dimer **1** (Table I) as has been predicted[7] by electronic arguments. The existence of a parallel, light-promoted reaction manifold that is markedly susceptible to external radical influences but is relatively insensitive to steric effects suggests that an ET mechanism related to the excited-state behavior[9] of compound **5** may overtake the associatively activated thermal reaction[1] under appropriate conditions.

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Registry No. **1**, 96280-42-1; **2**, 117687-35-1; **3**, 82484-38-6; **4**, 123266-64-8; MeI, 74-88-4.

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Utility of the 2,6-Dimethylphenoxide Ligand in Providing Chloride- and Oxide-Free $[Y(OR)_3(solvent)_a]_b$ Complexes with Accessible Coordination Sites

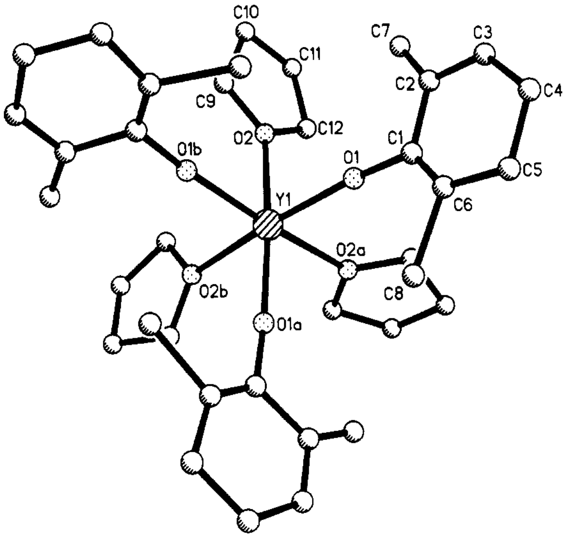

Figure 1. Molecular structure of $Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$ (**2**).

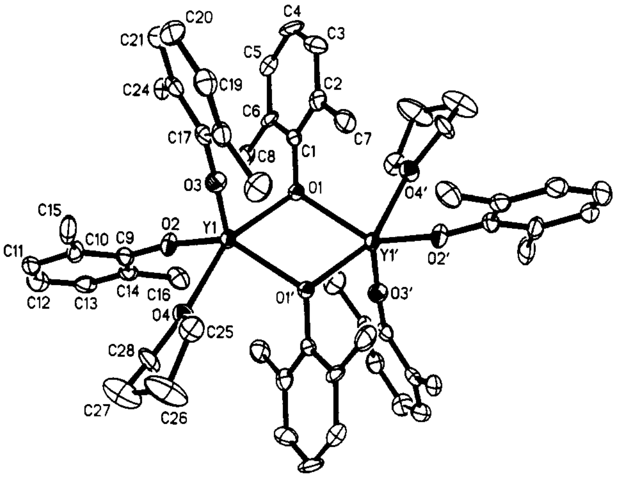

Figure 2. ORTEP diagram of $Y_2(OC_6H_3Me_2\text{-}2,6)_6(THF)_2$ (**3**) with probability ellipsoids drawn at the 40% level. Lattice toluene and hydrogen atoms are not shown.

Recently, the alkoxide chemistry of yttrium, barium, and copper has been of interest, since hydrolysis of heteropolymetallic alkoxides of these metals via sol-gel processes[1,2] offers a route to high-purity superconducting oxides such as $YBa_2Cu_3O_{7-x}$.[3] Although alkoxide complexes of yttrium have been known for years,[4,5] the precise structure and composition of some of these compounds has only recently been verified by X-ray crystallography.[6-11] These studies have shown that, with simple ligands such as $OCMe_3$ and $OCHMe_2$, polymetallic complexes that incorporate halide and oxide ligands are formed instead of simple $Y(OR)_3$ species. To date, the only way to obtain a fully characterized homoleptic $Y(OR)_3$ complex has been to use the 2,6-di-*tert*-butylphenoxide ligand, a ligand so large that the unusually low coordination number of 3 is observed in $Y[OC_6H_3(t\text{-}Bu)_2\text{-}2,6]_3$ (**1**).[11] We report here that the 2,6-dimethylphenoxide ligand[12,13] can provide halide- and oxide-free $[Y(OR)_3(solvent)_a]_b$ complexes with enough steric flexibility to achieve five- and six-coordination and to form bridged bimetallic species.

YCl_3 (200 mg, 1.02 mmol) reacted with $NaOC_6H_3Me_2\text{-}2,6$[14] (443 mg, 3.07 mmol) in THF (18 mL) to form a cloudy solution. After the reaction mixture was stirred for 24 h and centrifuged and the solvent was removed by rotary evaporation, $Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3$ (**2**)[16] (532 mg, 78%) was obtained as a white powder, as shown in eq 1. When this white powder was

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(14) Prepared[15] from the reaction of $HOC_6H_3Me_2\text{-}2,6$ (3.95 g, 0.032 mmol), which was vacuum-distilled from CaH_2 with sodium hydride (0.930 g, 0.039 mmol) in 70 mL of THF in the dry box. After being stirred for 24 h, the slightly cloudy solution was centrifuged and the solvent was removed from the supernatant by rotary evaporation. The resulting white powder was placed under vacuum (1×10^{-4} Torr) and heated to 40 °C for 24 h. ^1H NMR (C_6D_6): δ 7.10 (d, $J_{HH} = 7.3$ Hz, 2 H, $OC_6\mathit{H}_3Me_2\text{-}2,6$), 6.69 (t, $J_{HH} = 7.3$ Hz, 1 H, $OC_6\mathit{H}_3Me_2\text{-}2,6$), 1.87 (s, 6 H, $OC_6H_3\mathit{Me}_2\text{-}2,6$). IR (KBr): 3000 w, 2965 m, 2900 s, 2845 w, 1580 s, 1460 s br, 1425 s, 1370 m, 1340 w, 1300 s br, 1080 s, 970 m, 940 w, 905 m, 845 s, 755 s, 680 m cm^{-1}.

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(16) ^1H NMR (THF-d_8): δ 6.74 (d, $J_{HH} = 7.3$ Hz, 6 H, $C_6\mathit{H}_3Me_2\text{-}2,6$), 6.28 (t, $J_{HH} = 7.3$ Hz, 3 H, $C_6\mathit{H}_3Me_2\text{-}2,6$), 2.14 (s, 18 H, $C_6H_3\mathit{Me}_2\text{-}2,6$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 163.60 (s, $\mathit{C}_6H_3Me_2\text{-}2,6$), 129.44 (d, $J_{CH} = 155$ Hz, $\mathit{C}_6H_3Me_2\text{-}2,6$), 127.21 (s, $\mathit{C}_6H_3Me_2\text{-}2,6$), 116.34 (d, $J_{CH} = 157$ Hz, $\mathit{C}_6H_3Me_2\text{-}2,6$), 69.41 (THF), 27.50 (THF), 19.53 (q, $J_{CH} = 125$ Hz, $C_6H_3\mathit{Me}_2\text{-}2,6$). Anal. Calcd for $YC_{36}H_{51}O_6$: Y, 13.3. Found: Y, 13.7. IR (KBr): 3760 m, 3020 m, 2900 s br, 2700 m, 2395 m, 2000 w, 1580 s, 1250 s br, 1080 w, 760 m cm^{-1}.

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dissolved in toluene (10 mL) and the solvent was removed, $Y_2(OC_6H_3Me_2\text{-}2,6)_6(THF)_2$ (**3**)[17] was isolated as a white powder (441 mg, 82%) according to eq 2.

$$YCl_3 + 3NaOC_6H_3Me_2\text{-}2,6 \xrightarrow{THF} \underset{\mathbf{2}}{Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3} \qquad (1)$$

$$YCl_3 + 3NaOC_6H_3Me_2\text{-}2,6 \xrightarrow{THF} \xrightarrow{toluene} \underset{\mathbf{3}}{[Y(\mu\text{-}OC_6H_3Me_2\text{-}2,6)(OC_6H_3Me_2\text{-}2,6)_2(THF)]_2} \qquad (2)$$

The ^1H and ^{13}C NMR spectra of **2**[16] in THF-d_8 indicated that a single phenoxide ligand environment was present. This was confirmed by a preliminary single-crystal X-ray diffraction study,[18] which revealed the structure shown in Figure 1. The ^1H NMR spectrum of **3** in THF-d_8 was identical with that of **2**. However, in C_6D_6[17] two methyl resonances in a ratio of 2:1 were observed. White crystals of **3** were grown from toluene at −34 °C and were shown by single-crystal X-ray diffraction to have the bimetallic structure shown in Figure 2.[19] The solid-state structure is consistent with the ^1H NMR spectrum, assuming that the methyl groups of the bridging ligands resonate at lower field than those of the terminal ligands. *tert*-Butoxide ligands attached to yttrium exhibit this same trend in resonance shifts.[7,8]

Extraction of **3** with THF and removal of the solvent by rotary evaporation regenerated **2** (eq 3). Extraction of the regenerated

$$\underset{\mathbf{3}}{[Y(\mu\text{-}OC_6H_3Me_2\text{-}2,6)(OC_6H_3Me_2\text{-}2,6)_2(THF)]_2} \xrightleftharpoons[toluene]{THF} \underset{\mathbf{2}}{Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3} \qquad (3)$$

sample of **2** with toluene quantitatively regenerated **3**. This cycle could be traversed repeatedly; i.e., loss of THF from **2** to form phenoxide-bridged **3** is facile and reversible.

The structure of **2** contains a distorted *fac*-octahedral arrangement of ligands around yttrium. Six has been the common coordination number observed in all structurally characterized yttrium alkoxides in the literature except for the sterically crowded three-coordinate **1**.[11] Unfortunately, the quality of the structure of **2** does not allow a detailed discussion of bond distances and angles.[18]

In **3**, the yttrium atoms are five-coordinate. The geometry is best described as distorted square pyramidal with O(3) occupying the axial position. The bridging ligands are situated symmetrically between the two yttrium atoms (Y(1)–O(1) and Y(1)–O(1′) are 2.277 (5) and 2.275 (6) Å, respectively). As is typical,[6-10,22] these bridging Y–O distances are longer than the terminal Y–O distances (Y(1)–O(2) = 2.075 (6) Å, Y(1)–O(3) = 2.046 (6) Å). The terminal Y–O distances are similar to the 2.00 (2)-Å Y–O distances in **1**[11] and are in the 1.97–2.08-Å range of terminal Y–O distances in *tert*-butoxide complexes.[7,8] The Y(1)–O(2)–C(9) angle of 162.6 (5)° is smaller than the 171(1)–175(1)° range of Y–O–C angles in **1**, whereas the Y(1)–O(3)–C(17) angle of 168.7 (6)° is closer to this range. The 2.348 (6)-Å Y–O(THF) distance is in the 2.33–2.42-Å range observed for such distances in yttrium *tert*-butoxide complexes.[7,8]

Complexes **2** and **3** and their facile interconversion demonstrate that the 2,6-dimethylphenoxide ligand can provide a versatile $[Y(OR)_3(\text{solvent})_a]_b$ unit with yttrium in which *a* and *b* are variable. The sterically unsaturated "$Y(OR)_3(THF)$" moiety formed in the **2** to **3** conversion may be quite useful in synthesis, and its utility in the formation of heteropolymetallic alkoxide complexes is under study.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, thermal parameters, and hydrogen atom coordinates and thermal parameters and a summary of the structure solution method (10 pages); a listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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(17) ^1H NMR (C_6D_6): δ 7.09 (d, J_{HH} = 7.1 Hz, 6 H, $C_6\mathit{H}_3Me_2$-2,6); 6.79 (br m, 3 H, $C_6\mathit{H}_3Me_2$-2,6), 3.18 (s, 4 H, THF), 2.52 (s, 6 H, μ-$OC_6H_3\mathit{Me}_2$-2,6), 2.23 (s, 12 H, $OC_6H_3\mathit{Me}_2$-2,6), 0.66 (s, 4 H, THF). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 159.66 (s, $\mathit{C}_6H_3Me_2$-2,6), 153.85 (s, $\mathit{C}_6H_3Me_2$-2,6), 128.30 (s, $\mathit{C}_6H_3Me_2$-2,6), 128.20 (d, J_{CH} = 163 Hz, $\mathit{C}_6H_3Me_2$-2,6), 127.68 (d, J_{CH} = 158 Hz, $\mathit{C}_6H_3Me_2$-2,6), 124.77 (s, $\mathit{C}_6H_3Me_2$-2,6), 120.37 (d, J_{CH} = 156 Hz, $\mathit{C}_6H_3Me_2$-2,6), 116.73 (d, J_{CH} = 157 Hz, $\mathit{C}_6H_3Me_2$-2,6), 69.73 (t, J_{CH} = 155 Hz, THF), 23.75 (t, J_{CH} = 133 Hz, THF), 17.26 (q, J_{CH} = 125 Hz, $C_6H_3\mathit{Me}_2$-2,6). Anal. Calcd for $Y_2C_{56}H_{70}O_8$: Y, 17.0. Found: Y, 16.8. IR (KBr): 3000 w, 2940 w, 2900 s br, 1590 m, 1440 s br, 1270 s, 1235 m, 1195 m, 1090 m, 1010 w, 915 w, 860 s br, 755 s, 740 s, 700 m, 670 w cm^{-1}.

(18) **2** crystallized from THF/hexane at −34 °C in space group *P3cl* with unit cell parameters at 183 K of a = 18.340 (5) Å, c = 17.772 (5) Å, V = 5177 (2) Å^3, and D_{calcd} = 1.29 g cm^{-3} for Z = 6. The asymmetric unit consists of three independent molecules, each located on a crystallographic 3-fold rotation axis, Y(1) at ($^2/_3$, $^1/_3$, z), Y(2) at ($^1/_3$, $^2/_3$, z) and Y(3) at (0, 0, z). The poor quality of the data set prevented an accurate refinement of the model. Attempts to refine the structure by using the centrosymmetric space group *P*3*c*1 proved unsuccessful.

(19) Crystal data for $C_{56}H_{70}O_8Y_2\cdot 2(C_7H_8)$: The crystals belong to the monoclinic system with unit cell parameters at 183 K of a = 10.8392 (15) Å, b = 13.896 (2) Å, c = 22.065 (3) Å, β = 101.891 (11)°, and V = 3252.1(8) Å^3. The space group is $P2_1/c$ with Z = 2 dimers/unit cell and D_{calcd} = 1.26 g cm^{-3}. Intensity data (4517 total; $2\theta_{max}$ = 45.0°) were collected on the Nicolet R3m/V diffractometer system using monochromatized Mo Kα radiation (λ = 0.710730 Å) via the θ–2θ scan technique.[20] The structure was solved by direct methods and refined by full-matrix least-squares techniques[21] using those 2851 data with $|F_0| > 3.0\sigma(|F_0|)$. At convergence, R_F = 7.8%, R_{wF} = 7.7%, and GOF = 1.41 for 326 variables. A final difference-Fourier map yielded ρ(max) = 1.27 e Å^{-3} at a distance of 0.75 Å from C(30).

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Oxidation Photochemistry of Dimolybdenum(II) Diaryl Phosphate Promoted by Visible Light

Quadruply bonded metal–metal dimers are promising multielectron photoreagents. The lowest energy $^1(\delta\delta^*)$ excited state is long-lived[1] and is a two-electron source or sink in oxidation–reduction reactions.[2] Nevertheless the development of $M\overset{4}{-}M$ dimers for multielectron photochemical schemes has been hindered by the fact that $^1(\delta\delta^*)$ excited-state chemistry is an exceptional reaction pathway for these dimers. The photoredox chemistry of quadruply bonded metal–metal ($M\overset{4}{-}M$) dimers has generally been confined to photooxidation reactions derived from high-energy electronic excited states. Ultraviolet irradiation of acidic solutions containing $M\overset{4}{-}M$ dimers leads to one- or two-electron oxidation of the metal–metal core with the concomitant production of hydrogen.[3,4] Recent studies in our laboratories of dimolybdenum phosphates have shown that photochemical conversion of Mo_2-

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