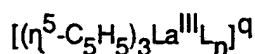


^{139}La -NMR: Investigations on Organolanthanum Compounds [1]

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Previous solution studies [2] of Lewis base (L) adducts of triscyclopentadienyl-lanthanum (III) of the type



($n = 0, 1$ and $q = 0$ or -1),

via ^{139}La -NMR spectroscopy, dealing mainly with nitrogen-coordinating ligands (e.g. nitriles, amines, pyridines), yielded comparatively sharp signals (minimum at $100\text{ Hz} = W_{1/2}$) in a new range of chemical shifts (-300 to -700 ppm rel. to $\text{La}(\text{NO}_3)_3$ aq). In the present contribution, these studies have been extended to some oxygen bonded ligands (L) to examine whether

- the features mentioned above (in view of chem. shifts and linewidth) are most common within the complex family $(\text{C}_5\text{H}_5)_3\text{La}\cdot\text{L}_n$,
- the exceptional properties are dominated by the influence of the ligands or the Cp_3La -system itself,
- the presently discussed sub-class will, similarly to that with N-bonded ligands, display any helpful analytical potential.

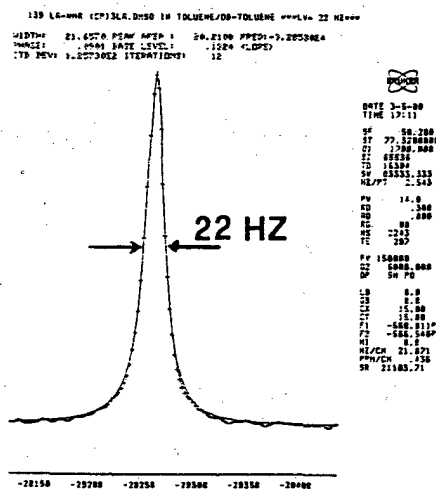
As is shown in Table 1, the chemical shifts are found in the same region as for the nitrogen-ligands, but so far the number of examples is too restricted to deduce any analytical potential from these observations.

Table 1: ^{139}La -NMR chemical shifts (CD_2Cl_2 , $\text{La}(\text{NO}_3)_3\text{aq} = 0\text{ ppm}$)

<u>Compound</u>	<u>ppm</u>
$\text{Cp}_3\text{La}\cdot\text{DMSO}$	-564
$\text{Cp}_3\text{La}\cdot\text{DMF}$	-576
$\text{Cp}_3\text{La}\cdot\text{OP}(\text{OMe})_3$	-576
$\text{Cp}_3\text{La}\cdot\text{CH}_3\text{COCH}_3$	-584
.....	
$\text{Cp}_3\text{La}\cdot\text{CH}_3\text{CN}$	-578

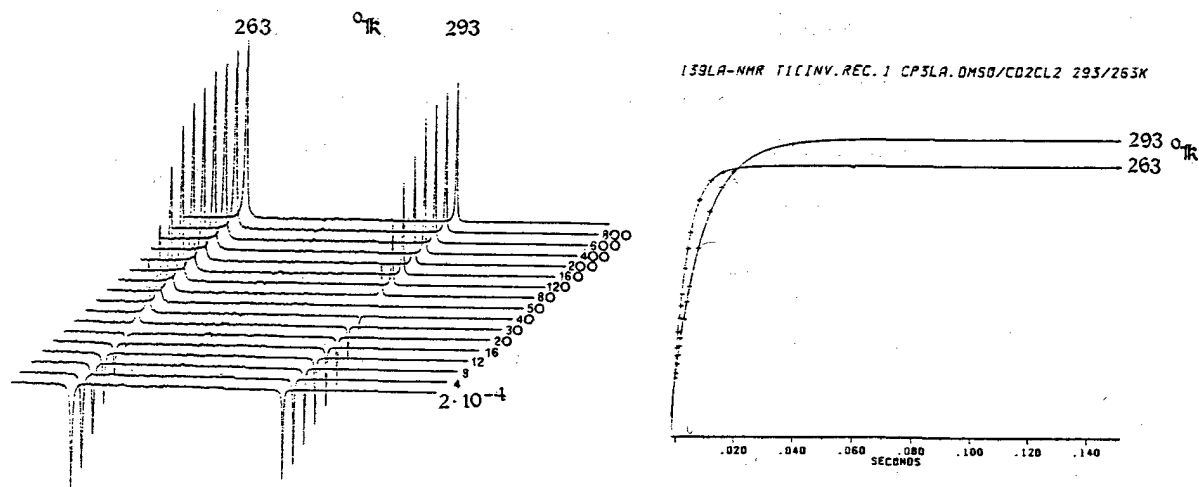
The positive trend in extraordinary linewidths culminates in a value for the Lorentzian line of 22 Hz for $\text{Cp}_3\text{La}\cdot\text{DMSO}$ in toluene- d_8 at 313K (Fig. 1). This is the best value we could achieve so far, and, to our knowledge, is the smallest value so far reported.

Fig. 1: ^{139}La -NMR signal of $\text{Cp}_3\text{La}\cdot\text{DMSO}$ in toluene- d_8 , 8.45T, 313K



Thus, the general trend of observing sharp lines is corroborated and it seems, that the Cp_3La -system dominates this behaviour, provided an electron-donating ligand is present. However, this extraordinary behaviour makes the complexes favourable for further studies, e.g. relaxation time measurements (Fig. 2). Thus, $\text{Cp}_3\text{La}\cdot\text{DMSO}$ may serve as a new ^{139}La -NMR standard in the future, not at least because its position is almost at the absolute upper end of the whole chemical shift scale.

Fig. 2: Inversion Recovery T_1 -measurements of $\text{Cp}_3\text{La}\cdot\text{DMSO}$ in $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ at two different temperatures (263 and 293K)



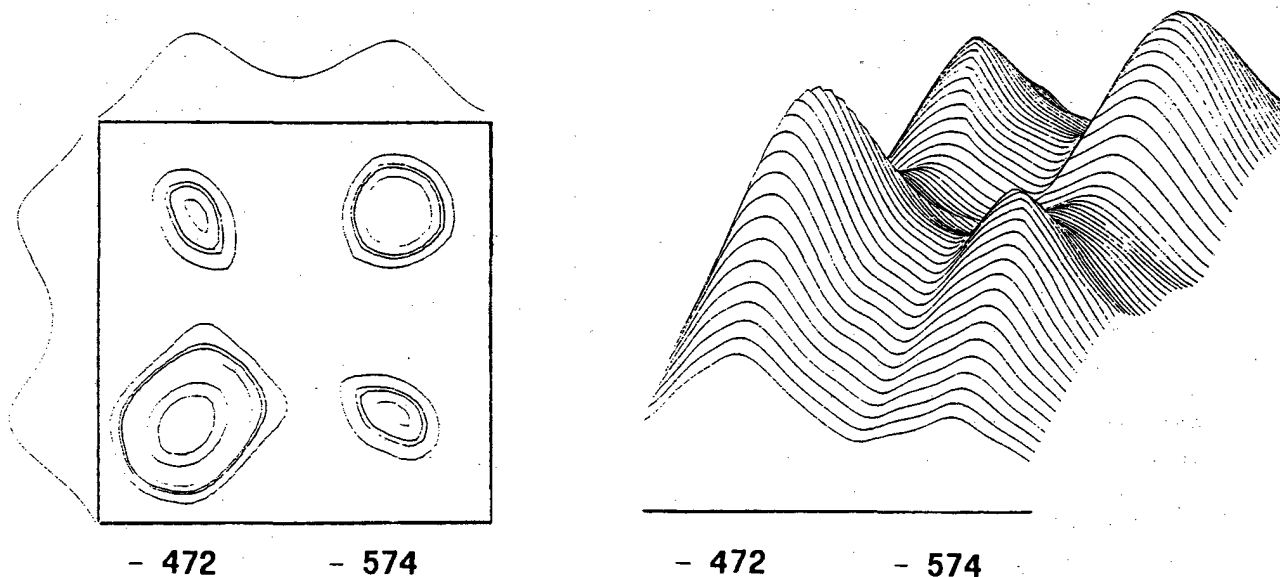
Moreover, fast exchange reactions have been made responsible for the behaviour of the ^{139}La -NMR chemical shifts in previous contributions [2,3]. The study of these reactions is complicated by obviously very fast exchange mechanisms and the very short relaxation times between 10^{-3} (Fig. 2) to 10^{-6} s of the ^{139}La nucleus. Now we have been so fortunate to find a system that allows the experimental confirmation of this exchange via 2D-EXSY-NMR spectroscopy with a very short mixing time of 10^{-6} s (Fig. 3). Thus, in suitable cases even this method seems to be a very helpful tool for the investigation of organolanthanum complexes.

Fig. 3: ^{139}La -2D-EXSY-experiment (mixing time = 2×10^{-6} sec):

$\text{Cp}_3\text{La}/\text{NBu}_4\text{BH}_3\text{CN}/\text{PPh}_4\text{Br}$ 2 : 1 : 1
(Bu = n-butyl, Ph = Phenyl)
in $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ 70:30 (% v/v)

isolated compounds:
 $[\text{NBu}_4][\text{Cp}_3\text{La}^a\text{BH}_3\text{CN}]^- = -574$ ppm
 $[\text{PPh}_4][\text{Cp}_3\text{La}^b\text{Br}]^- = -472$ ppm

Exchange reaction:



[1] Part IV of Lanthanum-139 NMR Spectroscopy of Organolanthanum(III) Complexes; for Part III see ref. 2.

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[3] Y. Ducommun, L. Helm, G. Laurenczy, A.E. Merbach
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