

# The Synthesis and Nuclear Magnetic Resonance Investigation of the Structure and Chemical Dynamics of New Anionic Tetra-allyl Complexes of Lanthanide Ions

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## Abstract

The synthesis and spectroscopic characterization of  $\text{LiLn}(\text{allyl})_4$  dioxane ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}$ ) from  $\text{LnCl}_3$  and  $\text{Sn}(\text{allyl})_4$  are described.

The dynamic behaviour of  $\text{LiSm}(\text{allyl})_4$  at high and low temperatures was studied and activation parameters were determined. An unusually pronounced broadening of line-width was observed at low temperature for  $\text{LiNd}(\text{allyl})_4$  and  $\text{LiCe}(\text{allyl})_4$  complexes.

## Introduction

The synthesis and catalytic properties of allyl compounds have been extensively dealt with in a number of papers and reviews. Neutral allyl complexes of trivalent lanthanide metals are unknown at this time and our attempts to synthesize them were also unsuccessful.

Several allyl compounds show temperature-dependent NMR spectra and the activation energy of the rotation-barrier is satisfactorily determined by line shape analyses.

Pure anionic compounds of the trivalent lanthanide metals were synthesized in our laboratories and preliminary data were presented by the authors at the NATO ASI conference held in Urbino in 1978

[1a]. A brief summary on the synthesis and catalytic properties has been given by Prof. A. Mazzei in a review [1b]. The present paper reports the complete data obtained in our study.

## Experimental

All operations were carried out under dry oxygen-free nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use.

Infrared spectra were recorded with a Perkin-Elmer 125 and 225 spectrophotometer. Nujol mulls were prepared in a nitrogen filled sleeve with dry, degassed Nujol.

$^1\text{H}$  NMR spectra were obtained in the FT mode on a Varian XL 100 instrument at 100.1 MHz. Samples for  $^1\text{H}$  NMR spectra were dissolved in deuteriotetrahydrofuran and sealed under vacuum. All chemical shifts were determined with reference to internal benzene or TMS. Probe temperatures were determined before and after every spectrum using methanol.

The DNMR3 computer program was used to calculate the simulated spectra [2a–c]. The best fit was obtained using  $T_2$  values = 0.032 and 0.079 s. The chemical shifts at high temperature were extrapolated by a graphical method.

TABLE I. Yields and Chemical Analyses

Complex <sup>a</sup>	Colour	Yield <sup>b</sup> (%)	Analyses (%)								Propylene <sup>c</sup> Ln	Dioxane <sup>d</sup> Ln
			Li		Ln		C		H			
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.		
$\text{LiCeA}_4\cdot\text{B}$	violet	90	1.65	1.74	33.8	35.11	48.5	48.12	7.35	7.02	3.8	1.3
$\text{LiNdA}_4\cdot\text{B}$	yellow	70	1.63	1.72	34.5	35.78	48.4	47.62	7.46	6.94	3.7	1.3
$\text{LiSmA}_4\cdot\text{B}$	orange	50	1.65	1.70	35.8	36.74	47.3	46.91	7.10	6.84	3.9	1.2
$\text{LiGdA}_4\cdot\text{B}$	yellow	50	1.58	1.67	35.2	37.78	47.5	46.13	7.20	6.73	3.7	1.4
$\text{LiDyA}_4\cdot\text{B}$	brown	65	1.56	1.65	36.6	38.56	46.7	45.56	6.95	6.64	3.7	1.3

<sup>a</sup>B = dioxane; Sn and Cl were absent (0.2%) in all cases.

<sup>b</sup>Based on recovered Ln after precipitation with dioxane.

<sup>c</sup>Gas-

volumetric analyses, butane was absent.

<sup>d</sup>GLC analyses.

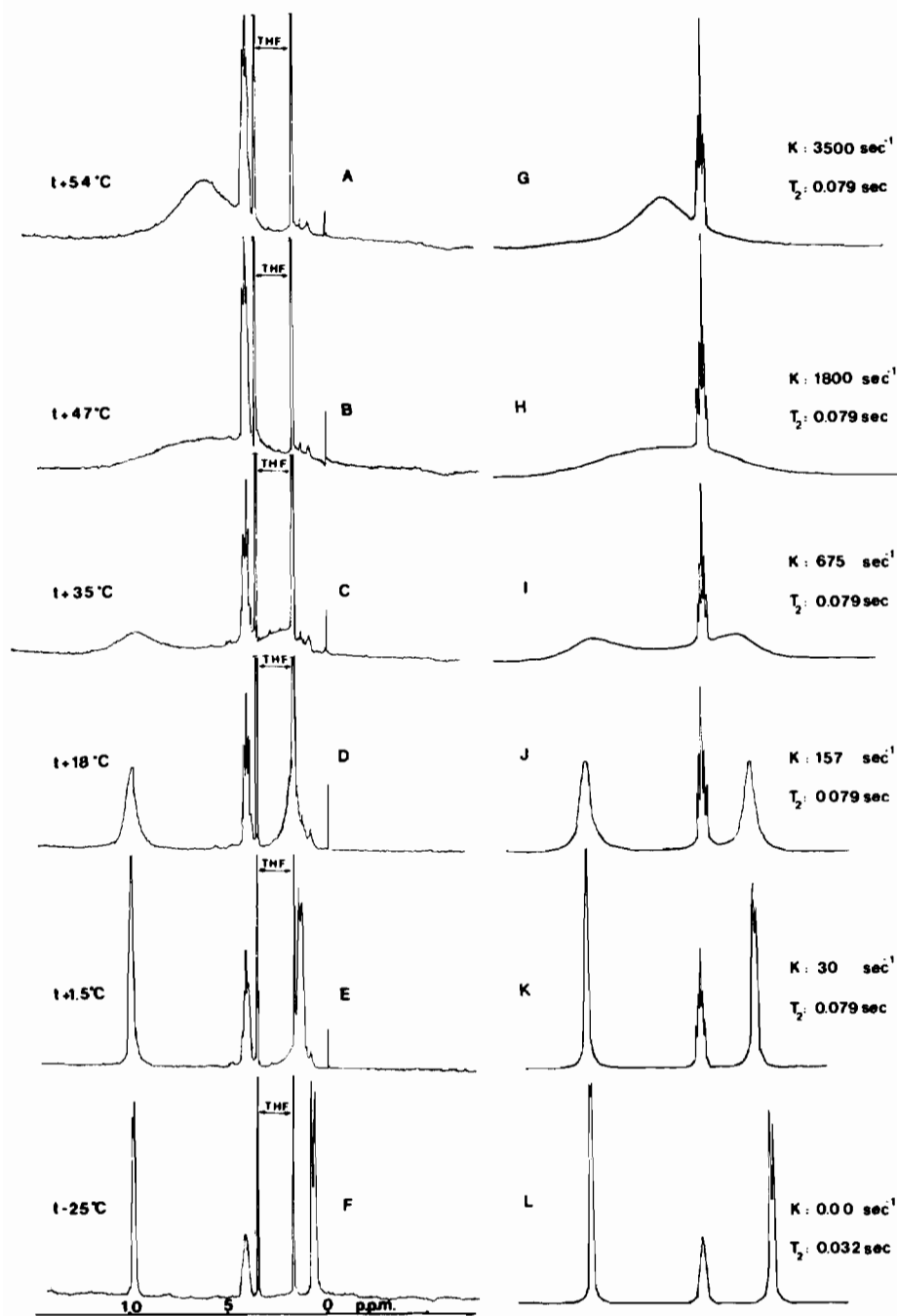


Fig. 1.  $^1\text{H}$  NMR spectra of  $\text{LiSm}(\text{allyl})_4$  at various temperatures in  $\text{THF-d}_8$ ; (A–F) experimental, (G–L) simulated.

#### Synthesis of $\text{LiLn}(\text{allyl})_4$

Butyllithium (2.35 N) in *n*-hexane was added dropwise at room temperature to a mixture of the appropriate lanthanide trichloride (0.015 mol) and tetra-allyltin (0.015 mol) in tetrahydrofuran (70  $\text{cm}^3$ ). The lanthanide trichloride dissolved slowly; the suspension was stirred overnight and the tetrahydrofuran became deeply coloured. Solvent was removed

*in vacuo* at room temperature and the residue washed with *n*-hexane ( $3 \times 20 \text{ cm}^3$ ) to remove tetrabutyltin, dried and then extracted with diethyl ether ( $5 \times 50 \text{ cm}^3$ ). Dry dioxane (50 ml) was added to the filtered ethereal solution. A coloured precipitate was formed which was collected and dried *in vacuo* at room temperature. Yields and analytical data are shown in Table I.

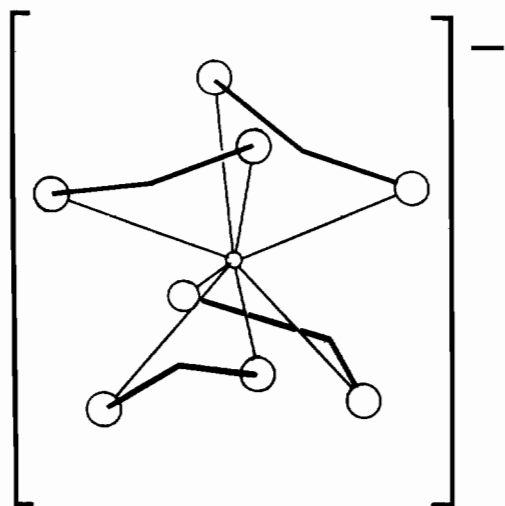


Fig. 2. Trihapto configuration of the four allyl ligands in a tetrahedral complex.

TABLE II. Proton Chemical Shifts for  $\text{LiLn}(\eta^3\text{-C}_3\text{H}_5)_4$  (Ln = Ce, Nd, Sm, in ppm from benzene)

Complex	Temperature (°C)	Chemical shifts <sup>a, b</sup>		
		H <i>syn</i>	H <i>anti</i>	H methine
LiCe(allyl)	28	-3.40	18.37	27.74
	-6.5	-5.22	20.51	32.94
	-18	-5.85	21.31	34.66
	-39	-7.19	22.60	38.02
	-62	-9.14	24.42	42.75
	-73	-9.61	25.88	45.47
	-96	-11.50	29.40	51.80
-108	-12.70	31.20	55.50	
LiNd(allyl)	26	15.67	35.65	25.68
	15	15.53	42.01	32.68
	-34	15.21	46.37	37.34
	-55	14.80	51.63	42.76
	-72	14.07	57.91	49.89
LiSm(allyl) <sup>c</sup>	26	-2.49	5.76	3.16
	-33	-2.54	6.62	2.98
	-52	-2.47	7.35	2.93
	-75	-2.77	7.23	2.83

<sup>a</sup>Chemical shifts are in ppm from benzene as internal standard. <sup>b</sup>The assignments of the *syn* and *anti* protons can be interchanged for Ce and Nd complexes. <sup>c</sup>The *J* values in LiSm(allyl) are 7.7 Hz for the low field and 15.3 Hz for the high field doublets.

#### Gas-volumetric Analysis

Hydrolysis was effected in a gas-volumetric apparatus by decomposing the sample with diglyme-water. The gas was collected, measured and analysed by GLC and the dioxane content in the liquid phase was also determined.

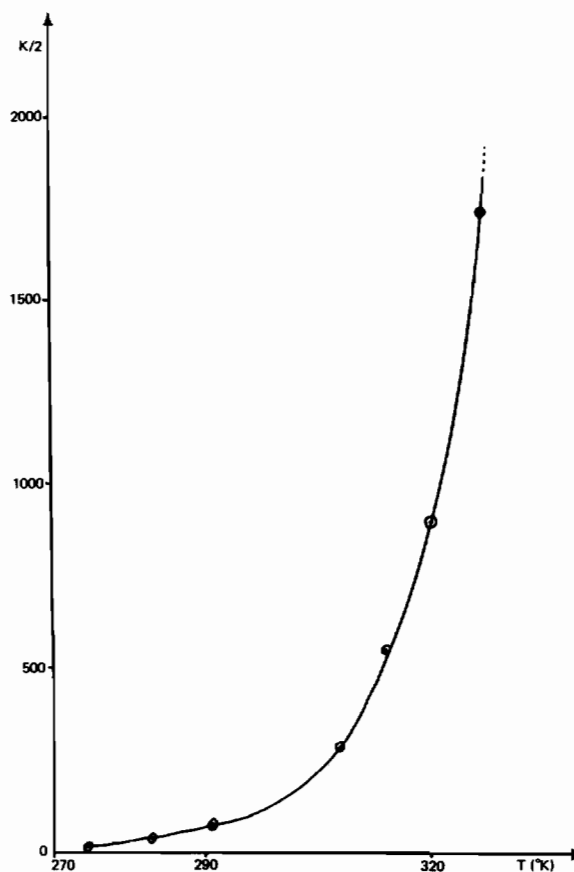
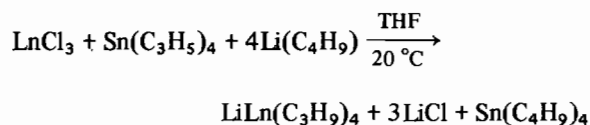


Fig. 3. Variation of  $K/2$  with temperature.

#### Results and Discussion

Lanthanide tetra-allyl complexes were prepared according to the reaction:



Ln = Ce, Nd, Sm, Gd, Dy

Although tetra-allyl derivatives can be recovered by removing the solvent after ether extraction, the best results were obtained by precipitating them as dioxane complexes. Their lack of solubility in common organic solvents prevented any further purification. Thus, the chemical analyses are not totally satisfactory especially as far as the dioxane/Ln ratio is concerned.

All derivatives are thermally stable but are oxygen and moisture sensitive; they burn in air and must be handled and stored under nitrogen.

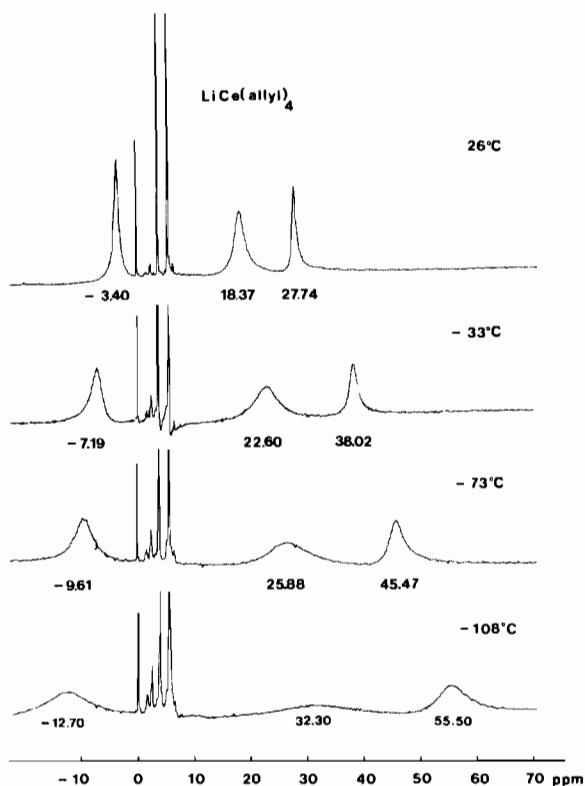


Fig. 4.  $^1\text{H}$  NMR spectra of  $\text{LiCe}(\text{allyl})_4$  at various temperatures.

The infrared spectra of all complexes are very similar and show absorptions at 3060, 1535, 1370, 1290, 1250, 1230, 1105, 1070, 1005, 995, 860, 720, 705, 670, 610 and  $590\text{ cm}^{-1}$ .

The trihapto conformation of the allyl group ( $C_{2v}$  local symmetry) is suggested by the presence of bands at about 1535, 1005 and  $670\text{--}590\text{ cm}^{-1}$ , which can be tentatively assigned to the ( $\nu_{\text{CCC}}$ ) asymmetric stretching, ( $\nu_{\text{CCC}}$ ) symmetric stretching and ( $\delta_{\text{CCC}}$ ) skeletal deformation, respectively. It should be noted that the asymmetric stretching appears at about 150 wavenumbers higher than the corresponding vibration mode recorded for the transition metal trihapto-allyl derivatives [3]. A similar trend was found in the case of the bis(allyl)-bis(alkoxo)uranium derivatives, where the trihapto conformation was confirmed by X-ray analyses [4].

$^1\text{H}$  NMR analyses were carried out only on Sm, Ce and Nd derivatives.  $\text{LiSm}(\text{allyl})_4$  spectra were recorded from  $-18$  to  $54^\circ\text{C}$ . The low temperature spectrum shows the usual  $\text{AM}_2\text{X}_2$  pattern with four equivalent trihapto allyl ligands (Figs. 1, 2). The coupling constants enabled the *syn* and *anti* protons to be assigned unequivocally (Table II). The pattern shows a considerable broadening of line width as the temperature increases up to  $+54^\circ\text{C}$  (Fig. 1a–f).

An intramolecular *syn*  $\rightleftharpoons$  *anti* exchange of the  $\text{AM}_2\text{X}_2 \rightleftharpoons \text{AX}_2\text{M}_2$  type was assumed to explain the dynamic behaviour. The  $K_1$  values were obtained by

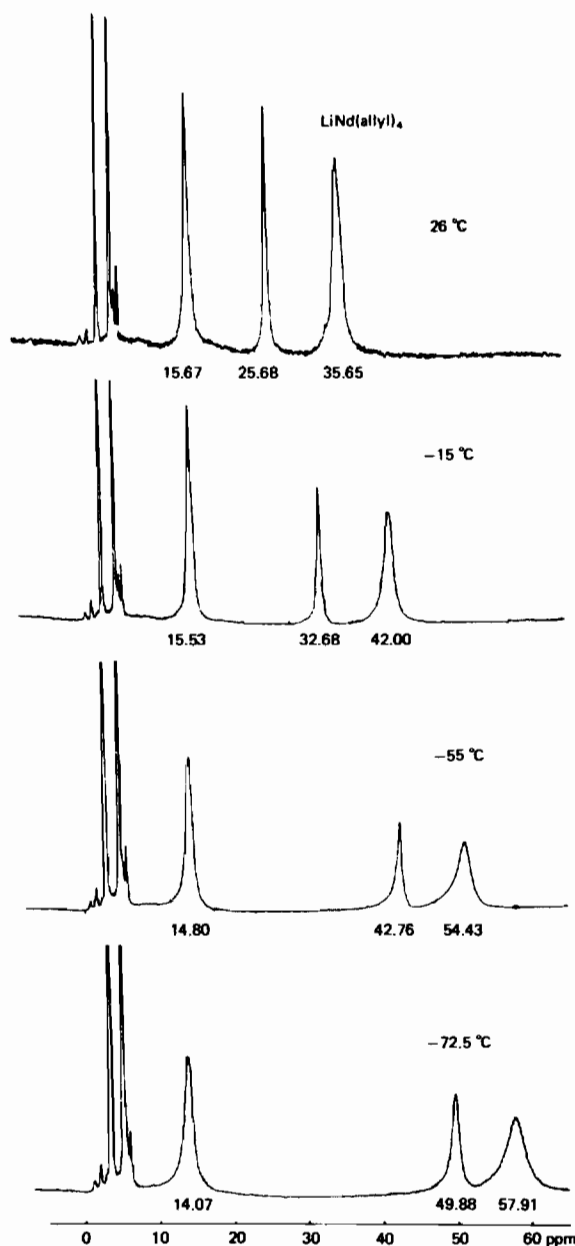


Fig. 5.  $^1\text{H}$  NMR spectra of  $\text{LiNd}(\text{allyl})_4$  at various temperatures.

matching experimental and calculated spectra using the DNMR3 program. From the  $K_1$  values an activation energy ( $\Delta G^\ddagger + 15.7\text{ kcal/mol}$ ) was obtained (Fig. 3). In both Ce and Nd complexes *syn* and *anti* exchange did not occur at room temperature (Figs. 4, 5).

As far as the isotropic shift is concerned, a linear dependence on the temperature was observed for all protons (Table II, Fig. 6). However, the best fit was obtained with an equation similar to that shown below (see refs. 7a–c).

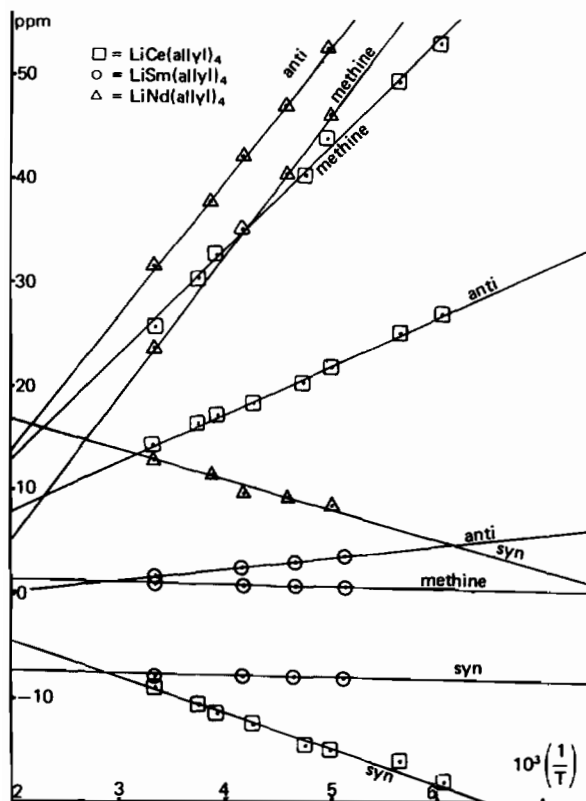


Fig. 6. Chemical shifts of some  $\text{LiLn}(\text{allyl})_4$  derivatives as a function of temperature.

$$\delta = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2}$$

It should be noted that an unusual pronounced broadening of resonance lines was observed when

the temperature was lowered. Two explanations merit attention:

(i) the lower the temperature the longer the electronic relaxation times ( $T_{1e}$ ). Hence modulated fields are produced which in turn reduce the life-times of nuclear states.

(ii) Lithium and lanthanoid ( $\text{C}_3\text{H}_5$ )<sub>4</sub> ions can be regarded as ion-pairs. At low temperature the lithium cation remains in a more fixed position and, as a consequence, the four allyl ligands become unequal.

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