were measured. The binding energies of both Ln$_{4d}$ and Cl$_{2p}$ decrease as Cp$_2$LnCl forms Cp$_2$LnCl·2,2′-bpy complexes. This fact also demonstrated that the lone pair of electrons on nitrogen is coordinated to the metal to form a coordinated covalent bond. It was unexpectedly found that the binding energies of Cl$_{2p}$ also decrease. It seems that the electron also shifts toward chlorine. The binding energies of N$_{1s}$ increase at the same time.

2. The second method of stabilizing early (f^0–f^3) lanthanocene chlorides we adopted is to use other types of chelate ligand, 2,2′-bipyridyl or *o*-phenanthroline to satisfy the coordination saturation, and thus improve the stabilization. We succeeded for the first time in synthesizing the dicyclopentadienyl early lanthanide chloride 2,2′-bipyridyl or *o*-phenanthroline coordination compounds (eqns. 4, 5).

They were allowed to react with sodium trifluoroacetate to afford the corresponding derivatives Cp$_2$-LnOCOCF$_3$·nB (eqn. 6). The ^{1}H NMR spectrum of Cp$_2$LaOCOCF$_3$·2phen was determined. It indicates that the δ values of coordinated *o*-phenanthroline shift to lower field as compared with that in *o*-phenanthroline.

$$\mathrm{LnCl_3 + nB \xrightarrow{THF} LnCl_3{\cdot}nB} \qquad (4)$$

$$\mathrm{LnCl_3{\cdot}nB + 2CpNa \xrightarrow{THF} Cp_2LnCl{\cdot}nB + 2NaCl} \qquad (5)$$

$$\mathrm{Cp_2LnCl{\cdot}nB + CF_3COONa \xrightarrow{THF} Cp_2LnOCOCF_3{\cdot}nB + NaCl} \qquad (6)$$

B = 2,2′-bpy; Ln = La, Nd
B = *o*-phen; Ln = La, Ce; N = 2; Ln = Pr, Nd; N = 1 or 2

By using ring-bridged dicyclopentadiene, 2,2′-bipyridyl or *o*-phenanthroline as a ligand the disproportionation of early lanthanocene chloride is thus prevented, the stabilization of early lanthanocene chlorides achieved, and the early lanthanocene chlorides can be isolated.

1 R. E. Maginn, S. Manastyskj and M. Dubeck, *J. Am. Chem. Soc., 85*, 672 (1963).
2 T. J. Marks, *Prog. Inorg. Chem., 24*, 51 (1978).
3 K. W. Bagnall, in 'Organometallics of the f-Elements', T. J. Marks, R. D. Fischer, Eds; Reidel, Dordrecht, Holland; p. 221–247, 1979.
4 A. L. Wayda and W. J. Evans, *Inorg. Chem., 19*, 2190 (1980).
5 T. Don Tilley and R. A. Andersen, *Inorg. Chem., 20*, 3267 (1981).
6 M. F. Lappert, A. Singh, J. L. Atwood and W. E. Hunter, *J. Chem. Soc. Chem. Comm.*, 1981, 1190, 1191.
7 Changtao Qian, Changqing Ye, Hanzhang Lu, Yuqin Li and M. Tsutsui, *YOUJI HUAXUE (Organic Chemistry)*, 1982 (No. 1), 50.
8 J. N. John and M. Tsutsui, *Inorg. Chem., 20*, 1602 (1981).

A24

Further Observations on the Reaction of Uranium Tetrachloride with Simple Lithium Alkyls

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A number of years ago, we reported a brief investigation of the thermally unstable products of the reaction of uranium tetrachloride with alkyl lithium reagents [1] (eqn. (1)). The purpose of this investigation was to ascertain whether β-hydride elimination might occur in a uranium hydrocarbyl with potential coordinative unsaturation. This being the object of the investigation, no attempt was made to characterize the intermediate organometallics nor was any structure or stoichiometric formulation specifically claimed for them (historically such species have been presumed to be tetrahydrocarbyls [2, 3]). Subsequent to this work, several groups have reported the successful use of eqn. (1) to generate finely divided uranium metal for synthetic purposes [4, 5], and evidence has been presented that, under certain conditions [6], greater than four alkyl groups may coordinate to uranium.

$$\mathrm{UCl_4 + 4RLi \xrightarrow[\text{or ether}]{\text{hydrocarbons}} organic\ products + U + 4LiCl} \qquad (1)$$

In hydrocarbon or ether solvents, eqn. (1) is obviously a highly complex, heterogeneous reaction, and the course of the transformation should be critically dependent on the state and history of the UCl$_4$. During a recent study of 'stabilized' actinide tetrahydrocarbyls [7], the sensitivity of reactions such as eqn. (1) to parameters involving the heterogeneity became apparent and stimulated a brief reinvestigation of our earlier work, using improved analytical techniques and a wider range of reaction conditions. We report here for two representative lithium reagents and the 'innocent' solvent heptane, further observations on eqn. (1) as regards optimization of RLi-derived products and, ultimately, metallic uranium.

Results

The principal goal of this investigation was to determine how, for constant solvent and lithium reagent, the course of eqn. (1) depends on the exact state of the UCl$_4$ and the reaction conditions. In Table I are compiled data for the gaseous organic products of eqn. (1) as a function of these

TABLE I. Gases Evolved in the $UCl_4 + 4RLi$ Reaction.

Experiment Lithium Reagent	UCl_4 Treatment[a]	Time (h)	Agitation	Cumulative Yield Rh + (RH)-H (%)[b]	Butene:Butane
1 $R = n\text{-}C_4H_9$	none	153	stirring	20	
		0.7	ultrasound	34	
		105	stirring	44	52:48[c]
2 $R = n\text{-}C_4H_9$	grinding, $SOCl_2$	110	stirring	48	
		26	ultrasound +		
		9	stirring	77	
		38	ultrasound	90	
		55	ultrasound	90	55:45[c]
3 $R = t\text{-}C_4H_9$	none	87	stirring	11	
		2.3	ultrasound +		
		33	stirring	28	
		3	ultrasound	30	
		30	stirring	30	56:44[d]
4 $R = t\text{-}C_4H_9$	$SOCl_2$	90	stirring	38	
		1	ultrasound +		
		24	stirring	52	
		1	ultrasound +		
		48	stirring	60	
		1	ultrasound +		
		38	stirring	63	
		1	ultrasound +		
		24	stirring	63	62:38[d]
5 $R = t\text{-}C_4H_9$	grinding, $SOCl_2$	118	stirring	58	
		1	ultrasound +		
		9	stirring	68	
		8	ultrasound +		
		37	stirring	81	
		21	ultrasound +		
		59	stirring	96	
		35	ultrasound +		
		47	stirring	98	
		47	ultrasound	98	60:40[d]

[a] None indicates that UCl_4 was employed as obtained from the procedure of ref. 9. [b] Estimated uncertainty: ±5%. [c] 1-Butene: n-butane. Estimated uncertainty in yields: ±3%. [d] Isobutene:isobutane. Estimated uncertainty in yields: ±3%.

parameters. For all experiments, the distribution of organic products (n-butane:1-butene, isobutane: isobutene) is similar to that reported in eqn. (1) for the longest reaction periods. The nature of the products is evidence that the intermediate uranium hydrocarbyls readily suffer β-hydride elimination. The yields are, however, found to be quite sensitive to the history of the UCl_4 and the agitation procedure. Thus, for practical reaction times, yields of butane and butene are significantly below stoichiometric if UCl_4 is employed as obtained from the synthesis, and simple stirring is carried out. These low yields are due to the heterogeneous nature of the conditions and incomplete reaction. Thus, finely pulverizing the UCl_4 and drying it with $SOCl_2$ both increase the hydrocarbon yields substantially*. Furthermore, the use of ultrasonic agitation, which is known to accelerate many types of heterogeneous reactions [8], increases the butane:butene yield to near quantitative. In the case of experiment 4, where the butane:butene yield is not quantitative, the additional equivalents of t-butyl functionality can be readily accounted for as unreacted lithium reagent.

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*In reference 1, a sample of anhydrous UCl_4 from a commercial source was subjected to grinding and drying with $SOCl_2$. This material, perhaps as a result of adventitious contamination by the supplier, appears to have been abnormally reactive.

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.

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1 T. J. Marks and A. M. Seyam, *J. Organomet. Chem., 67,* 61 (1974).
2 T. J. Marks and R. D. Ernst, in 'Comprehensive Organometallic Chemistry', G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds., Pergamon Press, Oxford, in press.
3 T. J. Marks, *Prog. Inorg. Chem., 25,* 224 (1979).
4 E. Cernia and A. Mazzei, *Inorg. Chim. Acta, 10,* 239 (1974).
5 M. J. Miller and A. Streitwieser, Jr., *J. Organomet. Chem., 209,* C52 (1981).
6 E. R. Sigurdson and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* 812 (1977).
7 A. M. Seyam, V. W. Day, C. S. Day and T. J. Marks, manuscript in preparation.
8 J.-L. Luche and J.-C. Damiano, *J. Am. Chem. Soc., 102,* 7926 (1980) and references therein.

A25

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].

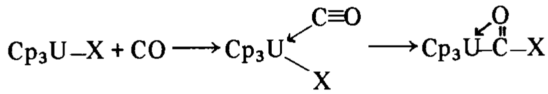
The usefulness of bis-cyclopentadienyl-uranium-bis-amides as reactive intermediates, has been firstly tested by Takats *et al.* [3] towards the carboxylic and thiocarboxylic acids [4] and some inserting molecules like CS_2, COS and CO_2 [5].

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.



$$Cp_3U{-}X + CO \longrightarrow Cp_3U\begin{smallmatrix}\swarrow C\equiv O\\ \searrow X\end{smallmatrix} \longrightarrow Cp_3U{-}\overset{\overset{O}{\swarrow\|}}{C}{-}X$$

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