# COMMUNICATION

## TETRAKIS(2,6-DI-t-BUTYLPHENOXY)URANIUM(IV): THE FIRST STRUCTURALLY CHARACTERIZED NEUTRAL HOMOLEPTIC ARYLOXIDE COMPLEX OF URANIUM(IV)

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(Received 8 January 1989; accepted 10 February 1989)

Abstract—The reaction of  $[(Me_3Si)_2N]_2UN(SiMe_3)SiMe_2CH_2$  with 4 equivalents of HO-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub> in toluene at 100°C provides orange U(O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub> in high yield. U(O-2,6-Bu'\_2C\_6H\_3)\_4 has been characterized by NMR, magnetic susceptibility ( $\mu_{eff} = 2.68$  BM), and X-ray crystallography. It is the first structurally characterized homoleptic uranium(IV) aryloxide complex. The UO<sub>4</sub> core is nearly tetrahedral with U(1)—O(2) = 2.135(4) Å, O(2)—U(1)—O(2') = 110.2(1)° and O(2)—U(1)—O(2'') = 108.0(2)°; the U(1)—O(2)—C<sub>ipso</sub> angle is 154.0(6)°.

We recently reported the synthesis and characterization of two uranium(III) phenoxide complexes, {U(O-2,6-R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>}<sub>x</sub> (R = Pr<sup>i</sup>, x = 2; R = Bu<sup>i</sup>, x = 1).<sup>1</sup> The uranium(IV) analogues of these complexes have not been reported, although [Li(THF)<sub>4</sub>][U(O-2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>5</sub>] has been isolated from the reaction of UCl<sub>4</sub> and LiOAr in THF and structurally characterized.<sup>2</sup> Lappert and co-workers<sup>3</sup> were unable to prepare U(O-2,6-Bu<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub> from [U(NEt<sub>2</sub>)<sub>4</sub>]<sub>2</sub> and excess phenol. Instead, the U(NEt<sub>2</sub>)(O-2,6-Bu<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> was isolated according to eq. (1):

$$0.5[U(NEt_{2})_{4}]_{2} + \ge 3HO-2,6-Bu_{2}^{t}C_{6}H_{3}$$
$$\xrightarrow{C_{3}H_{12}} U(NEt_{2})(O-2,6-Bu_{2}^{t}C_{6}H_{3})_{3}$$

 $+3HNEt_2$ . (1)

We have repeated this reaction in our laboratory and find that, even in refluxing toluene, the fourth diethylamide ligand [eq. (1)] cannot be metathesized.

Several years ago, Dormond *et al.*<sup>4</sup> described the reactions of the uranium(IV) metallacycle [(Me<sub>3</sub> Si)<sub>2</sub>N]<sub>2</sub> $UN(SiMe_3)SiMe_2CH_2$ ,<sup>5</sup> with both HOBu<sup>4</sup> and HO-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. They observed rapid protonation of the uranium–carbon bond and isolated two U(OR)[N(SiMe\_3)<sub>2</sub>]<sub>3</sub> complexes [eq. (2)]:

$$[(Me_3Si)_2N]_2UN(SiMe_3)SiMe_2CH_2 + HOR$$

$$\xrightarrow{C_6H_6} U(OR)[N(SiMe_3)_2]_3 \quad (2)$$

$$(R = Bu', 2,6-Me_2C_6H_3).$$

They also noted that cleavage of uranium-nitrogen bonds occurred but was not competitive with attack on the metal-carbon bond.

In agreement with Dormond *et al.*, we find that the reaction of one equivalent of HO-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub> with  $[(Me_3Si)_2N]_2UN(SiMe_3)SiMe_2CH_2$  in hexane at room temperature for 1 h, provides orange

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(3)

U(O-2,6-Bu<sub>2</sub>'C<sub>6</sub>H<sub>3</sub>)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> in essentially quantitative yield. This hydrocarbon soluble, air-sensitive compound has been characterized by elemental analyses and <sup>1</sup>H NMR.\* The room temperature <sup>1</sup>H NMR spectrum shows non-equivalent silyl amide ligands indicative of restricted rotation about the U—O bond and/or U—N bonds.

The reaction of  $[(Me_3Si)_2N]_2UN(SiMe_3)$ SiMe<sub>2</sub>CH<sub>2</sub> with slightly greater than 4 equivalents of HO-2,6-Bu<sup>1</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub> in toluene at 100°C for 6 h provides, after solvent removal and recrystallization from hexane, an orange, air-sensitive crystalline solid in 80% yield [eq. (3)]:

$$[(Me_{3}Si)_{2}N]_{2}UN(SiMe_{3})SiMe_{2}CH_{2}$$
  
+4HO-2,6-Bu'\_{2}C\_{6}H\_{3} \xrightarrow{PhCH\_{3},\Delta}  
U(O-2,6-Bu'\_{2}C\_{6}H\_{3})\_{4}+3HN(SiMe\_{3})\_{2}.

The <sup>1</sup>H NMR spectrum shows one type of phenoxide ligand and elemental analyses were consistent with the formula U(O-2,6-Bu<sup>'</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>.<sup>†</sup> The solid follows Curie–Weiss behaviour from 60 to 300 K with  $\mu_{\text{eff}} = 2.68$  BM, consistent with the presence of two unpaired electrons (U<sup>4+</sup> has a 5f<sup>2</sup> ground-state configuration).

X-ray quality crystals, in the form of orange cubes, were grown from a concentrated THF solution at  $-40^{\circ}$ C, and the structure was determined from X-ray diffraction data collected at  $-145^{\circ}$ C.<sup>‡</sup> The uranium lies on a crystallographic  $\overline{4}$  site (i.e. the molecule has  $S_4$  symmetry) and is coordinated by the oxygen atoms [U(1)—O(2) = 2.135(4) Å] of the

\* Found: C, 41.6; H, 8.0; N, 4.4. Calc. for UC<sub>32</sub> H<sub>75</sub>N<sub>3</sub>OSi<sub>6</sub>: C, 41.6; H, 8.2; N, 4.5%. <sup>1</sup>H NMR for U(O-2,6-Bu<sub>2</sub>'C<sub>6</sub>H<sub>3</sub>)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (22°C, benzene-d<sub>6</sub>):  $\delta$  16.2 (br s, *meta*);  $\delta$  15.1 (vbr s, Bu');  $\delta$  12.9 (br s, *para*);  $\delta$  3.4 (vbr s, TMS);  $\delta$  -7.4 (vbr s, TMS);  $\delta$  -20.9 (vbr s, TMS).

† Found: C, 63.5; H, 7.8; N, <0.05. Calc. for UO<sub>4</sub>C<sub>56</sub>H<sub>84</sub>: C, 63.5; H, 8.0; N, 0.0%. <sup>1</sup>H NMR for U(O-2,6-Bu<sub>2</sub>'C<sub>6</sub>H<sub>3</sub>)<sub>4</sub> (22°C, benzene-d<sub>6</sub>):  $\delta$  10.5 (d,  $J_{\text{HH}} = 7.3$  Hz, meta);  $\delta$  8.3 (t,  $J_{\text{HH}} = 7.3$  Hz, para);  $\delta$  -1.0 (br s, Bu').

<sup>‡</sup>X-ray analysis: U(O-2,6-Bu<sup>4</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub> crystallizes in the tetragonal space group I4 with cell constants (at -145°C): a = b = 14.066(2), c = 12.404(2) Å, V = 2652.1 Å<sup>3</sup>,  $d_{calc} = 1.327$  g cm<sup>-3</sup> and Z = 2. The structure was solved by a combination of Patterson and Fourier techniques and refined (positional and anisotropic thermal parameters for 16 non-hydrogen atoms; positional and isotropic thermal parameters for 21 hydrogen atoms; 229 variables) by full-matrix least-squares. Final discrepancy indices were  $R_F = 0.029$  and  $R_{wF} = 0.030$  for those 2020 reflections with  $F_o \ge 2.33\sigma(F_o)$ . The limits of data collection were  $6^\circ \le 2\theta \le 60^\circ$  (Mo- $K_z$ ).



Fig. 1. ORTEP drawing of U(O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>. U(1)— O(2) = 2.135(4) Å; O(2)—C(3) = 1.344(14) Å; U(1)— O(2)—C(3) = 154.0(6)°; O(2)—U(1)—O(2') = 110.2(1)°; O(2)—U(1)—O(2'') = 108.0(2)°.

four phenoxide ligands in a nearly tetrahedral fashion: angles O(2)—U(1)—O(2') and O(2)—U(1)—O(2'') are 110.2(1) and 108.0(2)°, respectively (Fig. 1). The U(1)—O(2)—C(3) angle is 154.0(6)°. U(NEt<sub>2</sub>)[O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>3</sub>, which also adopts a tetrahedral geometry, has an average U—O distance of 2.143(4) Å.<sup>3</sup> In the trigonal bipyramidal uranium(IV) anion, [U(O-2,6-Pr'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>5</sub>]<sup>-</sup>, the U—O distances range from 2.15(1) to 2.19(1) Å.<sup>2</sup>

The reason that U(NEt<sub>2</sub>)(O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> does not react with HO-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub> to form U(O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub> is most likely a consequence of the enhanced  $\pi$ -basicity of NEt<sub>2</sub><sup>-</sup> relative to N(SiMe<sub>3</sub>)<sub>2</sub><sup>-</sup>. For the latter, N  $\rightarrow$  Si  $p\pi$ - $d\pi$  bonding is possible and this will compete with N  $\rightarrow$  U  $\pi$ -bonding. In this context, we note that the U—N bond length of 2.162(5) Å in U(NEt<sub>2</sub>)(O-2,6-Bu'<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> is significantly shorter than the terminal U—N bonds of [U(NEt<sub>2</sub>)<sub>4</sub>]<sub>2</sub>, which range from 2.21(1) to 2.24(1) Å,<sup>6</sup> and that the average U—N bond length in HU[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> is 2.237(9) Å.<sup>7</sup>

Schrock and co-workers<sup>8</sup> have structurally characterized the  $d^2$  tungsten(IV) phenoxide complexes, W(O-2,6-R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub> (R = Me and Pr<sup>i</sup>), and found the coordination geometries to be nearly squareplanar. The latter has been explained in terms of oxygen lone-pair  $\rightarrow$  tungsten  $\pi$ -donation, which stabilizes the square-planar geometry relative to the tetrahedral geometry.<sup>8,9</sup> For U(O-2,6-Bu<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>, it is unclear whether the tetrahedral geometry is the result of the increased steric requirements of the phenoxide ligands, reduced oxygen  $\rightarrow$  metal  $\pi$ -bonding, or a combination of the two. Efforts are underway in our laboratory to prepare and structurally characterize the related 2,6-diisopropyl- and 2,6-dimethylphenoxide complexes.

Acknowledgements—We wish to thank the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy for financial support, and Dr D. L. Clark and Dr C. J. Burns for helpful discussions. We also thank Dr Clark for a preprint of ref. 9.

Supplementary Material Available. Tables of crystal data, fractional coordinates, anisotropic thermal parameters, and distances and angles have been deposited with the Cambridge Crystallographic Data Centre. A listing of observed and calculated structure factors has been deposited with the Editor at Indiana University and is also available from the Molecular Structure Center, Indiana University (Report no. 88901).

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