54 mmol) in THF (15 mL), and the mixture was stirred for 24 h. The cloudy mixture was centrifuged to remove the insoluble product, and the solvent was removed from the supernatant by rotary evaporation. The resulting white powder was extracted with toluene (12 mL). Removal of solvent from the toluene-soluble portion gave 304 mg (79%) of 1. Additional 1 could be recovered from the precipitates isolated by the above toluene extraction. Treatment of these precipitates with THF, removal of THF, and extraction with toluene yielded 26 mg (7%) of 1. Anal. Calcd for $YC_{11}H_{13}O$: Y, 35.54. Found: Y, 35.0. ^1H NMR (C_6D_6): δ 6.14 (s, 10 H, C_5H_5), 2.84 (s, 3 H, OCH_3). ^{13}C NMR ($C_6D_5CD_3$): δ 52.1 (q, J_{CH} = 140 Hz, OCH_3), 112.0 (C_5H_5). IR (KBr): 3075 s, 2800 s br, 2590 w, 2400 w, 2100 w, 1630 w, 1580 w, 1465 s, 1260 m, 1160 w, 1050 s br, 890 w, 750 s br cm^{-1}. Single crystals for X-ray studies were grown slowly from toluene at −34 °C over a 1-month period.[25]

Alternative Isolation Procedure for 1. A higher yield of 1 can be obtained directly by eliminating the initial centrifugation step in the above procedure. Hence, in a reaction identical to that described above, the THF solvent was removed by rotary evaporation at the end of the reaction *before* the solids (NaCl) were separated by centrifugation. The mixture of solids was extracted with toluene (12 mL) to yield 1 (362 mg, 94%).

$[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$ from KOMe. In the glovebox, $(C_5H_5)_2YCl(THF)$ (200 mg, 0.61 mmol) was added to a suspension of KOMe (43 mg, 0.61 mmol, prepared from $KN(SiMe_3)_2$ in THF (10 mL), and the mixture was stirred for 48 h. The cloudy mixture was centrifuged to remove insolubles, and the solvent was removed from the supernatant by rotary evaporation. The resulting white powder was extracted with toluene (10 mL). Removal of solvent gave 1 (118 mg, 77%). Treatment of the insoluble portion with THF followed by a second toluene extraction as described above for the NaOMe reaction yielded no additional toluene-soluble product. The THF-soluble fraction was found to contain $\{[(C_5H_5)_2Y]_3(\mu\text{-}OMe)_2(\mu_3\text{-}O)\}^-$, 2 (see below), by ^1H NMR. Elimination of the centrifugation step and direct toluene extraction of the crude reaction mixture did not give a higher yield of 1. When the above reaction was run with KOMe prepared by reacting potassium with MeOH, the yields of 1 were lower, the yields of 2 were higher, and other products such as $(C_5H_5)_5Y_5(OMe)_8O$, 3 (see below), and $(C_5H_5)_3Y(THF)$ were found.

$[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$, 4. Following the procedure originally described above for 1, $[(C_5H_4SiMe_3)_2YCl]_2$ (150 mg, 0.20 mmol) reacted with NaOMe (22 mg, 0.40 mmol) for 12 h to form $[(C_5H_4SiMe_3)_2Y(OMe)]_2$ (131 mg, 83%). Anal. Calcd for $YSi_2OC_{23}H_{29}$: Y, 22.53; Si, 14.24; C, 51.75; H, 7.42; O, 4.06. Found: Y, 22.50; Si, 13.95; C, 51.88;

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(25) 1 crystallized in space group $P\bar{1}$ with unit cell dimensions a = 16.747 (11) Å, b = 27.351 (14) Å, c = 8.404 (4) Å, α = 90.00 (4)°, β = 109.49 (4)°, γ = 90.05 (5)°, V = 3629 (3) Å^3, and Z = 6 for D_{calcd} = 1.14 g cm^{-3}. The crystal diffracted too weakly to provide a high-quality data set, but the connectivity of the atoms in the molecule was established. See supplementary material for details.

H, 7.22; O, 4.75. ^{1}H NMR (C_6D_6): δ 6.73 (m, 4 H, $C_5H_4SiMe_3$), 6.35 (m, 4 H, $C_5H_4SiMe_3$), 3.12 (s, 6 H, OCH_3), 0.36 (s, 18 H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 120.4, 114.9 ($C_5H_4SiMe_3$), 0.48 ($C_5H_4SiMe_3$). IR (KBr): 3084 m, 2954 s, 1653 m br, 1442 m, 1382 m, 1249 s, 1178 s, 1043 s, 906 s, 832 s br, 778 s, 754 s, 694 m, 650 m, 625 m.

$\{[(C_5H_5)_2Y(\mu\text{-}OCH_3)]_2[(C_5H_5)_2Y](\mu_3\text{-}O)\}\{K(THF)_4\}$, 2a. In the glovebox, $(C_5H_5)_2YCl(THF)$ (250 mg, 0.77 mmol) was added to a suspension of KOMe (71 mg, 1.01 mmol, prepared from potassium and methanol) in THF (14 mL), and the mixture was stirred for 48 h. The cloudy mixture was centrifuged to remove insolubles, and the solvent was removed from the supernatant by rotary evaporation. The resulting white powder was washed with toluene (8 mL) to remove any **1** and extracted with THF. The solvent was removed by rotary evaporation, and the resulting white powder was again washed with toluene to insure all toluene-soluble material was removed. The resulting THF-soluble material was **2a** (199 mg, 73%). Anal. Calcd for the mono-THF solvate $Y_3C_{36}H_{44}O_4K$: Y, 31.51; C, 51.08; H, 5.61; K, 4.62. Found: Y, 31.95; C, 48.66; H, 5.18; K, 3.54. ^{1}H NMR (THF-d_8): δ 6.11 (s, 20 H, C_5H_5), 5.95 (s, 10 H, C_5H_5), 3.51 (s, 6 H, μ-OCH_3). ^{13}C NMR (THF-d_8): δ 110.78 (s, C_5H_5), 109.25 (s, C_5H_5), 55.37 (q, J = 137 Hz, OCH_3). IR (KBr): 3050 s, 2880 s br, 1620 w, 1460 m, 1365 m, 1150 w, 1050 s br, 895 w, 875 w, 760 s br cm^{-1}. An analogous reaction using KOMe prepared from $KN(SiMe_3)_2$ and MeOH gave a 54% yield of **1**, a 25% yield of **2**, and a 16% yield of **3**.

In general the yields of **2a** have been found to vary from 10 to 70% depending on the particular KOMe sample used. Larger scale reactions were carried out in vessels connected to a vacuum line containing a Toepler pump in order to trap volatile products. For example, in the glovebox, $(C_5H_5)_2YCl(THF)$ (892 mg, 2.73 mmol) was added to a suspension of KOMe (from K/MeOH, 248 mg, 3.54 mmol) in THF (55 mL) in a 250-mL round-bottom flask fitted with a greaseless high-vacuum stopcock. The reaction vessel was attached to a high-vacuum line and immediately degassed. The mixture was stirred at room temperature for 48 h. The reaction mixture was cooled to −78 °C (dry ice/2-propanol bath), and the volatiles were collected using a Toepler pump (17.2 mL, 0.19 mmol). The gases were separated and analyzed on a Finnigan 4000 GC/MS using a 10-m 0.1% SP1000 column at 95 °C and found to contain Me_2O (0.05 mmol, 50% yield based on 0.099 mmol of **2a** isolated (11%)) and THF.

Since the yields of **2a** in these large-scale reactions were lower, four smaller scale reactions (200 mg each) were carried out simultaneously in four smaller vessels. Me_2O was again identified, but the yield of **2a** was still only 30%. Since the Toepler line reactions differed from those performed in the glovebox in that they were conducted at reduced pressure, two 200-mg-scale reactions were run simultaneously in which one reaction was under nitrogen and one was evacuated. The yields of **2a** in these reactions were 30 and 35%, respectively. The gases in the evacuated system contained Me_2O, and again the molar yield of the Me_2O was about 50% that of **2a**.

$\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_2[(C_5H_5)_2Y](\mu_3\text{-}O)\}\{[(THF)_3Na]_2(\mu\text{-}C_5H_5)\}$, 2b. Crystallization of a THF extract of the toluene-insoluble products of a $(C_5H_5)_2YCl(THF)$/NaOMe reaction gave single crystals of **2b** which were characterized by X-ray crystallography.[26]

Reaction of $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$ with NaOMe. THF-d_8 (0.66 mL) was condensed into an NMR tube containing **1** (20 mg, 0.040 mmol) and NaOMe (4.3 mg, 0.080 mmol). Within 30 min, the ^{1}H NMR spectrum showed over a dozen resonances in the C_5H_5 region (δ 5.7–6.4) and over a dozen resonances in the methoxide region (δ 3.3–4.0). The relative intensities of the peaks gradually changed as the sample was monitored at half-hour intervals, but after 7 h both regions were still complicated. After 3 days, the spectrum had simplified and one could identify the resonances of **2**, **3**, $(C_5H_5)_3Y(THF)$, and a complex with the following ^{1}H NMR resonances (THF): δ 6.23 (5 H), 4.05 (3 H), 3.90 (6 H), 3.80 (2 H).

$(C_5H_5)_5Y_5(\mu_3\text{-}OMe)_4(\mu\text{-}OMe)_4(\mu_5\text{-}O)$, 3. In the glovebox, NaC_5H_5 (550 mg, 5.12 mmol) was added slowly to a suspension of YCl_3 (1 g, 5.12 mmol) in THF (100 mL), and the mixture was stirred for 2 h. NaOMe (554 mg, 10.24 mmol) was added, and the reaction vessel was fitted with a reflux condensor, attached to a Schlenk line, and heated at reflux for 24 h. The cloudy mixture was brought into the glovebox and centrifuged to remove the solids (NaCl). The solids were reextracted with THF, and the THF fractions were combined. The solvent was removed by rotary evaporation, and the resulting powder was extracted twice with toluene (20 mL). Removal of toluene gave $(C_5H_5)_5Y_5(\mu_3\text{-}OMe)_4(\mu\text{-}OMe)_4(\mu_5\text{-}O)$ (989 mg, 93%). Treatment of the toluene-insoluble portion solids with THF, followed by another toluene extraction, yielded no additional toluene-soluble product. ^{1}H NMR (C_6H_6): δ 6.26 (s, 20 H, C_5H_5), 6.16 (s, 5 H, C_5H_5), 3.67 (s, 12 H, μ_3-OCH_3), 3.47 (s, 12 H, μ-OCH_3). ^{1}H NMR (THF-d_8): δ 6.38 (s, 5 H, C_5H_5), 6.23 (s, 20 H, C_5H_5), 4.15 (s, 12 H, μ_3-OCH_3), 3.69 (s, 12 H, μ-OCH_3). ^{13}C NMR (C_6D_6): δ 110.87 (C_5H_5, J_{CH} = 164 Hz), 110.50 (C_5H_5, J_{CH} = 165 Hz), 61.83 (CH_3), 54.51 (CH_3). IR (KBr): 3090 w, 2920 s br, 2810 s, 1457 m, 1258 m, 1154 w, 1072 s br, 1018 s br, 770 s br cm^{-1}. The crystal structure of **3** was previously described.[1]

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$ (**4**) and $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$ (**5**)

	4	**5**
formula	$Y_2C_{34}H_{58}O_2Si_4\cdot 2(C_6H_6)$	$Y_2C_{32}H_{52}Si_4Cl_2$
fw	945.2	797.8
temperature, K	173	183
crystal system	monoclinic	triclinic
space group	$C2/c$ (C_{2h}^6, No. 15)	$P\bar{1}$ (C_i^1, No. 2)
a, Å	24.930 (3)	8.676 (2)
b, Å	13.735 (2)	9.763 (2)
c, Å	14.764 (2)	12.487 (2)
α, deg		70.38 (1)
β, deg	91.90 (1)	76.69 (1)
γ, deg		88.67 (1)
V, Å^3	5052 (1)	967.7 (3)
Z	4	1 dimer
D_{calcd}, Mg/m^3	1.24	1.37
radiation (λ = 0.710 730 Å)	Mo Kα	Mo Kα
monochromator	highly oriented graphite	highly oriented graphite
data collected	$+h, +k, \pm l$	$+h, \pm k, \pm l$
scan type	θ–2θ	θ–2θ
scan width, deg	1.20° plus Kα separation	1.20° plus Kα separation
scan speed, deg min^{-1}	3.0 (in ω)	3.0 (in ω)
2θ range, deg	4.0–50.0	4.0–50.0
μ(Mo Kα), mm^{-1}	2.42	3.28
absorption correction	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)
transmsn factor (min/max)	0.194/0.218	0.534/1.000
reflections collected	4789	3684
observed reflections	3653 with $\lvert F_o\rvert > 2.0\sigma(\lvert F_o\rvert)$	3285 with $\lvert F_o\rvert > 0$
no. of variables	239	286
R_F, R_{wF}	5.3%, 5.7%	4.3%, 4.2%
goodness of fit	1.04	1.03

X-ray Data Collection and Structure Determination and Refinement for $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$, 4.[25,26] A clear crystal of approximate dimensions 0.46 × 0.46 × 0.53 mm was immersed in Paratone-N, mounted on a glass fiber, and transferred to the Siemens P3 automated four-circle diffractometer which is equipped with a modified LT-2 low-temperature system. The determinations of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.[27] Intensity data were collected at 173 K using a θ–2θ scan technique with Mo Kα radiation under the conditions described in Table I. All 4789 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The two possible C-centered monoclinic space groups are the noncentrosymmetric Cc (C_s^4, No. 9) or the centrosymmetric $C2/c$ (C_{2h}^6, No. 15). $C2/c$ was assumed and later proven to be the correct choice by successful solution and refinement of the model.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[28] or the SHELXTL PLUS program set.[29] The analytical scattering factors for neutral atoms were used throughout the analysis;[30a] both the

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[26] $\{[(C_5H_5)_2Y)]_3(OMe)_2O\}\{[(THF)_3Na_2](C_5H_5)\}$ crystallized from THF in space group *Pnam* with unit cell dimensions a = 18.854 (6) Å, b = 15.803 (3) Å, c = 22.355 (8) Å, and Z = 4 for D_{calcd} = 1.28 g cm^{-3}. The crystal did not provide a high-quality data set, but the connectivity of the atoms in the molecule was established. See supplementary material for details.

[27] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

[28] Strouse, C. Personal communication; UCLA Crystallographic Computing Package, UCLA, 1981.

[29] Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

Table II. Atomic Coordinates ($\times 10^4$) for $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$, **4**

	x	y	z
Y(1)	5597 (1)	1852 (1)	1870 (1)
Si(1)	7027 (1)	485 (1)	2549 (1)
Si(2)	5887 (1)	3161 (1)	−556 (1)
O(1)	4709 (1)	1846 (2)	1726 (2)
C(1)	6358 (2)	457 (3)	1951 (3)
C(2)	5882 (2)	25 (3)	2296 (3)
C(3)	5488 (2)	−54 (3)	1591 (3)
C(4)	5713 (2)	315 (3)	799 (3)
C(5)	6235 (2)	631 (3)	1011 (3)
C(6)	7303 (2)	1737 (3)	2723 (4)
C(7)	7502 (2)	−226 (4)	1874 (5)
C(8)	6966 (2)	−111 (5)	3679 (4)
C(9)	5886 (2)	3242 (3)	705 (3)
C(10)	5479 (2)	3651 (3)	1235 (3)
C(11)	5669 (2)	3755 (3)	2129 (3)
C(12)	6203 (2)	3415 (3)	2179 (3)
C(13)	6338 (2)	3109 (3)	1309 (3)
C(14)	6592 (2)	3035 (5)	−895 (4)
C(15)	5497 (3)	2113 (4)	−1038 (3)
C(16)	5585 (3)	4299 (4)	−1024 (4)
C(17)	4365 (2)	1900 (4)	950 (3)
	Benzene Solvent Molecule		
C(18A)	3313 (5)	2271 (9)	−501 (10)
C(18B)	3548 (6)	2131 (8)	−897 (10)
C(19A)	3685 (6)	2277 (10)	−1167 (9)
C(19B)	3871 (6)	2694 (14)	−1408 (9)
C(20A)	3920 (5)	3163 (14)	−1419 (8)
C(20B)	3872 (6)	3654 (16)	−1341 (12)
C(21A)	3767 (5)	4030 (9)	−999 (9)
C(21B)	3573 (8)	4122 (11)	−751 (13)
C(22A)	3387 (4)	4008 (9)	−337 (8)
C(22B)	3245 (6)	3566 (14)	−192 (9)
C(23A)	3165 (4)	3115 (11)	−65 (6)
C(23B)	3243 (5)	2569 (13)	−274 (10)

real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[30b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0015(|F_o|)^2$.

The structure was solved by direct methods (MITHRIL);[31] the position of the yttrium atom was determined from an "E-map". Subsequent difference Fourier syntheses (SHELXTL PLUS) revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. The molecule is a dimer and lies on a 2-fold rotation axis ($^1/_2$, y, $^1/_4$) which is perpendicular to the plane defined by Y(1)–O(1)–Y(1′)–O(1′). A benzene solvent of crystallization is present (two molecules per dimer). Residual electron density near each carbon of the benzene solvent molecule indicates that the two molecules are not perfectly crystallographically related by the 2-fold rotation axis. Twelve carbon atoms with a site occupancy factor of 0.5 were included to account for the approximately 30° "rotational disorder" of the solvent molecules. Refinement of positional and thermal parameters (isotropic for benzene carbons and all hydrogen atoms) led to convergence with R_F = 5.3%; R_{wF} = 5.7%, and GOF = 1.04 for 239 variables refined against those 3653 data with $|F_o| > 2.0\sigma(|F_o|)$ (R_F = 3.4% and R_{wF} = 4.6% for those 2907 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference Fourier map was "clean"; ρ(max) = 0.44 e Å^{-3}. Atomic positional parameters are given in Table II.

X-ray Data Collection and Structure Determination and Refinement for $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$, 5. A clear crystal of approximate dimensions 0.10 × 0.28 × 0.30 mm was oil-mounted on a glass fiber and handled as described for **4**. Details appear in Table I. All 3684 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o|$ = 0. A careful examination of a preliminary data set revealed no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The space group is either $P1$ or $P\bar{1}$. The centrosymmetric triclinic space group $P\bar{1}$ (C_i^1, No. 2) was chosen and later proved to be correct by successful solution and refinement of the model.

Table III. Atomic Coordinates ($\times 10^4$) for $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$, **5**

	x	y	z
Y(1)	262.7 (0.4)	9205.1 (0.3)	6677.1 (0.3)
Cl(1)	−1984 (1)	9297 (1)	5475 (1)
Si(1)	2950 (1)	11690 (1)	7701 (1)
Si(2)	−2214 (1)	5389 (1)	7842 (1)
C(1)	18 (4)	11822 (3)	6865 (3)
C(2)	−1514 (4)	11187 (4)	7250 (3)
C(3)	−1590 (4)	10004 (4)	8295 (3)
C(4)	−93 (4)	9939 (4)	8551 (3)
C(5)	956 (4)	11062 (3)	7655 (3)
C(6)	503 (4)	6704 (3)	8257 (3)
C(7)	2060 (4)	7257 (4)	7701 (3)
C(8)	2355 (5)	7231 (4)	6545 (3)
C(9)	977 (4)	6684 (3)	6408 (3)
C(10)	−217 (4)	6342 (3)	7470 (3)
C(11)	2673 (6)	13140 (5)	8384 (4)
C(12)	4222 (6)	12428 (7)	6188 (4)
C(13)	3930 (5)	10169 (5)	8620 (4)
C(14)	−2231 (5)	3572 (4)	8993 (3)
C(15)	−3784 (5)	6448 (5)	8449 (4)
C(16)	−2601 (6)	5181 (4)	6497 (4)

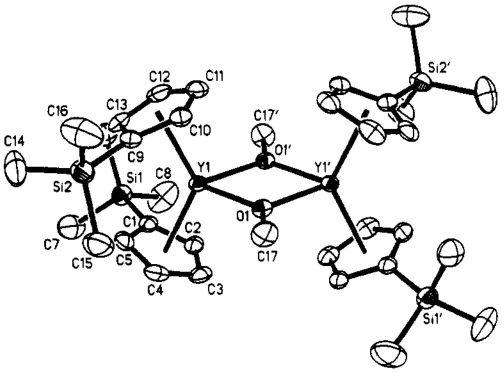

Figure 1. ORTEP diagram of $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$, **4**, with probability ellipsoids drawn at the 50% level.

All crystallographic calculations were carried out as described above for **4**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0008(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. All hydrogen atoms were located and refined isotropically. The molecule is a dimer and is located on a center of inversion at (0, 1, $^1/_2$). Refinement of positional and thermal parameters led to convergence with R_F = 4.3%, R_{wF} = 4.2%, and GOF = 1.03 for 286 variables refined against all 3285 unique data with $|F_o| > 0$ (R_F = 3.0% and R_{wF} = 3.8% for those 2721 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference Fourier map was devoid of significant features, ρ(max) = 0.51 e Å^{-3}. Atomic positional parameters are given in Table III.

Results

Synthesis. $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$. $(C_5H_5)_2YCl(THF)$ reacts with NaOMe over a 24-h period in THF to form $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$, **1**, as shown in eq 3. The reaction mixture can be

$$2(C_5H_5)_2YCl(THF) + 2NaOMe \rightarrow [(C_5H_5)_2Y(\mu\text{-}OMe)]_2 + 2NaCl \quad (3)$$

centrifuged to remove white THF-insoluble material presumed to be NaCl. Removal of solvent from the supernatant leaves a solid which can be extracted with toluene to give **1** in approximately 75% yield. Complex **1** was identified by complexometric analysis, ^{1}H NMR, ^{13}C NMR, and IR spectroscopies, and X-ray crystallographic studies on it and a derivative (Figure 1) as described in the section on crystallographic studies.

Surprisingly, additional quantities of **1** can be extracted from the toluene-insoluble solids after they are treated with THF. Hence, dissolution of the solids in THF followed by removal of THF and extraction with toluene increases the yield of **1** by 7–10%. These results suggest that **1** or its equivalent is initially tied up in some toluene-insoluble form which can be broken up by treatment with THF. It is interesting to note that a similar

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

(31) Gilmore, C. J. *MITHRIL, A Computer Program for the Automated Solution of Crystal Structures from X-ray Data*; University of Glasgow, Scotland.

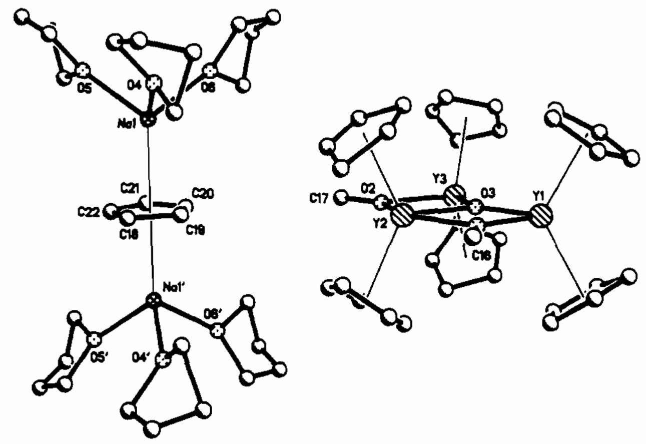

Figure 2. Ball and stick model of $\{[(C_5H_5)_2Y]_3(\mu\text{-}OMe)_2(\mu_3\text{-}O)\}\{[(THF)_3Na]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_5)\}$, **2b**. Unlabeled atoms are carbon.

situation is found in the procedure for optimizing the yield of the $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ starting material. As described in the Experimental Section, in that case, toluene-insoluble solids are formed which can be treated with THF and then extracted with toluene to give more $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$.

In contrast to the above procedure for the isolation of **1**, if the NaCl byproduct is *not* immediately removed by centrifugation from the reaction mixture of eq 3, a higher yield of **1** is directly obtainable by extraction. Hence, removal of THF from the crude reaction mixture of eq 3 followed by toluene extraction gives **1** in >90% yield. These results suggest that the presence of the NaCl byproduct diminishes the amount of **1** which is tied up in the toluene-insoluble form in the above procedure. Hence, we have the unusual situation that a *higher yield is obtained from a less pure reaction mixture.* This effect appears to depend on the identity of the alkali metal, since it is not observed in the KOMe reaction discussed below.

When KOMe is used instead of NaOMe in eq 3, the yield of **1** is invariably smaller and a variety of products can be obtained depending on the method of preparation of KOMe. In our hands, preparation of KOMe by adding freshly cut potassium to dried and distilled methanol and drying under vacuum (10^{-5} Torr) at 65 °C did not reliably give pure KOMe. The reaction of freshly sublimed $KN(SiMe_3)_2$ with dried, distilled methanol proved to be a cleaner synthesis of KOMe. The maximum yield of **1** observed from $(C_5H_5)_2YCl(THF)$/KOMe is 77%, and treatment of the toluene-insoluble byproduct with THF yields no additional **1**. Direct extraction of the crude reaction mixture prior to KCl removal did not give higher yields of **1**.

$\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_2[(C_5H_5)_2Y](\mu_3\text{-}O)\}^-$, 2. A constant byproduct in the $(C_5H_5)_2YCl(THF)$/KOMe reactions was a toluene-insoluble complex whose ^1H NMR spectrum contained two cyclopentadienyl resonances in a ratio of 1:2 and a single methoxide resonance with intensity consistent with two methoxides per three cyclopentadienyl groups. The ^{13}C NMR spectrum also agreed with this ratio of ligands. Other products were present in this THF-soluble portion, however, and prevented identification of this complex by X-ray crystallography. Samples of **2** were also obtained from THF extracts of a $(C_5H_5)_2YCl(THF)$/NaOMe reaction, but they appeared to contain NaC_5H_5 as a contaminant. The NaC_5H_5 could be removed from these mixtures by adding YCl_3 to form toluene-soluble $[(C_5H_5)_2Y(\mu\text{-}Cl)]_2$ which was subsequently removed by extraction. However, attempts to obtain X-ray-quality crystals of **2** from samples free of NaC_5H_5 were not successful. Only when NaC_5H_5 was present could crystals suitable for X-ray study be obtained. Most of these crystals diffracted only weakly, but one crystal was found which provided a data set good enough to determine the connectivity of the atoms in the complex.

The X-ray diffraction study revealed that NaC_5H_5 was not a contaminant in this case, but rather a component of the countercation for **2**; i.e., complex **2** crystallizes as the anion–cation pair $\{[(C_5H_5)_2Y]_3(OMe)_2O\}\{[(THF)_3Na]_2(\mu\text{-}C_5H_5)\}$ (Figure 2). The solid-state structure is consistent with the NMR data, and the ^1H and ^{13}C NMR spectra of the anion appear to be the same regardless of the cation present in solution. Complex **2** probably exists as the $M(THF)_x$ salt in solution and in the absence of free cyclopentadienide.

Since the ratio of the charge of oxygen-containing ligands to the number of yttrium atoms in **2** is 4:3, a reaction involving four methoxide ligands per three yttrium atoms was examined (reaction 4). When this reaction is carried out using K/MeOH-derived

$$3(C_5H_5)_2YCl(THF) + 4KOMe \rightarrow \{[(C_5H_5)_2Y(\mu\text{-}OMe)]_2[(C_5H_5)_2Y](\mu_3\text{-}O)\}^- \quad (4)$$

KOMe (which generates a 70% yield of $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$, **1**, and a 20% yield of **2** in a 1:1 reaction), **2a** can be isolated as the main product in as high as 70% yield. Little or no **1** is observed under these conditions. This clearly shows the importance of the relative concentrations of the reagents in this reaction system. Simply by increasing the amount of KOMe by one-third, the reaction can take an entirely different pathway.

When reaction 4 is carried out using KOMe obtained from $KN(SiMe_3)_2$/MeOH, the yield of **2** is also enhanced compared to the 1:1 reaction: 25% vs 4%. However, in this case, the yield of **1** is not negligible: it is 50% (cf. a 77% yield in the 1:1 reaction). Although these results are complicated by the variations depending on the source of KOMe, marked differences in product distributions due to the amount of methoxide present can be demonstrated by doing 1:1 and 4:3 stoichiometry reactions side by side with the same batch of reagents.

To determine if the oxide in **2** arose from the reaction vessel, reaction 4 was run in both Teflon and glass vessels in parallel experiments. No significant differences in the yield of **2** were observed. However, side by side reactions conducted in THF and toluene indicated that the solvent was important: **2** was not observed to form in toluene using reagents which gave yields of 25% when THF was the solvent.

Since **2** is formed by using a greater than 1:1 methoxide to yttrium ratio, it is possible that it would be formed by the reaction of the excess methoxide with initially-formed $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$. Accordingly, the reaction of **1** with methoxide ion was examined. An NMR study of the reaction of **1** with 1 equiv of NaOMe revealed a very complicated reaction system. At least a dozen cyclopentadienyl resonances were observed in the ^1H NMR spectrum after 30 min. This reaction mixture varied in composition over a period of days. After 3 days, **2**, $(C_5H_5)_5Y_5(OMe)_8O$,[1] **3** (see below), $(C_5H_5)_3Y(THF)$,[32] and one other main product (as yet unidentified) were observed. Clearly, $[(C_5H_5)_2Y(OMe)]_2$ reacts with methoxide, but this does not provide a simple route to **2**. The reaction of **1** with NaOMe was also examined in Teflon vessels, silylated glass vessels, glass vessels, and glass vessels containing glass shards to examine the effect of the container walls. No major changes in product distribution were observed. A high-dilution experiment also failed to show an effect.

The formation of gaseous byproducts in the synthesis of **2** via reaction 4 was examined by conducting large-scale reactions in a vessel attached to a Toepler pump. Me_2O was isolated and identified by mass spectroscopy as a byproduct in these reactions with yields of approximately 50% based on **2**. We attach no special significance to the 50% yield, given the volatility of this product, its isolation as a mixture with THF, and typical yields of gases in organolanthanide Toepler pump experiments (80–90% under ideal conditions). It is quite possible that Me_2O is formed in a 1:1 ratio with **2**, but we are able to isolate only half of that which is formed.

$[(C_5H_5)_5Y_5(\mu\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)]$, 3. When $(C_5H_5)_2YCl(THF)$ reacts with 1 equiv of NaOMe or KOMe which contains solvated MeOH, the reaction system becomes even more complicated than that described above. A new product, **3**, was generated in this reaction which had a characteristic ^1H NMR spectral

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[32] Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383–392.

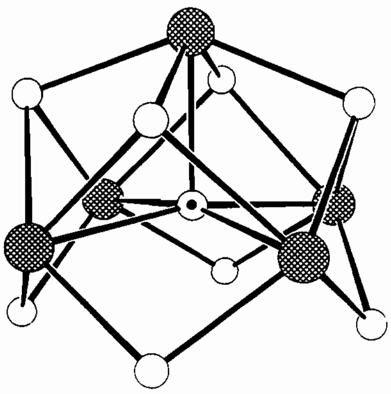

Figure 3. Diagram of the metal and oxygen framework of $[(C_5H_5)_5Y_5(\mu\text{-OMe})_4(\mu_3\text{-OMe})_4(\mu_5\text{-O})]$, **3** (open circles, OMe; cross hatched circles, $Y(C_5H_5)$; and circle with dot, oxide).

pattern containing two resonances with a 4:1 ratio in the C_5H_5 region and two resonances in a 1:1 ratio in the methoxide region. These NMR data are consistent with the solid-state structure determined to be $(C_5H_5)_5Y_5(\mu\text{-OMe})_4(\mu_3\text{-OMe})_4(\mu_5\text{-O})$ by an X-ray crystallographic study (Figure 3).[1]

The amount and form of the MeOH solvation appears to be crucial to the outcome of the reaction since the composition of the product mixtures can vary considerably. For example, **1** can be isolated in as much as 50% yield or just as a trace component. The other common product of these reactions, **3**, can be formed in trace amounts to as high as 60% yield. In some cases, the bulk of the product is not **1**, **2**, or **3**, but yet another material which is THF-insoluble. Formation of a specific $MOMe(MeOH)_x$ reagent by controlled addition of MeOH to desolvated MOMe has not given the same result as using a solvated methoxide reagent formed from MOMe in MeOH. The variability of the $(C_5H_5)_2YCl(THF)/MOMe$ reaction system with time and concentration, as described above, is consistent with this result. Simple addition of MeOH would not mimic the conditions of a solvated MeOH molecule being slowly released as the MOMe(MeOH) reagent dissolves and/or reacts.

The existence of a complex like **3** is not limited to yttrium. Since the initial discovery of **3**,[1] the preparation of the isostructural gadolinium complex has been reported.[17] Since **3** contains one C_5H_5 ring per yttrium, its independent formation from the monocyclopentadienyl complex $(C_5H_5)YCl_2(THF)_3$[33] was pursued. However, reactions of this complex with KOMe did not give good yields of **3**. Since the gadolinium complex was prepared from $(C_5H_5)GdCl_2(THF)_3$ prepared in situ, this route to **3** was examined. Following the procedure successful for the formation of the gadolinium complex, i.e., addition of NaOMe at −78 °C to the monocyclopentadienyl chloride generated in situ and stirring for 15 h at room temperature, little **3** was obtained. However, **3** can be made reproducibly in 85–95% yield by adding the NaOMe at room temperature and heating the $NaOMe/(C_5H_5)YCl_2(THF)_3$ mixture at reflux for 24 h as shown in reaction 5. Again, the specific reaction conditions appear to be crucial.

$$YCl_3 + NaC_5H_5 \xrightarrow{THF} [(C_5H_5)YCl_2(THF)_3] \xrightarrow{2NaOMe} \underset{\mathbf{3}}{(C_5H_5)_5Y_5(OMe)_8O} \quad (5)$$

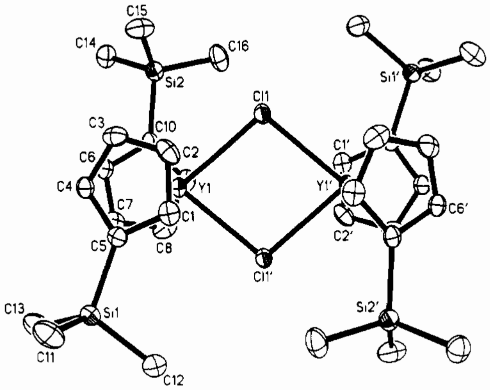

Figure 4. ORTEP diagram of $[(C_5H_4SiMe_3)_2Y(\mu\text{-Cl})]_2$, **5**, with probability ellipsoids drawn at the 50% level.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[(C_5H_4SiMe_3)_2Y(\mu\text{-OMe})]_2$, **4**

	Distances		
Y(1)–O(1)	2.217 (3)	Y(1)–O(1′)	2.233 (3)
Y(1)–C(1)	2.697 (4)	Y(1)–C(2)	2.677 (4)
Y(1)–C(3)	2.662 (4)	Y(1)–C(4)	2.658 (4)
Y(1)–C(5)	2.662 (4)	Y(1)–C(9)	2.683 (4)
Y(1)–C(10)	2.656 (4)	Y(1)–C(11)	2.646 (4)
Y(1)–C(12)	2.656 (5)	Y(1)–C(13)	2.679 (4)
Y(1)–Y(1′)	3.562 (1)	O(1)–C(17)	1.411 (5)
Y(1)–Cnt(2)	2.279	Y(1)–Cnt(1)	2.384
	Angles		
O(1)–Y(1)–O(1′)	73.6 (1)	Cnt(1)–Y(1)–O(1)	109.6
Cnt(1)–Y(1)–O(1′)	109.0	Cnt(2)–Y(1)–O(1)	108.7
Cnt(2)–Y(1)–O(1′)	109.7	Cnt(1)–Y(1)–Cnt(2)	131.3
Y(1)–O(1)–C(17)	131.0 (2)	Y(1)–O(1)–Y(1′)	106.4 (1)
C(17)–O(1)–Y(1′)	122.5 (2)		

Table V. Selected Interatomic Distances (Å) and Angles (deg) for $[(C_5H_4SiMe_3)_2Y(\mu\text{-Cl})]_2$, **5**[a]

	Distances		
Y(1)–Cl(1)	2.704 (1)	Y(1)–Cl(1′)	2.684 (1)
Y(1)–C(1)	2.643 (4)	Y(1)–C(2)	2.629 (4)
Y(1)–C(3)	2.604 (4)	Y(1)–C(4)	2.621 (4)
Y(1)–C(5)	2.648 (4)	Y(1)–C(6)	2.614 (3)
Y(1)–C(7)	2.614 (4)	Y(1)–C(8)	2.636 (4)
Y(1)–C(9)	2.634 (4)	Y(1)–C(10)	2.641 (3)
Y(1)–Cnt(1)	2.339	Y(1)–Cnt(2)	2.339
	Angles		
Y(1)–Cl(1)–Y(1′)	98.4 (1)	Cl(1)–Y(1)–Cl(1′)	81.6 (1)
Cnt(1)–Y(1)–Cl(1)	106.7	Cnt(1)–Y(1)–Cl(1′)	109.0
Cnt(2)–Y(1)–Cl(1)	109.5	Cnt(2)–Y(1)–Cl(1′)	109.3
Cnt(1)–Y(1)–Cnt(2)	130.1	Y(1)–O(1)–Y(1′)	106.4 (1)
C(17)–O(1)–Y(1′)	122.5 (2)		

[a] Cnt(1) is the centroid of the C(1)–C(5) ring. [b] Cnt(2) is the centroid of the C(9)–C(13) ring.

X-ray Crystallographic Studies. Bimetallic Complexes. Structural data were sought on **1** to determine if there were any unusual steric or bonding features of the methoxide ligand in the solid state. On the basis of related halide structures,[34,35] a dimeric structure, i.e., $[(C_5H_5)_2Y(\mu\text{-OMe})]_2$, was anticipated. On the other hand, the prevalence of trimeric yttrium alkoxide complexes in the literature[2-4,36] and the existence of the series $\{[(C_5H_5)_2Y]_3(OMe)_xH_{4-x}\}^-$ ($x = 0$–3)[37] and $[(Me_2C_5H_3)_2Y(\mu\text{-H})]_3$[38] made it conceivable that trimers could form. In addition, the ^1H NMR spectrum of **1** in C_6D_6 was unusual in that the δ 2.83 ppm shift of the methoxide resonance of **1** was upfield of the usual δ 3.26–3.47 region for μ-OMe ligands in cyclopentadienyl yttrium complexes.[1,37] In addition, this peak exhibited a temperature dependence and was observed to shift 0.2 ppm upfield as the temperature was lowered from +25 to −80 °C.

Unfortunately, crystals of **1** suitable for X-ray studies were difficult to obtain. The best crystal diffracted too weakly to provide sufficient data for satisfactory refinement of the structure, but

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Table VI. Comparative Crystallographic Data for $[(C_5H_4R)_2Y(\mu\text{-}Z)]_2$ Complexes

compound	Y–C(ring) av	(ring centroid)–Y –(ring centroid) angle	Y–Z–Y angle	Z–Y–Z angle	donor atom Y–Z distance	Y···Y distance	ref
$[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$	2.67 (1)	131.3	106.4 (1)	73.6	O 2.217 (3) 2.233 (3)	3.562 (1)	*a*
$[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$	2.63 (1)	130.1	98.4 (1)	81.6 (1)	Cl 2.704 (1) 2.684 (1)	4.079 (1)	*a*
$[(C_5H_5)_2Y(\mu\text{-}OH)]_2$	2.68 (3)	130	100.4 (7)	80.3 (9)	O 2.33 (2) 2.36 (2)	3.595 (6)	35
$[(C_5H_4Me)_2Y(\mu\text{-}OCH{=}CH_2)]_2$	2.651 (5)	128.1	106.9 (1)	73.1 (1)	O 2.275 (3) 2.290 (3)	3.667 (1)	36
$[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$	2.66 (2)	128.9	87.7 (3)	92.3 (3)	C 2.553 (10) 2.537 (9)	3.599 (8)	67

[a] This work.

Table VII. Comparative Structural Data on $M_5Z_{13}O$ Complexes (Z = Cp, OR)

distances (Å)	$Cp_5Y_5(OMe)_8O$, **3**	$Y_5(O^iPr)_{13}O$	$Yb_5(O^iPr)_{13}O$	$In_5(O^iPr)_{13}O$	$H_5Al_5(O^iBu)_8O$	$Cp_5Gd_5(OMe)_8O$
six-coordinate metal radius[43]	0.90	0.90	0.868	0.80	0.535	0.938
M(basal)–O(μ-OR)	2.19 (2)–2.25 (2) (2.22 av)	2.20 (5)–2.31 (3) (2.25 av)	2.171 (3)–2.229 (3) (2.190 av)	2.123 (11)–2.162 (11) (2.14 av)	1.817 (4)–1.824 (4) (1.821 av)	2.27 av
M(basal)–O(μ_3-OR)	2.40 (2)–2.46 (2) (2.43 av)	2.37 (4)–2.45 (4) (2.41 av)	2.285 (3)–2.397 (2) (2.366 av)	2.297 (10)–2.382 (10) (2.34 av)		2.45 av
M(apical)–O(μ_3-OR)	2.30 (2)–2.35 (2) (2.33 av)	2.18 (5)–2.32 (4) (2.27 av)	2.262 (3)–2.305 (3) (2.291 av)	2.204 (10)–2.222 (10) (2.22 av)		2.38 av
M(basal)–O(μ_5-O)	2.34 (2)–2.41 (2) (2.38 av)	2.31 (4)–2.39 (4) (2.35 av)	2.300 (2)–2.339 (2) (2.313 av)	2.220 (9)–2.260 (8) (2.24 av)	2.074 (3)–2.092 (2) (2.083 av)	2.42 av
M(apical)–O(μ_5-O)	2.27 (2)	2.34 (3)	2.285 (2)	2.211 (9)	1.900 (4)	2.30 (1)

it did establish the geometry of **1** as a dimer. Interestingly, five crystallographically distinct dimers were found in the unit cell.

To gain more definitive data on the bridging methoxide unit, a crystallographic study of the (trimethylsilyl)cyclopentadienyl derivative $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$, **4**, was carried out. For comparative purposes, the chloride analogue $[(C_5H_4SiMe_3)_2Y(\mu\text{-}Cl)]_2$, **5**, was also studied. Complexes **4** and **5** were prepared in direct analogy to their C_5H_5 analogues. Both complexes are more soluble than their C_5H_5 counterparts, and crystallization of **4** from benzene gave single crystals suitable for a detailed analysis. The ^1H NMR methoxide shift of **4** in C_6D_6, δ 3.12 ppm, was closer to the usual region than that of **1**.

The structures of **4** and **5** are shown in Figures 1 and 4, respectively, and summaries of bond distance and angle data are given in Tables IV and V. The overall structure of each complex is typical of $[(C_5H_4R)_2Ln(\mu\text{-}X)]_2$ complexes (R = H, Me, $SiMe_3$). The Me_3Si groups attached to the cyclopentadienyl rings bound to a single metal are positioned in a trans orientation with respect to each other to minimize steric interaction. This arrangement is also found in the recently published structure of $[(C_5H_4SiMe_3)_2Yb(\mu\text{-}OH)]_2$.[39] A comparison of bonding parameters between **4** and **5** and the closely related bimetallic yttrium complexes $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$,[40] $[(C_5H_4Me)_2Y(\mu\text{-}OCH{=}CH_2)]_2$,[41] and $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$[42] is given in Table VI. This shows that all four complexes have similar Y–C(ring) average distances, (ring centroid)–Y–(ring centroid) angles, ligand–Y–ligand angles, and Y–ligand–Y angles. The structure of $[(C_5H_4SiMe_3)_2Yb(\mu\text{-}OH)]_2$[39] also has structural parameters within these ranges when the difference in the size of the metals is considered. Interestingly, the bridging Y–O distances in **4** are shorter than those in the yttrium hydroxide and the yttrium enolate complexes. The short Y–O lengths in **4** evidently do not arise because of the trimethylsilyl substitution of the cyclopentadienyl ring, since they are also shorter than the Y–OH 2.29 (2) Å average Y–O length in $[(C_5H_4SiMe_3)_2Yb(\mu\text{-}OH)]_2$, which contains a metal which is 0.034 Å smaller than yttrium.[43]

In contrast to the data on **1**, there is a single crystallographically independent dimer in the unit cell of **4**. The bridging methoxide donor atoms are located rather symmetrically between the metals such that the Y–O distances are equivalent within experimental error. However, the Y–O–C angles are different: Y(1)–O(1)–C(17) is 131.0 (2)°, and Y(1′)–O(1)–C(17) is 122.5 (2)°.

A Trimetallic Complex. X-ray-quality crystals of $\{[(C_5H_5)_2Y]_3(\mu\text{-}OMe)_2(\mu_3\text{-}O)\}^-$, **2**, were difficult to obtain. The best crystal examined did not provide reliable bond distance and angle data, but the identity and connectivity of the atoms was determined. The structure of **2** shown in Figure 2 is an interesting variation of the structures of the trimetallic hydride chloride, polyhydride, and hydride methoxide complexes previously characterized: $\{[(C_5H_5)_2Er]_3(\mu\text{-}H)_2(\mu\text{-}Cl)(\mu_3\text{-}H)\}^-$,[44] $\{[(C_5H_5)_2Lu]_3(\mu\text{-}H)_3(\mu_3\text{-}H)\}^-$,[44] and $\{[(C_5H_5)_2Y]_3(\mu\text{-}OMe)_3(\mu_3\text{-}H)\}^-$.[37,45] In each of these complexes, there are three bis(cyclopentadienyl)metal moieties arranged in a triangle with three doubly-bridging monoanionic ligands spanning each edge of the trimetallic triangle and a central triply-bridging hydride ligand which lies in the plane of the three metals. Complex **2** also has three $(C_5H_5)_2Ln$ units arranged in a triangle and two of the edges bridged by monoanionic ligands (the methoxides). However, in place of the third bridging monoanion *and* the central hydride is an oxide ion. This ligand gives the same overall charge to the complex and occupies a coordination position essentially intermediate between those occupied in the other complexes by the central bridging hydride and one edge bridge.

The countercation in **2b**, $\{[(THF)_3Na]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_5)\}^+$, is the inverse of a metallocene sandwich complex. Although a variety of structures of alkali-metal cyclopentadienyl complexes are known[46–48] including some in which another metal is on the other

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side of the cyclopentadienyl ligand,[37,47,49–52] it is rare to find a homometallic inverse sandwich complex of this type. Examples have been reported for lithium with a dianion derived from acenaphthene in $[Li(TMEDA)]_2[\mu\text{-}\eta^5{:}\eta^5\text{-}C_{12}H_8]$[51] and with the methylcyclopentadienide ion in $\{[(TMEDA)Li]_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4Me)\}^+$.[52] To our knowledge, **2b** is the first example with sodium.

A Pentametallic Complex. The previously reported structure of $[(C_5H_5)Y]_5(\mu_3\text{-}OMe)_4(\mu\text{-}OMe)_4(\mu_5\text{-}O)$, **3**,[1] consists of a square-pyramidal arrangement of $(C_5H_5)Y$ units connected by μ_3-OMe ligands over each of the four triangular faces, μ-OMe ligands along each of the four edges of the base, and an internal oxide. The yttrium oxide framework, Figure 3, resembles a metal oxide lattice in which one metal had been removed from the six metals surrounding an oxide in an octahedral hole. When **3** was first described,[1] it was an unusual type of alkoxide oxide complex. The closest related structure in the literature was the aluminum isobutoxide $H_5Al_5(\mu\text{-}OCH_2CHMe_2)_8(\mu_5\text{-}O)$.[53] The aluminum complex differs from **3** structurally in that it has no triply-bridging alkoxide ligands. It has subsequently been shown that **3** is a prototype for an extensive series of pentametallic complexes containing five metals, thirteen monoanionic ligands (five terminal, four doubly bridging, and four triply bridging) and a central oxide ligand, $M_5(O^iPr)_{13}O$ (M = Y,[15,16] Yb,[15,18] In[15,18]). In addition, a direct analogue has been structurally characterized for gadolinium.[17] As shown in Table VII, the metrical parameters in **3** are very similar to those in $Y_5(O^iPr)_{13}O$, $In_5(O^iPr)_{13}O$, $Al_5H_5(O^iBu)_8O$, and $(C_5H_5)_5Gd_5(OMe)_8O$ when the differences in metallic radii are considered.[43]

Discussion

Synthesis. The reaction of $(C_5H_5)_2YCl(THF)$ with alkali-metal methoxides displays a surprisingly complex dependence on reaction conditions and procedures for isolating the products. The expected product of this system, $[(C_5H_5)_2Y(OMe)]_2$, **1**, is obtained most directly by the reaction of NaOMe with $(C_5H_5)_2YCl(THF)$ in THF at room temperature, eq 3.[54] The 80–90% yields are higher than that originally reported by Dubeck et al.[13] for the analogous erbium reaction which was run at reflux in THF, but the yields depend critically on the reaction workup.

Toluene extraction of the reaction mixture after separation of insoluble products by centrifugation does not provide the full yield of toluene-soluble **1** that is obtainable. Apparently, **1** can exist in some complexed form (e.g., $(C_5H_5)_2Y(\mu\text{-}OMe)(\mu\text{-}Cl)Na(THF)_2$ or some oligomer of this approximate constitution) which is toluene insoluble, since subsequent treatment with THF releases more toluene-soluble **1**. A similar situation is observed in the synthesis of $[(C_5H_5)_2YCl]_2$ from YCl_3 and NaC_5H_5.

The formation of less soluble adducts of complexes of general formula $(C_5R_5)_2LnZ$ (Ln = lanthanide or yttrium, Z = monoanionic monodentate ligand, R = H, Me, $SiMe_3$) is well known in yttrium and lanthanide chemistry. The most common examples are alkali-metal halide adducts of the type $(C_5R_5)_2LnZXM(ether)_x$,[55–57] (X = halide, M = alkali metal, and x = 1–3). These complexes are typically less soluble than their salt-free counterparts $(C_5R_5)_2LnZ(ether)$ or $[(C_5R_5)_2LnZ]_2$, and their stability, solubility, and degree of oligomerization depend on the identity and amount of ether present (e.g., compare $[(C_5Me_5)_2CeCl_2K(THF)]_n$[57] and $(C_5Me_5)_2CeCl_2Li(Et_2O)_2$[56]) as well as the specific alkali metal involved.

Interestingly, higher yields of **1** are best obtained by *not* separating the byproduct NaCl from the reaction mixture before extraction. Hence, the presence of NaCl seems to reduce the amount of **1** that is complexed as a toluene-insoluble product. Since an analogous effect is not observed in the KOMe preparations of **1**, this phenomenon seems to depend on the particular alkali metal present. Although the details of this observed dependence of yield on the presence or absence of alkali-metal halide and THF are unknown, the data seem explicable in terms of metal halide lattice energies, degree of solvation, and tendencies to form $(C_5R_5)_2LnZXM(ether)_x$ complexes.

In contrast to the high-yield synthesis of **1** from NaOMe, the analogous reaction of KOMe with $(C_5H_5)_2YCl(THF)$ is much more variable in its product distribution and it can give very low yields of **1**. The method of preparation of KOMe appears to be the most important factor influencing the product distribution obtained from this reaction, with the next most critical factor being the local ratio of methoxide to yttrium. Although this system proved to be too complicated for a detailed mechanistic analysis, it did provide two byproducts which in many respects are more interesting than the primary product **1**!

The two fully characterized byproducts consistently identified in these reactions are the oxides $\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_2[(C_5H_5)_2Y](\mu_3\text{-}O)\}^-$, **2**, and $(C_5H_5)_5Y_5(\mu\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$, **3**. The origin of oxide ligands in lanthanide and yttrium alkoxide reactions is a poorly understood area.[1–3,6,15–21] The oxide in $M_5(O^iPr)_{13}O$ (M = Y, Yb, In) is thought to arise[18,36] either by propene elimination ($MO^iPr \rightarrow MOH + H_2C{=}CHCH_3$) or by diisopropyl ether formation ($2MO^iPr \rightarrow M_2O + {}^iPr_2O$), since the oxo product forms even when "exceptional precautions" are taken to prevent hydrolysis.[19] However, neither propene nor isopropyl ether was isolated from these isopropoxide systems. Organic products which could form from alkoxide decomposition have been observed in some other cases. Propene has been reported to form upon thermolysis of yttrium isopropoxides,[21] isobutene forms upon thermolysis of $\{Ce[OCH(CMe_3)_2]_3\}_2$,[58] and propane has been observed in the reaction of $KN(SiMe_3)_2$ with $Zr_2(O^iPr)_8({}^iPrOH)_2$ to form $K_4Zr_2O(O^iPr)_{10}$.[59]

If the alkoxide ligands are not the source of the oxide, the other most likely source is adventitious water or water absorbed onto the glassware. Given the high reactivity of the cyclopentadienide ions in $(C_5H_5)_2YCl(THF)$ with H_2O, dicyclopentadiene would be expected to form if water were present. However, cyclo-

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(54) **1** can also be prepared by reacting $[(C_5H_5)_2Y(THF)(\mu\text{-}H)]_2$ with MeOH or CH_2O, but these reactions do not give higher yields of pure products.

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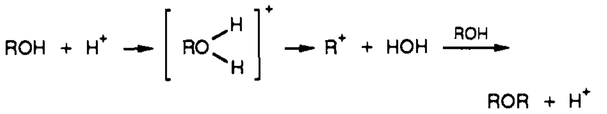
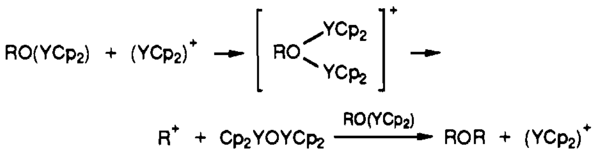
pentadienyl hydrolysis products were not observed in these reactions. On the other hand, the presence of water-derived oxide or hydroxide contaminants in the KOMe cannot be excluded. The synthesis of KOMe from sublimed $KN(SiMe_3)_2$ with MeOH was used to minimize such contamination, and separate attempts to make the oxide products in the presence of alkali-metal oxides failed. Comparison studies in glass versus Teflon reaction vessels indicated that water absorbed on glass was not the source of oxide.

The best evidence available to indicate that methoxide can be a source of oxide in the reactions reported here is the detection of Me_2O in reactions which form **2**. The yields of Me_2O are not quantitative, but given the difficulties in isolating and separating a product of this volatility, the 50% yields show that a significant amount of Me_2O is formed in reactions generating **2**. The formation of Me_2O in these reactions could be formally explained using an analogy between a cationic $[(C_5H_5)_2Y]^+$ unit and a proton[60] along with known reaction chemistry of alcohols. Equation 6 shows the acid-catalyzed formation of ethers from alcohols. An analogous reaction with $[(C_5H_5)_2Y]^+$ in place of the proton is given in reaction 7.



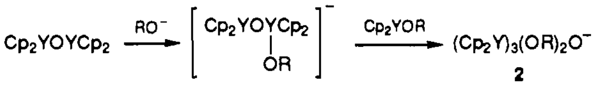
(6)



(7)

Neither the cation $[(C_5H_5)_2Y]^+$ nor the oxide $[(C_5H_5)_2Y]_2O$ have been observed in this reaction system. However, analogues of both are known. The cations $[(C_5Me_5)_2Sm(THF)_2]^+$[61] and $\{[C_5H_3(SiMe_3)_2]_2Ln(MeOCH_2CH_2OMe)(MeCN)\}^+$ (Ln = La, Ce)[62] and the oxides $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$,[63] $[(C_5H_5)_2Lu(THF)]_2(\mu\text{-}O)$,[64] and $[(C_5H_4Me)_2Yb(THF)]_2(\mu\text{-}O)$[65] have all been characterized by X-ray crystallography.[66] Attempts to synthesize and fully characterize $[(C_5H_5)_2Y(THF)_2]^+$ have not yet been successful.[67] As shown in reaction 7, only a catalytic amount of $[(C_5H_5)_2Y]^+$ is required by this scheme.

The $[(C_5H_5)_2Y]_2O$ which would accumulate in this reaction could react further to give the observed **2** as shown in reaction 8. The fact that **2** is not formed in high yield in toluene compared to THF is also consistent with the intermediacy of the cationic unit such as $[(C_5H_5)_2Y(THF)_2]^+$. Such a species would be expected to be stabilized in a more polar solvent and might not be expected to form or to be soluble and reactive in toluene.



(8)

The formation of the oxide ligand in **3** could be explained similarly although the route to this pentametallic complex obviously requires more steps. As discussed earlier, **3** is a prototype of an extensive series of pentametallic alkoxide oxide complexes containing five metals, thirteen monoanionic ligands, and a central oxide ligand.[15-18] These complexes are formed by a variety of routes, all of which have no intentionally added oxide ligands. Hence, there may be a variety of ways to generate the oxide in this system.

The formation of a product (**3**) which has a 1:1 C_5H_5:Y ratio is readily explained when MeOH-solvated KOMe is used. However, the lack of success we have had in attempts to reproduce the synthesis of **3** using a KOMe/MeOH reagent deliberately prepared from MeOH-free KOMe and MeOH suggests that the rate of release of MeOH into the system is important. Since **3** is also produced in MeOH-free reactions, other pathways to remove one C_5H_5 ring per yttrium must also exist. One possibility is a ligand redistribution reaction in which the ring lost from the $(C_5H_5)_2Y$-containing complexes ends up as the third ring in the observed byproduct $(C_5H_5)_3Y(THF)$.[32] Ligand redistribution reactions are common in lanthanide chemistry, and $(C_5H_5)_3Y(THF)$ is often the end product.

Another possible route to $(C_5H_5)Y$-containing products is methoxide-induced displacement of the cyclopentadienyl ligand. Previously, the removal of C_5H_5 from $(C_5H_5)_3Nd(THF)$ and $(C_5H_5)_3Lu(THF)$ by $LiCMe_3$ and $LiCH_2CHMe_2$ has been reported.[68] In support of this, it was found that C_5H_5 can be removed from $(C_5H_5)_3Y(THF)$ by NaOMe to form $[(C_5H_5)_2Y(OMe)]_2$. Again, reaction conditions and concentrations appear to be important since $(C_5H_5)_3Y(THF)$ is one of the final products in the $(C_5H_5)_2YCl(THF)$/MOMe reaction system.

After the identities of byproducts **2** and **3** were established, more systematic syntheses to these complexes could be developed. To date, the best synthesis of **2** involves the reaction of 4 equiv of KOMe prepared from potassium and MeOH with 3 equiv of $(C_5H_5)_2YCl(THF)$ in THF. As shown in eq 9, a balanced

$$3(C_5H_5)_2YCl(THF) + 4KOMe \xrightarrow{THF} \underset{\textbf{2a}}{\{[(C_5H_5)_2Y]_3(OMe)_2O\}\{K(THF)\}_y} + MeOMe + 3KCl \quad (9)$$

equation involving the formation of Me_2O can be written for this reaction. The reaction is not this simple, however, since **1** and **3** are consistently found as byproducts in this system. The reaction of $[(C_5H_5)_2Y(OMe)]_2$ with methoxide did not prove to be a more reliable route to **2**.[69]

It was expected that an improved synthesis of **3** might be achieved using the monocyclopentadienyl precursor $(C_5H_5)YCl_2(THF)_3$.[33] This complex did not give good yields of **3**, and syntheses following the procedure reported to form the gadolinium analogue[17] using a monocyclopentadienyl precursor generated in situ also failed to give good yields. However, using $(C_5H_5)YCl_2(THF)_3$ generated in situ and higher temperatures than used in the gadolinium system, **3** can be prepared consistently in 80–95% yields! These results again indicate the importance of specific reaction conditions in this system.

Structure. The structure of the bimetallic complex $[(C_5H_5)_2Y(\mu\text{-}OMe)]_2$ was surprisingly difficult to obtain considering the number of other $[(C_5H_5)_2Y(\mu\text{-}Z)]_2$ structures which are known.[34,35,40-42,70] X-ray crystallographic analysis of the Me_3Si derivative $[(C_5H_4SiMe_3)_2Y(OMe)]_2$ showed no unusual features except that the Y—O bond was shorter than the Y—O bonds in $[(C_5H_5)_2Y(\mu\text{-}OH)]_2$ and $[(C_5H_5)_2Y(\mu\text{-}OCH{=}CH_2)]_2$.

The structure of **2** is an interesting variation of the series of $\{[(C_5H_5)_2Ln(\mu\text{-}Z)]_3(\mu_3\text{-}Z')\}^-$ complexes characterized earlier in which Z could be halide, hydride, or methoxide and Z′ was hydride. Apparently, a dianionic ligand, in this case oxide, can effectively replace one doubly-bridging Z ligand and the central Z′ ligand which is coplanar with the three metals. The same charge and overall structure of the complex are maintained. The structure of **2** reinforces the idea that this trimetallic arrangement

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of $(C_5H_5)_2Ln$ units is favorable[2,3] and can be modified to some extent. Extensions to central S^{2-} and N^{3-} ligands are suggested by this result.

The existence of the inverse sandwich countercation $\{[(THF)_3Na]_2(\mu\text{-}\eta^5:\eta^5\text{-}C_5H_5)\}^+$ in **2** shows that the cyclopentadienyl ion can be more than an innocent contaminant in these reaction systems. In conjunction with alkali metals, it can provide a countercation of substantial size. Given that ligand disproportionation can occur and cyclopentadienyl ligands can be displaced in f element complexes,[68,71] the possible presence of $[M_2(\mu\text{-}C_5R_5)]^+$ cations must be considered in cyclopentadienyl systems containing alkali-metal ions.

The pentametallic structure of **3** has turned out to be a common form of self-assembly in alkoxide systems involving yttrium, lanthanide, and metals of similar sizes.[15-18] Comparison of these structures with **3** (Table VII) indicates that the combination of C_5H_5 and OMe ligand is sterically equivalent to the bulk provided by isopropoxide ligands.

In the sense that the square pyramid is comprised of four triangles, each of which contains a multiply-bridging ligand above and below the plane, this structure is also relatable to the trimetallic yttrium *tert*-butoxide complexes such as $Y_3(OCMe_3)_8Cl(THF)_2$ and $[Y_4(OR)_{10}Cl_2O]^{2-}$ which contain the basic unit $Ln_3(\mu\text{-}OR)_3(\mu_3\text{-}Z)_2$ (Z = OR, halide, or oxide).[2] In the case of **3**, the triply-bridging ligands are a methoxide on one side of the Y_3 triangle and the oxide on the other side, which since it is shared by all of the triangles is a μ_5-ligand. As in $[Y_4(OR)_{10}Cl_2O]^{2-}$, the edges of the triangles which are fused do not have the μ_2-alkoxide ligand, and hence **3** has only four μ_2-OMe ligands along the base. In this comparison, the C_5H_5/OMe ligand combination is functioning as the equivalent of the *tert*-butoxide ligand. If one considers the trimetallic bis(cyclopentadienyl)yttrium alkoxide complexes such as **2** and $\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_3(\mu\text{-}H)\}^{-}$[37] as additional variations on the basic $Ln_3(\mu\text{-}OR)_3(\mu_3\text{-}Z)_2$ unit, one can see a continuous series of structural possibilities based on triangular units with various combinations of alkoxide and cyclopentadienyl ligands.

Conclusion

The reaction of methoxide ion with $(C_5H_5)_2YCl(THF)$ has produced an unexpected amount of information on the chemistry of cyclopentadienylyttrium alkoxides. These reactions can be much more complicated than anticipated and demonstrate how carefully reaction details must be controlled in some lanthanide-based systems. A variety of reaction pathways are readily accessible, and small changes in the concentration of reagents can alter the course of the reaction in a major way. In addition, the preparation of the starting materials and product isolation procedures can have profound effects on the course of the reaction. This study also shows that oxide-containing products can be obtained in the presence of water-scavenging ligands such as $C_5H_5^-$ in reactions which form byproducts consistent with methoxide to oxide conversions. The variations observed in this reaction chemistry along with the considerable structural variety which appears to be accessible through bridged trimetallic complexes of these metals indicate that, to do future mechanistic studies of clean reaction systems, the components must be chosen very carefully.

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Supplementary Material Available: Tables of bond distances and angles, thermal parameters, crystal data, details of intensity data collection and structure refinement, atomic positional parameters, temperature factors, and H atom coordinates and displacement coefficients, ball and stick diagrams, ORTEP diagrams, and textual presentation of X-ray data collection and structure determination and refinement (43 pages); tables of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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Double Oxidative Carbon–Carbon Coupling of a Dimeric Orthopalladated Amido Complex Leading to Redox-Active Tetrapalladia Units $[Pd_4]^{n+}$ (n = 0–4)

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Chemical or electrochemical oxidation of the chiral orthometalated amido dimeric complex $[Pd\text{-}o\text{-}C_6H_4\text{—}C(Me)\text{=}N\text{—}NPh)L]_2$ ($L = P(OMe)_3$) leads to double carbon–carbon coupling on the para carbons of the phenyl groups, giving pure diastereomeric tetrapalladia units $[Pd_4]^{n+}$ (n = 0–4) related by fully reversible monoelectronic electron transfers. The species $[Pd_4]^{4+}$ undergoes splitting with Cl^-, giving dimeric units $[Pd_2]$ where a 4,4′-biphenylene quinone diimine is trapped and stabilized between two palladia atoms; reduction with $CoCp_2$ affords a mixture of both possible diastereomers of $[Pd_4]^0$. Near-infrared absorptions have been observed for paramagnetic $[Pd_4]^{3+}$, which can be regarded as a "mixed oxidation state" compound. The structure of $[Pd\text{-}o\text{-}C_6H_4\text{—}C(Me)\text{=}N\text{—}NPh\text{-}p\text{-}NO_2)L]_2$ ($L = P(OMe)_3$), where coupling is precluded by NO_2 groups, was determined crystallographycally [space group $P\bar{1}$ (triclinic), a = 10.901 (16) Å, b = 13.744 (9) Å, c = 14.242 (5) Å, α = 73.41 (4)°, β = 87.61 (6)°, γ = 81.00 (8)°, V = 2020 (5) Å^3, Z = 2].

Introduction

Mixed-valence polynuclear complexes are of current interest,[1] as they exhibit unusual structural, bonding, reactivity, spectroscopic, and magnetic properties[2] which can find applications in areas such as the study of electron-transfer processes[3] and the design of molecular electronics.[4]

We have previously prepared and described[5] binuclear orthometalated complexes of palladium(II) which could be used as precursors to prepare potentially mixed-valence compounds. The

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