Journal of Organometallic Chemistry, 309 (1986) 55–63
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOMETALLIC AMIDES OF URANIUM(IV) AND THORIUM(IV) INVOLVING ONE, TWO, OR THREE CYCLOPENTADIENYL LIGANDS

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(Received January 15th, 1986)

Summary

Both $U(NEt_2)_4$ and $Th(NEt_2)_4$ can be treated stoichiometrically and kinetically controlled with cyclopentadiene so that the various products $Cp_n{}^fM(NEt_2)_{4-n}$ ($n = 2, 3, {}^fM = U$; $n = 1, 2, 3, {}^fM = Th$) may be separately obtained in high yields. Cp_3UNEt_2 also reacts with an excess of HCp to give UCp_4. For the preparation of the complexes $Cp_2U(NR_2)_2$ (R = Et or Ph) and Cp_3UNEt_2, an alternative route, starting from UCl_4, TlCp and $LiNEt_2$ ($KNPh_2$) and from Cp_3UCl and $LiNEt_2$, respectively, has also been developed. The new complex $CpU(NEt_2)_3$ does not readily undergo ligand redistribution to give $Cp_2U(NEt_2)_2$ and $U(NEt_2)_4$, but it appears to react with another HCp molecule appreciably faster than does $U(NEt_2)_4$.

Compound numbers used below are as follows: $U(NEt_2)_4$ (**1**), $CpU(NEt_2)_3$ (**2**), $Cp_2U(NEt_2)_2$ (**3**) $Cp_2U(NPh_2)_2$ (**3a**), Cp_3UNEt_2 (**4**) Cp_3UNPh_2 (**4a**), Cp_4U (**5**) $Th(NEt_2)_4$ (**6**), $CpTh(NEt_2)_3$ (**7**) $Cp_2Th(NEt_2)_2$ (**8**) and Cp_3ThNEt_2 (**9**).

Transition metal amides are of considerable preparative value since the M–N bond readily undergoes protolytic cleavage and also facile insertion of small unsaturated molecules [1,2]. In 5*f*-transition metal chemistry, new organouranium amides have been obtained both by metathetical reactions [3] and by reactions of tetrakis(diethylamido)uranium(IV) with sufficiently proton acidic cyclopentadienes, HCp, [4–7] mainly to obtain some well-defined new organouranium amides. It has

0022-328X/86/$03.50

been shown that the rather weak acids pentamethylcyclopentadiene (pK_a 26.1 [8]) and tetramethylethylcyclopentadiene selectively displace only one NEt_2 ligand [6,7].

$$U(NEt_2)_4 + HCp''(\text{excess}) \rightarrow Cp''U(NEt_2)_3 + HNEt_2 \qquad (1)$$
$$(HCp'' = \text{peralkylated cyclopentadiene})$$

whereas e.g., HC_5H_5 (pK_a 18.0 [8]) successfully displaces a second NEt_2 ligand to give pure $Cp''CpU(NEt_2)_2$ [7].

$$Cp''U(NEt_2)_3 + HCp \xrightarrow{1/1} Cp''CpU(NEt_2)_2 + HNEt_2 \qquad (2)$$

A number of $Cp'_2U(NEt_2)_2$ systems including those with $Cp' = C_5H_5$ [4], indenyl (pK_a of HC_9H_7 20.1 [8]), or C_5H_4R (R = alkyl) have been prepared in one step by treating **1** with two equivalents of HCp′ [5]. However, an attempted step-by-step approach to arrive at pure $CpCp'U(NEt_2)_2$ complexes (free from Cp″) have only produced mixtures of the three species $Cp_2U(NEt_2)_2$, $Cp'_2U(NEt_2)_2$ and $CpCp'U(NEt_2)_2$ [5]. It has been suggested that complexes of the type $Cp'U(NEt_2)_3$ ($Cp' = C_5H_5$ or C_5H_4R) are always involved in facile ligand redistribution equilibria (eq. 3)

$$2Cp'U(NEt_2)_3 \rightleftarrows Cp'_2U(NEt_2)_2 + U(NEt_2)_4 \qquad (3)$$

which would seriously interfere with the isolation of pure products such as $Cp'U(NEt_2)_3$ [5]. We show in this paper that: (a) all four NEt_2-groups of **1** may be replaced by Cp in a stepwise procedure:

$$U(NEt_2)_2 \xrightarrow[-HNEt_2]{CpH,\ 1/1} CpU(NEt_2)_3 \xrightarrow[-HNEt_2]{CpH,\ 1/1} Cp_2U(NEt_2)_2 \xrightarrow[-HNEt_2]{CpH,\ 1/1}$$
$$Cp_3UNEt_2 \xrightarrow[-HNEt_2]{CpH,\ excess} Cp_4U \qquad (4)$$

(b) complexes **2** and **3** do not undergo ligand redistribution; (c) the corresponding stepwise replacement of one to three NEt_2 ligands by Cp is also possible in case of the thorium complex **6**. We also suggest facile alternative synthetic approaches to **3**, **3a** and **4** by avoiding the intermediate formation of $U(NEt_2)_4$. Thus both **3** and **3a** can be obtained by use of the appropriate stoichiometric amounts of UCl_4, TlCp and $LiNEt_2$ or $KNPh_2$; similarly **4** can be conveniently prepared from Cp_3UCl and $LiNEt_2$. Complexes of the type Cp_3UNR_2 have previously only been observed as by-products during the synthesis of $Cp_2U(NR_2)_2$ [4b], and not specifically produced by appropriate use of process 3. Finally a facile and quantitative route to **5** involving reaction of **4** with an excess of CpH has been shown to provide a convenient alternative to that previously used for this important organouranium compound [9].

Experimental

All sample preparations and manipulations were carried out in glove boxes under rigorously purified and monitored dinitrogen. Solvents were dried by standard methods [10] and used immediately after distillation. $LiNEt_2$ [11], $KNPh_2$ [4b], UCl_4 [12a], $U(NEt_2)_4$ [11], TlCp [12b], Cp_3UCl [12c] and $Th(NEt_2)_4$ [13] were synthesized by published procedures. Other reagents were commercial products and were used as supplied.

The C, H, and N analyses and the $HNEt_2$ determination (in which a weighed sample was decomposed with 2*N* KOH and the liberated $HNEt_2$ was distilled into an excess of 0.1*N* H_2SO_4, and the excess of the acid was back titrated with 0.1*N* NaOH) were performed by A. Berton at the C.N.R. Institute.

Visible IR (Nujol mulls in the range 4000–280 cm^{-1}), ^1H NMR (sample in sealed tubes), and mass spectra were recorded on Cary 17D, Perkin–Elmer 580B, Varian FT80A (equipped with a variable temperature acessory) and V.G. Ltd ZAB 2F (operating in EI at 70 eV) instruments, respectively.

$CpU(NEt_2)_3$

(a) A suspension of UCl_4 (0.38 g, 1 mmol), and $LiNEt_2$ (0.316 g, 4 mmol) in n-hexane or Et_2O (20 ml) was stirred at room temperature for 24 h, after which a solution of freshly distilled CpH (0.033 g, 0.5 mmol) in n-hexane (10 ml) was slowly added. Stirring continued for another 5 h. At intervals a few drops of the solutions were removed and evaporated, and the brown oily residue was dissolved in C_6D_6 and monitored by ^1H NMR spectrometry until the $U(NEt_2)_4/UCp(NEt_2)_3$ ratio remained constant for 1 h.

After addition of sufficient CpH for complete conversion of **1** into **2** and a further 5 h stirring, the resulting solution was filtered to remove LiCl and the solvent was evaporated under vacuo to leave a viscous red-brown oil (yield up to 90%). Analysis. Found: NEt_2 40.93. $C_{17}H_{35}N_3U$ calcd.: NEt_2 41.62%. The ^1H NMR spectrum in C_6D_6 (at 27°C with C_6D_5H as internal standard) showed the following signals: +17.98 (s, 5H, Cp), +8.07 (t, 18H, CH_3, *J* 5.2 Hz), −3.02 (q, 12H, CH_2, *J* 5.3 Hz), together with those of **3**, 2–3% of which was present. Further purification could not be achieved either by fractional crystallization or by cooling the solution at −80°C. In the latter case the light brown solid obtained still contained **3**.)

(b) Reaction of $CpUCl_3$ (1 mmol) in THF with $LiNEt_2$ (3 mmol) gave only traces of **2**.

$Cp_2U(NEt_2)_2$

(a) Following the procedure described in ref. 4b freshly distilled CpH (0.066 g, 1 mmol) was added to a solution of **1** in n-hexane or Et_2O (20 ml) prepared as described for **2** from 1 mmol of UCl_4 and 4 mmol of $LiNEt_2$. Stirring was continued 5 for h. The 2/3 molar ratio was determined by ^1H NMR spectroscopy and an additional amount of CpH necessary to convert the monocyclopentadienyl amide to the bis-derivative was added, and stirring was continued a further 5 h. After filtration of the solution and concentration to 10 ml, very pure **3** was obtained by cooling to −80°C.

(b) A suspension of UCl_4 (0.38 g, 1 mmol) and TlCp (0.54 g, 2 mmol) in 20 ml of THF or DME was stirred for 1 h at room temperature. After filtration of the resulting solution $LiNEt_2$ (0.158 g, 2 mmol) was added, and stirring was continued for 4 h. The solvent was pumped off under vacuo and the residue was treated with 50 ml of n-hexane or Et_2O and the mixture was stirred for another hour. The brown yellow mixture was filtered, the solid, on the filter was washed several times with the solvent and the combined filtrate and washings were reduced to 10 ml under vacuo. Cooling to −80°C gave very pure **3** (^1H NMR) in 87% yield. **3** was also obtained in very good yield by the following procedure: 48 h stirring of a 2/1 molar ratio Et_2O mixture of $LiNEt_2$ and UCl_4 and subsequent addition of 2 mmol of TlCp with further 3 h stirring.

When a solution of **3** contaminated by **4** was treated with $LiNEt_2$, complete conversion of the tricyclopentadienyl derivative into the dicyclopentadienyl species occurred. The analogous conversion of the dicyclopentadienyl derivative into the monocyclopentadienyl derivative did not take place.

$Cp_2U(NPh_2)_2$

As described above, a suspension of UCl_4 (0.38 g, 1 mmol), TlCp (0.54 g, 2 mmol) and $KNPh_2$ (0.414 g, 2 mmol) in THF was stirred for 1 h. The resulting deep red solution contained almost pure **3a** (by ^1H NMR) contaminated by a few per cent of Cp_3UCl and **4a**. The mixture was filtered to remove KCl and TlCl, and the filtrate concentrated to 5 ml in vacuo . When a 5/20 v/v mixture of n-hexane was added and the solution kept at −80°C pure microcrystalline **3a** slowly precipitated out (90% yield).

Cp_3UNEt_2

(a) A mixture of **2** and **3** was prepared from a suspension of 1 mmol of UCl_4, 4 mmol of $LiNEt_2$ and 1.5 mmol of CpH in hexane (20 ml). After filtration and addition of freshly distilled CpH (0.396 g, 6 mmol) stirring was continued for two days at room temperature. A red brown microcristalline powder slowly precipitated out and this was filtered off, washed with n-hexane, and dried under vacuo (78% yield). It was identified as **4** by comparison with the published ^1H NMR spectrum [4b]. The filtrate was evaporated to dryness and the solid residue was dissolved in C_6D_6 and shown by ^1H NMR spectroscopy to be a mixture of **3** and **4** (22.5 and 77.5%, respectively).

(b) A mixture of Cp_3UCl (0.468 g, 1 mmol) and $LiNEt_2$ (0.079 g, 1 mmol) in THF (30 ml) was refluxed for 1 h. The solvent was removed under vacuo and a suspension of the residue stirred for 1 h in 50 ml of a 1/1 v/v benzene/toluene mixture. The solution was filtered then concentrated to 10 ml, and the red solid obtained (0.2–0.3 g) by addition of n-hexane (50 ml) was identified as pure **4** [4c]. The same reaction carried out in a benzene/toluene mixture for 1 h under reflux gave only traces of **4** and **3**, together with unreacted Cp_3UCl. Complex **3** can be removed from **4** by washing with n-hexane.

Complex **4** is a red solid, soluble in THF, benzene, toluene and Et_2O, slightly soluble in n-hexane. It sublimes at 150°C and 10^{-4} mmHg. Its ^1H NMR spectrum agreed exactly with that reported by Takats [4b].

Mass spectrum (EI 70 eV; 150°C): parent ion M^+ m/e 505. Other characteristic ions: $M^+ - 65$ m/e 440 $(Cp_2UNEt_2)^+$; $M^+ - 72$ m/e 433 $(Cp_3U)^+$; m/e 434 $(Cp_3UH)^+$; $M^+ - 137$ m/e 368 $(Cp_2U)^+$; m/e 369 $(Cp_2UH)^+$; $M^+ - 202$ m/e 303 $(CpU)^+$; m/e 304 $(CpUH)^+$. Complex **4** also reacts readily with NH_4X (X = F, I) in THF to give Cp_3UX, as reported for Cp_4U [14].

Cp_4U

Freshly distilled CpH (0.5 ml) was added to a THF solution of **4** (0.190 g) and the mixture was stirred for 24 h. The bright red powder (0.140 g) was filtered off, washed with small portions of THF, and dried. Its ^1H NMR spectrum in C_6H_6 was identical to that previously reported for **5** [15]. The mass spectrum (EI 70 eV; 150°C) showed the parent ion M^+ at m/e 498 and some other characteristic ions due to the progressive loss of cyclopentadienyl groups: $M^+ - 65$ m/e 433 (Cp_3U^+);

$M^+ - 130$ m/e 368 $(Cp_2U)^+$; $M^+ - 195$ m/e 303 (CpU). The relative abundances of the various ions agree with those previously reported [16].

$CpTh(NEt_2)_3$

A solution of freshly distilled CpH (0.21 ml, 2.54 mmol) in 10 ml of toluene was slowly added to a toluene solution (25 ml) of **6** [13] prepared in situ from $ThCl_4$ (0.95 g, 2.54 mmol) and $LiNEt_2$ (0.803 g, 10.16 mmol). The solution was stirred for 20 h; then filtered, and the toluene was removed under vacuo. The white yellow solid (≃ 70% based on the taken $ThCl_4$) was characterized by its ^1H NMR spectrum and its NEt_2 content. Analysis. Found: NEt_2 41.5. $C_{17}H_{35}N_3Th$ calcd. NEt_2 42.10%. ^1H NMR (benzene-d_6: ppm from C_6D_5H as internal standard): 0.86 (s, 5H, Cp); 4.12 (q, 12H, CH_2); 6.16 (t, 18H, CH_3).

Comparable results were obtained when Et_2O or n-hexane were used as the solvent. Complex **7** is very soluble in n-hexane, toluene, benzene and Et_2O. It is very difficult to be obtained free from some **8** or **6**.

$Cp_2Th(NEt_2)_2$

To a solution of **6** prepared in situ starting from 2.54 mmol of $ThCl_4$ and 10.16 mmol of $LiNEt_2$ in 20 ml of toluene, small portions (0.05 ml, 0.06 mmol) of freshly distilled CpH were added until the $CpTh(NEt_2)_3/Cp_2Th(NEt_2)_2$ molar ratio (monitored by ^1H NMR) was approximately 1/9. The solution was filtered and the solvent evaporated off. Washing of the residue several times with small portions of n-hexane gave the insoluble **8** (white power) free from **7**, which is very soluble in n-hexane. Analysis. Found:NEt_2 28.46. $C_{18}H_{30}N_2Th$ calcd.: NEt_2 27.8%. ^1H NMR (ppm, C_6D_5H as internal standard): 1.02 (s, 10H, Cp); 3.88 (q, 8H, CH_2) 6.04 (t, 12H, CH_3).

Cp_3ThNEt_2

This compound was obtained as white insoluble powder by treating a solution of **8** (0.35 g) in Et_2O (20–30 ml) at room temperature with freshly distilled CpH. The solution was stirred for 10 h, then the precipitate was filtered off, washed, and dried under vacuo. Analysis. Found: NEt_2 13.9. $C_{17}H_{20}NTh$ calcd.: NEt_2 14.43%. ^1H NMR (C_6D_5H as internal standard): 1.07 (s, 15H, Cp); 3.90 (q, 4H, CH_2); 6.17 (t, 6H, CH_3). It is fairly insoluble in the usual solvents.

Some ^1H NMR experiments were carried out in order to investigate the possibility of the following conversions:

$$3Cp_2U(NEt_2)_2 \rightarrow 2Cp_3UNEt_2 + U(NEt_2)_4$$

and

$$2CpU(NEt_2)_3 \rightarrow Cp_2U(NEt_2)_2 + U(NEt_2)_4$$

Thus a solution of **3** in benzene-d_6 in a sealed NMR tube was kept at 26.5°C in an oil bath for 72 h and then at 67.5°C for 72 h. Its ^1H NMR spectrum which was recorded at various times, underwent no change. A similar result was obtained when a mixture of **3** (1.8%) and **2** (98.2%) was studied under similar conditions.

Results and discussion

Protolytic cleavage of M–N bonds ($M = U^{IV}$ and Th^{IV}) by cyclopentadiene (CpH) represents a very useful synthetic route to some mixed cyclopentadienyluranium(IV) and -thorium(IV) amides. Taken along with the results reported by other research groups [4,5], our data clearly indicate that the reaction proceeds stepwise as follows:

$$M(NEt_2)_4 + nCpH \xrightarrow[\text{temperature}]{\text{Room}} Cp_nM(NEt_2)_{4-n} + nHNEt_2$$

$$(M = Th, U;\ n = 1, 2, 3, 4) \qquad (A)$$

Thus there is initial formation of the new species **2**, followed by formation of the known **3**, **4** or **5** depending on the $U(NEt_2)_4/CpH$ ratio. Unfortunately **2** cannot be obtained as pure since compounds **1** and **3** which are present to the extent of ca. 3% have similarly high solubilities in organic solvents. The formation of **3** in the first stage of the procedure seems to be due to a comparable rate of reaction of CpH with **1** and **2** rather than to Cp ligand redistribution (see details of ^1H NMR study on the experimental). Diethyl ether solutions of **2** (98%) have a spectrum in the range 500–1600 nm typical of $CpUX_3 \cdot S$ (X = Cl, Br,; S = DME, 2THF) species; in particular, bands at 1031 and 1150 nm indicate a low symmetry and a high coordiation number (> 8) for the U^{IV} system and suggest the possibility of a species produced by association of two or more molecules via nitrogen bridging (Fig. 1). In the same range **4** has a spectrum very similar to those of Cp_3UX systems (where X = Cl, OPh, PPh_2) suggesting a pseudotetrahedral structure [17].

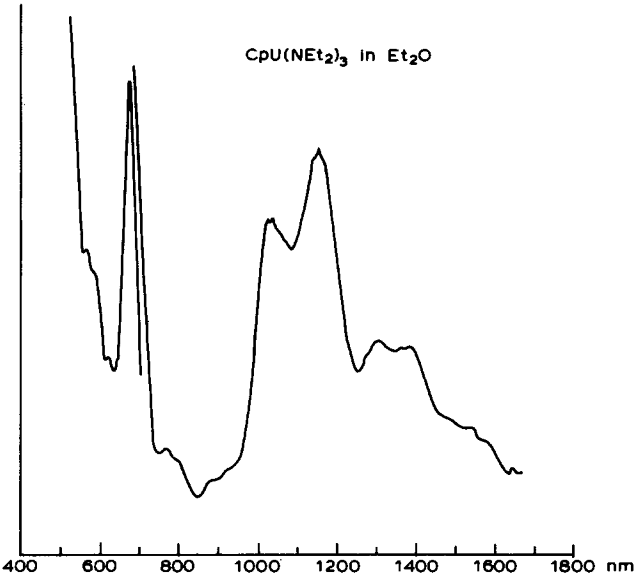


Fig. 1. NIR/VIS absorption spectrum of $CpU(NEt_2)_3$ in Et_2O.

Species **3** and **4** can be also obtained by replacement of Cl^- by NEt_2^- in processes 5–7.

$$\mathrm{UCl_4 + 2TlCp \xrightarrow{\text{DME or THF}} \text{“}Cp_2UCl_2\text{”} + 2TlCl} \tag{5}$$

$$\mathrm{\text{“}Cp_2UCl_2\text{”} + \begin{matrix} 2LiNEt_2 \\ \text{or} \\ 2KNPh_2 \end{matrix} \xrightarrow{\text{DME or THF}} \begin{matrix} Cp_2U(NEt_2)_2 \\ \text{or} \\ Cp_2U(NPh_2)_2 \end{matrix} + 2LiCl} \tag{6}$$

$$\mathrm{Cp_3UCl + LiNEt_2 \rightarrow Cp_3UNEt_2 + LiCl} \tag{7}$$

This alternative route which is analogous to that suggested for the preparation of $Cp'_2UClNMe_2$ and $Cp'_2M(NMe_2)_2$ ($M = U$, Th; $Cp' = C_5H_3(SiMe_3)_2$ [3]) appears more convenient than that based on protolytic cleavage of $U{-}NEt_2$ bonds by HCp since quantitative yields are obtained, especially for **3** since in this case species **4** which is also formed may be converted into **3** by reaction 8.

$$\mathrm{Cp_3UNEt_2 + LiNEt_2 \rightarrow Cp_2U(NEt_2)_2 + LiCp} \tag{8}$$

The new synthetic route to **3** (or **3a**) from “Cp_2UCl_2” and $LiNEt_2$ (or $KNPh_2$) is very interesting; it is consistent with results obtained previously in the synthesis of $Cp_2U(BH_4)_2$ [18]. It seems that while the compound “Cp_2UCl_2” cannot be isolated, it can be prepared in situ and then as an intermediate in the synthesis of other Cp_2UX_2 systems.

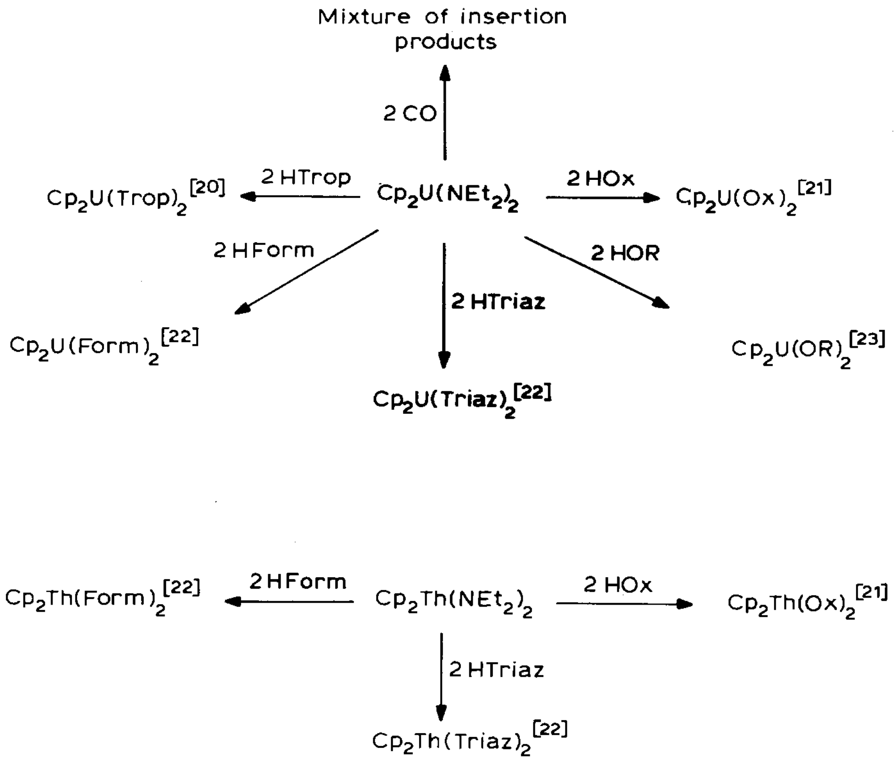
This behaviour suggests that the equilibrium 9

$$\mathrm{2\text{“}Cp_2UCl_2\text{”} \underset{\text{(DME, 2THF)}}{\underset{-S}{\overset{S}{\rightleftharpoons}}} CpUCl_3 + Cp_3UCl} \tag{9}$$

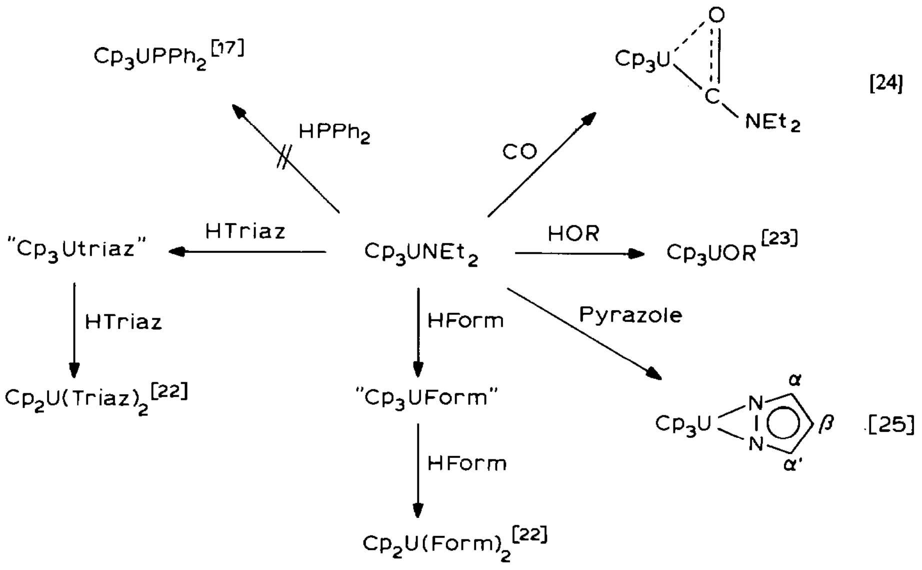
is shifted to the left by a subsequent reaction with bulky nucleophiles (X^-) when the rate of reaction of “Cp_2UCl_2” with X^- is higher than that for the corresponding Cp_3UCl and $CpUCl_3 \cdot S$ species. This seems to be confirmed by the observation that the reaction of $LiNEt_2$ with $CpUCl_3 \cdot S$ does not give **2**, while that with Cp_3UCl gives **4** only under reflux. (At room temperature step 7 is very much slower than 6). This behaviour is understandable since $CpUCl_3 \cdot S$ and Cp_3UCl are more coordinatively saturated than “Cp_2UCl_2”. Both **3** and **4** are very convenient starting materials in development of the organometallic chemistry of uranium(IV), as can be seen from Schemes 1 and 2. In particular, Cp_4U, Cp_3UBr, Cp_3UF can be very easily obtained by displacement of NEt_2 by use of HCp, NH_4Br, and NH_4F, respectively.

The reaction of **6** with HCp follows the course observed for **1**, i.e. in accord with equation (A); the products were separated and characterized in the usual way. However in this case the rate is slower, and more than the stoichiometric amount of CpH is needed for completion of the reaction [19]; moreover the separate products are always more or less contaminated by other members of the series $Cp_{4-n}Th(NR_2)_n$. This behaviour can be accounted for by assuming that during the time needed for the reaction the CpH can dimerize, with loss of protolytic ability, and that the reaction rates of CpH with the various species $Cp_{4-n}Th(NR_2)_n$ are comparable.

The solubilities of thorium derivatives (generally decrease with time, probably as a result of oligomerization by formation of nitrogen bonds between at least two thorium atoms, as indicated by the appearance of ions having *m/e* values higher than that for the molecular ion in the mass spectrum of **8**.



SCHEME 1. (Trop = tropolonato, Ox = oxinate, Form = *N,N'*-di-*p*-tolylformamide, Triaz = *N,N'*-di-*p*-tolyltriazenide).



SCHEME 2

In conclusion, as stated by Takats, stepwise protolytic scission of the M–N bond (M = U, Th) by CpH affords stable and characterizable organometallic compounds, which in turn are convenient starting material for interesting new complexes, as shown by the information in Schemes 1 and 2.

Acknowledgement

We thank Mr. F. Braga, and Mr. G. Agostini for skilled technical assistance.

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25 Analysed by ^{1}H NMR (benzene-d_6: ppm from C_6H_5H as internal standard): 16.67 (s, 15H, Cp); -1.68 (d, 2H, Hα,α'); -3.58 (t, 3H, Hβ).