Journal of Organometallic Chemistry, 247 (1983) 161–170
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND PROPERTIES OF NEW σ-BONDED ORGANOLANTHANIDE COMPLEXES AND STUDIES OF THEIR INFRARED SPECTRA *

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(Received June 17th, 1981; in revised form November 30th, 1982)

Summary

Five new solvated organolanthanide complexes containing Ln–C σ-bonds $(\eta^5\text{-}CH_3C_5H_4)_2ErC_6H_4CH_3\text{-}p \cdot THF$ (I), $(\eta^5\text{-}C_5H_5)_2LnC_6H_4X\text{-}p \cdot THF$, Ln = Er, X = CH_3 (II); Ln = Er, X = Cl (III); Ln = Yb, X = CH_3 (IV); Ln = Gd, X = CH_3 (V) were synthesized by the reaction of appropriate aryllithium derivatives with $(\eta^5\text{-}C_5H_5)_2LnCl$ or $(\eta^5\text{-}CH_3C_5H_4)_2LnCl$ in THF at low temperature (−78°C). The structures of these complexes were verified by elemental analyses, infrared spectra and mass spectra. Recrystallization of these complexes from non-polar solvents such as benzene-n-hexane or toluene-n-hexane led to removal of coordinated tetrahydrofuran resulting in unsolvated products. The thermal decomposition temperature and the variable temperature (77–291 K) magnetic susceptibilities of the five unsolvated complexes were measured. The relation between the structure and oxidative and thermal stability is also discussed.

Two new "mixed ligand" tri-η^5-cyclopentadienyllanthanide complexes Cp_2YbCp' (VI) and Cp'_2ErCp (VII) where Cp = η^5-cyclopentadienyl, Cp′ = η^5-methylcyclopentadienyl were also prepared. They are relatively more stable to air and moisture and more thermally stable than the complexes with Ln–C σ bonds.

The infrared spectra of fifteen organolanthanide complexes including those aforementioned compounds and eight known compounds, i.e. Cp_2GdCl, Cp'_2GdCl, Cp_2HoCl, Cp_2ErCl, Cp'_2ErCl, Cp_2YbCl, Cp_3Yb and Cp_3Er were measured from 4000 to 200 cm^{-1}. The absorption peak at 250 cm^{-1} was assigned as the characteristic absorption of the π-bonded cyclopentadienyl group to metal.

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* Part of this paper was presented at the China-Japan-U.S.A. Seminar on Organometallic Chemistry as a poster, June, 1980, Beijing.

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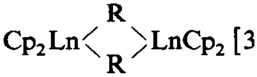
0022-328X/83/$03.00

Introduction

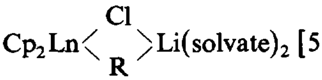
Important advances have been taking place in the organometallic chemistry of the lanthanides since the seventies [1]. Thus organolanthanide complexes containing either π-bonds or σ-bonds have been synthesized. In addition, organolanthanide complexes have also been reported as reagents and catalysts in organic synthesis [2].

The studies on the syntheses, structures and properties of organolanthanide complexes containing σ-bonds have been the focus of many studies. The σ-bonded organolanthanide complexes reported to date, that are stabilized by bulky cyclopentadienyl groups can be divided into three types: bridged dimers



$Cp_2Ln\langle\overset{R}{\underset{R}{}}\rangle LnCp_2$ [3],

THF solvated monomers $Cp_2LnR \cdot THF$ [4] and LiCl adducts



$Cp_2Ln\langle\overset{Cl}{\underset{R}{}}\rangle Li(solvate)_2$ [5].

Here we wish to report five new σ-bonded, tetrahydrofuran solvated complexes $Cp_2LnAr \cdot THF$. We found that unsolvated complexes can be obtained by recrystallization of solvated monomers in non-polar solvents. In other words, the tetrahydrofuran which is easily coordinated to the metal is also easily removed from the metal under certain conditions. In order to compare the properties of σ-bonded complexes with π-bonded complexes, two new π-bonded "mixed ligand" complexes (VI, VII) were also synthesized.

The infrared spectra of fifteen organolanthanide complexes, including those aforementioned compounds and eight known complexes were measured from 4000 to 200 cm^{-1}.

Results and discussion

New organolanthanide complexes containing a σ-bond were synthesized by the reaction of the di-η^5-cyclopentadienyl- or bis (η^5-methylcyclopentadienyl)-lanthanide chlorides with an appropriate *para*-substituted aryllithium as depicted in eq. 1 and 2.

$$(\eta^5\text{-}CH_3C_5H_4)_2ErCl + p\text{-}LiC_6H_4CH_3 \xrightarrow{THF}$$

$$(\eta^5\text{-}CH_3C_5H_4)_2ErC_6H_4CH_3\text{-}p \cdot THF + LiCl \qquad (1)$$

(I)

$$(\eta^5\text{-}C_5H_5)_2LnCl + p\text{-}LiC_6H_4X \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_2LnC_6H_4X\text{-}p \cdot THF + LiCl \qquad (2)$$

(II : Ln = Er, X = CH_3;
III : Ln = Er, X = Cl;
IV : Ln = Yb, X = CH_3;
V : Ln = Gd, X = CH_3)

These complexes containing a σ-bond are sensitive to oxygen and moisture, decomposing completely within 1–2 minutes upon exposure to air. They do not sublime. Compounds I, III and IV have definite melting points, but compounds II and V do not, only changing to a darker color at higher temperature. The physical properties of the complexes containing a σ-bond are listed in Table 1.

Besides the characteristic cyclopentadienyl, benzene ring and methyl absorption peaks, the infrared absorption spectra of compounds I, II, III, IV and V exhibited absorption peaks at 890 and 1045 cm^{-1}, respectively, which appear to be the characteristic absorption peaks of the coordinated tetrahydrofuran. The mass spectra of compound V showed a parent molecular ion peak at m/e 451 $[M+1]^+$ and other fragments as expected. Although the mass spectra of the other four compounds did not show the parent molecular ion, they showed tolyl, chlorophenyl, cyclopentadienyl, methylcyclopentadienyl and tetrahydrofuran ions and fragments which may be attributed to the moieties containing the aforementioned groups connected with metal. No ions with m/e higher than the parent molecular ion were observed. Flame tests showed that these complexes did not contain Li, so that the possibility for LiCl adducts was excluded.

By treatment of these solvated complexes with benzene/hexane or toluene/hexane, the unsolvated monomers $(\eta^5\text{-}C_5H_5)_2LnC_6H_4X\text{-}p$ without tetrahydrofuran were obtained. A recent paper also reported [6] that the solvated diethyl ether in pentamethylcyclopentadienyl complexes $Li[YbCl_2(C_5Me_5)_2]\cdot(\text{ether})_2$ can be removed after an appropriate treatment. Because of the removal of the coordinated tetrahydrofuran, the coordinated unsaturation of these compounds becomes greater, as does their sensitivity to moisture and oxygen. Similarly, they do not sublime and have no definite melting point. Their thermal decomposition temperatures are listed in Table 2. Comparison of the thermal decomposition temperatures of four erbium complexes suggests that their thermal stabilities are related to the substituent either on the ligand or on the benzene ring.

The infrared spectra of the five unsolvated σ-bonded complexes showed that the characteristic absorption peaks of tetrahydrofuran disappeared. Moreover, the mass spectra did not show the fragments of tetrahydrofuran. Ions larger than the parent molecular ions were not found and the molecular weight of di-η^5-cyclopentadienyl-

TABLE 1

σ-BONDED ORGANOLANTHANIDE COMPLEXES

Compound	Color	Melting point ^{a} (°C)	Yield (%)	Elemental analyses (Found (calcd.)(%))	
				Ln	O
$(\eta^5\text{-}CH_3C_5H_4)_2ErC_6H_4CH_3\text{-}p\cdot THF$ (I)	orange-red	130–134	36	36.80 (34.22)	3.06 (3.27)
$(\eta^5\text{-}C_5H_5)_2ErC_6H_4CH_3\text{-}p\cdot THF$ (II)	light-pink	92 ^{b}	69	36.22 (36.30)	3.45 (3.47)
$(\eta^5\text{-}C_5H_5)_2ErC_6H_4Cl\text{-}p\cdot THF$ (III)	orange-red	78–80	69	33.41 (34.76)	3.03 (3.33)
$(\eta^5\text{-}C_5H_5)_2YbC_6H_4CH_3\text{-}p\cdot THF$ (IV)	red	85–90	92	36.39 (37.09)	
$(\eta^5\text{-}C_5H_5)_2GdC_6H_4CH_3\text{-}p\cdot THF$ (V)	orange-yellow	115 ^{b}	85	34.23 (34.89)	

^{a} Melting points were determined in sealed argon filled capillaries. ^{b} Decomposition temperature.

TABLE 2

UNSOLVATED σ-BONDED ORGANOLANTHANIDE COMPLEXES

Compound	Color	Decomposition temperature (°C)	Yield[b] (%)	Analysis (Found(calcd.) (%)) Ln
$(\eta^5\text{-}CH_3C_5H_4)_2ErC_6H_4CH_3\text{-}p$ (I′)	light pink	150	58	40.89 (40.15)
$(\eta^5\text{-}C_5H_5)_2ErC_6H_4CH_3\text{-}p$ (II′)	light pink	94	40	43.98 (43.05)
$(\eta^5\text{-}C_5H_5)_2ErC_6H_4Cl\text{-}p$ (III′)	pink	76–78	33	39.57 (40.89)
$(\eta^5\text{-}C_5H_5)_2YbC_6H_4CH_3\text{-}p$ (IV′)	orange-red	100	38	44.51 (43.83)
$(\eta^5\text{-}C_5H_5)_2GdC_6H_4CH_3\text{-}p$ (V′)	pale yellow	144	26	41.53 (41.54)
$(\eta^5\text{-}C_5H_5)_2ErC_6H_5$[a]	light pink	128–130	52	

[a] N.M. Ely and M. Tsutsui, Inorg. Chem., 14, 2680 (1975). [b] Based on Cp_2LnCl.

p-tolylerbium (II′) was found to be 323. Therefore we considered these complexes to be monomeric [19]. The metal contents of these products obtained from non-polar solvents are consistent with the unsolvated form.

The variable temperature (77–292 K) magnetic susceptibilities of some organolanthanide complexes are listed in Table 3. The effective magnetic moments, which

TABLE 3

MAGNETIC SUSCEPTIBILITIES OF SOME ORGANOLANTHANIDES

Compound	(K)	χ_m (10^6 cgsu)	μ_{eff} (BM)	θ(K)
$Cp'_2ErC_6H_4CH_3\text{-}p$	77	125 000	9.22	
(I′)	195	52 165	9.21	8.0
	291	35 587	9.23	
$Cp_2ErC_6H_4CH_3\text{-}p$	77	116 009	9.30	
(II′)	195	50 968	9.28	16.0
	291	34 965	9.27	
$Cp_2ErC_6H_4Cl\text{-}p$	77	141 243	11.04	
(III′)	195	68 027	11.09	30.8
	291	47 710	11.09	
$Cp_2YbC_6H_4CH_3\text{-}p$	77	21 142	3.97	
(IV′)	195	9 302	3.97	16.0
	291	6 386	3.96	
Cp_3Er [13]	77		9.45	
	195		9.44	
	295		9.45	
Cp_3Yb [13]	77		4.00	
	195		4.00	
	295		4.00	

were obtained from treatment of the experimental results according to the Curie–Weiss rule, appeared to be independent of the temperature either for σ-bonded or for merely π-bonded cyclopentadienyl-organolanthanide complexes. These results are quite different from the results reported by Tsutsui [1], but they are in agreement with that reported by Raymond [7].

The effective magnetic moment of most complexes except III′ are close to the value of the trivalent state of lanthanide, although the reason why the effective magnetic moment of III′ is higher than the normal value still remains obscure.

Di-η^5-cyclopentadienylytterbium chloride and di-η^5-methylcyclopentadienylerbium chloride were allowed to react with methylcyclopentadienylsodium and cyclopentadienylsodium, respectively, in THF solution at room temperature. Volatiles were removed in vacuo. The residue was sublimed at 140–200°C in vacuo to give "mixed ligand" complexes which involve two different kinds of cyclopentadienyl groups in one molecule. The reactions are shown in the equations 3 and 4.

$$(\eta^5\text{-}C_5H_5)_2YbCl + CH_3C_5H_4Na \rightarrow \underset{\text{(VI)}}{(\eta^5\text{-}C_5H_5)_2Yb(\eta^5\text{-}CH_3C_5H_4)} + NaCl \qquad (3)$$

$$(\eta^5\text{-}CH_3C_5H_4)_2ErCl + C_5H_5Na \rightarrow \underset{\text{(VII)}}{(\eta^5\text{-}CH_3C_5H_4)_2Er(\eta^5\text{-}C_5H_5)} + NaCl \qquad (4)$$

The "mixed ligand" complexes have good thermal stability up to 200°C and definite melting points. Their melting points and sublimation temperatures are lower than those of the corresponding "homogeneous ligand" tri-η^5-cyclopentadienyllanthanide. Although they are still sensitive to oxygen and moisture, they are generally more stable than the complexes containing a σ-bond. The physical properties of the "mixed ligand" and "homogeneous ligand" complexes are compared and listed in Table 4. Infrared spectra of the "mixed ligand" complexes also showed that the Ln–C bonds are in η^5-form.

The infrared spectra of fifteen organolanthanide complexes including the aforementioned compounds and eight known compounds [8,12], i.e. Cp_2GdCl, Cp'_2GdCl, Cp_2HoCl, Cp_2ErCl, Cp'_2ErCl, Cp_2YbCl, Cp_3Er and Cp_3Yb were measured from 4000 to 200 cm^{-1}. The spectral data for the seven new compounds are shown in

TABLE 4

COMPARISON OF "MIXED LIGAND" AND "HOMOGENEOUS LIGAND" ORGANOLANTHANIDE COMPLEXES

Compound	Color	M.p. (°C)	Yield (%)	Anal. (Found (calcd.) (%)) Ln
$(\eta^5\text{-}C_5H_5)_3Er$	pink	285	69	46.58 (46.13)
$(\eta^5\text{-}C_5H_5)_3Yb$	green	273	47	47.75 (47.00)
$(\eta^5\text{-}CH_3C_5H_4)_2Er(\eta^5\text{-}C_5H_5)$	pink	115–118	50	42.77 (42.83)
$(\eta^5\text{-}CH_3C_5H_4)\,Yb(\eta^5\text{-}C_5H_5)_2$	green	135–137	44	44.20 (45.25)

TABLE 5. INFRARED SPECTRAL DATA OF SEVEN NEW COMPOUNDS (4000–200 cm^{-1})[a]

I	II	III	IV	V	VI	VII
3070s	3080s	3082m	3090s	3080m	3076s	3090s
3020w	3020s	3038w	3028s			
2970s		2980s	2980s	2970s		
		2960m(sh)			2960m(sh)	2960m(sh)
		2940w(sh)				
	2910s				2920s	2930s
					2900m(sh)	2900m(sh)
2880s	2870m	2880s	2880s	2880s	2860s	2864s
		2700w	2750m			
1607m	1607m		1604s	1606m	1620w	1605w
		1585m	1585m		1584w	
		1542m			1548s	
1505s	1505s		1504s	1504s	1518w	
		1485s	1495m		1490w	1490w
		1476s	1477w			
		1464w	1458m	1460w	1462m	
1445m	1445w	1445m	1446m		1450m	1450m
		1440w(sh)	1440m	1435m	1438s	1440s
1378s	1377m		1375m	1376s	1380s	1380s
1365m	1365w	1360w	1367w	1365m	1367w	1370w
			1355w			
			1344m		1346s	1346m
		1295w	1295w		1300m	1300w
1260s	1275s	1258s	1250s	1260m	1264m	
1240m (sh)		1220m	1225m			1240w
			1190s		1190m	1195w
1165w	1167m	1180m	1180m(sh)	1166w	1145w	1145w
			1120w			
1100w	1102w	1082m	1105m	1104w		
1066m		1068w			1065m	1065m
1045s	1045m	1044s	1045s	1044s	1048s	1048s
1030s(sh)					1032s	1032s
1015m	1010s	1013s	1012s	1010s	1014s	1014s
930w					934m	934m
915w	914w	914w	920w	915w		
890m	890m	886s	890m	890m	899w	899w
					886m	866m
855w	855s	860m			855w	855w
825m	828m			825w	830s	825s
770vs	780vs	780vs	780vs	780vs	775vs	775vs
		700s	728w	726w	732m	732m
670m		684w			674w	675w
		666m	665m	663m	665w	665w
645m	612m				625w	625w
		585s		580m	580w	590w
					560w	560w
	505m	472s			495w	485w
		415s			430s	425s
390s	390s		395m	385m	395s(sh)	395s
335m					330s	
		296w				
250s	250m(sh)	255s	250s	245m(sh)	254s	255s
	235s	230s(sh)	220s	225s	225m(sh)	225m

[a] w: weak; m: medium; s: strong; vs: very strong; sh: shoulder.

Table 5, while the far infrared spectral data of other eight known complexes are listed in Table 6. The infrared spectra at low frequencies for these complexes are reported for the first time.

All complexes exhibit four characteristic cyclopentadienyl or methylcyclopentadienyl absorptions at 770–782, 1010–1015, 1438–1450 and 3070–3100 cm^{-1}, respectively. When the ligand is methylcyclopentadiene, four absorption peaks appear in the 1000–1100 cm^{-1} region, i.e. 1014, 1032, 1048 and 1064 cm^{-1}, respectively. The four absorption peaks are similar in appearance and relative intensity for compounds I, VI, VII, Cp'_2GdCl and Cp'_2ErCl. The relative intensity of the absorption peak at 1032 cm^{-1} is higher than that at 1048 cm^{-1}. However, the relative intensities at 1032 and 1048 cm^{-1} in compound I are reversed, due to the characteristic absorption at 1045 cm^{-1} of coordinated tetrahydrofuran. The infrared spectra of unsolvated compounds I′ also show that the absorption peak at 1032 cm^{-1} is stronger than that at 1048 cm^{-1}.

Most of the complexes exhibit only a single sharp peak of medium intensity at the olefinic C–H stretching region (3000–3100 cm^{-1}), indicating that the cyclopentadienyl or methylcyclopentadienyl group is η^5-bonded to the metal in these complexes. If the cyclopentadienyl ring is linked to a metal in η^1 form, i.e. σ-bonded, multiple peaks should be observed [9]. It should be noted that di-η^5-cyclopentadienyllanthanide chloride exhibits multiple peaks at 3000–3100 cm^{-1}, e.g., Cp_2ErCl exhibits peaks at 3100, 3090 and 3080 cm^{-1}. It seems to be inconsistent with a η^5-linked form and, therefore, further investigation is necessary.

Tables 5 and 6 show that all complexes exhibit absorption peaks at about 250 cm^{-1} of medium to strong intensity. This peak is assigned to the characteristic absorption for the Ln–C bond of the π-bonded cyclopentadienyl group. These data agree well with the results of the Raman spectrum [10] of Cp_3Ln. Nakamoto [11] suggested that the characteristic absorption of metal–carbon bonding of σ-bonded phenyl derivatives was located at 500–200 cm^{-1}. The absorption peak at 390 cm^{-1} is very strong. Whether it is due to the characteristic absorption of the σ-bond of Ln–C needs further investigation.

TABLE 6

INFRARED SPECTRA OF EIGHT ORGANOLANTHANIDE COMPLEXES AT LOW FREQUENCIES (700–200 cm^{-1})

Cp_3Er	Cp_3Yb	Cp'_2GdCl	Cp'_2ErCl	Cp_2GdCl	Cp_2HoCl	Cp_2ErCl	Cp_2YbCl
665s	665s	676m	675s	664s	665m	663m	665s
		623m	625m				
	502m		560w				
480m							465w
430s	440s				405w	403w	
395s	390m	370w	368m				380w
351m	350m	342s	340s	350w	350w		
					272s	274s	274s
255s	255s	263s	250s	268s	256m	257m	256m
220m	220m	230s	235s	236w	225s	224s	225s
					206m	208s	205s

Experimental

All operations on these organolanthanide complexes were performed in an atmosphere of prepurified argon by using Schlenk techniques or in a dry box [13]. All solvents were refluxed and distilled over either finely divided $LiAlH_4$ or blue sodium benzophenone under argon immediately prior to use. Anhydrous lanthanide chlorides were obtained by the reaction of hydrated lanthanide chloride (obtained by the treatment of the lanthanide oxides with HCl) with thionyl chloride [14] or by the treatment of hydrated lanthanide chlorides with ammonium chloride [15]. The Cp_2LnCl and Cp'_2LnCl complexes were prepared by the method of Dubeck [8] et al. p-$CH_3C_6H_4Li$ and p-ClC_6H_4Li were prepared by the method of Gilman [16,17] et al. Melting points and thermal decomposition temperatures were determined in sealed argon filled capillaries and were uncorrected. Infrared spectra were recorded on Perkin–Elmer 580 spectrometers as Nujol and Fluorolube mulls and examined between disk-shaped CsI crystal plates. The mulls were prepared in the dry box. Magnetic susceptibilities were measured in solid state by the Faraday method on Shimdzu Magnetic Balance type MB-2. Mass spectra were recorded on Finnigan 4021GC-MS.

Metal analyses of lanthanides were accomplished using direct complexometric titration procedure with disodium EDTA. Approximately 15 mg of the organolanthanide complex was weighed in the inert atmosphere [18]. The weighed solid and weighing tube together were placed into a modified Kjeldahl flask and 5 ml of concentrated nitric acid was added, then the flask was heated to boiling for 1 h to digest the sample completely. After cooling the solution was transferred to a beaker. The solution was diluted to about 50–60 ml, adjusted to pH 3–4 with ammonium hydroxide and then buffered to pH 5.5 with hexamethyltetramine. The indicator, xylenol orange, was added to give the solution a red color and the stirred mixture was titrated with standard 0.01 *M* disodium ethylenediamine tetraacetic solution to an end-point change of red to yellow.

Di-η^5-cyclopentadienyl-p-tolylerbium · THF (II)

Into a centrifuge Schlenk flask was placed 2.51 g (7.54 mmol) of Cp_2ErCl and 100 ml of THF, and was cooled to −78°C. 25 ml of ether solution containing 7.54 mmol of p-tolyllithium was syringed to the Schlenk flask. The reaction mixture was allowed to warm to room temperature during a 2 h period and then stirred overnight. The reaction mixture was then concentrated to about 5 ml in vacuo and 100 ml of toluene was added, a white or light organge precipitate immediately appeared. The Schlenk flask was centrifuged and the precipitate was removed from the solution. The toluene solution was again concentrated to about 3 ml. Addition of 60 ml of benzene gave a light orange precipitate. The Schlenk flask was centrifuged again and the precipitate was removed from the solution. The benzene solution was concentrated and dried in vacuo to give a crude product. To the crude product 60 ml of benzene was added. Some precipitate remained. After the removal of the precipitate, the benzene solution was concentrated then dried in vacuo and resulted in light pink solid, the yield of di-η^5-cyclopentadienyl-p-tolylerbium · THF is 2.39 g (69%).

Di-η^5-cyclopentadienyl-p-tolylerbium (II′)

To a centrifuge Schlenk flask was placed 2.39 g di-η^5-cyclopentadienyl-*p*-tolylerbium · THF and 10 ml of benzene. After removing the insoluble solid, the benzene solution was then concentrated to about 3 ml in vacuo and 70 ml of n-hexane was added. The product precipitated out as a light pink solid, which was collected by centrifugation. The product was dried in vacuo and gave 1.70 g (84%) of unsolvated di-η^5-cyclopentadienyl-*p*-tolylerbium.

Other compounds (I, III, IV, V, I′, III′, IV′ and V′) containing σ-bonds were synthesized in a similar way. The yields and elemental analyses of these compounds are listed in Table 1 and Table 2.

Di-η^5-cyclopentadienyl(methylcyclopentadienyl)ytterbium (VI)

To a centrifuge Schlenk flask was placed 1.32 g (3.9 mmol) of $(\eta^5\text{-}C_5H_5)_2YbCl$. THF was added to give a wine red solution. To the reaction vessel 30 ml of a THF solution containing 8 mmol of methylcyclopentadienylsodium was added in fifteen minutes. The dark green reaction mixture was allowed to stir overnight at room temperature. After removal of the solvent under reduced pressure, the dry residue was transferred to a sublimation apparatus. Sublimation at 140–200°C under 10^{-4} mmHg pressure gave 0.65 g (44%) of Cp_2YbCp' as a dark green solid. Di-η^5-methylcyclopentadienylcyclopentadienylerbium (VII) was prepared in similar way. The elemental analyses and yields of "mixed ligand" tri-η^5-cyclopentadienyllanthanides are shown in Table 4.

Since the reactivity of methylcyclopentadiene is lower than that of cyclopentadiene, the reaction of methylcyclopentadiene with sodium sand must be carried out by refluxing in THF in order to form the sodium derivative, and the reaction period should be 3–4 times longer than that of cyclopentadiene.

Acknowledgements

The authors wish to express their cordial thanks to Prof. Yaozeng Huang and Prof. Weihua Xu for their effort to organize the cooperation between the Department of Chemistry, Texas A&M University and Shanghai Institute of Organic Chemistry, Academia Sinica on the research of organolanthanide chemistry. We are also indebted to Prof. Chongshi Nie and Dr. Peili Yao for the measurement of the infrared spectra and to the mass spectra group of our Institute for the measurement of the mass spectra. We are also obliged to Prof. Yaozeng Huang for the encouragement of this work.

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