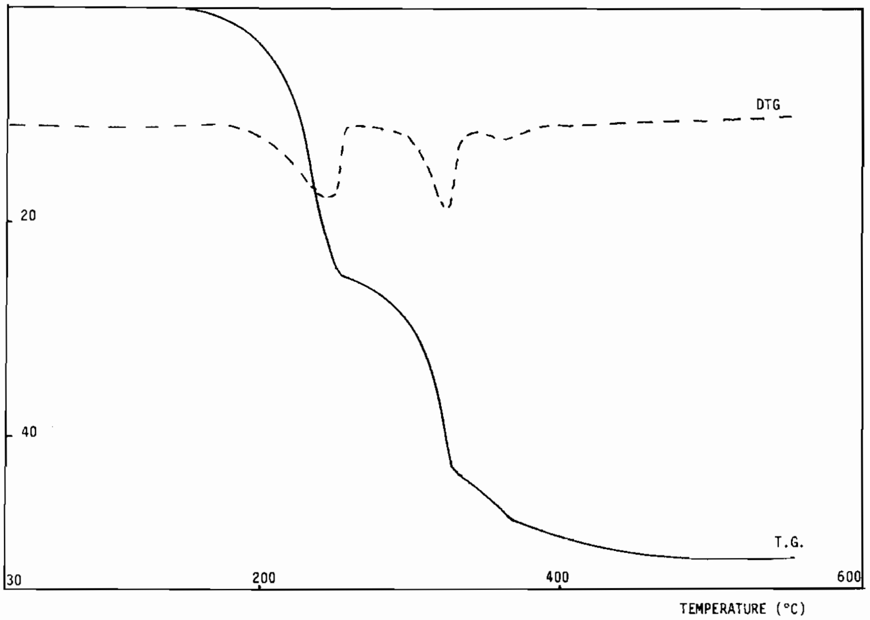

Fig. 1. TG and DTG curves for the oxidation of $UCl_4 \cdot 2tmu$.

(i) $UCl_4 \cdot 2tmu + O_2 \longrightarrow UO_2Cl_2 \cdot tmu +$

+ volatile products

This reaction started at ±150 °C and was completed at ±250 °C and

(ii) $UO_2Cl_2tmu + O_2 \rightarrow U_3O_8$ + volatile products

over the temperature range ±260 °C to ±480 °C.

Only the first reaction was studied fundamentally. The profiles of the TG and DTG curves, Fig. 1, suggested that the oxidation and dissociation reactions are occurring simultaneously. Isothermal measurements were performed over the temperature range 180–205 °C. The data suggested that the mechanism for the reaction can be described by the equation

$$1 - (1 - \alpha)^{1/2} = kt$$

where α = fraction decomposed. Using this equation an apparent activation energy was calculated and found to be 164 kJ mol^{-1}.

The DSC trace obtained for the oxidation reaction gave series of exothermic peaks over the temperature range 175–500 °C. The two overlapping peaks between 178 and 275 °C were assigned to the reaction,

$UCl_42tmu + O_2 \longrightarrow UO_2Cl_2 \cdot tmu$ + volatile products

The enthalpy of the reaction was estimated as –271 kJ mol^{-1}. The total enthalpy *i.e.* for the reaction

$UCl_42tmu + O_2 \longrightarrow U_3O_8$ + volatile products

was estimated as –765 kJ mol^{-1}. These results as well as isothermal measurements which were carried out in a argon atmosphere suggested that although the dissociation and oxidation reactions seem to occur simultaneously, the dissociation of the neutral ligand is a prerequisite for the reaction to occur.

A22

A Cone Packing Model Applied to Lanthanide(III) Organometallic Chemistry

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Statistics based on the structures of more than 30 organolanthanide(III) compounds give:

$\overline{SAS} = 0.72$ and $\delta = 0.05$

where $\overline{SAS}$ is the average value of the solid angle sum (SAS), δ is the standard deviation [1]. A stable region can thus be defined for SAS around 0.72 ± 0.10 (Fig. 1) where 0.10 is the intrinsic error in our cone packing model [1, 2]. Steric parameters of common ligands are listed in Table I. In this way steric crowding around the metal ion in compounds of the

TABLE I. Steric Parameters of Common Ligands.[a]

Ligand	Bond length	SAF	FA	Remark
$C_5H_5^-$	2.42	0.215	55	Second order steric para-
$Me_5C_5^-$	2.42	0.27	63	meters of modified Cp:
$C_8H_8^{2-}$	1.9	0.29	65	$C_5H_nX_{5-n}^-$
$C_9H_7^-$	2.42	(0.25)	55/67	
Cl^-	2.58	0.14	45	(SAF) = 0.215 +
$O(OR^-)$	2.35	0.10	37	$\frac{5-n}{5}$ XC;
(OR_2)	2.48	0.087	34	when X = Me, C = 0.055;
N(neutral)	2.7	0.085	33	when X = $SiMe_3$, C = 0.090
C(Me)mono.	2.5	0.13	43	
bridg.	2.58	0.12		
CH_2R^-	2.50	0.17* 0.16**	40/60	*R = $SiMe_3$
CHR_2^-	2.50	0.21* 0.19**	40/60	**R = CMe_3
CMe_3^-	2.50	0.183	51	
BH_4^- triden.		0.168	48	
biden.		0.12		
$HBPz_3^-$ triden.		0.26		estimated values based on
biden.		0.17		the U(IV) corresponding
NCS^-		0.105		parameters (ref. 1)
allyl$^-$ triden.		0.22	66/39	
mono.		0.13	43	

[a] $R_{Ln^{3+}} = 0.95$ Å.

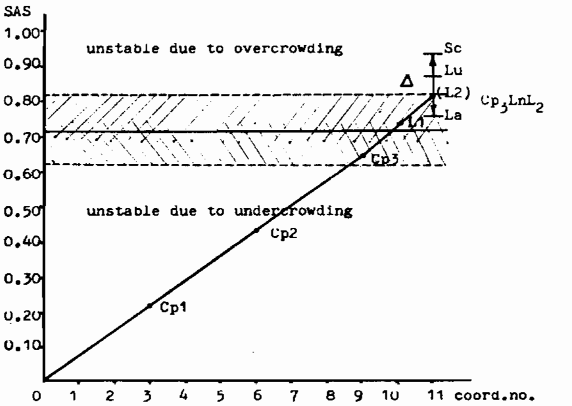

Fig. 1. Steric crowding for lanthanide organometallic compounds of the type Cp_3LnL_2.

type $LnA_mB_nC_p$ can be estimated by the following equation

$$SAS = mSAF_A + nSAF_B + pSAF_C + \Delta$$

where SAF is the related steric parameters, and Δ a correction accounting for the radius of individual

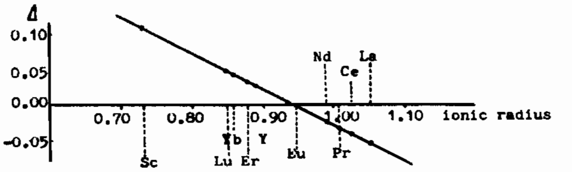

Fig. 2. Corrections Δ for individual lanthanide ions due to increasing ionic radius.

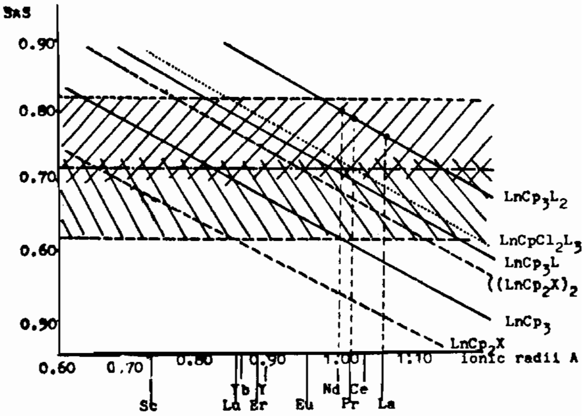

Fig. 3. Stability of lanthanide(III) cyclopentadienyl compounds.

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.

This work is supported by the Friedrich Ebert Stiftung (to Li X.f). We also thank the Chinese Academy of Science and the Hamburg University for supporting the research cooperation.

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A23

Synthesis and Properties of Organolanthanide Complexes with Chelate Ligands

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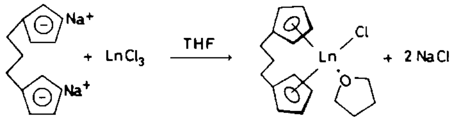
Dicyclopentadienyl lanthanide chlorides, $(C_5H_5)_2$-LnCl, are key intermediates for the synthesis of the compounds containing LN—C σ bonds, Ln—N and Ln—O bonds. However, probably due to lanthanide contraction effect, the early lanthanocene chloride complexes, particularly for La, Ce, Pr and Nd, have 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 pentamethylcyclopentadienyl 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.

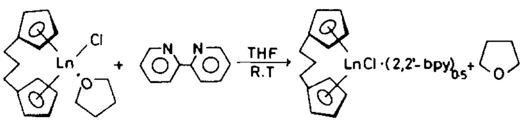
1. By using ring-bridged dicyclopentadiene instead of two separated cyclopentadienes as a ligand we have succeeded in synthesizing the stabilized early lanthanocene chlorides tetrahydrofuran coordinated neutral complexes [7]. Because our results are different from Tsutsui's [8], we further synthesized 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-dicyclopentadienylpropane 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).



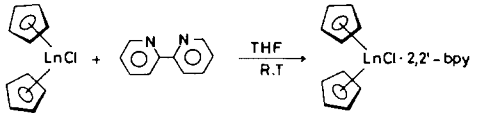
(2)

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