tallization from pentane (eq 1). Spectroscopic properties[9] for

$$(\mathrm{Me_3CO})_3\mathrm{MCl} + (\mathrm{THF})_3\mathrm{LiSi(SiMe_3)_3} \xrightarrow{-3\mathrm{THF},\ -\mathrm{LiCl}} (\mathrm{Me_3CO})_3\mathrm{MSi(SiMe_3)_3} \quad (1)$$

$$\mathbf{1},\ \mathrm{M} = \mathrm{Zr}$$
$$\mathbf{2},\ \mathrm{M} = \mathrm{Hf}$$

these air- and water-sensitive complexes resemble those observed for other group 4 –$\mathrm{Si(SiMe_3)_3}$ derivatives. However, in contrast to other d^0 silyl compounds which are highly colored, **1** and **2** are colorless.

The molecular structure of **1** is shown in Figure 1.[10] A crystallographically imposed mirror plane at $y = 0.2500$ bisects the molecule and contains C(21), Si(2), Si(1), Zr(1), O(1), C(51), and C(52). Additionally, two noncrystallographic mirror planes give the molecule nearly C_{3v} symmetry, with the 3-fold rotation axis containing the Zr(1)–Si(1) bond. This symmetry is reflected in the Si–Si–Zr–O dihedral angles of 179.3, 179.3, and 180.0°. A view down the Zr–Si bond (Figure 2) illustrates the staggered conformation about these two tetravalent atoms. The geometry about Si(1) is nearly tetrahedral, with average Si–Si–Si angles of 108.5 (3)°, and Zr–Si–Si angles averaging 110.4 (2)°. In other complexes containing the $\mathrm{Si(SiMe_3)_3}$ ligand, distortions of these angles about the metal-bound silicon atom, apparently due to steric interactions, are observed.[4b,11] The Zr(1) center also exhibits an approximate tetrahedral coordination geometry, with a mean Si–Zr–O angle of 107.6 (3)° and a mean O–Zr–O angle of 111.4 (4)°. The average Zr–O bond distance (1.89 (1) Å) and Zr–O–C angle (166 (1)°) compare favorably with other zirconium alkoxide structures in which some degree of O(pπ)–Zr(dπ) bonding is presumed.[12] The Zr–Si bond distance of 2.753 (4) Å is shorter than either of the two previously reported Zr–Si distances, 2.813 (2) Å in $\mathrm{Cp_2Zr(SiPh_3)Cl}$[13] and 2.815 (1) Å in $\mathrm{Cp_2Zr(SiMe_3)S_2CNEt_2}$.[2a] This is consistent with the formally lower coordination number in **1**. According to Shannon, the effective ionic radius of four-coordinate Zr(IV) is 0.25 Å smaller than that of eight-coordinate Zr(IV).[14] Since the Zr–Si distance in **1** is only 0.06 Å less than other reported Zr–Si distances, the Zr–Si bond in **1** is longer than expected. Apparently there are no crystal structures of $\mathrm{(RO)_3Zr(alkyl)}$ complexes available for comparison.

Preliminary experiments show that these compounds are surprisingly inert. **1** and **2** are unreactive toward carbon monoxide (24 h, 70 psi, pentane), ethylene (24 h, 70 psi, pentane), and $\mathrm{PhSiH_3}$ (1 equiv, 3 days, benzene-d_6). However, both compounds react with $\mathrm{2,6\text{-}Me_2C_6H_3NC}$ to afford the insertion products $\mathrm{(Me_3CO)_3M[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]}$ (**3**, M = Zr; **4**, M = Hf).[15] Heating **1** and **2** to 90 °C in benzene-d_6 results in only slow thermal decomposition, to $\mathrm{HSi(SiMe_3)_3}$ and as yet uncharacterized metal-containing species. Studies are under way to examine further aspects of the synthesis, structure and reactivity of mixed alkoxy/silyl complexes of the early transition metals.

Acknowledgment is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, for support of this work under Grant No. AFOSR-88-0273, and to the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–90).

Supplementary Material Available: Tables of crystal and data collection parameters, atomic coordinates (Table 1), bond distances and angles (Tables 2 and 3), anisotropic thermal parameters (Table 4), and hydrogen atom coordinates and their isotropic thermal parameters (Table 5) (6 pages); a listing of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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(9) Data for **1**: mp 225–228 °C dec. Anal. Calcd for $\mathrm{C_{21}H_{54}O_3Si_4Zr}$: C, 45.2; H, 9.75. Found: C, 45.1; H, 9.72. IR (Nujol, CsI, $\mathrm{cm^{-1}}$): 1361 s, 1254 m, 1240 s, 1206 s, 1182 s, 1042 s, 998 vs, 862 s, 832 vs, 791 m, 746 w, 735 w, 681 m, 621 m, 548 w, 480 w, 439 w, 388 w, 350 w. UV (pentane, $\lambda_{\max}$/nm (ϵ/$\mathrm{M^{-1}\ cm^{-1}}$): 228 (21 500). ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.48 (Si*Me*$_3$), 1.28 (OC*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 3.61 (Si*Me*$_3$), 32.29 (OC*Me*$_3$), 77.46 (O*C*Me$_3$). ^{29}Si{^{1}H} NMR (benzene-d_6, 59.6 MHz, 23 °C): δ −115.82 (*Si*SiMe$_3$), −7.20 (Si*Si*Me$_3$). Data for **2**: mp 144–147 °C dec. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.47 (Si*Me*$_3$), 1.31 (OC*Me*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 4.75 (Si*Me*$_3$), 33.53 (OC*Me*$_3$), 78.40 (O*C*Me$_3$). ^{29}Si{^{1}H} NMR (benzene-d_6, 59.6 MHz, 23 °C): δ −103.47 (*Si*SiMe$_3$), −5.04 (Si*Si*Me$_3$).

(10) Crystal data for **1**: $\mathrm{C_{21}H_{54}O_3Si_4Zr}$, orthorhombic, *Pnma*, $a = 21.48$ (1) Å, $b = 16.850$ (8) Å, $c = 10.033$ (5) Å, $V = 3631$ (3) Å^3, $Z = 4$, $D_c = 1.021\ \mathrm{g\ cm^{-3}}$, $F(000) = 1200$, $\mu = 4.41\ \mathrm{cm^{-1}}$, Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å). An irregularly shaped colorless crystal of approximate dimensions 0.4 mm × 0.4 mm × 0.4 mm was mounted under N_2 in a glass-walled capillary and flame-sealed. Data was collected at ca. 23 °C on a Nicolet R3m/V automated diffractometer with a highly ordered graphite monochromator, using $\theta/2\theta$ scans (variable scan speed, 1.5–15° $\mathrm{min^{-1}}$) and was corrected for slight crystal decay (3.3%). No absorption correction was applied. Of the 4793 reflections collected (3° $\le 2\theta \le$ 45°), 2480 were considered independent ($R_{\mathrm{int}} = 2.62\%$). Systematic absences indicated the space group to be either of the nonstandard settings *Pc*2$_1$*n* or *Pcmn*. After conversion to the standard space group, only the centrosymmetric group *Pnma* gave a solution that could be refined. The Zr atom was located by Patterson methods, and all remaining non-hydrogen atoms were located and refined anisotropically by difference Fourier and full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI). The refinement was based on 1190 observed reflections ($F_o > 6\sigma(F)$). Hydrogen atoms were fixed in calculated, idealized positions (d(C–H) = 0.96 Å, with fixed isotropic thermal parameters 1.2 times the isotropic thermal parameter for the carbon to which the hydrogen is attached). $R_F = 6.00\%$, $R_{wF} = 6.77\%$, GOF = 1.82, data/parameter = 8.4, mean $\Delta/\sigma = 0.001$, and $\Delta(\rho) = 0.53$ e Å^{-3} (1.24 Å from Si(2), 1.47 Å from C(22)).

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(15) Data for **3**: mp 64–67 °C dec. Anal. Calcd for $\mathrm{C_{30}H_{63}NO_3Si_4Zr}$: C, 52.3; H, 9.21; N, 2.03. Found: C, 51.7; H, 9.17; N, 2.13. IR (Nujol, CsI, $\mathrm{cm^{-1}}$): $\nu_{\mathrm{C=N}}$ 1509 w. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.26 (s, Si*Me*$_3$), 1.34 (s, OC*Me*$_3$), 2.06 (s, *o-Me*), 6.90 (m, *m,p*-C*H*). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 2.24 (Si*Me*$_3$), 19.04 (*o-Me*), 33.20 (OC*Me*$_3$), 75.27 (O*C*Me$_3$), 125.55 (*p-C*), 127.41 (*o-C*), 128.62 (*m-C*), 155.35 (ipso *C*), 299.01 (Zr*C*N). Data for **4**: IR (benzene-d_6 solution, CsF, $\mathrm{cm^{-1}}$): $\nu_{\mathrm{C=N}}$ 1503 w. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.26 (s, Si*Me*$_3$), 1.35 (s, OC*Me*$_3$), 2.08 (s, *o-Me*), 6.89 (m, *m,p*-C*H*). ^{13}C{^{1}H} NMR (benzene-d_6, 75.5 MHz, 23 °C): δ 2.26 (Si*Me*$_3$), 19.01 (*o-Me*), 33.34 (OC*Me*$_3$), 75.36 (O*C*Me$_3$), 125.68 (*p-C*), 128.62 (*m-C*), 155.21 (ipso *C*), 310.21 (Zr*C*N).

Chemistry Department, D-006
University of California at San Diego
La Jolla, California 92093-0506

Richard H. Heyn
T. Don Tilley*

Received December 21, 1988

Synthesis and Redox and Structural Chemistry of Monomeric Rhenium(IV) Phenoxide Complexes

Next to molybdenum and tungsten, rhenium catalysts are the most widely used for olefin metathesis[1] and remain the catalysts of choice for metathesizing certain functionalized olefins.[2] Two important principles have emerged from studies of homogeneous

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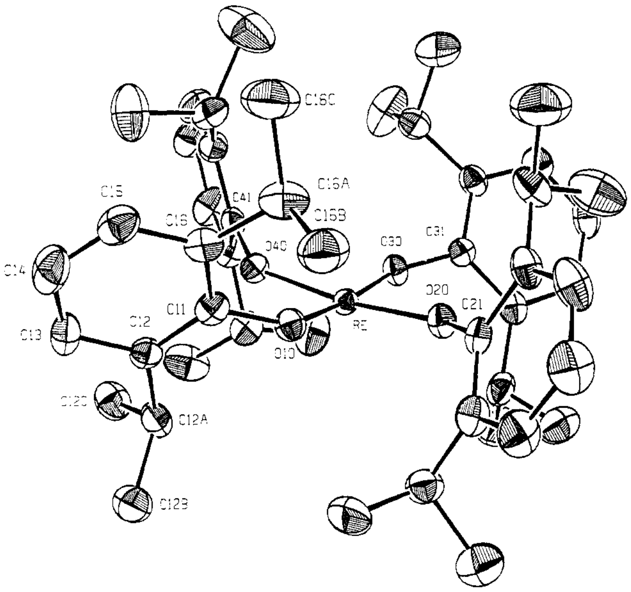

Figure 1. Molecular structure of $Re(O-2,6-C_6H_3-i-Pr_2)_4$ (**1**), with atoms shown as 30% probability ellipsoids.

group 6 olefin[3] and acetylene[4] metathesis systems: (i) the d^0 configuration seems to be the only viable oxidation state in either homogeneous reaction;[5] (ii) metathesis is typically not a *catalytic* process until halide ligands are replaced by better π-donor ligands, e.g. alkoxides.[4,6] A puzzling feature of rhenium chemistry is that although d^0 Re(VII) alkylidynes and metallacyclobutadienes have been shown to participate in acetylene metathesis,[7] d^0 alkylidenes are poor olefin metathesis catalysts.[8] Of possible relevance to this question are two recent reports that document a high activity for acetylene[9] and olefin[10] metathesis in rhenium systems where *intermediate oxidation state* complexes are implicated as catalytically active species.[9,10] We have attempted, therefore, to combine midvalent metal centers and π-donor ligation in designing rhenium compounds relevant to metathesis chemistry. Herein, we report rare examples of monomeric ReX_4 species (where X is a monodentate anionic ligand), viz. the phenoxide compounds $Re(O-2,6-C_6H_3R_2)_4$, and undertake a preliminary examination of their redox chemistry and their reactions with acetylenes.

The reaction between $ReCl_4(THF)_2$[11] and $Li(DIPP)\cdot Et_2O$ (DIPP = $O-2,6-C_6H_3-i-Pr_2$) proceeds smoothly in diethyl ether according to eq 1, in spite of $ReCl_4(THF)_2$ being almost insoluble in the reaction solvent. Reaction 1 is complete after 24 h (room temperature), and dark red-brown, paramagnetic $Re(DIPP)_4$ (**1**) is isolated in 75% yield.[12] The ^1H NMR spectrum of $Re(DIPP)_4$ shows sharp, though shifted, resonances resulting from the compound's paramagnetism ($\mu_{eff} = 1.5\ \mu_B$). The reaction between $ReCl_4(THF)_2$ and $Li(DMP)\cdot THF$ (DMP = $O-2,6-C_6H_3Me_2$) in diethyl ether also occurs smoothly, and $Re(DMP)_4$ (**2**) can be isolated as a dark brown, paramagnetic solid in 77% yield (reaction 2).[13] A combustion analysis confirms that less crowded $Re(DMP)_4$ (**2**) is not a dinitrogen complex.

$$ReCl_4(THF)_2 + 4Li(DIPP)\cdot OEt_2 \xrightarrow{Et_2O} \underset{\mathbf{1},\ 75\%}{Re(DIPP)_4} + 4LiCl \qquad (1)$$

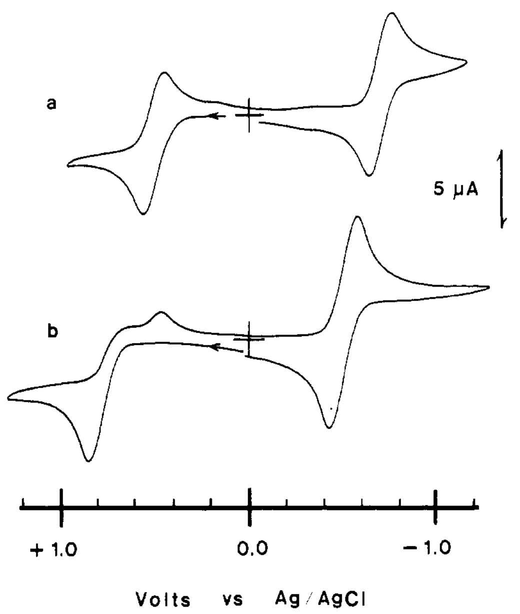

Figure 2. Cyclic voltammograms of 0.1 M $n-Bu_4NPF_6/CH_2Cl_2$ solutions of (a) $Re(O-2,6-C_6H_3-i-Pr_2)_4$ (**1**) and (b) $Re(O-2,6-C_6H_3Me_2)_4$ (**2**), recorded at 150 mV/s.

$$ReCl_4(THF)_2 + 4Li(DMP)\cdot THF \xrightarrow{Et_2O} \underset{\mathbf{2},\ 77\%}{Re(DMP)_4} + 4LiCl \qquad (2)$$

An X-ray structural study[14,15] of $Re(DIPP)_4$ shows the local coordination of the metal to be square planar (Figure 1). The

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(12) The physical properties of $Re(O-2,6-C_6H_3-i-Pr_2)_4$ (**1**) are as follows. ^1H NMR (C_6D_6, probe temperature): δ 11.35 (d, 2 H, H_m, J_{HH} = 8 Hz), 9.05 (br, 2 H, C*H*Me$_2$), 6.17 (t, 1 H, H_p, J_{HH} = 8 Hz), 1.74 (br s, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 203.1 (br s, C_{ipso} or C_{ortho}), 146.4 (d, C_{meta}), 127.0 (d, C_{para}), 27.0 (q, CH*Me*$_2$), 23.6 (d, C*H*Me$_2$). Magnetic moment (NMR method, C_6D_6): $\mu_{eff} = 1.50\ \mu_B$. ESR (THF solution, room temperature): Six-line signal at $g = 2.04$, $A_{Re} \approx 580$ Hz. Anal. Calcd for $C_{48}H_{68}O_4Re$: C, 64.39; H, 7.66; Cl, 0.0. Found: C, 64.26; H, 7.79; Cl, 0.0.

(13) The physical properties of $Re(O-2,6-C_6H_3Me_2)_4$ (**2**) are as follows. ^1H NMR (C_6D_6): broad, featureless resonances at δ 10.0, 9.4, and 8.8. Magnetic moment (NMR method, C_6D_6): $\mu_{eff} = 1.52\ \mu_B$. Anal. Calcd for $C_{32}H_{36}O_4Re$: C, 57.29; H, 5.41; N, 0.0. Found: C, 57.07; H, 5.53; N, 0.0.

(14) A dark red block crystal of $Re(O-2,6-C_6H_3-i-Pr_2)_4$ (approximate dimensions 0.16 × 0.29 × 0.56 mm) crystallized in the monoclinic space group $P2_1/c$ (No. 14) with a = 22.657 (3) Å, b = 11.498 (2) Å, c = 18.605 (3) Å, β = 110.62 (1)°, V = 4536.2 Å^3 for Z = 4 (ρ_{calcd} = 1.31 g cm^{-3}), and μ = 27.5 cm^{-1}. Data were collected on a Syntex $P2_1$ diffractometer at room temperature with Mo Kα radiation. A total of 8948 reflections were collected in the $+h,+k,\pm l$ octants (8035 unique) in the range $2° \leq 2\theta \leq 50°$, with 5163 reflections having $I \geq 3\sigma(I)$. The agreement factors for the 566 observed and accepted reflections were 2.8% based upon I and 2.4% based on F_o. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques, for a final R = 0.035 and R_w = 0.044. The largest peak in the final difference-Fourier map had a height of 0.48 e/Å^3. A numerical absorption correction was applied. Complete structural details will be provided in a full report.

(15) Selected interatomic distances (Å): Re–O(10) = 1.867 (4), Re–O(20) = 1.879 (4), Re–O(30) = 1.868 (4), Re–O(40) = 1.864 (4). Selected bond angles (deg): O(10)–Re–O(20) = 89.4 (2), O(10)–Re–O(30) = 173.9 (2), O(10)–Re–O(40) = 88.6 (2), O(20)–Re–O(30) = 90.6 (2), O(20)–Re–O(40) = 170.6 (2), O(30)–Re–O(40) = 90.5 (2), Re–O(10)–C(11) = 138.1 (4), Re–O(20)–C(21) = 141.9 (4), Re–O(30)–C(31) = 143.8 (4), Re–O(40)–C(41) = 138.5 (4).

trans O–Re–O angles are 173.9 (2) and 170.6 (2)°, while the cis O–Re–O angles average 89.8°. Metal–oxygen bond lengths vary from 1.864 (4) to 1.879 (4) Å and Re–O–C_{ipso} angles fall in a narrow range between 138.1 (4) and 143.8 (4)°. In Figure 1, the Re atom is displaced 0.13 Å below the O_4 plane, while all of the C_{ipso} atoms are located above this plane (0.31 Å on average). The metal center is well protected from above and below the ReO_4 square plane by the *o*-isopropyl groups of the phenoxide ligands. This d^3 rhenium complex can be compared to the related d^2 complexes $W(DIPP)_4$ and $W(DMP)_4$, both of which are also square planar.[16] The observed geometry in $Re(DIPP)_4$ (like $W(OR)_4$) no doubt reflects an electronic effect, as the delocalization of oxygen π electrons over the entire ReO_4 core (possible in a square-planar conformation) may offer significant energetic advantages to the complex.[16] In the recently reported compound $Re(2\text{-}MeC_6H_4)_4$ where π interactions of this type are not possible, the compound assumes a tetrahedral geometry.[17]

An oxidation and a reduction couple are observed for both compounds **1** and **2** by cyclic voltammetry (Figure 2).[18] Redox couples for $Re(DIPP)_4$ feature cathodic/anodic peak separations between 120 and 155 mV (at 150 mV/s scan rate), and $i_{p,a}/i_{p,c}$ for the +0.49-V oxidation is not strictly 1.0, although plots of peak anodic current vs the square root of the sweep rate ($v^{1/2}$) are linear, *implying* electrochemical reversibility.[19] However, bulk electrolysis reveals that these processes transfer only 0.5 (±0.05) electron, which could reflect the stoichiometric reaction of $[Re(DIPP)_4]^+$ (or $[Re(DIPP)_4]^-$) with neutral $Re(DIPP)_4$ (an EC process).[20] The electrochemistry of $Re(DMP)_4$ parallels that of $Re(DIPP)_4$ except in one regard: the oxidation of $Re(DMP)_4$ is completely irreversible. The reactivity differences we observe between the neutral DMP and DIPP compounds (vide infra) are presumably sterically regulated and are likely to be augmented in reactive $[Re(OR)_4]^+$ cations, which could account for the EC process being fast on the CV time scale for the $Re(DMP)_4$ oxidation.

Preliminary reactivity studies of **1** and **2** have focused on their reactions with acetylenes.[21] No reaction was seen to occur between $Re(DIPP)_4$ (**1**) and an excess of 2-butyne or diphenylacetylene, a behavior which parallels that of the related $W(DIPP)_4$.[16] However, the reaction of $Re(DMP)_4$ with 1 equiv of MeC≡CMe (Et_2O, −20 °C, 45 min) provides a dark red solid that we formulate as the acetylene adduct, $Re(MeC{\equiv}CMe)(DMP)_4$, (**3**, 59% yield).[22] The cyclic voltammogram of $Re(MeC{\equiv}CMe)(DMP)_4$ (**3**) reveals an irreversible[19] oxidation ($E_{p,a}$ = +0.80) and an apparently reversible (on the CV time scale) reduction ($E_{1/2}$ = −0.57 (120)) in dichloromethane. Both couples are shifted to more negative potentials relative to "base-free" $Re(DMP)_4$,[18] a result that is consistent with adduct formation, since, in general, one would expect the addition of an electron to be more difficult (and the removal of an electron to be more facile) in the adduct.

Because it is likely that some homogeneous rhenium metathesis systems involve $d^{n>0}$ complexes, and because π-donor ligation may be important in activating these species to catalysis, the alkoxide compounds reported here may provide a means by which to substantiate and understand the role of *midvalent* rhenium in metathesis chemistry.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the U.S. Army Research Office for a Short Term Innovative Research Program Grant. This project was supported in part by Grant BRSG S07 RR07002 awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health. Thanks are also due the University of Arizona Foundation for partial support of this work.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters, anisotropic thermal parameters, and bond distances and bond angles and figures showing ORTEP views of $Re(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$ (**1**) (6 pages). Ordering information is given on any current masthead page.

Carl S. Marvel Laboratories of Chemistry
Department of Chemistry
University of Arizona
Tucson, Arizona 85721

Ian M. Gardiner
Michael A. Bruck
David E. Wigley*

Received December 21, 1988

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Lewis Base Adducts of Uranium Triiodide: A New Class of Synthetically Useful Precursors for Trivalent Uranium Chemistry

It is interesting, from a historical perspective, that, after some 50 years of synthetic actinide research, very little is known about the nonaqueous chemistry of trivalent uranium.[1] The paucity of molecular uranium(III) compounds is undoubtedly due to a lack of suitable starting materials.[2] The anhydrous uranium trihalides have all been prepared, but they are polymeric solids,[3,4] insoluble in common organic solvents, and quite unreactive.[5] Uranium tetrachloride, UCl_4, dissolved in tetrahydrofuran can be reduced (e.g., with NaH, $NaC_{10}H_8$, or Na/Hg) to give a sparingly soluble purple solid formulated as $UCl_3(THF)_x$.[6] The exact identity of the latter material is unknown, and its utility as a precursor to uranium(III) compounds is apparently limited.[6–11] We have encountered some difficulties using "$UCl_3(THF)_x$" as a starting material. For example, we find that the synthesis of $U[N(SiMe_3)_2]_3$ from $UCl_3(THF)_x$ (generated in situ) and sodium

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