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Lanthanum-139 NMR Spectroscopy of Triscyclopentadienyllanthanum(III) Derivatives: a Promising New Tool for Solution Studies*[†]

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Lanthanum-139 belongs to the three most promising 'NMR nuclei' out of the 17 'earliest' transition elements Sc, Y and La–Lu [1] (Table I). Because of the paramagnetism of all tripositive lanthanoid ions (except Lu(III)), and the reportedly [1, 2] rather long scanning time in ^{89}Y NMR spectroscopy, ^{139}La appears, from a practical point of view, superior to all other principally suitable nuclei of genuine lanthanoids including even ^{89}Y.

TABLE I. Properties of the Nuclei ^{45}Sc, ^{89}Y and ^{139}La (from ref. 6)

Nucleus	^{45}Sc	^{89}Y	^{139}La
Natural abundance (%)	100	100	99.1
Nuclear spin, I	7/2	1/2	7/2
Nuclear quadrupole moment[a]	−0.22	0	0.21
Relative sensitivity[b]	0.301	1.18×10^{-4}	0.059

[a]Qe in barns. [b]By comparison with ^{1}H.

Although the first ^{139}La NMR experiments date back to 1949 [3], comparatively few ^{139}La NMR studies have been reported in the meantime [4, 5]. Most of these investigations deal with analytically ambiguous samples in aqueous solution.

The present communication is, after two short notes [6, 7], the first more systematic consideration of one distinct and principally quite well-understood class of organolanthanoid(III) complexes [8] with lanthanum as the central metal:

$$[\mathrm{Cp_3La{\cdot}L}_n]^q \quad (\mathrm{Cp} = \eta^5\text{-}\mathrm{C_5H_5} \text{ or } \eta^5\text{-}\mathrm{C_5H_4CH_3};$$
$$\mathrm{L} = \text{monodentate ligand}; n = 0\text{–}2; q = 0 \text{ or } -1)$$

Although the majority of the La(III) complexes considered here have not been described before*, it appears justified to assume pseudotetrahedral (ψ-T$_d$) coordination for $n = 1$ (with a total hapticity of 16 for η^1-L), and trigonal bipyramidal (tbp) coordination in the case of $n = 2$ (with a total hapticity of 17). In view of the high electric quadrupole moment of the ^{139}La nucleus which makes the half-width $W_{1/2}$ of its resonance signal very sensitive to changes in the symmetry and the electric field gradient of the ligand sphere, it is important to emphasize here that, for example within the most abundant sub-class with $n = 1$, only minor variations of the spatial ligand arrangement can occur.

Experimental

All complexes investigated were analytically well characterized*, and handled strictly under pure N_2; most of them have also been examined by infrared and ^{1}H NMR spectroscopy. Until now, around 50 individual samples of more than 30 different compounds have been subjected to ^{139}La NMR spectroscopy. Apart from only a few exceptions, CH_2Cl_2/CD_2Cl_2 mixtures (1:1) were used as the optimal solvent; saturated solutions were studied in 10 mm NMR tubes containing a coaxially centered 4 mm tube with a solution of $La(NO_3)_3{\cdot}6H_2O$ in H_2O as external standard.

A Bruker multinuclear NMR spectrometer AM 360 was used throughout (50.87 MHz, deuterium lock, room temperature). Average scanning time: 30–60 min; reproducibility of $\delta(^{139}\mathrm{La})$: ±1 ppm (depending on the $W_{1/2}$ value).

Results

While the majority of the NMR samples (group a) give rise to usually one well-detectable resonance signal, a few samples appear either fully 'NMR-silent' (group b) or do not show any signal until the ligand L has been added in excess (group c). To date, the only representative of group b is the base-free complex $(C_5H_5)_3La$ [6] which is known to form poorly soluble oligomers $[(C_5H_5)_3La]_n$ [9]. The considerably more soluble, but likewise notably associated [10], homologue $(C_5H_4CH_3)_3La$ belongs to group a, but both its $\delta(^{139}\mathrm{La})$ value and the line-width $W_{1/2}$ reach the largest values of all so far examined samples (Table II). The observability of a ^{139}La resonance

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*Earlier described adducts of $(C_5H_5)_3La$ have been marked in the Tables by an asterisk. Space limitations imposed on the present paper will delay a detailed description of all other compounds.

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TABLE II. Present Extension of the Chemical Shift $\delta(^{139}La)$; Standard ($\delta \equiv 0$): $La(NO_3)_3 \cdot 6H_2O$ in H_2O

	Hitherto reported range of $\delta(^{139}La)$	Extended range of $\delta(^{139}La)$
$\delta(^{139}La)$ (ppm)	+1090 to −129	−380 to −614
Samples	$[LaBr_6]^{3-} \cdots [La(NCCH_3)_n]^{3+}$	$(C_5H_4CH_3)_3La \cdots (C_5H_5)_3La(CNR)_2$
Reference	5	present work

signal is thus indicative of a reaction of $(C_5H_5)_3La$ and L. First examples of group c have been the three well-isolable 1:1 adducts with L = dioxane, 2,6-dimethylxylylamine and *p*-cyanopyridine (Tables IV–VI).

The three pentahapto-coordinated cyclopentadienyl ligands displace all chemical shifts $\delta(^{139}La)$ towards dramatically higher magnetic field strengths than have so far been reported for any ^{139}La NMR sample [4, 5] (Table II). This pronounced high-field shift which has also been observed in the case of other NMR nuclei surrounded by at least two η^5-cyclopentadienyl [7] or even η^6-arene [11] ligands, respectively, seems to reflect the generally observable dependence of the position of the resonance line from the actual coordination number.

1:1 Adducts ($(C_5H_5)_3La \cdot L$ with $q = 0$) display uniformly one La resonance signal in the range −508 to −578 ppm. As long as some special findings are ignored, ^{139}La appears to behave, in accordance with earlier findings [4], as a so-called 'inverse-order nucleus'. Thus for a selected number of examples (Table IV) even a satisfactorily linear variation of $\delta(^{139}La)$ with the pK_B value of the base L can be formulated. A more detailed view of the sub-group of amine adducts (Table V), leads, however, to the impression that proton basicity might not necessarily be an optimal quantity for further correlations.

TABLE III. ^{139}La Spectroscopic Results of some $(C_5H_4CH_3)_3La$ Derivatives

L^q	δ (ppm)	$W_{1/2}$ (Hz)	$\lvert\Delta\delta\rvert$ (ppm)[a]
CH_3CN	−533	1450	45
THF	−513	3300	44
F^- [b]	−437[c]	500	44
−*	−380	11800	

[a] From corresponding $[(C_5H_5)_3La \cdot L]^q$ (q = electric charge) [b] Cation: $[(CH_3)_4N]^+$. [c] No other resonance detectable (see, for comparison, Table VIII).

TABLE IV. Attempted Correlation of $\delta(^{139}La)$ and the (Proton) Basicity of L

Nature of L	$\delta(^{139}La)$ (ppm)	pK_B [14]
Aliphatic amines	−508 to −525	3.5 ± 1.0
Pyridines	−540 to −545	8.5 ± 0.5
Cyclic ethers	−549 to −558	13 ± 3
p-Cyanopyridine	−556	15.9
Aliphatic nitriles	−575 to −578	22 ± 2

The line widths $W_{1/2}$ of analytically pure samples range from *ca.* 100 to 2650 Hz, and turn out to be more strongly governed by the steric bulk of the ligand L than the chemical shift (Tables V and VI). In view of the uniform construction of the ligand sphere around the ^{139}La nucleus in all $(C_5H_5)_3La \cdot (\eta^1\text{-}L)$ species, a strong increase in $W_{1/2}$ could be best explained by a notable enhancement of adduct dissociation according to the equilibrium:

$$n(C_5H_5)_3La \cdot L \xrightleftharpoons[\text{(rapid exchange)}]{\text{solvent}} [(C_5H_5)_3La]_n + nL$$

Actually, the adduct with triethylamine has, like that with diethylether, turned out to be too labile for isolation.

Table VII presents a few examples that demonstrate the influence of the concentration of L (c_L) and/or of the nature of the solvent on $\delta(^{139}La)$ and $W_{1/2}$: while the signal of the dioxane adduct is not observable until dioxane has been added in considerable excess (group c, *vide supra*), both δ and $W_{1/2}$ of the diethylamine adduct remain insensitive to wide variations in c_L. In good accordance with the different spectroscopic data of the piperidine and

TABLE V. Comparison of pK_B of L and of $\delta(^{139}La)$ and $W_{1/2}$ of the Corresponding Complexes $(C_5H_5)_3La \cdot L$

Base	pK_B of L	$\delta(^{139}La)$ (ppm)	$W_{1/2}$ (Hz)
$NH(CH_2)_5$[a]	2.72	−520	200
$NHEt_2$	2.98	−525	500
$NHMe_2$	3.22	−519	550
NH_2Me	3.37	−514	100
$NH_2(CH_2)_2Me$	3.40	−514	200
NH_2CHMe_2	3.44	−518	200
NMe_3	4.20	−508	2450
NH_3	4.75	−518	150
NH_2CH_2Ph	4.97	−515	350
$NH(CH_2)_4O$[b]	5.64	−522	500
NH_2Ph	9.31	−519	2100

[a] Piperidine [b] Morpholine.

TABLE VI. Comparison of $\delta(^{139}La)$ and $W_{1/2}$ of Pairs of Complexes with Chemically Similar Ls of Different Steric Congestion

Base L	$W_{1/2}$ (Hz)	$\delta(^{139}La)$ (ppm)
THF*	450	−558
2-Me-THF	2650	−549
NH_3	150	−518
NMe_3	2450	−508
NH_2CHMe_2	200	−518
$NH_2(2,6\text{-}Me)_2C_6H_3$	2450	−518
γ-Picoline	250	−540
α-Picoline	2100	−544

dioxane adducts, respectively (Tables V and VII), morpholine seems to be exclusively N-coordinated. On the other hand, both β-picoline and (−)-nicotine (≙3-(1-methyl-2-pyrrolidyl)-pyridine) display rather similar changes of δ and $W_{1/2}$ when the solvent CH_2Cl_2 is replaced by $C_6H_5CH_3$. This feature, as well as the incompatibility of the actual values of δ and $W_{1/2}$ with those of the NR_3- and NHR_2-adducts, are strongly in favour of exclusive coordination of the aromatic N atom in the 1:1 adduct with nicotine. *p*-Cyanopyridine, another principally ambidentate N-base, is, on the other hand, most probably involved in rapid exchange of its two isomeric 1:1 adducts.

The notable decrease in both δ and $W_{1/2}$ as c_L of $NCCH_3$ is increased signals a concomitant growth of the concentration of the tbp-configurated 1:2 adduct:

$$(C_5H_5)_3La\cdot NCCH_3 \xrightarrow[\text{(rapid exchange)}]{NCCH_3} (C_5H_5)_3La(NCCH_3)_2$$

Corresponding variations of δ and $W_{1/2}$ as a function of an increasing average coordination number take

TABLE VII. Variation of $\delta(^{139}La)$ and $W_{1/2}$ with the Nature of the Solvent and/or of the Concentration of L

Base	Solvent	Analytically pure 1:1-adduct[a]	Adduct plus excess L[b]
Dioxane	CD_2Cl_2/CH_2Cl_2	[c]	−552 (1800)
$NHEt_2$	CD_2Cl_2/CH_2Cl_2	−525 (450)	−524 (450)
β-Picoline	CD_2Cl_2/CH_2Cl_2	−540 (300)	
β-Picoline	toluene/toluene-d_8		−545 (700)
(−)-Nicotine	CH_2Cl_2/CD_2Cl_2	−541 (450)	
(−)-Nicotine	toluene/toluene-d_8		−552 (1350)
$NCC(CH_3)_3$	CH_2Cl_2/CD_2Cl_2	−575 (1000)	
$NCCH_3$[d]*	CH_2Cl_2/CD_2Cl_2	−578 (1200)	
$NCCH_3$	CH_2Cl_2/CD_2Cl_2	−577 (900)[e]	−596 (500)
$NCCH_3$	CH_3CN/CD_3CN		−606 (600)

[a] $W_{1/2}$ values in parentheses. [b] *ca.* 10^3-fold. [c] Signal not observable. [d] Or NCC_2H_5. [e] Pure 1:2 adduct.

TABLE VIII. ^{139}La Spectroscopic Results of Various Adducts with Anionic Ligands L^-

Sample dissolved in CH_2Cl_2/CD_2Cl_2	$\delta(^{139}La)$[a] (ppm)	
$[P(C_6H_5)_4][(C_5H_5)_3LaCl]$	−474 (150)	
$[P(C_6H_5)_4][(C_5H_5)_3LaBr]$[b]	−472 (200)	
$[N(n\text{-}C_4H_9)_4][(C_5H_5)_3LaI]$	−430 (1900)	
$[P(C_6H_5)_4][(C_5H_5)_3LaBr]$	−475 (200)	−450 (250)
$[K(18\text{-crown-}6)][(C_5H_5)_3LaF]$	−481 (200)	−446 (300)
$[K(18\text{-crown }6)][(C_5H_5)_3LaOH]$	−475 (300)	−447 (600)
$[N(n\text{-}C_4H_9)_4][\{(C_5H_5)_3La\}_2CN]$	−536 (750)	−492 (1750)
$[N(n\text{-}C_4H_9)_4][(C_5H_5)_3LaNCBH_3]$	−574 (140)	
$[N(n\ C_4H_9)_4]_2[(C_5H_5)_3La(NCBH_3)_2]$		
$[N(n\text{-}C_4H_9)_4][(C_5H_5)_3LaBH_4]$	−550 (300)	−474 (550)[c]
$[Na(15\text{-crown-}5)][(C_5H_5)_3La(C_5H_5)]$	−772 (3070)[d]	−489 (250)
$[Li(THF)_4][(C_5H_5)_3La(n\text{-}C_4H_9)]$[e]	−556 (750)	−526 (5830)

[a] $W_{1/2}$ values in parentheses in Hz. [b] In the presence of strong excess of $[P(C_6H_5)_4]Br$. [c] Two weaker ^{139}La resonances occur as well. [d] Less intense than signal at −489 ppm. [e] Dissolved in THF/THF-d_8.

place when the ratio cyclohexylisocyanide/$(C_5H_5)_3La$ is varied between 1 and *ca.* 10^3 [7].

Coordination of an anionic ligand L^- to $(C_5H_5)_3La$ (Table VIII) leads frequently, but not exclusively, to displacements of $\delta(^{139}La)$ towards lower fields than -500 ppm (*i.e.*, δ is more positive than for the uncharged adduct with $N(CH_3)_3$). Deviations towards $\delta < -500$ ppm might be due to effective separations of the negatively charged atom in L^- from the ^{139}La nucleus (e.g., as with $L^- = |N{\equiv}C{-}BH_3|^-$ or $|N{\equiv}C{-}\overline{S}|^-$) and/or to a higher hapticity of L^- than one (e.g., as with $L^- = BH_4^-$ or η^5-$C_5H_5^-$). Further complications arise in the case of $L = NCBH_3^-$ in view of its capability to also form tbp adducts (making use of both $La \leftarrow N$ and $La \cdot\cdot H$ bonds).

One particularly interesting feature is that a number of analytically pure, apparently mononuclear complexes with anionic ligands L^- give rise to spectra with two well-separated ^{139}La resonances. These findings are most reasonably explained in terms of slow (on the ^{139}La NMR time-scale) equilibria of the kind:

$$2[(C_5H_5)_3LaL]^- \underset{\text{(slow exchange)}}{\overset{CH_2Cl_2}{\rightleftharpoons}} [\{(C_5H_5)_3La\}_2(\mu\text{-}L)]^- + L^-(\text{solv.})$$

$\delta(^{139}La)$ of the L-bridged binuclear anions with $L = Br^-$, F^-, and OH^- is even less negative than $\delta(^{139}La)$ of the mononuclear adduct; one plausible reason might be even more pronounced $L \rightarrow La$ π-donor bonding in the dimer.

While the assumption of a $[(\eta^5\text{-}C_5H_5)_3La(\eta^n\text{-}C_5H_5)]^-$ anion with $n = 1$ or 2 (and $\delta(^{139}La) = -489$ ppm) appears also well-supported by ^1H NMR and IR spectroscopic results*, the interpretation of the to date most negative highfield shift of -772 ppm in terms of a more labile, and less abundant, isomer $[(\eta^5\text{-}C_5H_5)_4La]^-$ may be tempting but is at present still highly speculative.

The data of Table II demonstrate that replacement of the three C_5H_5 ligands by the more electron-donating, and somewhat bulkier, $C_5H_4CH_3$ ligands leads to ^{139}La resonances which are fairly constantly shifted ($\Delta\delta(^{139}La) \sim 44$ ppm) relative to the non-methylated congeners. Not unexpectedly, the presence of the three methyl groups prevents the formation of an F-bridged binuclear anion.

In conclusion, it should be emphasized that the rather new, but undoubtedly very promising, tool of ^{139}La NMR spectroscopy of organolanthanum complexes has not yet passed from its initial 'age of collectors and hunters' into a scientifically more mature and consolidated stage. This intermediate situation should be kept in mind in view of most of the still rather tentative explanations given above.

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*See footnote on p. 315.

*Another, non-organometallic example of 'type b' is the complex $La\{N[Si(CH_3)_3]_2\}_3$.