

Hydrocarbon-soluble, Crystalline, Four-co-ordinate Chloro(aryl oxide)s, Dialkylamido(aryl oxide)s, and Di[bis(trimethylsilyl)cyclopentadienyl]s of Th^{IV} and U^{IV}; X-Ray Crystal Structure of Diethylamidotris(2,6-di-*t*-butylphenoxo)uranium(IV)[†]

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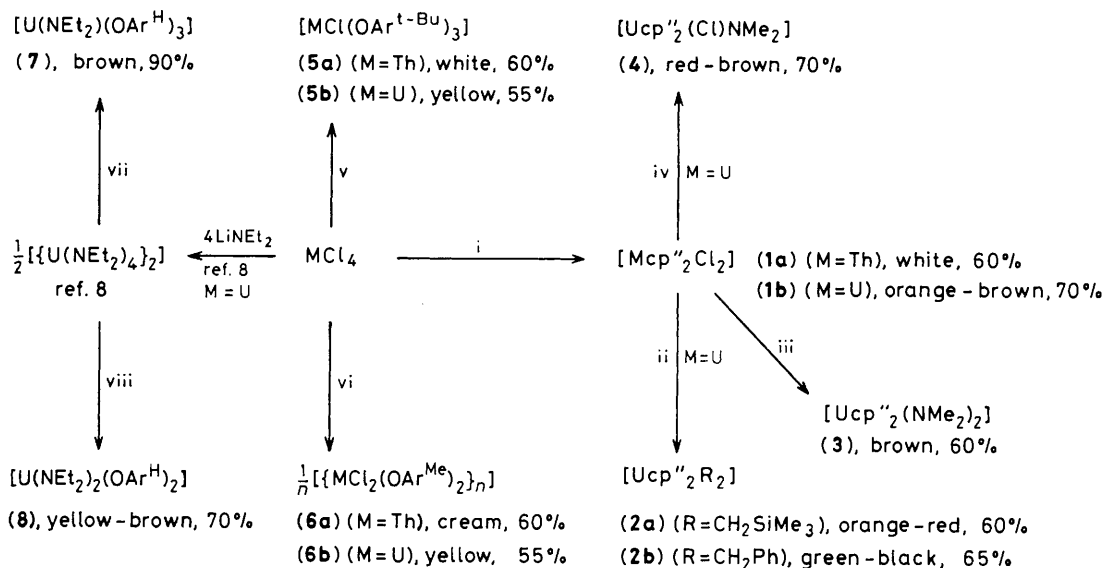
Two types of reactions [$\bar{\text{Cl}}/\text{X}^-$ or $\bar{\text{N}}\text{Et}_2/\bar{\text{OAr}}^{\text{R}}$ exchange; $\text{X} = \eta\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$ (cp''), $\text{OC}_6\text{H}_2\text{Bu}^t\text{-2,6-R-4}$ (OAr^{R}), CH_2SiMe_3 , or CH_2Ph] gave $[\text{Mcp}''_2\text{Cl}_2]$, $[\text{Ucp}''_2\text{R}'_2]$ ($\text{R}' = \text{NMe}_2$, CH_2SiMe_3 , or CH_2Ph), $[\text{Ucp}''_2(\text{Cl})\text{-NMe}_2]$, $[\text{MCl}(\text{OAr}^{\text{t-Bu}})_3]$, $[\{\text{MCl}_2(\text{OAr}^{\text{Me}})_2\}_n]$; ($\text{M} = \text{Th}$ or U), $[\text{U}(\text{NEt}_2)(\text{OAr}^{\text{H}})_3]$ (**7**), and $[\text{U}(\text{NEt}_2)_2(\text{OAr}^{\text{H}})_2]$; the title compound (**7**) has tetrahedrally co-ordinated U and trigonal N with U–N 2.162(5) and av. U–O 2.143(4) Å and av. O–U–O 114, av. O–U–N 104, and av. U–O–C 154°.

We report a range of novel complexes of thorium and uranium [(**1**)–(**8**) in Scheme 1], which are crystalline and hydrocarbon-

soluble. With two exceptions, (**6a**) and (**6b**), they are rare examples of mononuclear actinoid complexes. They are all in the +4 oxidation state, and are available as precursors to +3, +5, and +6 analogues.

The metallocene chlorides of (i) the early (4f⁰–4f⁸) lantha-

[†] No reprints available.



Scheme 1. Abbreviations: cp'' = $\eta\text{-C}_5\text{H}_5(\text{SiMe}_3)_2$, $OAr^R = OC_6H_4Bu^t\text{-}2,6\text{-R-}4$. Reagents and conditions: i, 2 Lcp'', thf (+ OEt₂, for M = Th), -23°C to ca. 20°C , 7 days; ii, 2 LiR, OEt₂, -78°C to ca. 20°C , 1 day; iii, 2 LiNMe₂, OEt₂, -78°C to ca. 20°C , 1 day; iv, 1 LiNMe₂ and as in iii; v, excess of $[LiOAr^{t-Bu}(OEt_2)]_2$, thf, 20°C , 4 days, then refluxed 4 h; vi, $[LiOAr^{Me}(OEt_2)]_2$, thf (+ OEt₂, for M = Th), 0°C to ca. 20°C , 7 days; vii, excess of $Ar^H\text{OH}$, $n\text{-C}_5\text{H}_{12}$, 0°C to ca. 20°C , 1 day; viii, 2 $Ar^H\text{OH}$ and as for vii. Isolation procedure: for each of (1)–(8), successive solvent removal, extraction into PhMe (1, 5, 6) or $n\text{-C}_5\text{H}_{12}$, concentration, and crystallisation at -30°C . Characterisation: compounds (1)–(8) are crystalline and gave satisfactory microanalytical results as well as ¹H and ¹³C n.m.r. spectra; X-ray crystal data for (7) and (1b) (J. L. Atwood and W. E. Hunter, unpublished work) are also available.

noids $[Lncp_2(\mu\text{-Cl})_2]$ or (ii) the actinoids $[Mcp_2Cl_2]_n$ (M = Th or U) have proved to be elusive for the case of cp = $\eta\text{-C}_5\text{H}_5$; attempted preparation leads to their disproportionation products $[Lncp_3]$ or $[Mcp_3Cl]_m$. We

recently showed that the use of the ligand $\bar{C}_5\text{H}_5(\text{SiMe}_3)_2$ (abbreviated as cp'') makes accessible the series (i),¹ and now find that (ii) may likewise be obtained [(1a) and (1b) in Scheme 1]; an alternative strategy, valid for (ii) but not (i),

was based on $\bar{C}_5\text{EtMe}_4^2$ or $\bar{C}_5\text{Me}_5$.³ From $[Ucp''_2Cl_2]$, (1b), simple metathetical reactions (Scheme 1) give the crystalline complexes $[Ucp''_2(\text{CH}_2\text{R})_2]$ (R = SiMe₃ or Ph), (2), $[Ucp''_2(\text{NMe}_2)_2]$, (3), and $[Ucp''_2(\text{Cl})\text{NMe}_2]$, (4). Of these, compounds (2) and (3) have precedents in other uranocene dialkyls³ or diamides.⁴

Another series of bulky ligands which confer lipophilic character upon their metal (M) complexes are the 2,6-di-*t*-butylphenoxides (e.g., OAr^R or OAr^{Me} , where the superscript defines the substituent in the 4-position, as shown previously *inter alia* for $M'(OAr^{Me})_2$ (M' = Ge or Sn),⁵ $[Ticp_2(OAr^{Me})]$,⁶ and $[HfCl(OAr^R)_3]$.⁷ We now report data on two new series of heteroleptic complexes of actinoids: namely the chloro(aryl oxide)s, exemplified by $[ThCl(OAr^{t-Bu})_3]$, (5a), and $[MCl_2(OAr^{Me})_2]$ [M = Th, (6a); or U, (6b)]; and the dialkyl-amido(aryl oxide)s, as in $[U(NEt_2)(OAr^H)_3]$, (7), and $[U(NEt_2)_2(OAr^H)_2]$, (8). The compounds were made by the following exchange reactions: \bar{Cl} by \bar{OAr}^R from MCl_4 and $[LiOAr^R(OEt_2)]_2$, or \bar{NEt}_2 by \bar{OAr}^H from $[U(NEt_2)_4]_2$ and $Ar^H\text{OH}$, Scheme 1. It is interesting that, even when using an excess of the aryl oxide or phenol, the homoleptic aryl oxide $[M(OAr^R)_4]$ was not obtained but only the heteroleptic $[MCl(OAr^R)_3]$, (5) or (7); similarly $ThCl_4$ and an excess of $LiN(\text{SiMe}_3)_2$ yielded $ThCl\{N(\text{SiMe}_3)_2\}_3$.⁹ By contrast, UCl_4 with an excess of a phenol (e.g., PhOH or *o*-MeC₆H₄OH) in liquid ammonia yielded the hydrocarbon-insoluble and presumably oligomeric $[U(OAr)_4(\text{NH}_3)_n]_m$ ($n = 1$ or 2).¹⁰

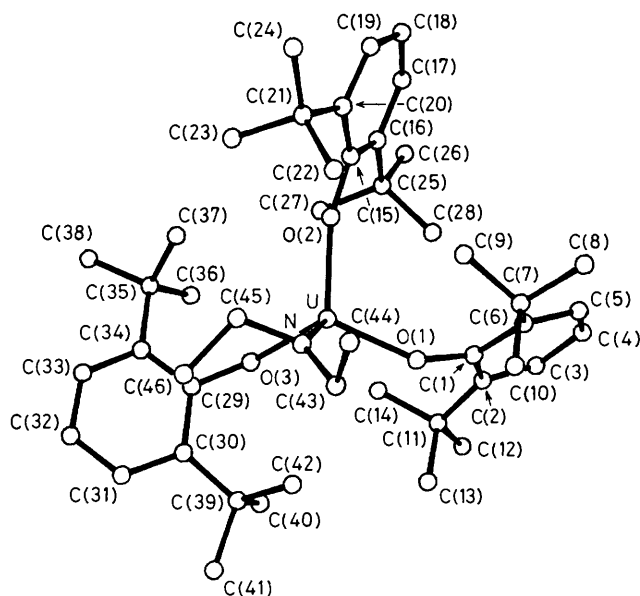


Figure 1. The molecular structure and atom numbering scheme. Relevant dimensions are: U–O(1) 2.140(4), U–O(2) 2.146(4), U–O(3) 2.143(4), U–N 2.162(5) Å, U–O(1)–C(1) 149.4(3), U–O(2)–C(15) 163.4(4), U–O(3)–C(29) 150.4(4)°.

The only other Th or U aryl oxides to have been described appear to be $U(O)_n(\text{OPh})_2$, $U(\text{OPh})_4(\text{OEt})$,¹¹ $U(\text{Cl})(\text{OPh})_4\text{-}\{\text{OC}(\text{NMe}_2)\text{H}\}$, and the sole previously X-ray characterised complexes $[U^V(\text{OPh})_3(\text{thf})]_2$ $\{U^{VI}(\text{O})_2(\text{thf})_2\}_2(\mu\text{-OPh})_4(\mu_2\text{-O})_2$ (thf = tetrahydrofuran)¹² and $[U(\text{OPh})_4(\text{dmpe})_2]$ (dmpe = $\text{Me}_2\text{P}[\text{CH}_2]_2\text{PMe}_2$)¹³ (the Th analogue was also made).

Crystal data for (7): C₄₆H₇₃NO₃U, $M = 926.1$, triclinic, $P\bar{1}$, $a = 10.802(1)$, $b = 10.885(2)$, $c = 21.033(2)$ Å, $\alpha = 92.63(1)$, $\beta = 97.39(1)$, $\gamma = 114.64(1)^\circ$, $Z = 2$. The structure of $[U(NEt_2)(OAr^H)_3]$, (7), (Figure 1) was solved by routine

heavy atom methods and refined by least squares to $R = 0.053$, $R' = 0.071$ for 6390 reflections measured on a CAD-4 diffractometer with Mo- K_{α} radiation.†

The uranium atom is co-ordinated tetrahedrally by three aryloxy and one amido ligand. {In actinoid chemistry there appear to be only two prior proven examples of monomeric crystalline complexes with four monohapto ligands: $[\text{U}(\text{NPh}_2)_4]^{14}$ and $[\text{U}(\text{H})\{\text{N}(\text{SiMe}_3)_2\}_3]^{15}$ (although the hydrogen was not located).} The O-U-O angles (average 114°) are larger than the O-U-N angles (average 104°) presumably for steric reasons. The U-N bond length of 2.162(5) Å is shorter than that found for the tetrahedral U^{IV} complexes $[\text{U}(\text{NPh}_2)_4]^{14}$ [av. 2.27(5) Å] or $[\text{U}(\text{H})\{\text{N}(\text{SiMe}_3)_2\}_3]^{15}$ [av. 2.237(9) Å]. The amido N atom is in an essentially planar environment. The U-O bonds average 2.143(4) Å and the U-O-C angles average 154° , and may be compared with the values for the terminal isopropoxy groups in $[\{\text{U}^{\text{IV}}(\eta\text{-C}_3\text{H}_5)_2(\text{OPr}^1)(\mu\text{-OPr}^1)\}_2]$, 2.06(1) Å and 178° ,¹⁶ and with av. 2.17(1) Å in $[\text{U}(\text{OPh})_4(\text{dmpe})_2]^{13}$. Similar values have been seen in the $\text{U}^{\text{V}}/\text{U}^{\text{VI}}$ phenoxide mentioned above, where the terminal phenoxy-uranium bonds average 2.08(5) Å and the U-O-C angles average 165° .¹² Large M-O-C angles have also been seen in $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{OAr}^{\text{Me}})]$ [142.3(2)°]⁶ and $[\text{HfCl}(\text{OAr}^{\text{H}})_3]$ (av. 156°).⁷

In $[\text{U}(\text{NEt}_2)(\text{OAr}^{\text{H}})_3]$, (7), the arrangement of the aryloxy groups is such that for two of the groups the phenyl rings and the U-N bond are approximately coplanar and each of these two rings has one Bu^t group close to the N atom and one on the opposite side of the molecule. The third aryloxy group is rotated approximately 90° about the C-O bond such that the two Bu^t groups are roughly equidistant from the N atom.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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