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Preliminary communication

ACTINIDE—AMIDE COMPLEXES

I. SYNTHESIS AND UTILITY OF DI-η-CYCLOPENTADIENYLBIS-(DIETHYLAMIDO)URANIUM(IV)

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Summary

The reaction of two moles of cyclopentadiene with $U[N(C_2H_5)_2]_4$ results in the formation of $(\eta\text{-}C_5H_5)_2U[N(C_2H_5)_2]_2$ in excellent yields. The synthetic utility of the complex as a potential starting material for other $(\eta\text{-}C_5H_5)UX_2$ compounds is commented upon.

Despite the current renaissance of interest in organouranium chemistry studies up to now have mainly been limited to two systems: derivatives of Cp_3UX ($Cp = \eta\text{-}C_5H_5$) (for instance X = halide [1], C_5H_5 [2], alkyl [3] and complexes related to uranocene, $(\eta\text{-}C_8H_8)_2U$ [4]. The new possibilities offered by the reported synthesis of Cp_2UCl_2 [5] were indeed shortlived since it was shown [6] that the product of the reaction is $[Cp_3UCl]_2UCl_4$ and not the dichloride as originally postulated.

Our interest in the amido derivatives of uranium, coupled with the well established synthetic utility of the corresponding transition metal amides [7], led us to investigate the reactivity of $U[N(C_2H_5)_2]_4$ toward cyclopentadiene*. In this communication we wish to describe the synthesis of $Cp_2U[N(C_2H_5)_2]_2$ and its potential utility toward the preparation of other Cp_2UX_2 compounds.

$Cp_2U[N(C_2H_5)_2]_2$ can be obtained in excellent yield by the reaction scheme shown in eqns. 1 and 2 making use of the in situ preparation of $U[N(C_2H_5)_2]_4$ [9]. This type of reaction sequence has been used by Chandra

$$UCl_4 + 4LiN(C_2H_5)_2 \xrightarrow{THF} \underset{(I)}{U[N(C_2H_5)_2]_4} + 4LiCl \qquad (1)$$

$$I + 2C_5H_6 \xrightarrow{Pentane} Cp_2U[N(C_2H_5)_2]_2 + 2HN(C_2H_5)_2 \qquad (2)$$

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*A recent report by Bagnall and Yanir [8] described the insertion of CS_2, COS and CO_2 into the uranium—nitrogen bond.

and Lappert for the amides of Zr and Hf [7]. However, in contrast to $Zr[N(C_2H_5)_2]_4$ and $Hf[N(C_2H_5)_2]_4$ which react with only two equivalents of C_5H_6, the uranium amide will react with three equivalents of C_5H_6 to form $Cp_3U(NEt_2)$. Hence the stoichiometry in eqn. 2 must be closely followed.

$Cp_2U[N(C_2H_5)_2]_2$, which can be crystallized from pentane at −78°C as golden leaves, was characterized by NMR (^1H and ^{13}C), analysis, and mass spectral data (molecular ion seen at *m/e* 512). In addition to the sharpness of the resonances the NMR data on the bis-amide is quite interesting. Both the CH_2 and CH_3 groups experience downfield shifts from their normal positions, ^1H NMR of $Cp_2U[N(C_2H_5)_2]_2$ in ppm from internal benzene; Cp 20.94 (s), CH_2 −1.54 (q), CH_3 + 5.70 (t). However the shifts are much less substantial than in Cp_3UOR type complexes [10]. The unexpected upfield shift for the CH_2 carbon atom in the ^{13}C NMR spectrum[*] of the complex could be an indication of contact contribution to the observed chemical shifts. The importance of such mechanisms has been previously observed in other organouranium complexes [3,10]. Further work currently in progress is designed to settle this point.

$CpU[N(C_2H_5)_2]_2$ reacts with ligands which have protons which are more acidic than that of diethylamine. Hence toluene-3,4-dithiol (tdt), *o*-mercaptophenol (omp), catechol (cat), and 1,2-ethanedithiol (edt) react with $Cp_2U[N(C_2H_5)_2]_2$ according to eqn. 3[**]. In contrast to the nearly constant position of the Cp resonance in the ^1H NMR spectra of Cp_3UR (where

$$Cp_2U[N(C_2H_5)_2]_2 + 2H{-}X \rightarrow Cp_2U(X)_2 + 2HN(C_2H_5)_2 \qquad (3)$$

R = alkyl, aryl, alkenyl) [3], the Cp resonances vary considerably in the chelated complexes, i.e. from 0.12 ppm in $Cp_2U(tdt)$ to 6.88 ppm in Cp_2U-(cat) with respect to internal C_6H_6. Again whether this is due to changes in the contact or pseudocontact contribution is not known at the present time. Another unexpected feature, as revealed by a variable temperature ^1H NMR investigation of $Cp_2U(tdt)$, is the apparent existence of dimeric materials for these chelated complexes. The room temperature singlet for the Cp protons splits into two peaks having an intensity ratio of approximately 2/1 at −60°C. The possibility of rapid conformational changes of a puckered five-membered ring, as observed for $Cp_2Ti(tdt)$ [12], to account for the obtained variable temperature results can be dismissed since such mechanism should result in an intensity ratio of 1/1 for the two peaks. A possible explanation is a rapid monomer—dimer equilibrium which is slowed down at low temperature. This dimeric tendency is also seen in the mass spectra which showed *m/e* 984, 952, and 920 for $[Cp_2U(omp)]_2$, $[Cp_2U(cat)]_2$, and $[Cp_2U(edt)]_2$, respectively. The mass spectrum of $Cp_2U(tdt)$ did not show the expected dimer. However $Cp_2U(tdt)$ is much less volatile than the other complexes as reflected by the fact that a higher temperature was needed to obtain a spectrum and that its peaks were of low intensity.

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[*] ^{13}C NMR of $Cp_2U[N(C_2H_5)_2]_2$: Cp (d, *J* 161 Hz) at 125 ppm below TMS, CH_3 (q, *J* 125 Hz) at 59.5 ppm below TMS, and CH_2 (t, *J* 129 Hz) at 120.4 ppm above TMS.

[**] Brady and Marianelli [11] reported on the preparation and synthetic utility of $(\eta\text{-}C_5H_5)_2U$-$(acac)_2$ (acac = acetylacetonate) at a conference. However, nothing has yet appeared in the literature.

Although the chelated complexes could easily be prepared and handled, attempts to prepare monodentate thiol derivatives were far less successful. For instance two equivalents of ethanethiol react with $Cp_2U[N(C_2H_5)_2]_2$ to give a mixture of $Cp_2U(SC_2H_5)_2$ and $Cp_3U(SC_2H_5)$. Similar results were obtained with thiophenol. t-Butanethiol (tbt) reacts in THF to give essentially pure $Cp_2U(tbt)_2$ and in pentane about 5% of $Cp_3U(tbt)$ is also formed. These results tend to support the monomer—dimer equilibrium with the resulting disproportionation of $Cp_2U(SR)_2$. The fate of $CpU(SR)_3$ or $U(SR)_4$, the other possible disproportionation products, is not known at the present time.

Carbon disulfide inserts into the uranium—nitrogen bond to give the corresponding dithiocarbonate, $Cp_2U[S_2CN(C_2H_5)_2]_2$. This was verified by its mass spectrum (highest peak at *m/e* 664) and ^1H NMR spectrum.

Further work on the synthetic utility of $Cp_2U[N(C_2H_5)_2]_2$ and other amido derivatives is in progress. This work is also being extended to thorium.

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