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LANTHANIDE SHIFT REAGENTS AS A STRUCTURAL PROBE FOR ALKENES

P.A.Krasutsky, A.G.Yurchenko, V.N.Rodionov
Department of Chemical Technology, Kiev
Politechnic Institute, Kiev, 252056, USSR

Maitland Jones,Jr.
Department of Chemistry, Princeton University
Princeton, New Jersey, 08544, USA

SUMMARY: The utility of LSR for structural analysis of the Ag^+ complexes of 3,7-dimethylenebicyclo[3.3.1]nonane and its derivatives is demonstrated.

Being weak Lewis acids, lanthanide shift reagents (LSR) are widely used for clarification of complex NMR spectra of compounds containing nucleophilic functional groups such as $-NH_2$,-OH,-C=O,ets. Hitherto olefins could not be studied by this method because of the inability of a double bond to produce a complex with LSR. That is why the study of the molecular geometry of 3,7-dimethylenebicyclo[3.3.1]nonane (1) had required an introduction of an additional 1-hydroxymethyl group [1]. Three studies presented evidence that LSR induced shifts of olefinic proton signals in the presence of silver propionate, trifluoroacetate [2] and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate (fod) [3,4].

We have found that stable complexes of (1) with different silver salts form binuclear complexes with LSR and this results in paramagnetic shifts of NMR signals.

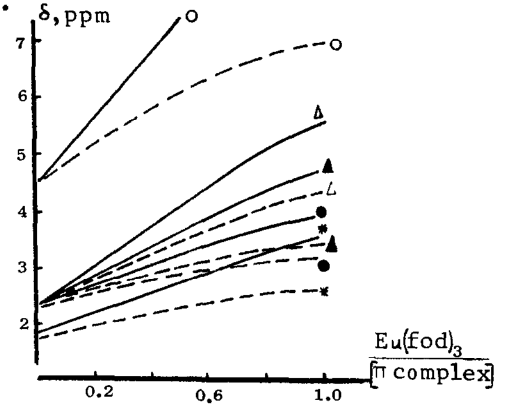


Figure 1. Plots of shifts (δ,ppm) vs.the ratio $\frac{Eu(fod)_3}{[\pi complex]}$,
— complex (1)•••Ag(fod),
--- complex (1)•••$AgNO_3$

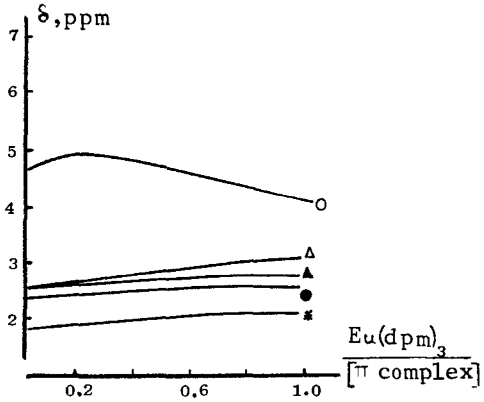
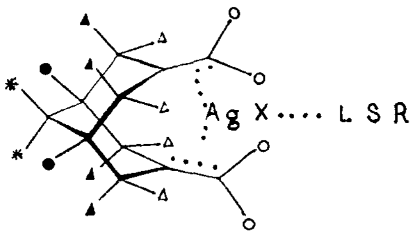


Figure 2. Plots of shifts (δ,ppm) vs.the ratio $\frac{Eu(dpm)_3}{[\pi complex]}$, complex (1)•••$AgNO_3$



Figures 1 and 2 demonstrate the effect of LSR concentration on the magnitude of the induced shifts.

Typically, different amounts of LSR were added to the saturated solution of the complex in $CDCl_3$ or CCl_4 up to the ratio $\frac{\text{LSR}}{[\pi\text{ complex}]} = 1$.* The largest induced shifts were found for the complex (1)···Ag(fod)···Eu(fod)$_3$ (see Table).

TABLE

INDUCED SHIFTS (Δδ,ppm) FOR BINUCLEAR COMPLEX (1)···AgX···Eu(fod)$_3$

Ag X	Solvent	H Index				
		H°	H^{Δ}	$H^{\blacktriangle}$	$H^{\bullet}$	H^{*}
$AgBF_4$	$CDCl_3$	0	0	0	0	0
$AgClO_4$	$CDCl_3$	0,29	0,2	0,2	0,06	0,06
AgO_2CCH_3	$CDCl_3$	2,7	2,2	1,02	0,9	0,64
$AgNO_3$	$CDCl_3$	3,24	2,69	1,14	0,96	0,78
Ag(fod)	CCl_4	7,77	3,25	2,2	1,55	1,52

The qualitative interpretation of spectra prompts us to suggest a symmetrical structure for the binuclear complex. This suggestion was proved by application of McConnel-Robertson equation [5] and X-Ray diffraction investigations [6] wich will be published subsequently.

The influence of chiral shift reagents on spectra of chiral olefins was of special interest. Using silver nitrate and Eu(hfbc)$_3$ as a chiral shift reagent, we succeeded in demonstrating the bifurcating of some narrow peaks in the spectrum of racemic chiral 3-methylene-7-benzylidenebicyclo[3.3.1]nonane (2). Figure 3 presents a comparison of unshifted, shifted with nonchiral Eu(fod)$_3$ and shifted with chiral Eu(hfbc)$_3$ spectra of racemic diene (2). The increase in the difference in chemical shift of bifurcated signals vs. the concentration of Eu(hfbc)$_3$ proves this effect to be due to the enantiomeric composition of the diene (2). It was surprising that the use of Ag(fod) [3] and newly synthesized Ag(hfbc) instead of $AgNO_3$ was completely unsuccessful for determination of the olefin (2) enantiomers. Probably this is because the structures of the binuclear complexes (2)···$AgNO_3$···Eu(hfbc)$_3$ and (2)···Ag(hfbc) ···Eu(hfbc)$_3$ are different.

* ^{1}H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer.

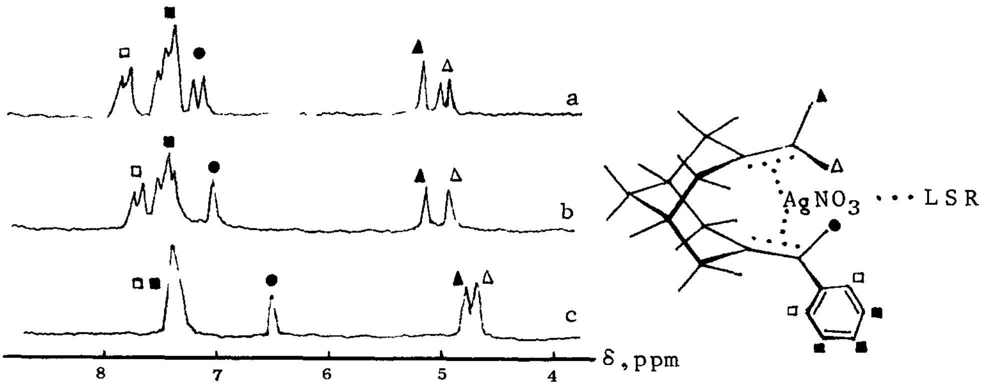


Figure 3. NMR spectra fragment of (a) (2)···$AgNO_3$···$Eu(hfbc)_3$,
(b) (2)···$AgNO_3$···$Eu(fod)_3$,
(c) (2)···$AgNO_3$.

The comparison of the lanthanide induced shifts (LIS) for the complexes (2)···$AgNO_3$ and (2)···Ag(fod) supports this view. The different structures of the binuclear complexes follow from this analysis (see Figure 4a and 4b).

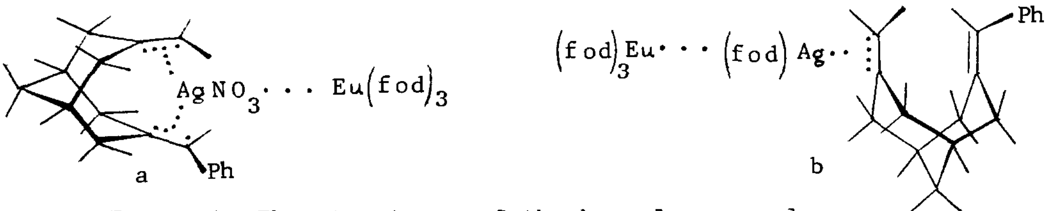


Figure 4. The structures of the binuclear complexes
(a) (2)···$AgNO_3$···$Eu(fod)_3$, (b) (2)···Ag(fod)···$Eu(fod)_3$

One more distinguishing feature of the binuclear complexes based on $AgNO_3$ and Ag(fod) was revealed when 1-hydroxymethyl-3,7-dimethylenebicyclo[3.3.1]-nonane (3) was used as unsaturated substrate. The character of the LIS for complex (3)···$AgNO_3$···$Eu(fod)_3$ is similar to that of complex (3)···$Eu(fod)_3$. This means that HO-group in the complex (3)···$AgNO_3$ is the coordination center for $Eu(fod)_3$. However for the complex (3)···Ag(fod) the picture is different and rather unusual (see Figure 5). The LIS up to the ratio $\frac{\mathrm{Eu(fod)}_3}{[\pi \mathrm{complex}]} < 0.55$ are such as if the Eu^{3+} ion is located in the region of the double bonds and similar to the LIS for the complex (1)···Ag(fod). The LIS of H$^{\blacksquare}$-proton signals (OCH_2-group protons) are the most informative. The coordination of the $Eu(fod)_3$ with HO-group became perceptible when the ratio $\frac{\mathrm{Eu(fod)}_3}{[\pi \mathrm{complex}]} = 0{,}55$. That is why H$^{\blacksquare}$-proton signals have the largest LIS when the ratio is 2. The same analysis may be performed for every proton of the olefin (3) (see Figure 5).

The most plausible explanation for this result is the formation of a stable eight-coordinate adduct $AgEu(fod)_4$, as it was mentioned earliar [4]. The lanthanide

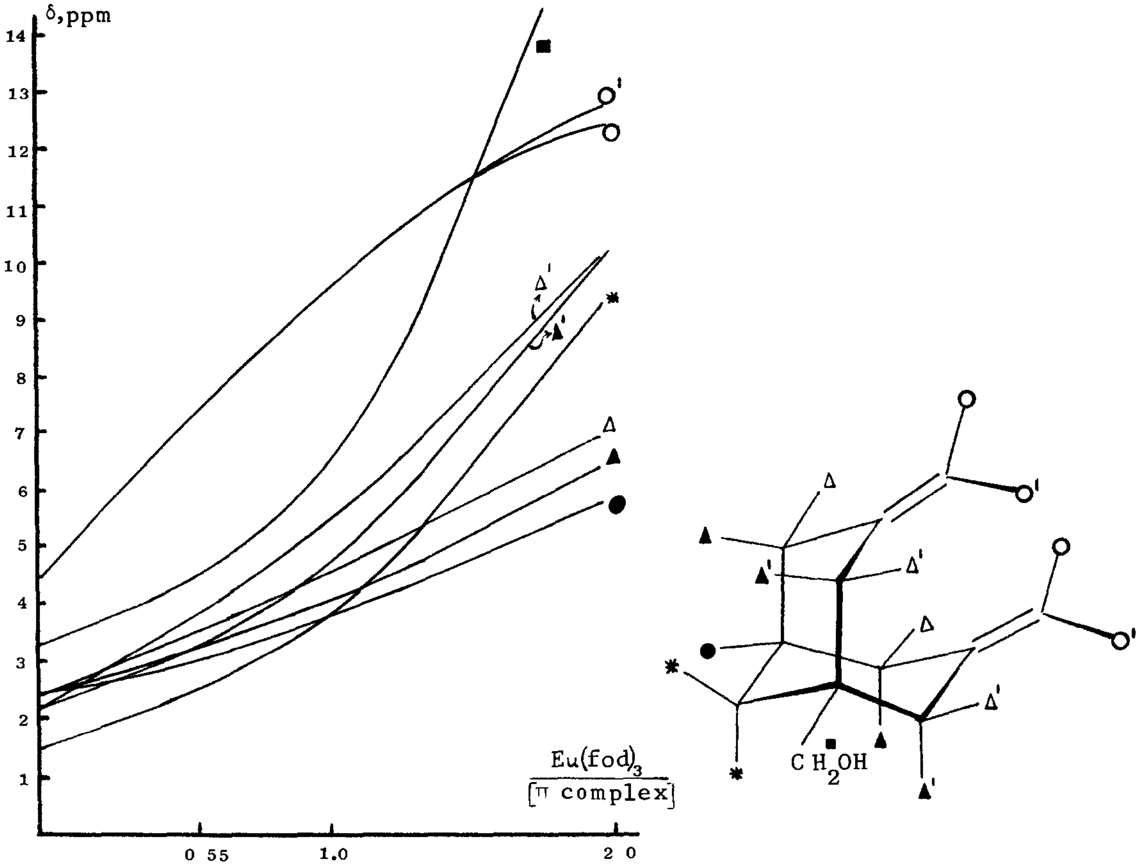


Figure 5. Plots of shifts (δ, ppm) vs.the ratio $\frac{Eu(fod)_3}{[(3)\cdots Ag(fod)]}$

Eu^{3+}-ion in this case has to be surrounded with four bulky β-diketonate ligands and this makes it inaccessible to nucleophile. Possibly the Ag$^+$-ion is responsible for the stability of the complex Ag Eu(fod)$_4$. More detailed discussion of the Ag Eu(fod)$_4$ structure will be published separately.

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