

STUDIES ON ORGANOLANTHANIDE COMPLEXES

VII *. FORMATION AND CLEAVAGE OF CARBON-METAL BONDS OF DICYCLOPENTADIENYL-EARLY LANTHANIDE COMPLEXES

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Summary

Four new 1,10-phenanthroline-coordinated early lanthanide complexes containing a σ -carbon-metal bond (1-4) were synthesized by the reaction of alkynylsodium or alkyllithium with $(\eta^5\text{-C}_5\text{H}_5)_2\text{LnCl} \cdot n\text{Phen}$ in THF at 0 or -78°C . The complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{LnCl} \cdot n\text{Phen}$ were prepared from $\text{LnCl}_3 \cdot n\text{Phen}$ and $\text{C}_5\text{H}_5\text{Na}$. 1,1'-Trimethylenedicyclopentadienyl(phenylacetylenylneodymium)·THF (5) was also prepared. These complexes were identified by elemental analysis, IR, ^1H NMR spectroscopy and thermogravimetry. Protolysis reactions of these complexes with H_2O , CH_3OH and $t\text{-C}_4\text{H}_9\text{OH}$ show that different protolytic reagents give the products with different cleavage extents of σ - and π -bonds. The ligands in the complexes also affect the cleavage of π -bonds. β -Hydrogen elimination of complex 3 takes place with thermal decomposition.

Introduction

The unsolvated σ -bonded later lanthanocene complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{LnR}$ have been reported by Tsutsui [1]. Schumann reported the synthesis of series of lutetium complexes containing Lu-C σ -bonds, $(\eta^5\text{-C}_5\text{H}_5)_2\text{LuR} \cdot \text{THF}$ [2]. Recently, we synthesized the tetrahydrofuran solvated aryl-later lanthanocene complexes [3]. There is, however, very little knowledge about the σ -bonded complexes of early lanthanides [4]. Probably due to the lanthanide contraction effect, the early lanthanides have larger ionic radii and further disproportionation will take place during the syntheses of dicyclopentadienyl-early lanthanide chlorides. We succeeded in stabilizing the early lanthanocene chlorides by applying ring-bridged 1,1'-trimethylenedicyclopentadiene instead of separated dicyclopentadiene as ligand, and tetra-

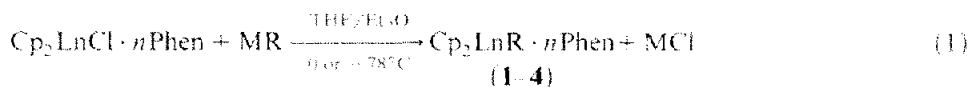
* For part VI see ref. 10

hydrofuran-coordinated 1,1'-trimethylenedicyclopentadienyl-early lanthanide chlorides have been obtained [5]. Moreover, through coordination with the chelated ligand 1,10-phenanthroline, the coordination saturation of early lanthanocene chloride is achieved, and the early lanthanocene chlorides coordinated with 1,10-phenanthroline were successfully isolated [6].

We now report the syntheses of 1,10-phenanthroline-coordinated early lanthanocene complexes containing Ln-C σ -bonds, and their protolysis reactions with several reagents. We also describe the effects of different ligands on the cleavage of their π -bonds and β -hydrogen elimination reactions with thermal decomposition of the complex Cp₂Nd-t-C₄H₉·Phen.

Results and discussion

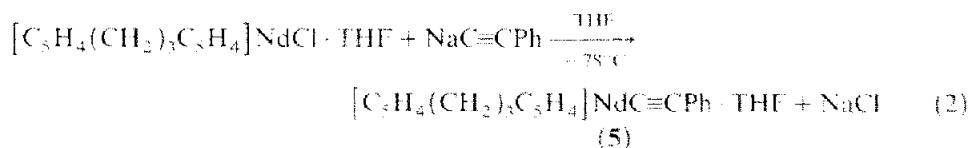
1,10-Phenanthroline-coordinated lanthanocene chlorides [6] were allowed to react with alkynylsodium or alkyllithium giving 1,10-phenanthroline-coordinated lanthanocenes containing σ -bonds according to eq. 1.



- (1): R = C≡CPh, M = Na, Ln = Nd, n = 1;
 2: R = C≡CPh, M = Na, Ln = La, n = 2;
 reaction temp. 0°C.
 3: R = t-C₄H₉, M = Li, Ln = Nd, n = 1;
 4: R = t-C₄H₉, M = Li, Ln = La, n = 2;
 reaction temp. -78°C)

(Cp = cyclopentadienyl, Ph = phenyl, Phen = 1,10-phenanthroline)

For studying the effects of ligands on protolysis reactions, tetrahydrofuran-coordinated 1,1'-trimethylenedicyclopentadienyl(phenylacetylenyl)neodymium was synthesized as shown in eq. 2.



All the new σ -bonded organolanthanide complexes are extremely sensitive to air and moisture, but have higher thermostability. The complexes, stored in sealed tubes filled with argon at room temperature, were identified by elemental analysis, IR and ¹H NMR spectroscopy, thermogravimetry and protolysis. The physical properties, yields and analytical data of these complexes are shown in Table 1.

The infrared spectra of complexes 1-5 were recorded from 4000 to 200 cm⁻¹. The major absorption peaks are listed in Table 2. The absorption peak at about 250 cm⁻¹ is characteristic for absorption of π -bonds between the metal and cyclopentadienyl groups [3]. All complexes exhibit characteristic absorptions of cyclopentadienyl and 1,10-phenanthroline. In addition, complexes 1, 2 and 5 show absorption peaks of PhC≡C, while complexes 3 and 4 show absorption peaks of t-C₄H₉.

The ¹H NMR spectra of the diamagnetic complexes 2 and 4 are listed in Table 3.

The chemical shifts of the coordinated 1,10-phenanthroline move apparently to

TABLE 1
PHYSICAL PROPERTIES, YIELDS AND ELEMENTAL ANALYSES OF PRODUCTS

Compound	Color	M.p. (°C)	Yield (%)	Analysis (Found (calcd.) (%))		
				Ln	C	H
1 ($\eta^5\text{-C}_5\text{H}_5$) ₂ NdC≡CPh·Phen	brown	210–212	37	26.40 (25.95)	64.71 (64.84)	4.51 (4.17)
2 ($\eta^5\text{-C}_5\text{H}_5$) ₂ LaC≡CPh·2Phen	brown	128–130	53	18.64 (19.01)	70.07 (69.04)	5.19 (4.27)
3 ($\eta^5\text{-C}_5\text{H}_5$) ₂ Nd-t-C ₄ H ₉ ·Phen	purple-red	185–187 (dec.)	27	27.15 (28.19)	58.87 (61.02)	5.49 (5.32)
4 ($\eta^5\text{-C}_5\text{H}_5$) ₂ La-t-C ₄ H ₉ ·2Phen	purple-red	184–186	47	20.21 (20.23)	64.14 (66.47)	5.37 (5.14)
5 [C ₅ H ₄ (CH ₂) ₃ C ₅ H ₄]NdC≡CPh·THF	yellow-green	210–213 (dec.)	41	29.03 (29.57)	59.83 (61.56)	5.01 (5.58)

TABLE 2
INFRARED SPECTRAL DATA OF PRODUCTS (cm⁻¹)

Compound	Low frequency region	Cp	<i>o</i> -Phen	PhC≡C	t-C ₄ H ₉	THF
1	203 (m)	774 (s)	414 (m), 733 (s), 751 (s)	531 (m)		
	243 (w)	1011 (s)	841 (s), 1418 (s), 1505 (m)	751 (s)		
	347 (m)	1441 (m)	1563 (m), 1586 (m), 1618 (m)	1485 (m)		
2		3070 (s)				
		765 (s)	415 (m), 735 (s), 750 (s)	540 (m)		
	250 (m)	1010 (s)	842 (s), 1416 (s), 1504 (s)	750 (s)		
3	320 (m)	1446 (m)	1564 (m), 1587 (m), 1617 (m)	1493 (m)		
		3075 (s)				
	215 (m)	770 (s)	418 (w), 732 (s), 753 (s)		1138 (m)	
4	243 (m)	1014 (s)	842 (s), 1420 (m), 1509 (m)		1170 (m)	
	350 (w)	1440 (s)	1563 (m), 1588 (m), 1609 (m)		1472 (m)	
		3080 (m)				
5		780 (m)	414 (w), 733 (s), 753 (s)		1137 (m)	
	255 (w)	1011 (m)	842 (m), 1420 (m), 1510 (m)		1170 (w)	
	350 (w)	1445 (w)	1567 (m), 1590 (m), 1610 (m)		1473 (m)	
	3070 (m)					
5	235 (m)	755 (s)		540 (s)		
	350 (s)	1012 (m)		755 (s)		890 (m)
	540 (s)	1440 (s)		1490 (m)		1045 (m)
	3060 (s)		1598 (m)			
			1660 (m)			

TABLE 3
¹H NMR OF COMPLEXES 2 AND 4

Complex	δ (ppm)			
	<i>o</i> -Phen	PhC≡C	C ₅ H ₅	C(CH ₃) ₃
2	8.83 (d-d), 8.08 (d-d), 7.58 (s), 7.45 (d-d)	7.02 (m)	5.46 (s)	
4	8.46 (d-d), 7.65 (d-d), 7.11 (s), 6.99 (d-d)		5.21 (s)	0.80 (s)
free <i>o</i> -Phen	8.42 (d-d), 7.65 (d-d), 7.13 (s), 6.98 (d-d)			

TABLE 4

PROTOLYSIS OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{NdC}\equiv\text{CPh}\cdot\text{Phen}$ (Protolysis conditions: 10°C, shaking in CCl_4 , protolysis reagent/complex = 5/1)

Time (h)	Cleavage (%)					
	in H_2O		in CH_3OH		in $t\text{-C}_4\text{H}_9\text{OH}$	
	σ	π	σ	π	σ	π
0.5	100	100	100	76		
2			100	76		
8			100	100	trace	trace
24					100	29
72					100	29
96					100	29

lower field in complex **2** and are almost unchanged in complex **4** as compared to shifts of free 1,10-phenanthroline. The coordination between 1,10-phenanthroline and lanthanum is increased by the $\text{PhC}\equiv\text{C}$ group with delocalization of π -bonds. The lone pair electron on nitrogen in 1,10-phenanthroline transfers to lanthanum to greater extent which lowers the electron density on the 1,10-phenanthroline ring. Another feature is the magnetic anisotropic effect of the alkynyl group. However, because the lanthanum is bound to an electron-donating group, $t\text{-C}_4\text{H}_9$, coordination between 1,10-phenanthroline and lanthanum in complex **4** becomes weaker and gives almost unchanged δ values for 1,10-phenanthroline.

However, no obvious shift was noticed comparing infrared absorption peaks of coordinated 1,10-phenanthroline in these complexes with those of free 1,10-phenanthroline.

Complexes **1** and **5** were protolysed with various reagents such as H_2O , CH_3OH and $t\text{-C}_4\text{H}_9\text{OH}$. The protolysis results of complex **1** are shown in Table 4. The σ - and π -bonds of $(\eta^5\text{-C}_5\text{H}_5)_2\text{NdC}\equiv\text{CPh}\cdot\text{Phen}$ are cleaved readily with generation of phenylacetylene and cyclopentadiene under the attack of water. With methanol, σ -bond cleavage also occurred readily, whereas π -bond cleavage proceeded slowly. In the reaction with *t*-butyl alcohol, cleavages of both σ - and π -bonds were slow and no evidence was found for protolysis of this complex after 8 h, but the σ -bond was cleaved completely after 24 h, while the π -bond was cleaved for about 29% only.

TABLE 5

PROTOLYSIS OF $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{NdC}\equiv\text{CPh}\cdot\text{THF}$ (Protolysis conditions: 10°C, shaking in CCl_4 , protolysis reagent/complex = 5/1)

Time (h)	Cleavage (%)					
	in H_2O		in CH_3OH		in $t\text{-C}_4\text{H}_9\text{OH}$	
	σ	π	σ	π	σ	π
0.5	100	80	100	60	100	0
2	100	100	100	60	100	0
8			100	60	100	0
24			100	60	100	0
48			100	60	100	0
72			100	60	100	0

The protolysis results of complex **5** are shown in Table 5. The lanthanide-carbon σ -bonds underwent rapid protolysis with water and methanol, and cleavage of the metal-ring bonds was not competitive with attack on the σ -bonds. However, with *t*-butyl alcohol, no cleavage of the $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]$ ligands was found after 72 h at 10°C.

The π -bond certainly is more stable than the σ -bond on protolysis. However, the protolytic reagent affects the protolysis rate and cleavage extent of the π -bond. The results are similar to those for 5*f* elements [7], and seem to be related to the different $\text{p}K_{\text{a}}$ values of protolytic reagents. The following order of $\text{p}K_{\text{a}}$ values is found: 15.7 (H_2O) < 16 (CH_3OH) < 19 (*t*- $\text{C}_4\text{H}_9\text{OH}$). The protolysis results also showed that the stability of the π -bond between 1,1'-trimethylenedicyclopentadienyl and lanthanide is higher than that of the π -bond between separated dicyclopentadienyl and lanthanide.

Thermogravimetric analysis of complex **3** under nitrogen indicated that weight losses of 11.8, 33.1 and 23.6% at 74–186, 186–435 and 435–687°C, respectively. This is in accordance with the loss of one *t*-butyl, *o*-phenanthroline and two cyclopentadienyl groups respectively. Finally, the residual weight is equal to 31.5%, and the neodymium content is the residue is 85.8%, which is consistent with Nd_2O_3 . Therefore the measured molecular weight of the complex is 533 (C_5H_5)₂Nd-*t*- C_4H_9 · Phen calcd.: 511).

Because of β -hydrogen elimination the M-C σ -bonded *d*-transition metal complex containing β -hydrogen atoms usually could not be obtained. Contrary to the *d*-transition metal complex, the σ -bonded lanthanide metal complex containing β -hydrogen can be isolated at room temperature. However, on heating β -hydrogen elimination occurs in the case of complex **3**. Thermolysis results in vacuo of complex **3** at various temperatures are listed in Table 6.

Complex **3** is stable at 50°C. It decomposes very slowly in vacuo at 75°C. Upon heating for 4 h in vacuo at 100°C, complex **3** decomposed partially due to β -hydrogen elimination. The gaseous products are a mixture of 2-methylpropene and 2-methylpropane with a ratio of about 1/1.5. At 200°C, complex **3** decomposed completely and the final residue changed into a brown solid.

Experimental

All operations were performed under prepurified argon using Schlenk techniques or in a drybox. All solvents were refluxed and distilled over LiAlH_4 or benzophenonesodium under argon immediately before use. Anhydrous lanthanide chlorides were

TABLE 6
THERMOLYSIS DATA IN VACUO OF COMPLEX **3**

Temp. (°C)	Time (h)	Residue		Gas evolved
		Color	Nd (%)	
50	4	purple-red	27.74	no
75	4	purple-red	27.24	trace
100	4	rusty	26.40	$(\text{CH}_3)_2\text{C}=\text{CH}_2 + t\text{-C}_4\text{H}_{10}$
150	4	yellow	27.67	$(\text{CH}_3)_2\text{C}=\text{CH}_2 + t\text{-C}_4\text{H}_{10}$
200	4	brown	30.91	$(\text{CH}_3)_2\text{C}=\text{CH}_2 + t\text{-C}_4\text{H}_{10}$

obtained by treatment of hydrated lanthanide chlorides with ammonium chloride [3]. Phenylacetylenylsodium [4] *t*-butyllithium [8] and 1,1'-trimethylenedicyclopentadienylneodymium chloride [5] were prepared by literature methods. Melting points or thermal decomposition temperatures were determined in a sealed argon-filled capillary and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 580B spectrometer as Nujol and Fluorolube mulls which were prepared in an argon-filled glovebox and examined between diskshaped CsI crystal plates. ^1H NMR spectra were recorded on an EM 360 L (60 MHz) spectrometer and referenced to external Me_2Si . THF-*d*₈ (Merck for NMR spectroscopy) was dried over Na/K alloy and was degassed by freeze-thaw cycles on a vacuum line. Thermogravimetry was performed on a WRT-1 thermobalance. Gas chromatographic analysis was carried out on a 103 gas chromatographic instrument. Metal analyses of lanthanides were accomplished using the direct complexometric titration procedure with disodium EDTA [9]. Carbon and hydrogen analyses were carried out by direct combustion in aluminium tube.

Di- η^5 -cyclopentadienyl(phenylacetylenyl)neodymium·Phen (1)

A 40-ml THF solution of 2.08 g (11.56 mmol) of 1,10-phenanthroline was added to a 30-ml THF suspension of 2.84 g (11.36 mmol) anhydrous NdCl_3 . The reaction mixture was allowed to stir overnight at room temperature. To this suspension was added dropwise under stirring a solution of cyclopentadienylsodium (23.48 mmol) in 50 ml of THF. The reaction mixture was stirred overnight at room temperature. A brownish green solution (105 ml), the chlorine content of which is 8.82 mN, was isolated by centrifugation. The above-mentioned solution (62 ml) was allowed to react with 5.22 mmol of $\text{PhC}\equiv\text{CNa}/\text{Et}_2\text{O}$ overnight at room temperature. The resulting brown solution was centrifuged and concentrated in vacuo. By addition of *n*-hexane a brown solid precipitated out which was washed with *n*-hexane, and dried in vacuo. Product **1** (1.39 g, 37%) was obtained.

Di- η^5 -cyclopentadienyl(phenylacetylenyl)lanthanum·2Phen (2)

Compound **2** was synthesized similarly to **1**, but the $(\eta^5\text{-C}_5\text{H}_5)_2\text{LaCl}\cdot 2\text{Phen}$ -THF suspension prepared was not isolated and treated in situ with an equivalent portion of $\text{PhC}\equiv\text{CNa}/\text{Et}_2\text{O}$ (yield 53%).

*Di- η^5 -cyclopentadienyl-*t*-butylneodymium·Phen (3)*

A 40 ml THF solution of 1.67 g (9.27 mmol) of 1,10-phenanthroline was added under stirring to a 30-ml THF solution of 2.38 g (9.50 mmol) of NdCl_3 . The reaction mixture was stirred overnight. A solution of cyclopentadienylsodium (19.13 mmol) in 50 ml of THF was added and again stirred overnight at room temperature; a brownish green solution (110 ml), the chlorine content of which is 7.22 mN, was isolated by centrifugation. This solution (85 ml) was cooled to -78°C and a solution of $t\text{-C}_4\text{H}_9\text{Li}/\text{Et}_2\text{O}$ (5.6 mN) kept between -35 and -40°C was syringed into it. The reaction mixture was maintained for 1 h at -78°C and then allowed to warm to room temperature. A purple-red solution formed which was stirred overnight. The solvent was removed in vacuo and the solid extracted with benzene. Upon concentration of the resulting purple-red solution, followed by addition of *n*-hexane, a purple-red crude product precipitated out, which was extracted with benzene and precipitated two times with *n*-hexane. A product free from chloride was obtained (1.03 g, 27%).

*Di- η^5 -cyclopentadienyl-*t*-butyllanthanum · 2Phen (4)*

The method is similar to that of **3**, but the $(\eta^5\text{-C}_5\text{H}_5)_2\text{LaCl} \cdot 2\text{Phen}/\text{THF}$ suspension prepared was not isolated and treated in situ with an equivalent portion of $t\text{-C}_4\text{H}_9\text{Li-Et}_2\text{O}$. (yield 47%).

1,1'-Trimethylenedicyclopentadienyl phenylacetylene neodymium · THF (5)

A $\text{PhC}\equiv\text{CNa}/\text{Et}_2\text{O}$ suspension (5.21 mmol) was added into a $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{NdCl} \cdot \text{THF}$ solution [4], the chlorine content of which is 5.20 mN. The pale-blue mixture was kept for 1 h at -78°C , then allowed to warm to room temperature and stirred overnight. The colour of the solution changed to brown-green. After centrifugation, the solution was concentrated in vacuo and a yellow-green solid precipitated out upon addition of *n*-hexane to give 1.60 g of product. (yield 40% based on NdCl_3).

Protolysis reaction

Complexes were placed in a series of centrifuge tubes. CCl_4 was added, then an excess of H_2O , CH_3OH or $t\text{-C}_4\text{H}_9\text{OH}$ was added into each of these tubes. The reaction mixtures were shaken at 10°C and centrifuged after different reaction times. Clear solutions were placed in NMR tubes and ^1H NMR spectra were recorded (referenced to internal Me_4Si). The product of σ -bond cleavage is $\text{PhC}\equiv\text{CH}$ and that of π -bond cleavage is cyclopentadiene or 1,1'-trimethylenedicyclopentadiene. According to their integral intensity the contents of protolysis products were measured.

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