

Strategy for Synthesis of an Yttrium/Copper(I) Complex with an Oxo Ligand Environment

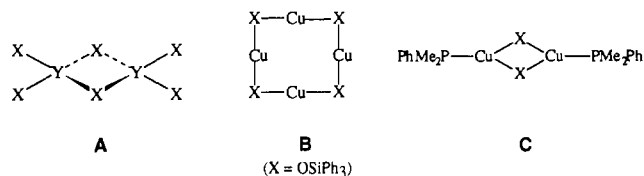
Paul S. Coan, John C. Huffman, and Kenneth G. Caulton*

Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Received March 10, 1992

Introduction

We have shown earlier¹ that $Y[N(SiMe_3)_2]_3$ reacts with Ph_3SiOH in noncoordinating solvents to yield $[Y(OSiPh_3)_2]_2$, which has the $(AlCl_3)_2$ structure (A). This molecule (unlike $[La-$



$(OSiPh_3)_2]_2$) retains its dimeric form in toluene solvent, as established by ²⁹Si NMR studies. Four-coordinate yttrium in this dimer is clearly electrophilic as judged³ by its reaction with THF (to give $Y(OSiPh_3)_3(THF)_3$) and by the coordination of silanol to the analogous $[Y(OSiMe_2^tBu)_2]_2$. We have pursued the idea that a late transition-metal silyl oxide, because of diminished $O \rightarrow M \pi$ -donation associated with the higher valence electron count, should retain Lewis basicity at the silyl oxide oxygen. Monovalent copper, in particular, should be a good candidate because of its low metal oxidation state and filled d-shell. Moreover, we have characterized $[Cu(OSiPh_3)_n]$ as a planar tetramer (B) and its PMe_2Ph adduct as a dimer (C), each with some evidence of pyramidal (hence basic) character at the silyl oxide oxygen.⁴ Acting on our proposal that neutral silyl oxides of yttrium and copper might selectively form a complex based on the Lewis acidity and basicity described above, we report here the synthesis and characterization of $YC_u(OSiPh_3)_4(PMe_2Ph)$.

Experimental Section

Materials and Procedures. All manipulations were performed using standard Schlenk techniques either in vacuo or in an atmosphere of nitrogen or using a nitrogen-filled drybox. Solvents were dried over appropriate desiccants (potassium metal/benzophenone for hexanes; CaH_2 for CH_2Cl_2 distilled under nitrogen and subjected to freeze-evacuate-thaw cycles prior to use). $[Y(OSiPh_3)_2]_2$ ³ and $[Cu(OSiPh_3)(PMe_2Ph)]_2$ ⁴ were synthesized according to methods in the literature.

Physical Measurements. Infrared spectra were recorded as KBr pellets using a Nicolet 510P FT-IR spectrometer. Hydrogen-1 and phosphorus-31 NMR spectra were recorded on either a Bruker AM500 instrument (¹H NMR at 500.14 MHz; ³¹P at 202.40 MHz) or a Nicolet 360 instrument (¹H NMR at 361.07 MHz; ³¹P at 146.17 MHz). Silicon-29 and yttrium-89 NMR spectra were recorded on a Bruker AM500 instrument (²⁹Si NMR at 99.36 MHz; ⁸⁹Y at 24.5 MHz). Hydrogen-1 NMR spectra were referenced via solvent residuals to Me_4Si . Silicon-29, phosphorus-31, and yttrium-89 NMR spectra were externally referenced to Me_4Si/C_6D_6 (50/50), 85% H_3PO_4 , and 3 M YCl_3 in D_2O . NMR sample temperatures were monitored using a thermocouple. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis of $YC_u(OSiPh_3)_4(PMe_2Ph)$. In a Schlenk flask, $[Y_2(OSiPh_3)_6]$ (0.192 g, 0.210 mmol) and $[Cu(OSiPh_3)(PMe_2Ph)]_2$ (0.100

g, 0.210 mmol) were combined. To this mixture, CH_2Cl_2 (30 mL) was added to form a colorless solution. This solution was stirred for 2 h at 23 °C. The solution was filtered through Celite to remove trace particulate and reduced in vacuo to 10 mL. Hexanes (30 mL) were carefully layered on the CH_2Cl_2 solution. After several days, X-ray quality crystals had formed. IR (KBr): $\nu(OH)$; $\nu(CH)$, 3061, 3002, 2907 cm^{-1} ; aromatic overtones, 1960, 1890, 1823 cm^{-1} ; other bands 1587, 1483, 1428, 1111, 1022, 972, 730, 710, 540 cm^{-1} . ¹H NMR (C_6D_6): δ 7.71 (d, 7.2 Hz, ortho Si-Ph), 7.186 (m, P-Ph), 7.10 (m, para Si-Ph), 7.02 (t, 7.2 Hz, meta Si-Ph), 6.85 (t, 7.0 Hz, meta P-Ph), 0.24 (d, 7.2 Hz, P-Me). ³¹P NMR (C_6D_6): δ -27.7 (br). ²⁹Si NMR (CH_2Cl_2/C_6D_6 , 80/20): δ -24.1. ⁸⁹Y NMR (CH_2Cl_2/C_6D_6 , 80/20): δ 300.7. Anal. Calcd for $C_{80}H_{71}CuO_4PSi_4Y$: C, 69.02; H, 5.14. Found: C, 68.58; H, 5.33.

X-ray Structure Determination. A suitable crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to -160 °C for characterization (Table I) and data collection ($6^\circ < 2\theta < 45^\circ$). All manipulations were performed using inert atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space failed to locate any symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement confirmed the centrosymmetric choice, $P\bar{1}$. Data were collected using a standard moving-crystal/moving-detector technique with fixed background counts at each extreme of the scan. After correlation for Lorentz and polarization effects, equivalent data were averaged ($R = 0.035$). No absorption correction was deemed necessary. The two metal atoms were located by direct methods (MULTAN78), and all remaining non-hydrogen atoms were located by successive Fourier analysis. The positions of most hydrogen atoms were clearly visible in a final difference Fourier map phased on the non-hydrogen atoms, and they were placed in idealized fixed positions for the final least-squares refinement. A final difference Fourier map was featureless, the largest peak being $0.37 e/\text{\AA}^3$, and the largest valley was $0.34 e/\text{\AA}^3$. The results of the structure determination are shown in Tables II and III and Figure 1. Additional details are available as supplementary material.

Results

Reaction of $[Y(OSiPh_3)_2]_2$ with $[Cu(OSiPh_3)PMe_2Ph]_2$ (1:1 Y:Cu ratio) in CH_2Cl_2 at 23 °C, followed by slow crystallization from CH_2Cl_2 /hexanes yields X-ray quality crystals. The product was shown by X-ray diffraction (Figure 1) to have structure $(Ph_3SiO)_2Y(\mu-O-SiPh_3)_2Cu(PMe_2Ph)$, comprised of a distorted tetrahedral YO_4 unit sharing an edge with a planar CuO_2P unit. The bridging oxygens are essentially co-planar with their three attached groups (angles about oxygen sum to 357.3 and 359.0°), the terminal silyl oxides are nearly linear ($\angle Y-O-Si = 165.4$ (1) and 169.8 (2)°), and the distances from Y to the $\mu-O$ atoms are 0.08 Å longer than from Y to the terminal silyl oxide oxygen. Although the $SiPh_3$ groups of the bridges bend toward the copper ($\angle Y-\mu-O-Si = 140.3$ (2) and 142.4 (2)°), there is no compelling evidence for phenyl-to-copper or -yttrium bonding. The shortest Cu/C and Y/C distances are 3.27 and 3.47 Å.^{5,6} The compound is unusual for linking electron-rich and electron-poor metals⁷ but the Y/Cu separation, 3.127 Å, does not strongly indicate direct Cu→Y donation. The bridging silyl oxide oxygens show polarization of the M/O bonds in $YC_u(OSiPh_3)_4(PMe_2Ph)$ in comparison to those in $Cu_2(OSiPh_3)_2(PMe_2Ph)_2$ and $Y_2(OSiPh_3)_6$: the Y-($\mu-O$) distances are 0.09 Å shorter and the Cu-($\mu-O$) distances are 0.05 Å longer in the heterometallic compound as a result of the dominant electrophilicity of yttrium.

Solution NMR studies are useful to define the behavior of the compound in the absence of any solid-state effects. Although ²⁹Si NMR spectroscopy has proven to be effective in resolving

- (1) Coan, P. S.; McGeary, M. J.; Lobkovsky, E. B.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 3570.
- (2) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1991**, *30*, 4963.
- (3) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1723.
- (4) McGeary, M. J.; Wedlich, R. C.; Coan, P. S.; Folting, K.; Caulton, K. G. *Polyhedron*, in press.

(5) Pasquai, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191.

- (6) (a) The shortest Y/C distance is 0.491 Å longer than the Ce/C distance observed in a complex with a similar ligand set.² Yttrium has a smaller radius than cerium. Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. (b) In the case of a metal of similar size to yttrium, $Yb(O-2,6-Ph_2C_6H_3)_3$ shows both Yb/phenyl and an agostic Y/C(Ph) interaction, of lengths 2.98 Å (average) and 2.88 Å. See: Deacon, G. B.; Nickel, S.; MacKinnon, P.; Tickink, E. R. T. *Aust. J. Chem.* **1990**, *43*, 1245.
- (7) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

Table I. Crystallographic Data for YCu(OSiPh₃)₄(PMe₂Ph)

chem formula	C ₈₀ H ₇₁ PSi ₄ O ₄ CuY	fw	1392.21
a, Å	13.915 (5)	space group	P1̄
b, Å	22.265 (9)	T, °C	-160
c, Å	13.613 (6)	λ, Å	0.710 69
α, deg	92.35 (2)	ρ _{calcd} , g cm ⁻³	1.316
β, deg	119.11 (1)	μ(Mo Kα), cm ⁻¹	12.67
γ, deg	73.67 (2)	R ^a	0.0412
V, Å ³	3512.87	R _w ^b	0.0422
Z	2		

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}, \quad w = 1/\sigma^2|F_o|.$$

Table II. Selected Fractional Coordinates and Isotropic Thermal Parameters^a for YCu(OSiPh₃)₄(PMe₂Ph)

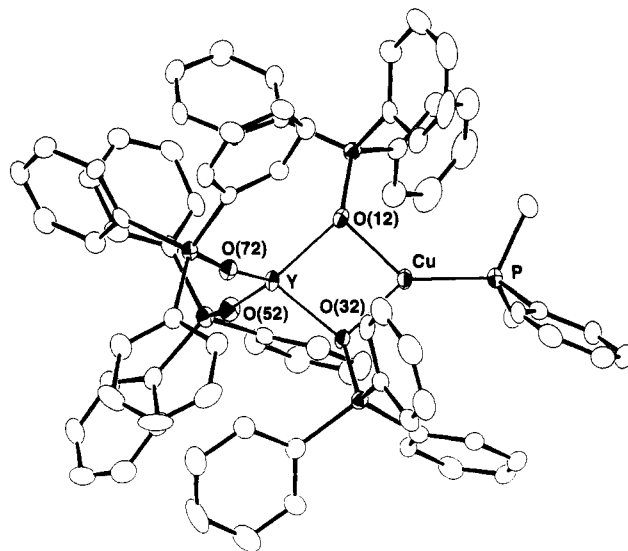
	10 ⁴ x	10 ⁴ y	10 ⁴ z	10B _{iso} , Å ²
Y(1)	7098.3 (4)	2453.6 (2)	8041.6 (4)	12
Cu(2)	4708.6 (5)	2453.7 (3)	7703.2 (5)	15
P(3)	3010 (1)	2413 (1)	7213 (1)	16
O(12)	6255 (3)	1792 (1)	8142 (3)	17
O(32)	5476 (3)	3109 (1)	7709 (3)	14
O(52)	7276 (3)	2531 (2)	6632 (3)	21
O(72)	8378 (3)	2552 (1)	9629 (3)	16

^a Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

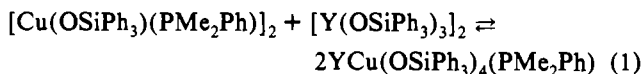
Table III. Selected Bond Distances (Å) and Angles (deg) for YCu(OSiPh₃)₄(PMe₂Ph)

Y(1)-O(12)	2.170 (3)	Si(13)-C(26)	1.881 (5)
Y(1)-O(32)	2.154 (3)	Si(33)-O(32)	1.626 (3)
Y(1)-O(52)	2.071 (3)	Si(33)-C(34)	1.877 (5)
Y(1)-O(72)	2.080 (3)	Si(33)-C(40)	1.881 (5)
Cu(2)-P(3)	2.1492 (17)	Si(33)-C(46)	1.875 (5)
Cu(2)-O(12)	2.048 (3)	Si(53)-O(52)	1.607 (3)
Cu(2)-O(32)	2.033 (3)	Si(53)-C(54)	1.874 (5)
P(3)-C(4)	1.825 (5)	Si(53)-C(60)	1.871 (5)
P(3)-C(5)	1.815 (5)	Si(53)-C(66)	1.878 (5)
P(3)-C(6)	1.819 (5)	Si(73)-O(72)	1.605 (3)
Si(13)-O(12)	1.617 (3)	Si(73)-C(74)	1.880 (5)
Si(13)-C(14)	1.879 (5)	Si(73)-C(80)	1.878 (5)
Si(13)-C(20)	1.879 (5)	Si(73)-C(86)	1.887 (5)
O(12)-Y(1)-O(32)	80.76 (12)	C(34)-Si(33)-C(40)	109.98 (22)
O(12)-Y(1)-O(52)	119.23 (13)	C(34)-Si(33)-C(46)	110.90 (21)
O(12)-Y(1)-O(72)	111.89 (12)	C(40)-Si(33)-C(46)	113.60 (22)
O(32)-Y(1)-O(52)	108.07 (13)	O(52)-Si(53)-C(54)	109.48 (20)
O(32)-Y(1)-O(72)	108.86 (12)	O(52)-Si(53)-C(60)	109.90 (20)
O(52)-Y(1)-O(72)	120.14 (13)	O(52)-Si(53)-C(66)	109.50 (20)
P(3)-Cu(2)-O(12)	134.39 (10)	C(54)-Si(53)-C(60)	110.00 (22)
P(3)-Cu(2)-O(32)	138.26 (10)	C(54)-Si(53)-C(66)	110.48 (22)
O(12)-Cu(2)-O(32)	86.70 (13)	C(60)-Si(53)-C(66)	107.46 (21)
Cu(2)-P(3)-C(4)	117.13 (18)	O(72)-Si(73)-C(74)	108.90 (20)
Cu(2)-P(3)-C(5)	111.06 (17)	O(72)-Si(73)-C(80)	109.68 (19)
Cu(2)-P(3)-C(6)	116.49 (16)	O(72)-Si(73)-C(86)	110.05 (19)
C(4)-P(3)-C(5)	102.20 (25)	C(74)-Si(73)-C(80)	109.68 (21)
C(4)-P(3)-C(6)	102.44 (23)	C(74)-Si(73)-C(86)	109.31 (21)
C(5)-P(3)-C(6)	105.97 (23)	C(80)-Si(73)-C(86)	109.20 (21)
O(12)-Si(13)-C(14)	107.13 (20)	Y(1)-O(12)-Cu(2)	95.64 (13)
O(12)-Si(13)-C(20)	110.29 (20)	Y(1)-O(12)-Si(13)	140.31 (18)
O(12)-Si(13)-C(26)	109.62 (20)	Cu(2)-O(12)-Si(13)	123.14 (18)
C(14)-Si(13)-C(20)	111.03 (22)	Y(1)-O(32)-Cu(2)	96.61 (13)
C(14)-Si(13)-C(26)	109.46 (22)	Y(1)-O(32)-Si(33)	142.40 (18)
C(20)-Si(13)-C(26)	109.28 (22)	Cu(2)-O(32)-Si(33)	118.28 (17)
O(32)-Si(33)-C(34)	107.79 (19)	Y(1)-O(52)-Si(53)	165.39 (22)
O(32)-Si(33)-C(40)	107.62 (19)	Y(1)-O(72)-Si(73)	169.82 (20)
O(32)-Si(33)-C(46)	106.68 (19)		

similar silyl oxide environments in other complexes, including the bridging and terminal ligands of Y₂(OSiPh₃)₆,⁸ the ²⁹Si NMR spectrum of YCu(OSiPh₃)₄(PMe₂Ph) (in CH₂Cl₂/C₆D₆, 80/20) shows only one chemical shift down to -65 °C. This resonance is located near the weighted average of the shifts of the homo-

**Figure 1.** ORTEP diagram of YCu(OSiPh₃)₄(PMe₂Ph) omitting hydrogens.

metallic parent complexes. Since the two ²⁹Si NMR resonances of Y₂(OSiPh₃)₆ are relatively broad at room temperature, suggesting the onset of bridge-terminal exchange, the corresponding dynamic process is likely for YCu(OSiPh₃)₄(PMe₂Ph). That this process is more difficult to freeze out in the heterometallic species is consistent with the expected smaller chemical shift difference between bridging and terminal silyl oxides in this complex: while the terminal ligands on yttrium should have a δ value similar to that of the yttrium dimer (-26.1 ppm), the bridging ligands are expected to lie somewhere between the value for the bridging ligands in the parent yttrium (-17.9 ppm) and copper (-24.5 ppm) complexes. Probably as a consequence of the facile bridge-terminal exchange in YCu(OSiPh₃)₄(PMe₂Ph), no ²J_{Y-Si} coupling is observed. This coupling is expected to be small (cf. 7 Hz terminal, <2 Hz bridging for [Y₂(OSiPh₃)₆]).⁸ As a result, the averaged coupling may be obscured by the line width of the resonance. The ¹H NMR spectrum of YCu(OSiPh₃)₄(PMe₂Ph) (in CDCl₃) is consistent with the ²⁹Si NMR and indicates only one silyl oxide environment. The ⁸⁹Y NMR chemical shift (300.7 ppm) for YCu(OSiPh₃)₄(PMe₂Ph) is to be compared to that of the parent yttrium dimer (263.2 ppm). This shift is consistent with a four-coordinate yttrium silyl oxide complex.⁸ If the equilibrium (eq 1) were occurring, the room temperature yttrium-89



chemical shift of YCu(OSiPh₃)₄(PMe₂Ph) would be a weighted average between the "true" shift of the complex and the shift of parent yttrium dimer. The "true" chemical shift value of YCu(OSiPh₃)₄(PMe₂Ph) would therefore be ≥300 ppm. Lowering the temperature would shift the equilibrium toward the ground-state complex, YCu(OSiPh₃)₄(PMe₂Ph), and the observed chemical shift should move *downfield*. Cooling the sample to -65 °C causes the yttrium-89 chemical shift of Y(Cu(OSiPh₃)₄(PMe₂Ph)) to move *upfield* (285 ppm). This is inconsistent with the movement of the chemical shift expected with an equilibrium. Moreover, since [Y(OSiPh₃)₃]₂ is significantly less soluble than either YCu(OSiPh₃)₄(PMe₂Ph) or [Cu(OSiPh₃)₂(PMe₂Ph)]₂, any of this yttrium complex available via such an equilibrium would precipitate out before the mixed-metal product, making YCu(OSiPh₃)₄(PMe₂Ph) difficult (at best) to isolate. These observations provide confirmation that YCu(OSiPh₃)₄(PMe₂Ph) remains intact in solution.

There has been considerable effort directed toward the synthesis of heterometallic complexes that contain the metals found in

(8) Coan, P. S.; Hubert-Pfalzgraf, L. G.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 1262.

high-temperature superconducting materials.⁹⁻¹⁸ These complexes are sought as both soluble precursors (via sol-gel processing) to the solid-state materials and as soluble analogues to be used in an attempt to determine what structural factors influence the electrical properties of these materials. The low number of metals contained within $\text{YCu}(\text{OSiPh}_3)_4(\text{PMe}_2\text{Ph})$ is unique among known complexes. This feature might allow more facile synthesis of complexes containing a stoichiometry richer in copper. Examination of space-filling diagrams of $\text{YCu}(\text{OSiPh}_3)_4(\text{PMe}_2\text{Ph})$ indicate that the coordination sphere about the two metals is

- (9) Goodgame, D. M. L.; Williams, D. J.; Winpenny, R. E. P. *Polyhedron* **1989**, *8*, 1531.
- (10) Blake, A. J.; Milne, P. E. Y.; Thornton, P.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1139.
- (11) Wang, S. *Inorg. Chem.* **1991**, *30*, 2253.
- (12) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1750.
- (13) Sauer, N. N.; Garcia, E.; Salazar, K. V.; Ryan, R. R.; Martin, J. A. J. *Am. Chem. Soc.* **1990**, *112*, 1524.
- (14) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *6*, 969.
- (15) Purdy, A. P.; George, C. F. *Inorg. Chem.* **1991**, *30*, 1969.
- (16) Rupich, M. W.; Lagos, B.; Hachey, J. P. *Appl. Phys. Lett.* **1989**, *55*, 2447.
- (17) Guillou, O.; Bergerat, P.; Kahn, O.; Bakalbassis, E.; Boubekeur, K.; Betail, P.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 110.
- (18) Blake, A. J.; Gould, R. O.; Milne, P. E. Y.; Winpenny, R. E. P. *J. Chem. Soc., Chem. Commun.* **1991**, 1453.

quite crowded. This indicates that grafting of further copper silyl oxide units onto $\text{YCu}(\text{OSiPh}_3)_4(\text{PMe}_2\text{Ph})$ might be sterically unfavorable. Indeed, reaction of $[\text{Y}_2(\text{OSiPh}_3)_6]$ with excess $[\text{Cu}(\text{OSiPh}_3)(\text{PMe}_2\text{Ph})]_2$ (Y:Cu 1:3) yields only $\text{YCu}(\text{OSiPh}_3)_4(\text{PMe}_2\text{Ph})$, as indicated by silicon-29 NMR spectroscopy. Reducing the steric bulk of the silyl oxide ligands may allow for mixed-metal complexes of different metal stoichiometry.

Although $\text{YCu}(\text{OSiPh}_3)_4(\text{PMe}_2\text{Ph})$ remains intact in "non-coordinating" solvents, the bridging interactions between yttrium and copper are cleaved in THF solution. The silicon-29 NMR spectrum of $\text{YCu}(\text{OSiPh}_3)_4(\text{PMe}_2\text{Ph})$ in THF shows resonances corresponding to $\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$ and $[\text{Cu}(\mu\text{-OSiPh}_3)(\text{PMe}_2\text{Ph})]_2$. This is probably due to the stability of six-coordinate yttrium in $\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$. Several other workers have also reported that mixed-metal alkoxide complexes are cleaved to homometallic complexes by Lewis bases.^{15,19}

Acknowledgment. This work was supported under DOE Grant DE-FG02-90ER45427 through the Midwest Superconductivity Consortium.

Supplementary Material Available: Tables of crystallographic details, positional parameters, and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

- (19) Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4519.