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New dinuclear bis(cyclopentadienyl)lanthanoid chlorides containing η^5-C_5H_4 ligands linked by a metal-coordinated 2,6-dimethylenepyridyl unit

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Abstract

The salts $M_2[2,6\text{-}(CH_2C_5H_4)_2C_5H_3N]$ (*i.e.* Na_2L, Li_2L) react under mild conditions with anhydrous $LnCl_3$ in the molar ratio 1 : 1 to afford complexes of the type $[(LLnCl)_2]$ (Ln = Y, Pr, Nd, Sm, Dy, Er, Yb, or Lu; **1–8**). The dinuclear nature of the products **1–8** has been confirmed by mass spectrometry. Extended B/E-linked scans of metastable transitions suggest that L is chelating and not metal-bridging. Direct coordination of the pyridine-N atom to the Ln ion has been deduced from XPS measurements. Reaction of $PrCl_3 \cdot (THF)_x$ and Na_2L in the molar ratio 2 : 3 leads to the compound $[L_3Pr_2]$ (**9**) which has been characterized by elemental analysis, ^1H NMR and mass spectrometry. Some preliminary results on the catalytic activity of **1–8** during hydrogenation of 1-hexene by $LiAlH_4$ suggest the formation of catalytically active, intermediate hydrides.

Key words: Rare earth metals; Lanthanum; Lutetium; Lanthanoid; Chloride

1. Introduction

Bis(cyclopentadienyl) lanthanoid chlorides, $(Cp_2LnCl)_n$ are valuable precursors for the synthesis of derivatives with Ln–H, Ln–C (alkyl or aryl), Ln–N and Ln–O σ bonds [1]. All dinuclear bis(cyclopentadienyl) lanthanoid chlorides with the unsubstituted cyclopentadienyl except those of the early lanthanoids are available [1,2]; however, because of the rather large ionic radii of the lightest lanthanides La, Ce, Pr, and Nd, the coordination sphere of even a dinuclear complex is incapable of providing sufficient coordinative saturation to avoid rapid ligand redistribution processes.

Nevertheless, several research groups have developed methods to stabilize derivatives of the lighter bis(cyclopentadienyl)lanthanoid chlorides. By enhanced steric congestion around the metal ion, *e.g.* by employment of bulky mono- [3] or peralkyl-substituted cyclopentadienyls [4], as well as of trimethylsilyl- [5] or polytrimethylsilyl [6] -substituted cyclopentadienyls, intermolecular ligand redistribution processes may frequently be avoided. Equally favourable results have been obtained by linking two otherwise unsubstituted cyclopentadienyls by a suitable group μ-X [X = $(CH_2)_n$; $n = 1$ [7], 3, 5 [7,8], Me_2Si [7,9], $(CH_2)_2$-2,5-C_6H_4 or $(CH_2)_2$-2,4-C_6H_4 [10], $(CH_2)_2$–O–$(CH_2)_2$ [11,12], $(CH_2)_2$-2,6-C_5H_3N [13], or $\{Si(Me_2)\}_2O$ [14], as well as by linking two peralkylcyclopentadienyls [15] or one unsubstituted cyclopentadienyl and one peralkylated cyclopentadienyl [16] by a dialkylsilyl group. It has become apparent that the stoichiometric and catalytic reactivity of organo-f-element hydrocarbyls and hydrides derived from the corresponding bis(cyclopentadienyl)lanthanoid monochlorides depends strongly on the specific vacancies within the coordination sphere of the equatorial girdle (*i.e.* on the actual occupation of the usual frontier orbitals of a Cp''_2LnR system).

With the background of the successful synthesis and structural analysis of the mononuclear organouranium(IV) complex: $[2,6\text{-}C_5H_3N(CH_2C_5H_4)_2UCl_2]$ [13b] we have also focused on the properties of lan-

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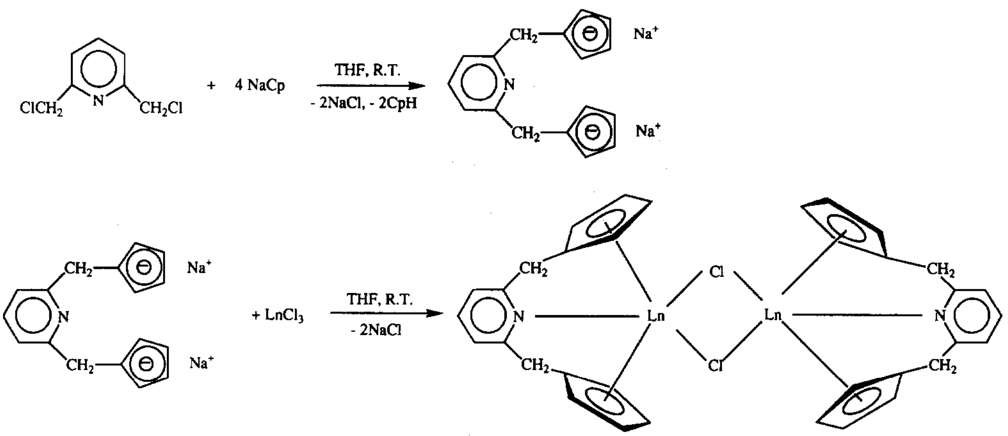
TABLE 1. Elemental analyses of compounds **1**–**8**

Compound	C%		H%		N%		M%		Cl%	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
[(LYCl)$_2$] (**1**) (light yellow, 65% yield)	57.50	57.09	4.30	4.23	4.40	4.25	25.10	24.86	9.70	9.91
[(LPrCl)$_2$] (**2**) (yellow-green, 67% yield)	50.00	49.84	3.75	3.69	3.50	3.42	34.45	34.39	8.75	8.65
[(LNdCl)$_2$] (**3**) (light blue, 72% yield)	50.00	49.44	3.65	3.66	3.50	3.39	35.10	34.92	8.65	8.58
[(LSmCl)$_2$] (**4**) (yellow lemon, 74% yield)	49.20	48.72	3.70	3.61	3.45	3.34	36.05	35.87	8.55	8.46
[(LDyCl)$_2$] (**5**) (yellow-orange, 70% yield)	47.55	47.35	3.80	3.50	3.50	3.25	37.35	37.68	8.35	8.22
[(LErCl)$_2$] (**6**) (pink, 73% yield)	47.05	46.83	3.65	3.47	3.40	3.21	38.65	38.36	7.85	8.13
[(LYbCl)$_2$] (**7**) (orange, 70% yield)	46.50	46.22	3.55	3.42	3.10	3.17	39.50	39.17	8.30	8.02
[(LLuCl)$_2$] (**8**) (yellow orange, 70% yield)	46.05	46.01	3.55	3.41	3.30	3.16	39.45	39.43	7.45	7.99



Scheme 1.

TABLE 2. Mass spectrometric data (EI, 70 eV, T_{probe} = 120–150°C) of [(LLnCl)$_2$] compounds [m/z (Rel. ab. %)]

Fragment	Ln = ^{89}Y	Ln = ^{141}Pr	Ln = ^{144}Nd	Ln = ^{150}Sm	Ln = ^{163}Dy	Ln = ^{168}Er	Ln = ^{174}Yb	Ln = Lu
$P^{+\bullet}$	714(2)	818(6)	824(8)	836(6)	862(8)	870(6)	884(7)	886(5)
$P^{+\bullet} - Cl$	679(1)	783(2)	789(2)	801(2)	827(2)	835(3)	846(4)	851(4)
$P^{+\bullet} - C_5H_6$	648(5)	752(2)	758(1)	770(2)	796(1)	804(2)	818(2)	820(1)
$[C_{29}H_{27}N_2Ln]^{+\bullet}$ (**A**)	492(2)	544(2)	545(1)	553(2)	566(2)	570(2)	577(2)	578(10)
$P^{+\bullet}/2 + Cl$			447(2)	453(2)	466(2)	471(1)	477(2)	478(2)
$P^{+\bullet}/2$	357(19)	409(36)	412(15)	418(18)	431(20)	436(17)	442(64)	443(48)
$P^{+\bullet}/2 - Cl$	322(100)	374(100)	377(100)	393(100)	396(100)	401(100)	407(100)	408(100)
$P^{+\bullet}/2 - C_5H_5$	292(8)	344(1)	347(8)	353(10)	366 (18)	371(2)	377(2)	378(2)
$[C_{11}H_9NLnCl]^{+\bullet}$	279(7)	331(1)	334(10)	340(8)	353(22)	358(2)	364(3)	365(3)
$[C_{12}H_{10}LnCl]^{+\bullet}$	278(10)	330(2)	333(10)	339(6)	352(18)	357(2)	363(2)	364(3)
$[C_{11}H_9NLn]^+$	244(2)	296(2)	299(40)	305(40)	318(2)	323(1)	329(3)	330(3)
$[C_7H_7LnCl]^{+\bullet}$	229(40)	281(9)	284(6)	290(32)	303(2)	308(< 1)	314(2)	315(2)
$[C_7H_7NLn]^+$	194(2)	246(< 1)	249(2)	255(1)	268(2)	273(< 1)	279(2)	280(4)
LH^+	234(12)	234(44)	234(25)	234(46)	234(69)	234(95)	234(23)	234(7)
$L^{+\bullet}$	233(8)	233(12)	233(23)	233(32)	233(53)	233(48)	233(15)	233(4)

thanide complexes with the novel ligand $L^{2-} = 2,6\text{-}C_5H_3N\text{-}(CH_2C_5H_4)_2$. Below we describe a number of $[(LLnCl)_2]$ systems, the dinuclear complex $[L_3Pr_2]$ and the important starting reagents M_2L with M = Na [13] or Li.

2. Results and discussion

The new bis(cyclopentadienyl)lanthanoid chlorides $[(LLnCl)_2]$ are obtained according to eqn. (1) (Scheme 1).

$$2M_2L + 2LnCl_3 \xrightarrow{THF} [(LLnCl)_2] + 4MCl \qquad (1)$$

where Ln = Y, Pr, Nd, Sm, Dy, Er, Yb, or Lu (**1–8**)

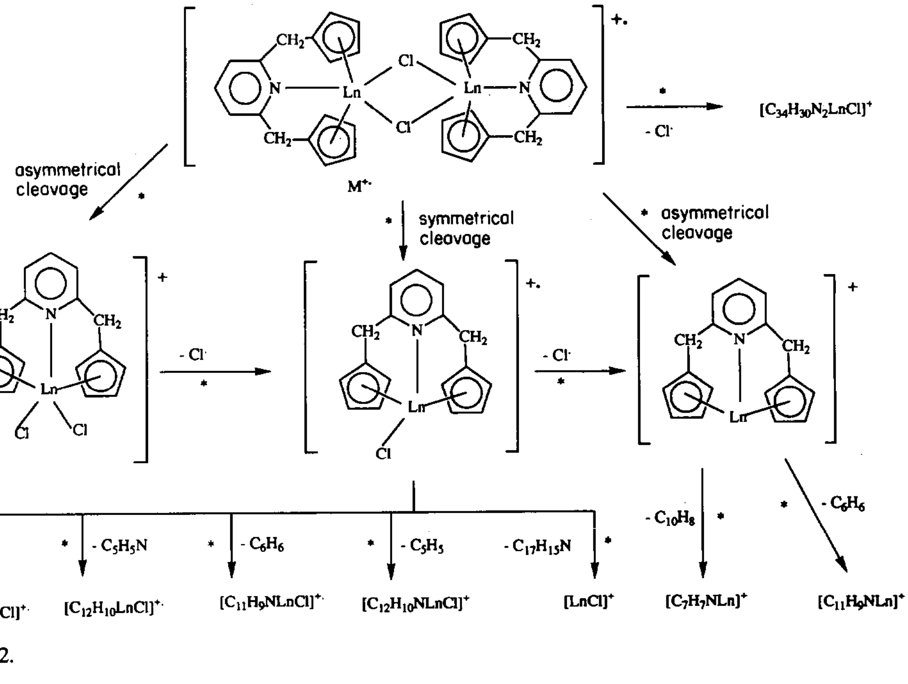
The resulting new bis(cyclopentadienyl)lanthanoid chlorides have been identified by elemental analysis (Table 1), and extensively characterized by IR spectroscopy, mass spectrometry (MS), and ^1H NMR and X-ray photoelectron spectroscopy (XPS).

The infrared spectra of **1–8** (4000–180 cm^{-1}, Nujol mulls between CsI disks) are all very similar. Whereas absorptions characteristic of the methylene, cyclopentadienyl and pyridyl groups appear, no absorption bands due to coordinated THF could be observed. On the other hand, the strong pyridyl ν(CN) band of the disodium salt, Na_2L (1591 cm^{-1}) is shifted to ~1610 cm^{-1} probably as a consequence of significant pyridine-N-coordination to the lanthanoid ions. This is supported by significant shifts of the pyridyl ring breathing vibration from 997 cm^{-1} in Na_2L to higher wavenumbers by about 15 cm^{-1}.

The mass spectra of the new chlorides (Table 2) display the dinuclear molecular ion, $[(LLnCl)_2]^{+\bullet}$, as well as some fragments, indicating that all products are dimeric at least in the vapour phase, and thus most probably also in the solid state. The lack of fragments at *m/z* 72 or 71 confirms that the complexes are THF-free. On the basis of B/E linked scan studies, the fragmentation pathway shown in Scheme 2 may be inferred.

The mass spectra of **1–8** (Table 2) show, in addition to the parent molecular ion $[P]^{+\bullet}$, peaks whose *m/z* values correspond to the mononuclear species $[P/2]^{+\bullet}$ and its daughter fragments. Owing to the much higher relative abundances of the latter peaks, the dinuclear species is more likely to contain L in the chelating mode (from **I**). The B/E-linked scans of $P^{+\bullet}$ confirm that symmetric and asymmetric cleavage clearly dominates over alternative fragmentation pathways still leading to dinuclear ions. Where two cyclopentadienyl rings are linked by a dimethylsilyl group [7,9], dinuclear species may form with either chelating or bridging $(C_5H_4)_2SiMe_2$ units (Scheme 3).

Elimination of either C_6H_6 or C_5H_5N from $P/2^{+\bullet}$ is non-trivial and deserves more comment. In the latter case, the metal-containing fragment $[C_{12}H_{10}LnCl]^+$ is likely to involve an ethylene bridge between the two C_5H_4 units. Surprisingly, CAD MIKE experiments comparing the $[C_6H_6]^{+\bullet}$ fragments with genuine benzene show that the latter is not formed. In contrast the



Scheme 2.

TABLE 3. ^{1}H NMR data of the diamagnetic complexes [(LYCl)$_2$] and [(LLuCl)$_2$] [a]

Compound	CH_2	CH in cyclopentadienyl	3,5-CH in pyridine ring	4-CH in pyridine ring
$Na_2[2,6\text{-}C_5H_3N(CH_2C_5H_5)_2]$ (L)	4.06(s, 4H)	5.31(t, 4H) 5.49(t, 4H)	7.01(d, 2H)	7.54(t, 1H)
[(LYCl)$_2$]	4.04(q, AB, 4H, J = 18.2 Hz)	5.57(t, 2H) 5.72(t, 2H) 5.94(m, 4H)	7.05(d, 2H)	7.59(t, 1H)
[(LLuCl)$_2$]	4.20(q, AB, 4H J = 18 Hz)	5.68(t, 2H) 5.98(t, 2H) 6.17(m, 4H)	7.18(d, 2H)	7.70(t, 1H)

[a] (δ ppm); THF-d_8 was used as solvent for Na_2L and [(LYCl)$_2$], but $CDCl_3$ for [(LLuCl)$_2$].

ligands of tris(methylcyclopentadienyl)lanthanoid complexes were shown to undergo metal-assisted ring-enlargement to generate free benzene [17].

Unlike the ^{1}H NMR spectra of Na_2L, those of the diamagnetic yttrium and lutetium chlorides display magnetically non-equivalent cyclopentadienyl and CH_2 protons (Table 3). Whereas the CH_2 signal of the disodium salt is a singlet, an AB quartet appears in the spectra of the metal complexes. Correspondingly, the two pseudo-triplets of the α- and β-cyclopentadienyl protons of the disodium salt have changed to three multiplets of relative intensities 4:2:2. This indicates a comparatively rigid structure in which the two non-parallel cyclopentadienyl rings give rise to prochiral C_5H_4 and CH_2 units. Corresponding structural features are reflected by the ^{1}H NMR spectra of the paramagnetic Pr, Nd, Sm, and Yb derivatives (Table 4). The significant broadening of the CH_2 resonances of the complexes with Pr, Nd, or Yb is reminiscent of the behaviour of the uranium complex [$LUCl_2$] [13].

XPS was used to compare the ionization energies of core electrons of the rare earth ions and of the pyridine-N atom. The data (Table 5) demonstrate that the binding energies of all metal core electrons of LLnCl systems are smaller than those of the corresponding "parent" dicyclopentadienyl complexes, $[(C_5H_5)_2\text{-}LnCl]_2$ [18]. Conversely, the 1s-binding energies of the N atoms in the new complexes exceed those of the salt Na_2L. Both features imply strongly that the lone pair of the nitrogen atom of these lanthanoid complexes is partially transferred to the coordinatively unsaturated rare-earth ion. A genuine coordinative N → M bond has been deduced from the X-ray data of [$LUCl_2$] [13b]. In an earlier study, XPS has been used to demonstrate that an oxygen atom located in a chain connecting two C_5H_4-units is likewise coordinated to the central metal ion [18].

The mass spectra of all complexes showed a very weak fragment corresponding to the composition $[LM\text{-}(C_5H_4\text{-}CH_2\text{–}C_5H_3N\text{–}CH_3)]^{+\bullet}$ (fragment A in Table

TABLE 4. ^{1}H NMR data for the paramagnetic compounds [(LLnCl)$_2$] (Ln = Pr, Nd, Sm, or Yb) [a]

Compound	CH_2	CH in cyclopentadienyl	3,5-CH in pyridine ring	4-CH in pyridine ring
[(LPrCl)$_2$]	13.10(br. s, 8H)	105.61(br. s, 4H) 17.92(br. s, 4H) −24.79(br. s, 4H) −51.96(br. s, 4H)	3.87(d, 4H)	2.91(t, 2H)
[(LNdCl)$_2$]	11.05(br. s, 8H)	47.06(br. s, 4H) 15.60(br. s, 4H) −23.81(br. s, 4H) −40.14(br. s, 4H)	5.34(br. s, 4H)	4.85(br. s, 2H)
[(LSmCl)$_2$]	5.68(br. s, 8H)	14.86(br. s., 4H) 8.66(br. s, 4H) 1.87(br. s, 4H) 0.92(br. s, 4H)	7.18(br. s, 4H)	7.42(br. s, 2H)
[(LYbCl)$_2$]	−19.04(br. s, 8H)	135.75(br.s, 4H) 43.72(br. s, 4H) −22.00(br. s, 4H) −148.38(br. S, 4H)	16.18(br.s, 4H)	18.69(br. s, 2H)

[a] (δ ppm); $CDCl_3$.

TABLE 5. Binding energy data (eV)

Compound	N_{1s}		Y_{3d}		$Dy_{4d5/2}$		$Er_{4d5/2}$		Lu_{4f}	
	BE	ΔE_1 [a]	BE	ΔE_2 [b]	BE	ΔE_2 [b]	BE	ΔE_2 [b]	BE	ΔE_2 [b]
Na_2L	398.6									
Cp_2YCl			159.6							
Cp_2DyCl					157.7					
Cp_2ErCl							160.9			
Cp_2LuCl										
$[(LYCl)_2]$	399.6	+1.0	158.9	−0.7					10.4	
$[(LDyCl)_2]$	399.5	+0.9			155.0	−2.7				
$[(LErCl)_2]$	399.4	+0.8					159.8	−1.1		
$[(LLuCl)_2]$	399.7	+1.1							9.6	−0.8

[a] ΔE_1 = BE $N_{1s}[(LLnCl)_2]$ − 398.6. [b] ΔE_2 = BE $[(LLnCl)_2]$ − BE $[(Cp_2LnCl)]$.

2), suggesting traces of another dinuclear, possibly halide-free, species of the type $[L_3M_2]$.

In fact, reaction of $PrCl_3 \cdot 3THF$ and Na_2L in the molar ratio 2:3 yields the new halide-free complex $[L_3Pr_2]$ (**9**) in high yield (*ca.* 70%). Absence of chlorine, and ^1H NMR and mass spectrometric data have confirmed the formulation $[(LPr)_2(\mu\text{-}L)]$ for **9**. First, in the ^1H NMR spectrum of **9** (CD_2Cl_2, see Fig. 1) two distinct groups of pyridyl protons are observed: (a) δ −6.69 (t, 2H, J = 7.5 Hz), δ −19.95 (d, 4H, J = 7.5 Hz); (b) δ −16.91 (t, 1H, J = 8.0 Hz), δ −28.49 (d, 2H, J = 8.0 Hz). Owing to the usually rigid nature of the two LPr units, the methylene protons of the two chelating L give rise to two doublets, δ −3.68 (d, 4H, J = 18 Hz) and δ −9.21 (d, 4H, J = 17.8 Hz). The remaining seven equally intense and broad singlets ($W_{1/2} \approx 20$ Hz) belong to the C_5H_4 protons of the chelating (4 signals) and bridging (2 signals) L's, re-

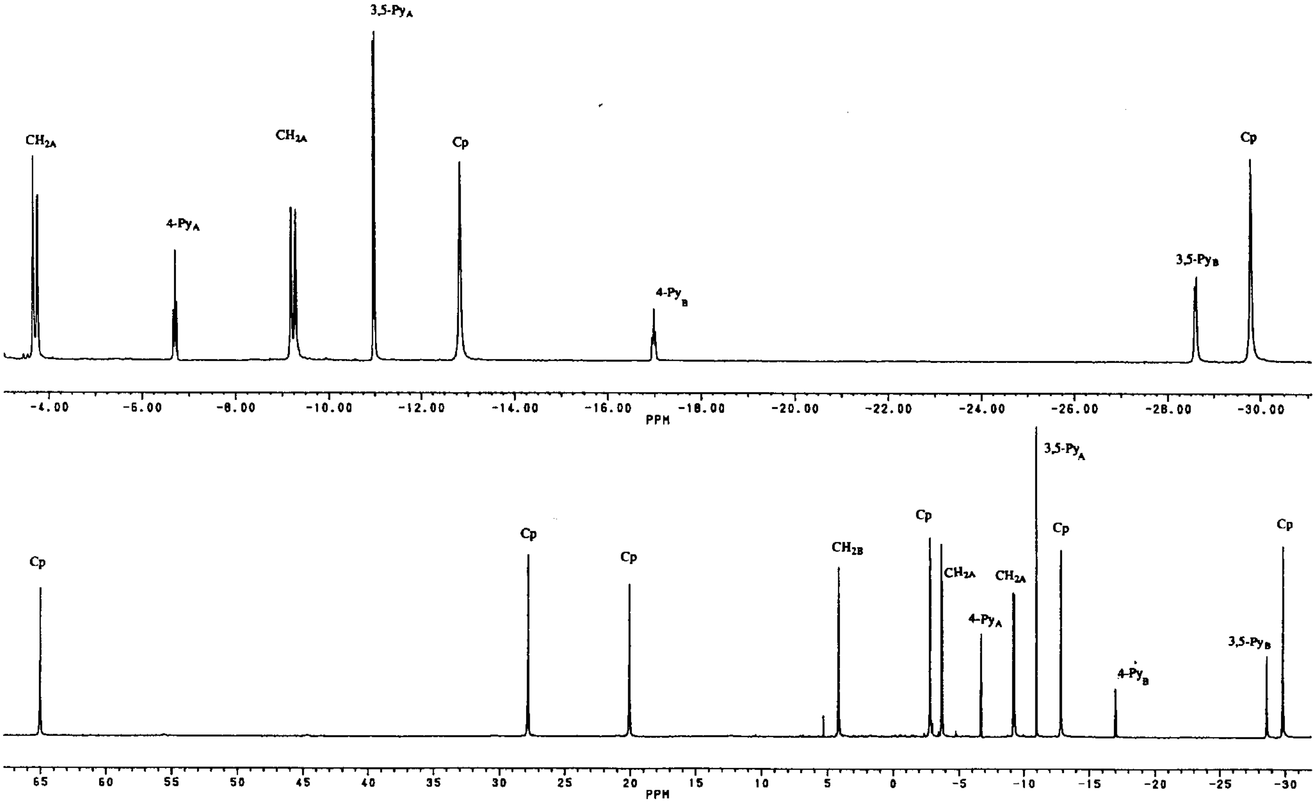
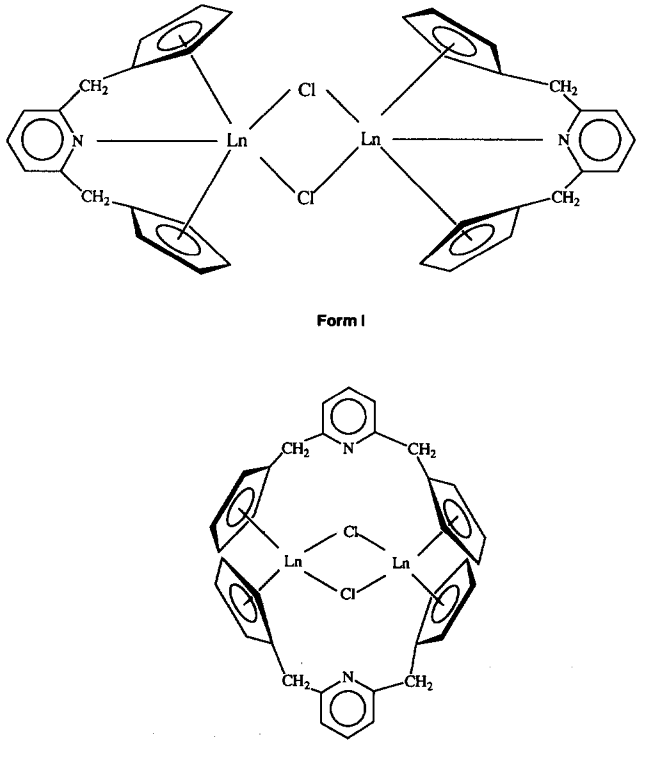


Fig. 1. ^1H NMR spectrum (CD_2Cl_2, T = 296 K) of $[L_3Pr_2]$ (**9**) (δ ppm from TMS).



Form I

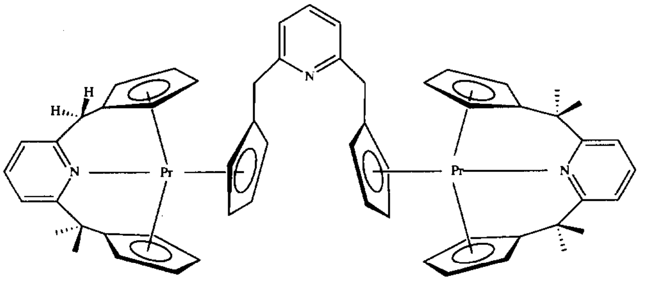
Form II

Scheme 3.

spectively, and to the CH_2 protons of the more flexible μ-L unit: δ 64.99, 27.78, 20.04, 4.15, −2.80, −12.80, −29.72 (s, 4H each). Apparently, in solution the flexibility of the bridging ligand L of **9** is similar to that of L^{2-} in its disodium salt (*vide supra*) (Scheme 4).

Complex **9** may be easily converted into $[(LPrCl)_2]$ (**2**) by reaction with equimolar quantities of $PrCl_3$. In view of the very different solubilities of Na_2L and $LnCl_3$ in THF, the product $[(LLnCl)_2]$ should always be contaminated with some $[(LLn)_2(\mu\text{-}L)]$.

The mass spectrum of **9** (EI, 70 eV, $T_{probe} = 300°C$) displays the molecular ion at m/z 981 in low relative abundance (1%), together with peaks at m/z 608 (2) and 607 (3) assignable to the ions $[LPrLH]^{+\bullet}$ and $[LPrL]^+$, respectively, and at m/z 544 (3), 543 (5), 542 (10) and 529 (9) assignable to the ions $[LPr(C_5H_4)CH_2C_5H_3NCH_3]^{+\bullet}$, (**A**), $[\mathbf{A} - H]^+$, $[\mathbf{A} - 2H]^{+\bullet}$ and $[\mathbf{A} - Me]^+$, respectively. Moreover, the presence of ions at m/z 439 (2) assignable to $[LPr(C_5H_5)]^{+\bullet}$, at m/z 206 (11) due to $[C_5H_5Pr]^+$ and at m/z 171 (9) and 170 (10) assignable to $[C_5H_5CH_2\text{-}C_5H_3N\text{-}CH_3]^{+\bullet}$ and $[C_5H_5CH_2\text{-}C_5H_3N\text{-}CH_2]^+$, respectively, is indicative of asymmetric cleavage of the bridging L unit in $P^{+\bullet}$. The low abundance of $P^{+\bullet}$ prevents reproducible B/E-linked scan experiments.



Scheme 4.

TABLE 6. Hydrogenation of hex-1-ene with $[(LLnCl)_2]$/NaH [a]

Molar ratio		Yield (%)
1-Hexene/$LiAlH_4$/[LDyCl]	(1:4:0.2)	97
1-Hexene/$LiAlH_4$/[LDyCl]	(1:4:0.1)	68
1-Hexene/$LiAlH_4$/[LDyCl]	(1:2:0.2)	99
1-Hexene/$LiAlH_4$/[LErCl]	(1:2:0.2)	72
1-Hexene/$LiAlH_4$/[LLuCl]	(1:2:0.2)	23
1-Hexene/$LiAlH_4$/[LYCl]	(1:4:0.2)	47

[a] Reaction conditions: 65°C, 24 h, THF.

2.1. Catalytic activity

Complexes $[(LLnCl)_2]$ with Ln = Pr and Nd could not be converted by NaH into the corresponding hydrides, $(LLnH)_n$, initial experiments of the type shown in eqn. (2)

$$\text{hex-1-ene} \xrightarrow[{[(LLnCl)_2]}]{LiAlH_4/THF(refl.)} \text{hexane} \qquad (2)$$

indicate that apparently catalytically active, intermediate, $(LLnH)_n$ may be obtained.

Some preliminary results on the catalytic properties of $[(LLnCl)_2]$ in the reduction of hex-1-ene by $LiAlH_4$ are reported in Table 6.

3. Experimental details

All manipulations were carried out with rigorous exclusion of oxygen and moisture, either in flamed Schlenk-type glassware or a dual manifold Schlenk line interfaced with a high-vacuum line. Alternatively, a prepurified dinitrogen-filled BRAUN 200 MB glovebox with a high capacity recirculator was used (average concentrations of O_2 and H_2O in the glovebox monitored by the BRAUN Oxygen and Moisture Analyzers were ≤ 1 ppm). Dinitrogen and argon (SIAD) were purified by passage through a supported MnO oxygen-removal column and a Davison 4-Å molecular sieve column. Tetrahydrofuran was sequentially refluxed and distilled over finely divided $LiAlH_4$ and K/benzophenone immediately before use. Aliphatic hydrocarbons were pretreated with concentrated sulphuric acid. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all ≥ 99 at.% D) and were degassed (by freeze-thaw cycles) and dried over Na/K alloy (benzene-d_6, toluene-d_8, tetrahydrofuran-d_8) or P_2O_5 ($CDCl_3$) before use. Anhydrous metal trichlorides were prepared from the corresponding oxides [19] and used either as obtained or after conversion to the corresponding THF adducts by Soxhlet extraction with THF. 2,6-Pyridinedimethanol (Aldrich) and $SOCl_2$ (Aldrich) were used as obtained.

Infrared spectra were recorded on Perkin Elmer 983 IR spectrometer as Nujol and Fluorolube mulls and examined between disk-shaped CsI and KBr plates, respectively, in an O-ring sealed, air-tight holder. Mass spectra were recorded on either a Finnigan 4021 or a ZAB 2F (V.G.) spectrometer. Samples were prepared in the glovebox in sealed gass capillaries; these capillaries were opened under argon and introduced by a direct inlet procedure.

^1H NMR spectra were recorded on either a JEOL FX-90Q (90 MHz) or a Bruker A 200 (200 MHz) spectrometer. Chemical shifts were referred to internal solvent resonances and finally referenced to TMS.

X-Ray photoelectron spectra (XPS) were recorded on a NP-1 spectrometer equipped with a Mg Kα X-ray source.

Elemental analyses (C, H, N, Cl) were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, Germany. Analyses of rare earth metals were carried out using a direct complexometric titration procedure with disodium EDTA [20].

3.1. $Na_2[2,6\text{-}(CH_2C_5H_4)_2\text{-}C_5H_3N]$

To a magnetically stirred solution of sodium cyclopentadienide (12.637 g, 0.1436 mol) in 400 ml of THF, a solution of 2,6-bis(chloromethyl)pyridine (6.318 g, 3.59×10^{-2} mol) in THF (150 ml) was added during 2 h. The mixture was stirred overnight and the NaCl then filtered off. The volume of the yellow-brown solution was reduced under vacuum to 200 ml, then hexane (100 ml) was added. The solution was set aside overnight and the extremely air- and moisture-sensitive, white crystals were filtered off, washed with several portions of hexane, and dried under vacuum (8.57 g, 85% yield). Anal. Found: C, 73.05; H, 5.45; N, 5.25. $C_{17}H_{15}NNa_2$ calcd.: C, 73.11; H, 5.41; N, 5.02%. The major infrared peaks occurred at 1591, 1572, 1452, 1447, 1415, 1377, 1365, 1155, 1055, 1036, 1022, 997, 899, 796, 714, 661, 548 cm^{-1}. ^1H NMR (THF-d_8): δ 7.54 (t, 1H, Py-$H4$, $J = 7.5$ Hz); 7.01 (d, 2H, py-$H3,5$, $J = 7.5$ Hz); 5.49 (t, 4H, Cp-protons); 5.31 (t, 4H, Cp-protons); 4.06 (s, 4H, CH_2).

3.2. $Li_2[2,6\text{-}(CH_2C_5H_4)_2C_5H_3N]$

2,6-Dichloromethylpyridine (3.159 g, 1.795×10^{-2} mol) was allowed to react in THF (150 ml) with NaC_5H_5 (3.159 g, 3.59×10^{-2} mol) (molar ratio 1:2) at 0°C. After evaporation of THF the residue was extracted with cold hexane (*ca.* −5°C). The resulting extract was reacted with Li^{n}Bu (molar ratio 1:2) at −30°C. The red-violet precipitate of pure dilithium salt was filtered off and dried under vacuum. This product is extremely air- and moisture-sensitive, and when exposed to air it becomes instantaneously colourless and only some minutes thereafter dark-brown.

3.3. $[(LYCl)_2]$ (1)

To a magnetically stirred suspension of anhydrous yttrium trichloride (0.388 g, 1.895 mmol) in 40 ml of THF at −30°C (or at room temperature), a solution of pyridine-2,6-bis(methylenecyclopentadienyl) disodium salt (0.563 g, 1.895 mmol) in 30 ml of THF was added during 1 h. The reaction mixture was stirred for 2 h at −30°C, then allowed to warm up to room temperature, and stirred for 2 days. The suspension was filtered through a Celite-packed frit, and the solvent removed under reduced pressure. The crude product was extracted with three portions of toluene (30 ml each). The toluene solution was evaporated to dryness under reduced pressure giving an analytically pure yellow-orange solid (0.44 g ≈ 65% yield). IR: 3078m, 2964s, 2923m, 2890s, 1605m, 1575m, 1460s, 1417m, 1260w, 1160w, 1095w, 1038m, 1008m, 828m, 780s, 660w, 374w, 359w, 322vw, 281w, 230m cm^{-1}.

3.4. $[(LPrCl)_2]$ (2), $[(LNdCl)_2]$ (3), $[(LSmCl)_2]$ (4), $[(LDyCl)_2]$ (5), $[(LErCl)_2]$ (6), $[(LYbCl)_2]$ (7), $[(LLuCl)_2]$ (8)

The preparations followed closely the synthesis of **1**. The colours, yields and analytical data of the compounds **1**–**8** are summarized in Table 1.

3.5. $[(LPr)_2(\mu\text{-}L)]$ (9)

To a solution of $PrCl_3 \cdot 3THF$ (0.927 g, 2 mmol) in 120 ml of THF a solution of Na_2L (0.837 g, 3 mmol) in 100 ml of THF was added slowly under magnetic stirring (room temperature). After 24 h, the yellow precipitate was collected, washed with small portions of THF and dried. The crude product was extracted with CH_2Cl_2 (80 ml), insoluble NaCl was filtered off, and an equivalent volume of hexane was added to the clear solution. The resulting pale-yellow solid (**9**) was analytically pure (0.590 g, 60% yield). A further amount (0.177 g, 17% yield) of the product was obtained from the THF solution after solvent evaporation to small volume under vacuum. Anal. Found: C, 61.85; H, 4.30; N, 4.10; Pr, 28.25. $C_{51}H_{45}N_3Pr_2$ calcd. C, 62.39; H, 4.62; N, 4.28; Pr, 28.71%.

4. Conclusions

The 2,6-dimethylenepyridine bridging two cyclopentadienyls prevents ligand redistribution processes and allows the synthesis of the corresponding biscyclopentadienyl(lanthanoid) chlorides without any restrictions due to the different ionic radii of the lanthanides. $[(\mathrm{LLnX})_n]$ systems (where $X = H$, alkyl, etc.) may have catalytic applications (olefin hydrogenation or polymerization) and further experimental work is in progress. In addition, compound **9** is, to our knowledge, a new example of the still rare class of polynuclear organolanthanide complexes that contain the same ligand $(C_5H_4)_2(\mu\text{-}X)$ both in the chelating and the metal-bridging mode. An analogous behaviour has most recently been observed for some related U^{IV} and Zr^{IV} [21] complexes.

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