Thus, addition of water to the filtrate from the reaction mixture liberates a 43% yield if isobutane.

The nature of the black reaction residue from eqn. (1) was investigated to determine whether residual hydrocarbyls are present and whether, in the case where the organic products indicate quantitative reaction, the expected stoichiometry is obeyed. In regard to the first question, the C, H contents (%) from the residues of experiments 1, 2 and 5 were found to be 2.77, 0.76; 1.68, 0.66; and 4.43, 1.20, respectively, indicating only minor incorporation of carbonaceous products (perhaps ether from the washing). The residue from experiment 5 was found to contain: Li, 6.69; Cl, 33.62; U, 55.20. If eqn. (1) proceeds as written, the stoichiometry of the inorganic residue should be Li_4UCl_4 or Li, 6.81; Cl, 34.79; U, 58.40. If eqn. (1) did not proceed to completion, there would be a deficiency of lithium, since the soluble lithium alkyl would be washed from the residue. Clearly there is no deficiency of lithium.

I am grateful to Professor Tobin J. Marks for helpful discussion, financial support, and making available his research laboratory at Northwestern University.

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The Reactivity of the Cyclopentadienyl Uranium(IV) and Thorium(IV) Amides. An Inviting Approach to Some New Organometallic Actinide Derivatives

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Transition metal amides are known to show a very useful reactivity of the metal-nitrogen bonds towards molecules containing acidic hydrogens and dipolar double bonds [1].

This behaviour has been videly used in order to provide a quite easy synthetic approach to many transition metal complexes [2].

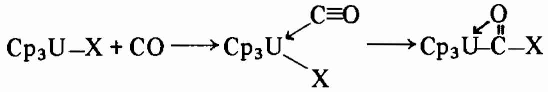
The usefulness of bis-cyclopentadienyl-uranium-bis-amides as reactive intermediates, has been firstly tested by Takats *et al.* [3] towards the carboxylic and thiocarboxylic acids [4] and some inserting molecules like CS_2, COS and CO_2 [5].

With the aim to extend the use of Actinide amides as reagents in the synthesis of new organometallic actinide derivatives, recently we reported the routes to $Cp_nM(NEt_2)_{4-n}$ (M = U(IV); Th(IV); $n \leqslant 4$) [6].

In this paper we report the results concerning the reactivity of uranium mono-, bis-, and tris-cyclopentadienyl amides towards molecules containing acidic hydrogens, and the CO insertion reaction; the Schemes 1 and 2 summarize these results.

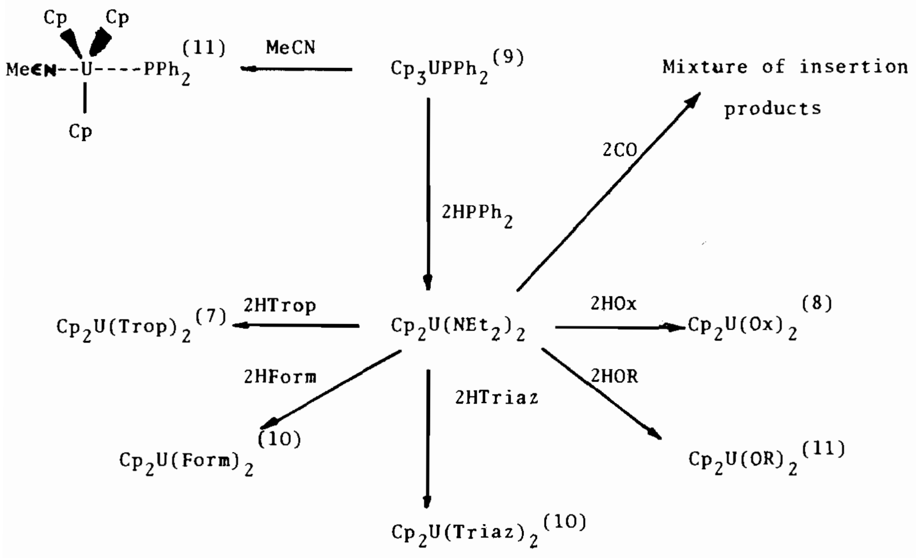
One of the most interesting aspects resulting from the Scheme 1 is the possibility of obtaining stable Cp_2UX_2 products, without any redistribution of ligands, by using very bulky and/or polydentate X-ligands. This behaviour confirms that the steric hindrance is the limiting factor to the ligands redistribution and that a good stability of the Cp_2UX_2 systems can be obtained either by using polysubstituted cyclopentadienyls or bulky X-ligands. In the Table I the ^1H NMR spectra of the new Cp_2UX_2 compounds are reported.

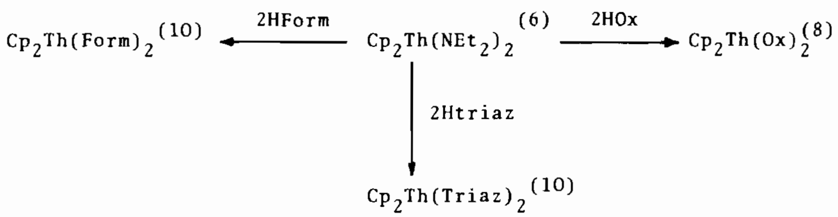
The CO insertion into the U–N bond represents the first example of such an insertion in systems like $Cp_3U–X$ [12, 13], to date considered coordinatively saturated.



$$Cp_3U{-}X + CO \longrightarrow Cp_3U\genfrac{}{}{0pt}{}{\swarrow C{\equiv}O}{\searrow X} \longrightarrow Cp_3U{-}\overset{\overset{O}{\swarrow\Vert}}{C}{-}X$$

This insertion reaction together with the reactivity of Cp_3UNEt_2 and Cp_3UPPh_2 towards MeCN are





HTrop = Tropolone
HForm = N,N'-di(p-tolyl)formamidine
HTriaz = N,N'-di(p-tolyl)triazene
HOx = 8-hydroxyquinoline
$HPPh_2$ = Diphenylphosphine

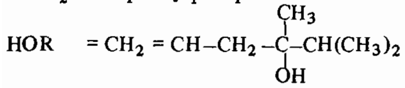
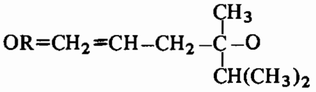

$HOR = CH_2=CH{-}CH_2{-}\underset{OH}{\overset{CH_3}{C}}{-}CH(CH_3)_2$

TABLE I. ^1H NMR Spectra of the New Cp_2MX_2 Compounds: M = U(IV), Th(IV) (Benzene-d_6; ppm from Benzene-d_6 as Internal Standard).

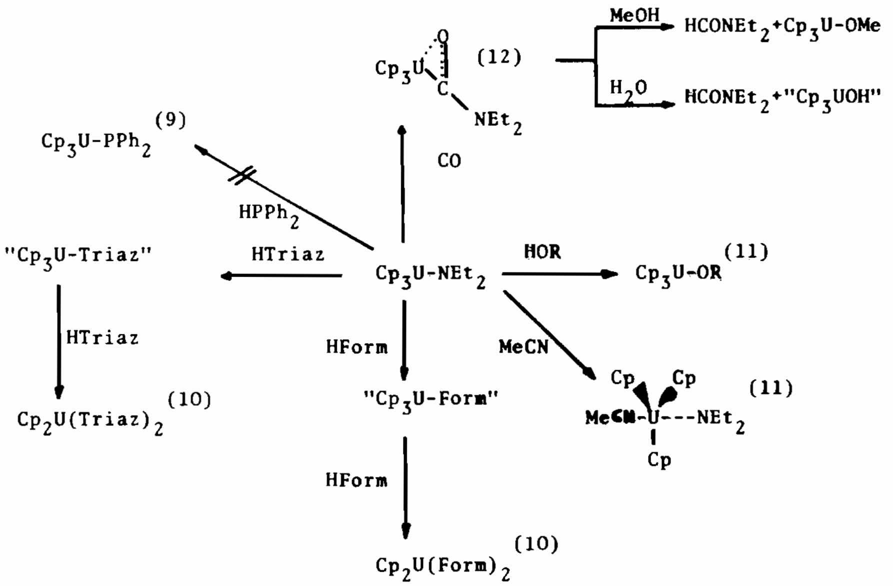
Compounds	ppm (T = 27 °C)
$Cp_2U(Ox)_2$	+19.19(d,2H,C_7–H, $J_{6,7}$ = 7.7 Hz); +5.20(t, 2H, C_6–H, $J_{5,6}$ = 8.0; $J_{6,7}$ = 7.7 Hz); + 1.73(d, 2H, C_4–H; $J_{3,4}$ = 7.5 Hz); +0.16(d, 2H, C_5–H, $J_{5,6}$ = 8.0Hz); –8.9(dd, 2H, C_3–H, $J_{2,3}$ = 4.6; $J_{3,4}$ = 7.5 Hz); –10.72(d, 2H, C_2–H, $J_{2,3}$ = 4.6 Hz) –23.01(s, 10H, Cp).
$Cp_2U(Form)_2$	+11.59(bs, 4H, meta-phenyls); +4.73(bs, 4H, meta'-phenyls); –2.08(bs, 6H, CH'_3); –3.86(s, 10H, Cp); –10.65(bs, 10H ortho'-phenyls + CH_3); –23.86(s, 2H, CH); –34.86 (bs, 4H, ortho-phenyls).

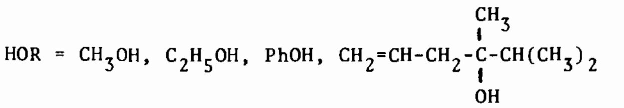
(continued on facing page)

TABLE I. *(continued)*

Compounds	ppm (T = 27 °C)
$Cp_2U(Triaz)_2$	+10.70(d, 4H, meta-phenyl, J = 7.9); +4.04(d, 4H, meta'-phenyls J = 7.8); –2.91(s, 6H, CH'_3); –3.33(s, 10H, Cp); –10.39(s, 6H, CH_3); –10.90(d, 4H, ortho'-phenyl, J = 6.6); –38.92(d, 4H, ortho-phenyl, J = 6.4 Hz).
$Cp_2U(OR)_2$  $OR{=}CH_2{=}CH{-}CH_2{-}\overset{CH_3}{\underset{CH(CH_3)_2}{C}}{-}O$	+8.47(m, 4H, $-CH_2-CH=$); + 6.41(sept., 2H $-CH(CH_3)_2$); +5.74(s, 6H, $-O-C-CH_3$); +4.62(m, 2H, $-CH_2-CH=CH_2$); +0.85 (d, 2H, trans $=CH_2$); –0.52(d, 2H, *cis* $=CH_2$, J = 10 Hz); –2.03(d, 12H, $-CH-(CH_3)$, J = 6.6 Hz); –31.78(s, 10H, Cp)
$Cp_2Th(NEt_2)_2$	–1.02(s, 10H, Cp); –4.00(q, 4H, α–CH_2); –6.17(t, 6H, β–CH_3, J = 6.8 Hz)
$Cp_2Th(Triaz)_2$	+0.08(q, 16H, AA'BB', phen.); –0.84(s, 10H, Cp); –4.99(s, 12H, CH_3

The negative sign is indicative of upfield shift, and the positive one downfield shift from benzene-d_6.





$HOR = CH_3OH,\ C_2H_5OH,\ PhOH,\ CH_2{=}CH{-}CH_2{-}\overset{CH_3}{\underset{OH}{C}}{-}CH(CH_3)_2$

further a confirmation that under particular conditions the Cp_3UX compounds behave as coordinatively unsaturated systems [14].

The $CpU(NEt_2)_3$, firstly isolated and characterized by us [6], shows an unexpected behaviour towards weakly acidic molecules like $HPPh_2$. In fact by reacting $CpU(NEt_2)_3$ at room temperature with one equivalent of $HPPh_2$, $Cp_2U(NEt_2)_2$ as the major products is obtained together with a mixture of hardly separable products. Such a behaviour can be interpreted by making two hypotheses: a) $CpU(NEt_2)_3$ does not react with $HPPh_2$ and completely rearranges to $Cp_2U(NEt_2)_2$ and $U(NEt_2)_4$ during the reaction time.

b) $CpU(NEt_2)_3$ reacts with $HPPh_2$ giving rise to an unstable intermediate (A) containing both $-NEt_2$ and $-PPh_2$ groups, which rearranges immediately to $Cp_2U(NEt_2)_2$.

By considering the hypothesis (a) the reaction mixture should contain $Cp_2U(NEt_2)_2$ and $U(NEt_2)_4$ in the presence of $HPPh_2$. As we reported, $Cp_2U(NEt_2)_2$ reacts with $HPPh_2$ to produce Cp_3UPPh_2 and in addition we observed that $U(NEt_2)_4$ and $HPPh_2$ (in molar ratio 1:1) quantitatively afford $U(NEt_2)_3(PPh_2)$ [9]; the lack of the Cp_3UPPh_2 and $U(NEt_2)_3(PPh_2)$ in the reaction mixture suggests that the hypothesis (a) has to be excluded while the (b) one seems to be acceptable.

On the other hand, the reaction of $U(NEt_2)_3(PPh_2)$ and cyclopentadiene in the molar ratio 1:1 produces the same reaction mixture as previously observed for the reactions between $CpU(NEt_2)_3$ and $HPPh_2$, making realistic the hypothesis (b) concerning the rearrangement of an unstable intermediate (A):

$$\left.\begin{array}{l} CpU(NEt_2)_3 \quad + HPPh_2 \\ U(NEt_2)_3(PPh_2) + CpH \end{array}\right\rangle \longrightarrow CpU(NEt_2)_2(PPh_2) \qquad (A)$$

$$\downarrow$$

$$Cp_2U(NEt_2)_2 + \text{`}U(NEt_2)_2(PPh_2)\text{'}$$

Analogous studies on reactivity of the corresponding thorium amides are in progress.

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Preparation and Properties of Hydrated Uranium Trichlorides

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The preparation of the hydrated uranium trichlorides: $UCl_3 \cdot 7H_2O$, $UCl_3 \cdot 4H_2O$, $UCl_3 \cdot 3H_2O$ and $UCl_3 \cdot 2H_2O$ as well as some of their structural, spectroscopic and magnetic properties are reported.

The compounds were prepared by means of a general method presented in Ref. 1. The navy blue heptahydrate and the purple tetrahydrate could be directly obtained from solutions, whereas the remaining hydrates have been obtained by a controlled vacuum thermal dehydration. The compounds are relatively stable towards oxygen but are readily oxidized in presence of moisture. Vacuum dehydration at 600–700 K gives the anhydrous chloride. The composition of the hydrates has also been confirmed by a thermogravimetric analysis.

The solution and solid state spectra of the compounds are discussed. The heptahydrate exhibits an absorption spectrum almost identical with that of the aqueous ion. The less hydrated compounds show an intense absorption at about 18000 cm^{-1} which is characteristic for uranium(III) complex chlorides.

Magnetic susceptibilities of polycrystalline samples were measured by the Faraday method in the 6.5–295 K range. The uranium trichloride heptahydrate follows in this region the Curie–Weiss law with $C = 1.0839$ emu K mol^{-1} and $\theta = -32.72$ K.

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