lanthanide ions. By definition, this correction is zero for the ion Eu^{3+} (R = 0.95 Å, Fig. 2). Part of the steric crowding for lanthanide(III) cyclopentadienyl complexes is shown in Fig. 3. It is clearly seen that neither 'Cp_2LnCl' nor 'Cp_3Ln' can have as simple structures as suggested by the chemical formula. It is also expected from Fig. 3 that a new coordination pattern, corresponding to trigonal bipyramidal Cp_3LnL_2 complexes is likely to be stabilized as the ionic radius of the metal increases. Experimental results have confirmed this prediction.

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A23

Synthesis and Properties of Organolanthanide Complexes with Chelate Ligands

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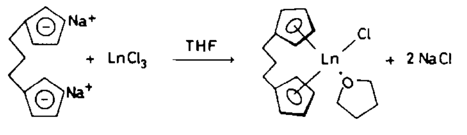
Dicyclopentadienyl lanthanide chlorides, $(C_5H_5)_2$-LnCl, are key intermediates for the synthesis of the compounds containing LN–C σ bonds, Ln–N and Ln–O bonds. However, probably due to lanthanide contraction effect, the early lanthanocene chloride complexes, particularly for La, Ce, Pr and Nd, have not yet been synthesized [1–3]. Recently, some organometallic chemists have made their efforts to study how to stabilize the dicyclopentadienyl early lanthanide chloride. Using the di(trimethylsilyl)-lanthanide chlorides. By using a bulky pentamethyl-cyclopentadienyl as a ligand, Evans [4] and Andersen [5] had succeeded in stabilizing dicyclopentadienyl cyclopentadienyl as a ligand, Lappert [6] succeeded in stabilizing early (f^0–f^3) lanthanocene chlorides by generating an anionic complex.

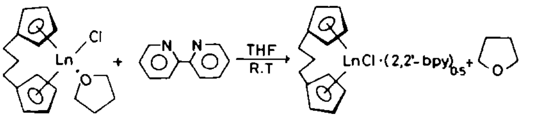
We now wish to report here two methods for the stabilization of early lanthanocene chlorides by using a chelate ligand.

1. By using ring-bridged dicyclopentadiene instead of two separated cyclopentadienes as a ligand we have succeeded in synthesizing the stabilized early lanthanocene chlorides tetrahydrofuran coordinated neutral complexes [7]. Because our results are different from Tsutsui's [8], we further synthesized six 1,1'-trimethylenedicyclopentadienyl lanthanide chlorides. All the products so far obtained were found to be tetrahydrofuran coordinated neutral complexes without exception. Anhydrous lanthanide chlorides reacted with disodium salt of 1,3-dicyclopentadienyl-propane in THF at –50 °C to give tetrahydrofuran coordinated 1,1'-trimethylenedicyclopentadienyl lanthanide chlorides (eqn. 1).

 (1)

Ln = Pr, Nd, Gd, Dy, Ho, Er, Yb, Lu

Furthermore, we found that the coordinated tetrahydrofuran could be replaced by 2,2'-bipyridyl to afford 2,2'-bipyridyl complexes which exhibit better stability to air and moisture (eqn. 2).

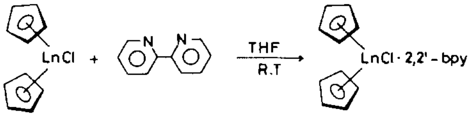
 (2)

Ln = Pr, Nd, Dy, Ho, Er, Yb, Lu

It should be noted that even when the molar ratios of chlorides to 2,2'-bipyridyl in starting material were changed from 1:1 to 1:2, the atomic ratios of lanthanide metal to nitrogen in products remained 1:1. The infrared spectra of 2,2'-bipyridyl complexes indicate that four characteristic absorption peaks of pyridine ring at 408, 621, 994 and 1580 cm^{-1} all shift to higher frequencies as compared with that in $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot 2,2'\text{-bpy})_{0.5}$. It implies that a pair of electrons on nitrogen is coordinated to the metal to form a coordinated covalent bond.

However, the dicyclopentadienyl lanthanide chlorides reacted with 2,2'-bipyridyl giving 2,2'-bipyridyl complexes, the atomic ratios of metal to nitrogen in products always were 1:2 and the coordination number is nine (eqn. 3).

The infrared spectra of these complexes indicate that four characteristic absorption peaks of pyridine ring all shift to higher frequencies too, in agreement with that of $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot (2,2'\text{-bpy})_{0.5}$. The X-ray photoelectron spectra of five dicyclopentadienyl lanthanide chlorides and their corresponding bipyridyl complexes ($Cp_2LnCl \cdot 2,2'$-bpy)



Ln = Gd, Dy, Ho, Er, Yb, Lu

were measured. The binding energies of both Ln_{4d} and Cl_{2p} decrease as Cp_2LnCl forms $Cp_2LnCl \cdot 2,2'$-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 $Cp_2LnOCOCF_3 \cdot nB$ (eqn. 6). The ^1H NMR spectrum of $Cp_2LaOCOCF_3 \cdot 2phen$ was determined. It indicates that the δ values of coordinated *o*-phenanthroline shift to lower field as compared with that in *o*-phenanthroline.

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

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

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

$B = 2,2'$-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.

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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.

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

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