STUDIES ON LANTHANIDE SHIFT REAGENTS

A thesis submitted for

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by

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ABSTRACT

Proton magnetic resonance studies of lanthanide shift reagents with olefin-transition metal complexes, monoamines and diamines as substrates are described.

Shift reagents for olefins are reported : $Ln^{III}(fod)_3$ can induce substantial shifts in the nmr spectra of a variety of olefins when silver 1-heptafluorobutyrate is used to complex the olefin. The preparation, properties and efficiency of such systems are described and various other transition metal-olefin complexes are investigated.

Configurational aspects and exchange processes of $Ln^{III}(fod)_3$ complexes with secondary and tertiary monoamines are analysed by means of dynamic nmr. Factors influencing the stability and the stoïchiometry of these complexes and various processes such as nitrogen inversion and ligand exchange are discussed.

At low temperature, ring inversion can be slow on an nmr time-scale for $Ln^{III}(fod)_3$-diamino chelates. Barriers to ring inversion in substituted ethylenediamines and propanediamines are obtained. Steric factors appear to play an important role in the stability and kinetics of these bidentate species.

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ABBREVIATIONS

Aghfb	Silver 1-heptafluorobutyrate
DEA	Diethylamine
DMen	NN'-dimethylethylenediamine
DMp	1,4-dimethylpiperazine
DMPA	NN-dimethyl-n-propylamine
dnmr	Dynamic nuclear magnetic resonance
DPA	Di-n-propylamine
dpm	Dipivaloylmethane
d_9-fod	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-d_6-4,6-octanedione-8,8,8-d_3
en	Ethylenediamine
facam	3-(trifluoromethylhydroxymethylene)-d-camphorate
fod	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione
HMP	Hexamethylphosphoramide
LIS	Lanthanide induced shift(s)
Ln	Lanthanide
LSR	Lanthanide shift reagent(s)
MDEA	N-methyldiethylamine
MDPA	N-methyl-di-n-propylamine
MEPA	NN-methylethyl-n-propylamine
MePi	1-methylpiperidine
MePi-d_{10}	1-methylpiperidine-d_{10}
MPA	N-methyl-n-propylamine

MTA	N-methyl-t-butylamine
OML	Olefin - transition metal - lanthanide system(s)
TEen	NNN'N'-tetraethylethylenediamine
TMbn	NNN'N'-tetramethyl-1,4-diaminobutane
TMen	NNN'N'-tetramethylethylenediamine
TMpn	NNN'N'-tetramethyl-1,2-diaminopropane
TMtn	NNN'N'-tetramethyl-1,3-diaminopropane.

CONSTANTS

Boltzmann's constant : $k = 1.38053 \times 10^{-23}\ JK^{-1}$

Gas constant : $R = 1.9872\ cal\ deg^{-1}mol^{-1} = 8.3143\ JK^{-1}mol^{-1}$

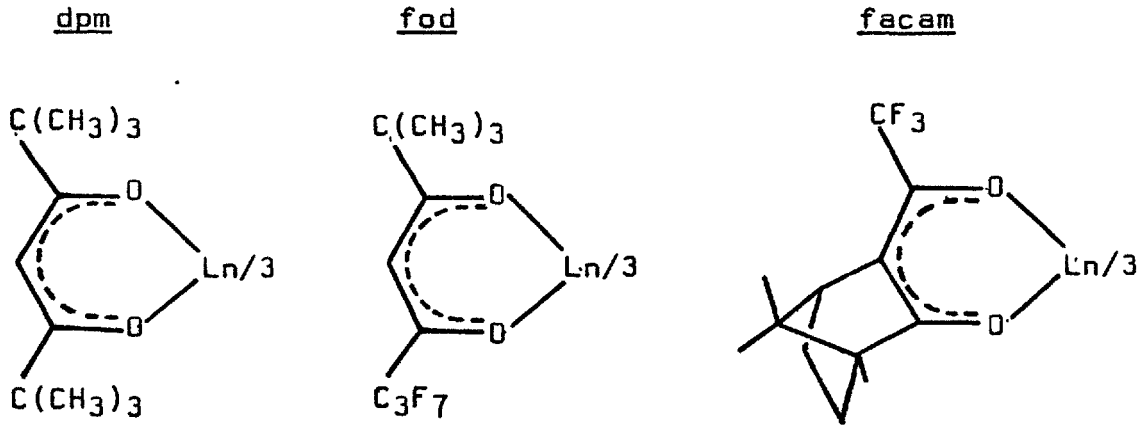
Planck's constant : $h = 6.62559 \times 10^{-34} Js.$

I N T R O D U C T I O N

The chemistry of lanthanide shift reagents has known an explosive development since Hinkley's demonstration of their practical application in nmr spectroscopy.[1] A very large number of publications have now appeared and there are comprehensive reviews covering most of the known aspects of LSR chemistry.[2-7]

The most popular uses of LSR have been nmr spectra interpretation and configurational elucidation.[8] The principal reagents are $Ln(dpm)_3$,[8a] $Ln(fod)_3$[9] and optically active $Ln(facam)_3$;[10] Ln is normally Eu, Pr and Yb.

Fig. 1 Usual LSR



1) Theory of lanthanide induced shifts (L.I.S.)

Nmr shifts induced by paramagnetic ions can arise from both contact interaction and dipolar (pseudo-contact) [11] interaction.

The Fermi-contact interaction involves delocalisation of the unpaired electrons into the substrate molecular orbitals thus inducing a contact shift[12] that declines rapidly through σ-bonds.[13]

The dipolar induced shift ΔH_{dip}, in complexes containing a paramagnetic metal ion with an anisotropic ligand field, is described by the following equation :[14]

$$\Delta H_{dip}/H = -D\langle(3\cos^2\vartheta - 1)/r^3\rangle - D'\langle\sin^2\vartheta\cos 2\Omega/r^3\rangle$$

D and D' are functions of the principal molecular susceptibilities and r, ϑ, Ω are the spherical polar co-ordinates of the resonating nucleus in the co-ordinate system of the principal magnetic axes. The second term of the equation can be neglected with the assumption of axial symmetry equal or greater than three-fold, or if the substrate ligand undergoes free rotation about an axis passing through the lanthanide ion, or if there are three or more interconverting rotamers which are equally populated.[15]

In transition metals, the 3d electrons participate in the bonding process thereby inducing contact shifts as in $Ni(acac)_2$.[16] In the rare-earth series, the 4f orbitals are shielded by the s and p electrons and the shifts are predominantly dipolar[3,11,17] although the contact contribution cannot always be ignored.[18]

2) Properties

Lanthanide shift reagents have now been used for over six years and those containing europium or praseodymium have been the most popular : they can induce large shifts with basic substrates [19] (values of over 60ppm have been obtained in the present work) and they do not cause too much signal broadening.[20,21] These chelates are soluble in ordinary nonpolar solvents such as carbon tetrachloride, chloroform, benzene, toluene, and their adducts often remain soluble in the appropriate solvent at low temperature.

Other lanthanides can also be used. Ytterbium chelates usually induce downfield shifts which are larger than those of europium but they cause slightly more signal broadening.[20,21] The gadolinium (III) ion has an isotropic g-tensor ($X_x=X_y=X_z$) so no dipolar shifts are expected although contact shifts have been measured.[22] Gd^{III} chelates have been used as broadening probes (see ref.23 and also p.28 in the present work) as a result of the ion's long electron relaxation time (τ_e). Table 1 gives comparative induced shifts and line-widths of some $Ln(dpm)_3$ adducts.

$Ln(dpm)_3$ and $Ln(fod)_3$ are the most widely-used shift reagents. The latter is usually more soluble and often induces larger shifts due to the higher Lewis acidity of the β-diketonate induced by the perfluoro alkyl group.[9,18] One of the roles of bulky substituents in making lanthanide β-diketonates more efficient as shift reagents is that internal steric constraints

Table 1

LIS and line widths of some $Ln(dpm)_3$ adducts and radii of eight-co-ordinate Ln^{III} ions.

Ln	αCH_2* ppm (a)	$\delta\nu$(H-1) Hz (a)	H-1* ppm (b)	$\delta\nu(CH_3)$ Hz (c)	ionic radius Å (d)
Pr	11.25	> 20	4.73	5.6	1.14
Nd	5.55	> 20	1.33	4.0	1.12
Sm	—	> 20	—	4.4	1.09
Eu	-2.95	ca. 15	-3.11	5	1.07
Gd	—	—	—	—	1.06
Tb	26.25	75	16.58	96	1.04
Dy	54.00	85	24.3	200	1.03
Ho	51.45	92	10.5	50	1.02
Er	-25.55	61	-4.6	50	1.00
Tm	46.65	90	-11.37	65	0.99
Yb	-12.15	23	-5.68	12	0.98

* All positive LIS upfield, negative LIS downfield.

(a) from cyclohexanol [20]

(b) from 1-hexanol [21]

(c) from 2-picoline [21]

(d) reference [25]

may limit the number of stable geometrical isomers present in solution : if a very large number were present, dipolar shifts would tend to average to zero.[24]

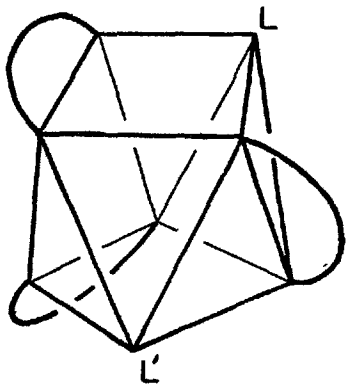
3) Chelate structure.

The size of the Ln^{III} ion can affect the structure of the LSR complex. The ionic radii of the lanthanide series decrease with increasing atomic number (see table 1). The imperfect shielding of 4f electrons by one another as they increase in number and as the nuclear charge also increases causes a reduction in size of the entire $4f^n$ shell. The accumulation of successive contractions with increasing atomic number is called the total lanthanide contraction.

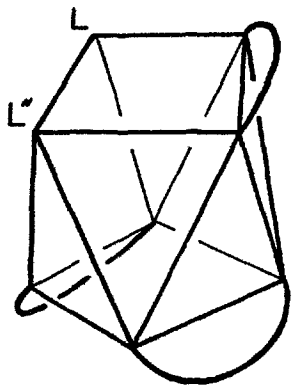
High co-ordination numbers of Ln^{III} ions ranging from 7 to 10 (as in $[La(OH_2)_4EDTAH].3H_2O$ [26])or even 12 (as in $Ce(NO_3)_6^{3-}$) can be found but the most common co-ordination numbers are 7,8 and 9. As a result of the lanthanide contraction, larger co-ordination numbers are to be expected in elements at the beginning of the rare-earth series.

X-ray studies of $Eu(dpm)_3(L)_2$ adducts (L= pyridine,[27] picoline,[24] DMF [15a] show that the geometry displayed by these complexes is that of a distorted square-antiprism (fig.2) where the picoline and pyridine ligands occupy corners of opposite square faces as far apart from one another as possible (L & L' fig. 2a) and, in the DMF complex, the two ligands occupy cis-positions on the same square face (L & L" on fig. 2b).

Fig. 2 Square antiprismatic co-ordination polyhedra :

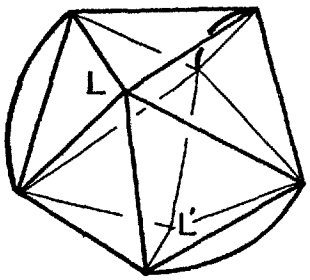


(2a)



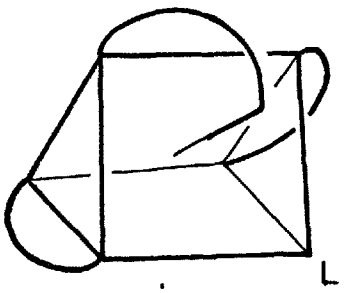
(2b)

Fig. 3 Dodecahedron



However dodecahedral structures are also possible and might be expected with unsymetrical β-diketonates where one of the substituents is much less bulky than the other. An example was recently reported[28] from X-ray studies of tris(thenoyltrifluoroacetonato)bis(triphenylphosphine oxide)neodymium(III).

Fig. 4 Capped trigonal prism



The 7-co-ordinate $Lu(dpm)_3$(3-methylpyridine) has, in the solid state, the structure of a distorted capped trigonal prism[29] where the substrate ligand (L in fig. 4) occupies one of the four corners of the capped face.

While these structures are not necessarily the only ones present in solution, they are likely to be important species..

4) Equilibria and exchange processes

A solution containing a shift reagent (R) and a substrate (S) is a complicated system in which many equilibria can be involved. The main equilibria are listed below[30]:

$$R + S \rightleftharpoons RS \qquad ((1)) \qquad K_1$$

$$RS + S \rightleftharpoons RS_2 \qquad ((2)) \qquad K_2$$

$$R + R \rightleftharpoons R_2 \qquad ((3)) \qquad K_d$$

$$S + A \rightleftharpoons SA \qquad ((4)) \qquad K_A$$

$$R + I \rightleftharpoons RI \qquad ((5)) \qquad K_I$$

A and I represent the solvent and an impurity. K_2 is the equilibrium constant for dimerization.

Equilibria involving reagent and substrate

These include equilibria ((1)) and ((2)). The formation constants of the 1:1 adduct is $K_1 = [RS] / [R] \times [S]$ and that of the 1:2 adduct is $K_2 = [RS_2] / [RS] \times [S]$.

Initially, LSR-substrate systems have been studied at room-temperature in fast exchange conditions. The observed chemical shifts were the averaged values of the chemical shifts of each species.

Although the complexed species were thought, at first, to be entirely 1:1 adducts and calculations were made of absolute chemical shifts and of K_1[31], evidence was soon provided of the existence of 1:2 adducts. Attempts were made to calculate formation constants (K_1 and K_2) and 'bond' chemical shifts

(δ_1 and δ_2)[32,33] via indirect and not always entirely satisfactory methods.

Direct evidence of the existence of RS_2 adducts has been provided by Evans & Wyatt[34] who obtained solvation numbers, chemical shifts and kinetic data of LSR-substrate systems in the slow exchange region at low temperature. On sufficiently cooling a solution containing shift reagent and substrate, resonances broaden and finally split into signals corresponding to free and complexed species. Integration of these signals leads to direct determination of solvation numbers, and line-shape analysis, when possible, to the calculation of kinetic data.

The equilibrium between RS and RS_2 adducts can be influenced by the following factors :

- The Lewis acid character of the LSR : $Ln(fod)_3$ reagents are better acceptors than $Ln(dpm)_3$ complexes.

- The donor properties of the substrate : HMP or basic substrates like amines form particularly stable adducts.

- Steric effects will tend to increase with bulky β-diketones, with bulky substrates or with a decrease in the lanthanide ionic radius. However, if interatomic distances between substrate and reagent are such that Van der Waals forces are attractive rather than repulsive, the RS_2 adduct may be stabilized.

Other equilibria

- Solid state studies[35] and osmometric analysis of $Pr(fod)_3$ solutions[36] have shown that shift reagents can

dimerize readily (equilibrium ((3)) : $2R \rightleftharpoons R_2$) and probably even trimerize ($R_2 + R \rightleftharpoons R_3$)[36]. This tendency towards self-association decreases in the heavier, hence smaller, lanthanides.[33,37]

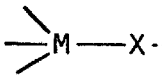
- Strong interactions can be observed between the substrate and various solvants (equilibrium ((4)) : $S + A \rightleftharpoons SA$). Thus, hydrogen-bonding between chloroform and HMP can affect equilibrium ((2)) as compared with an inert solvent such as toluene.[34,38]

- Impurities, and particularly water, can form very stable adducts with shift reagents, and even traces of water can diminish their shift-inducing capacity.[15a] Dehydration of an LSR can be obtained by vacuum pumping at elevated temperatures (see experimental part).

CHAPTER I

SHIFT REAGENTS FOR OLEFINS

Lanthanide shift reagents do not co-ordinate with molecules in which a carbon-carbon double bond is the only function; they cannot be used directly to simplify the nmr spectra of the latter compounds.[19,39] However, a number of transition metals M form co-ordination compounds with olefins :[40,41] these complexes could also co-ordinate to a shift reagent R through another ligand X[42] and form an olefin - metal complex - LSR (OML) system of the type :

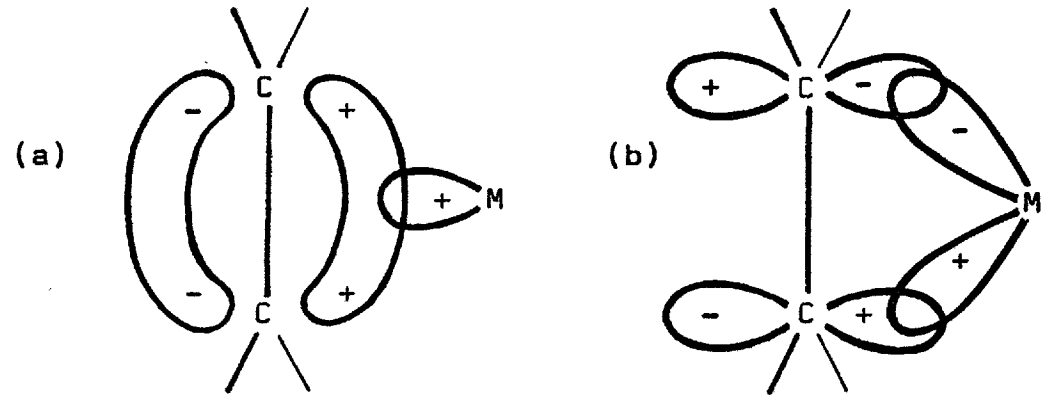


Studies on the application of LSR to organometallics[43,44] have shown that a variety of transition-metal complexes (Fe, Mo, Ti, Sn, Ru, W and Ir) containing ligands such as F, Cl, N_3, CN, and bridging -CO groups, interact with shift reagents; important induced shifts can be obtained.

Nature of the bonding in olefin-transition metal complexes

A model proposed by Dewar[45] and later modified by Chatt[46] is usually considered to describe satisfactorily metal-olefin bonding.

Fig. 5 Molecular orbital view of olefin-metal bonding according to Dewar.[47]



The model comprises two types of bonding :

σ-bonding formed by a donation of π-electrons from the olefin into the vacant σ-type orbital of the metal.(Fig. 5a)

π-bonding formed by back-donation of electrons from d-orbitals of the metal into the lowest-lying π^*-antibonding orbitals of the olefin.(Fig. 5b)

The contribution of either σ-bonding or π-bonding will vary from one transition metal to another.[41,47,48] It is generally accepted that silver-olefin bonding is predominantly of σ-type.[49]

A number of transition metal complexes known to form adducts with olefins have been studied and are described in this chapter. They comprise mainly silver salts but also Rh, Ir, Pt, and Pd complexes.

1. Silver Salts

The olefin - metal complex - LSR (OML) system should meet the following requirements :

(a) solubility in inert solvents such as carbon tetrachloride,

deuterochloroform, dideuterodichloromethane. Note : benzene or toluene would compete with the olefin.
(b) fast olefin-metal exchange on an nmr time-scale at room temperature so that an alteration of the LIS values may be made possible by varying the LSR to substrate ratio.
(c) lanthanide-olefin distances as short as possible in order to have significant induced shifts.

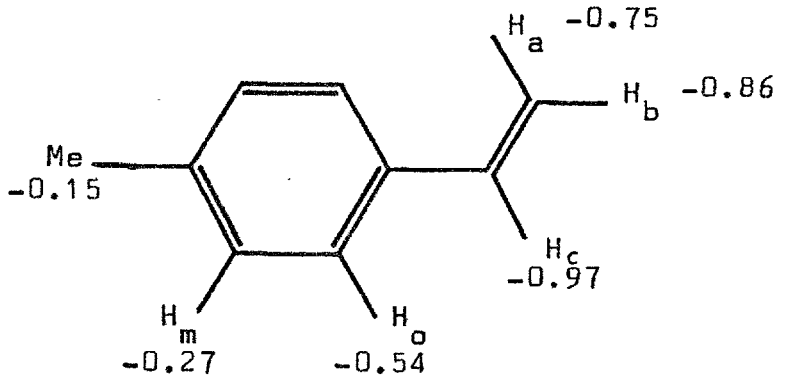
Silver salts have been widely used to separate olefins by glc.[49] The requirements of such techniques (weak olefin-silver interactions, fast exchange rates) are similar to those stated in (b). Salts such as silver 1-heptafluoro-butyrate (Aghfb), trifluoroacetate and trifluoromethyl-sulphonate fulfill the requirements stated above; they have roughly the same characteristics and can be used indiscriminately. Other silver salts have been tried unsuccesfully : $AgNO_3$, $AgBF_4$, $AgClO_4$ and AgF. None of the corresponding OML systems are soluble in CCl_4, $CDCl_3$ or CD_2Cl_2.

Eu $(d_9\text{-fod})_3$ was mostly used together with Aghfb in carbon tetrachloride. $Pr(d_9\text{-fod})_3$ and $Yb(d_9\text{-fod})_3$ were also used on several occasions. CD_2Cl_2 or $CDCl_3$ proved to be no better as solvents than CCl_4. Solutions were always made in vigorously dry conditions.[50,51]

4-Methylstyrene

The effect of an equimolar Aghfb-$Eu(d_9\text{-fod})_3$ system on 4-methylstyrene is illustrated by the spectra in figure 6 and figures 7a and 7b.

Fig. 6 Shifts (in ppm)* of 4-methylstyrene (0.4M) induced by Aghfb-Eu(d_9-fod)$_3$ (0.2M) in CCl_4. T = 35°C



The olefinic protons H_a, H_b and H_c are shifted significantly more than the aromatic ring protons H_o and H_m. The ortho proton, which is the closest to the double bond, is shifted twice as much as the meta proton. Complexation by the silver takes place on the double bond rather than on the aromatic ring.

Maximum LIS values of ca. 1 to 1.5 ppm are typical for most of the olefins studied in the present work. In the absence of LSR, very small upfield shifts were observed (table 2) and 4 equivalents of olefin were needed to dissolve the silver salt.

Table 2 Shifts (ppm) induced by Ag^+ complexation (in CCl_4).

4-methylstyrene : Aghfb	H_a	H_b	H_c	H_o	H_m	Me
0.8M : 0.2M	0.04	0.07	0.07	0.02	0.00	0.01

*The L.I.S. sign convention used throughout the present work is + for upfield shifts and - for downfield shifts.

Comparison of various lanthanides

The efficiency of europium, praseodimium and ytterbium are compared in the following table.

Table 3 Comparative $Ln(d_9\text{-fod})_3$ induced shifts in the 4-methylstyrene - Aghfb system.

Ln	olefin : Ag^+ : LSR *	H_a	H_b	H_c	H_o	H_m
Eu	0.4 : 0.2 : 0.2	-0.97	-0.86	-0.75	-0.54	-0.27
Pr	0.4 : 0.2 : 0.2	+1.29	+1.66	+1.61	+0.90	+0.42
Yb	0.4 : 0.2 : 0.18	-1.40	-0.70	-1.09	-1.07	-0.61

* Moles. CCl_4 solution. T = 35°C.

The shifts obtained with the three different LSR follow the same pattern and have the expected sign, i.e. downfield for europium and ytterbium and upfield for praseodymium. With $Eu(fod)_3$, the shifts are not as large as with $Pr(fod)_3$ (cf. spectra 7b,c,d). Shifts induced by $Yb(fod)_3$ are also greater than those induced by $Eu(fod)_3$ but the Aghfb-$Yb(fod)_3$ system gives unpredictable results with a number of olefins such as hex-1-ene where protons close to the complexing site can be shifted upfield at low olefin to Ag^+:LSR ratio and only revert to the expected downfield shifts when enough olefin is added to the solution .

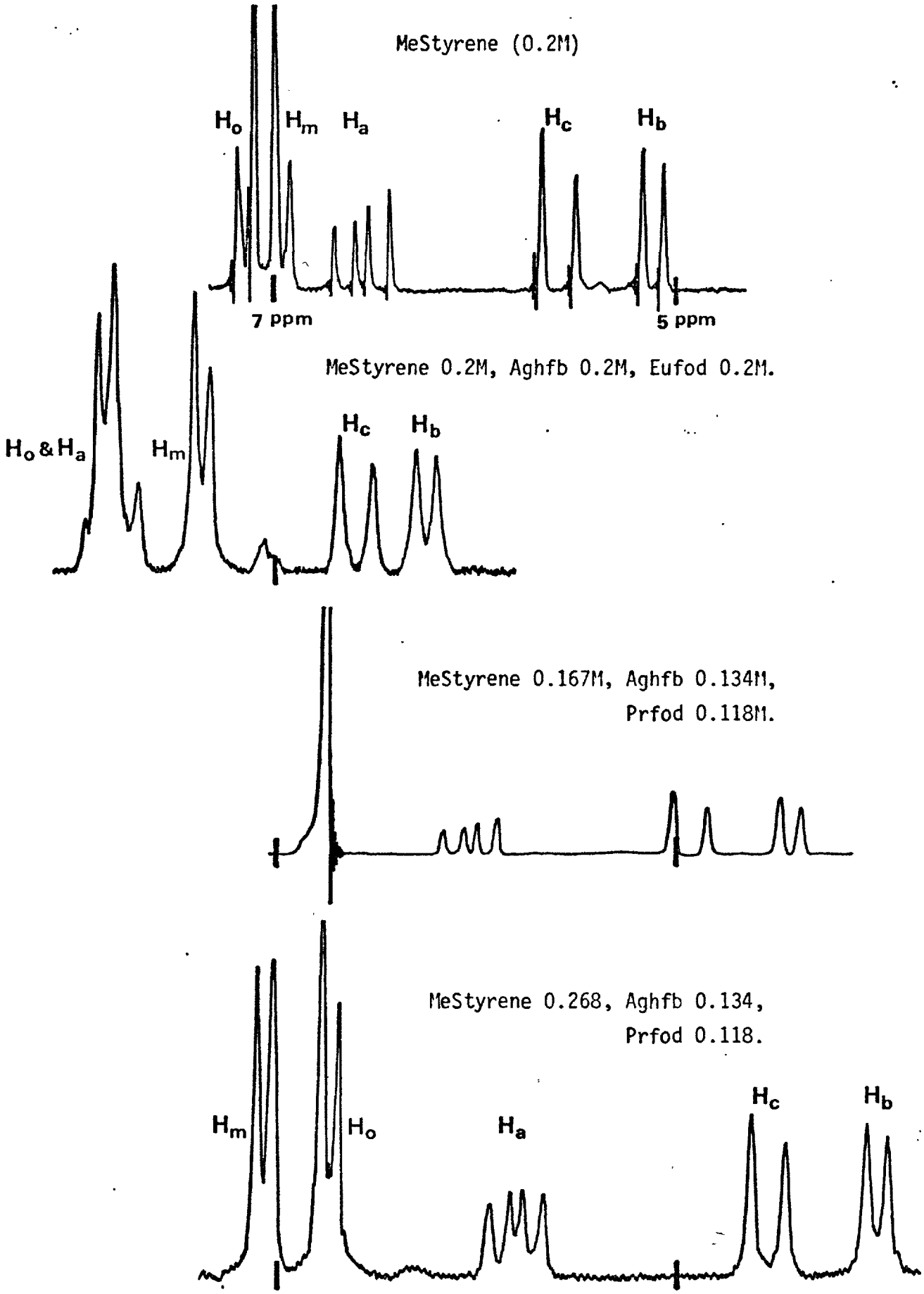
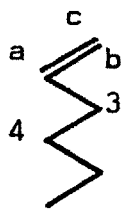


Fig. 7 100 MHz spectra of pMeStyrene-Aghfb-Ln(d_9-fod)$_3$ systems in CCl_4
T = 35°C, Reference TMS.

Table 4

Influence of the olefin to Aghfb-$Yb(fod)_3$ ratio.



Hexene : Ag^+ : Yb (a)	H_a (b)	H_b	H_c	H_3	H_4
0.3 : 0.2 : 0.21	-1.37	+0.71	+0.04	-1.42	-0.95
0.8 : 0.2 : 0.21	-0.86	-0.13	-0.39	-0.78	-0.38

(a) moles; CCl_4 solution; T = 35°C. (b) ppm.

The reason for such behaviour is unknown. It is not due to contact interaction as the Yb ion is distant from the olefin and contact shifts are smaller with Yb^{III} chelates than with those of Eu^{III} or Pr^{III}.

The small ionic radius of Yb^{3+} may be an influencing factor. Geometrical parameters (ϑ values) must be taken into account. In any case, $Yb(fod)_3$ is not a very useful shift reagent for our purpose.

Influence of the olefin : Ag^+ : LSR ratios

Table 5

Variation of the $Eu(fod)_3$ concentration

Hexene : Ag^+ : Eu (a)		H_a (b)	H_b	H_c	H_3	H_4
0.3 : 0.2 :	0.1	-0.89	-0.68	-0.59	-0.53	-0.25
	0.2	-1.56	-1.33	-1.15	-1.00	-0.57
	0.3	-1.41	-1.20	-1.01	-0.88	-0.50

(a) moles; CCl_4 solution; T = 35°C. (b) ppm.

The values listed above clearly illustrates that induced shifts reach a maximum for a silver : LSR molar ratio of approximately 1:1 (see also spectra 7c, 7d). In addition when the molar ratio is greater than 1, i.e. in presence of excess Ag^+, solubility problems arise, and accordingly a 1:1 ratio was subsequently used.

The following table shows, as expected, a steady decrease of induced shifts as more olefin is added to an OML solution.

Table 6

Variation of the olefin concentration.

Hexene : Ag^+ : LSR (a) (b)	H_a (c)	H_b	H_c	H_3	H_4
0.3 : 0.2 : 0.2	-1.56	-1.33	-1.15	-1.00	-0.57
0.4 : 0.2 : 0.2	-1.15	-0.99	-0.84	-0.74	-0.38
2.0 : 0.2 : 0.2	-0.24	-0.22	-0.19	-0.16	-0.07

(a) Moles; CCl_4 solution; T = 35°C. (b) $Eu(d_9\text{-fod})_3$. (c) ppm

The dilution effect

A slight decrease of the induced shifts is observed (table 7) in a diluted OML solution. This is a sign of increasing dissociation of the OML complex as the total concentration decreases.

Table 7

Variation of the total concentration.

Olefin[(a)] : Ag^+ : $Eu(fod)_3$	H_a[(b)]	H_b	H_c	H_o	H_m
0.3 : 0.2 : 0.2	-1.25	-1.13	-0.98	-0.70	-0.33
0.15 : 0.1 : 0.1	-1.10	-0.99	-0.87	-0.60	-0.28
0.075 : 0.05 : 0.05	-1.00	-0.88	-0.76	-0.56	-0.26

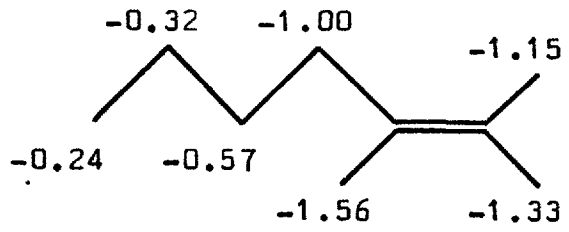
(a) 4-methylstyrene (moles) ; CCl_4 solution; T = 35°C.

(b) ppm.

Effect of the lanthanide-proton distance

As expected, the closer the observed proton is to the complexing site, the greater is the induced shift :

Fig. 8 Shifts (in ppm) of hex-1-ene (0.3M) induced by Aghfb-$Eu(d_9$-fod$)_3$ (0.2M) in a CCl_4 solution, T = 35°C.



Temperature dependence

Two factors can be taken into account in the variation of lanthanide induced shifts as a function of temperature :

- a modification of equilibrium constants giving rise to a variation in the concentration of the complex.[(2)]

- the usual pseudocontact temperature dependence which, in the case of Eu^{3+} shift reagents, is approximately proportional to T^{-1}, and in the case of Yb^{3+} or Pr^{3+} to T^{-2}.(52)

Table 8

Temperature dependence of OML chemical shifts in a 4-methylstyrene (0.35M) - Aghfb (0.2M) - $Eu(fod)_3$ (0.2M) system.

T (°C)	H_a*	H_b	H_c	H_o	H_m	CH_3
45	-0.92	-0.76	-0.64	-0.55	-0.29	-0.16
35	-0.98	-0.83	-0.71	-0.58	-0.30	-0.17
25	-1.02	-0.91	-0.78	-0.60	-0.33	-0.18
15	-1.10	-1.01	-0.87	-0.69	-0.37	-0.22
5	-1.13	-1.10	-0.94	-0.72	-0.39	-0.24

* Shifts in ppm; CCl_4 solution.

As expected, an increase in LIS is observed as the temperature decreases. The resonances tend to broaden and the solution reaches its solubility limit at about 0°C.

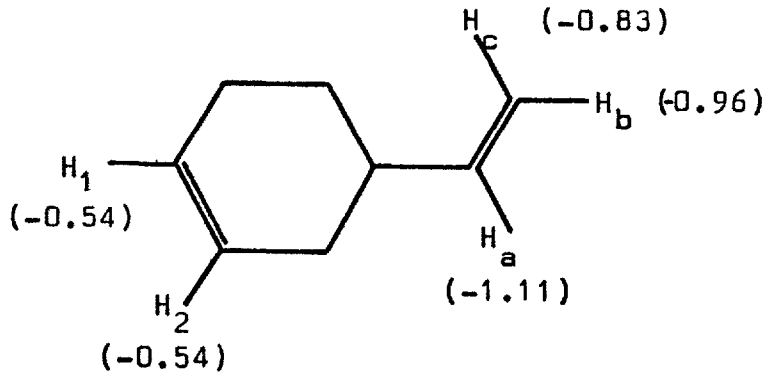
Diolefins

In molecules with two competing complexation sites, LIS values reflect the equilibrium between the adducts formed at each site.

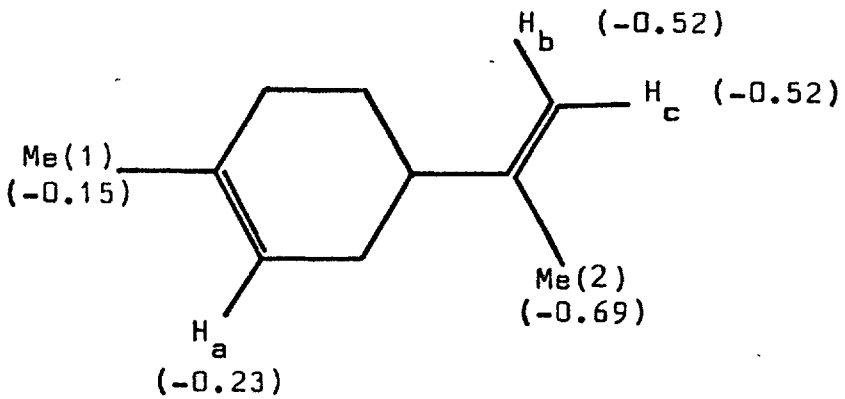
As illustrated in figure 9a, a preferred complexation by Aghfb at the less substituted terminal double bond of 4-vinylcyclohexene is evident where induced shifts are about twice as big as those of the cycle olefinic protons.

Figure 9

(a) 4-vinylcyclohexene (0.3M), Aghfb-Eu(fod)$_3$ (0.2M);



(b) limonene (0.4M), Aghfb-Eu(fod)$_3$ (0.2M); CCl_4 solutions, LIS in ppm, T = 35°C.



Similarly, in limonene (fig. 9b) the shifts observed for H_b and Me(2) are substantially greater than those observed for H_a and Me(1). Gadolinium chelates are used as broadening probes[50,53] since the Gd^{3+} ion has a long electron-spin relaxation time giving rise to important nuclear relaxation and nmr line broadening (proportional to r^{-6}). $Gd(fod)_3$ can be useful in OML systems and confirms the result obtained above: a 1.05M:0.2M:0.0016M limonene-Aghfb-Gd(d_9-fod)$_3$ spectrum shows much more extensive broadening of the Me(2)

resonance than of the Me(1) resonance.

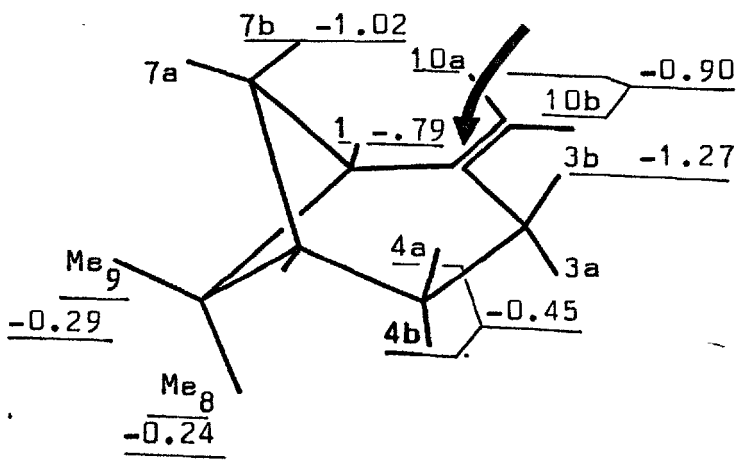
These results are consistent with those obtained by Muhs and Weiss[49] who found by glc that increasing the number of substituents about the double bond causes a reduction of the olefin-Ag^+ equilibrium constant. They point out the strong influence of steric factors on equilibrium constants for the formation of $AgNO_3$ - olefin complexes. Inductive effects of alkyl substituents on the double bond are thought to be less important than steric factors: bulky substituents restrain overlap of the metal and olefin orbitals thus diminishing complex stability.

Applications

The immediate potential of the OML system is apparent from fig. 11 where the spectra of β-pinene with and without shift reagent are compared to the 300 MHz spectrum of β-pinene without shift reagent.[54]

Figure 10

Shifts (in ppm) of β-pinene(0.3M) induced by Aghfb(0.2M)-$Eu(d_9\text{-fod})_3$(0.215M) in CCl_4. T = 35°C.



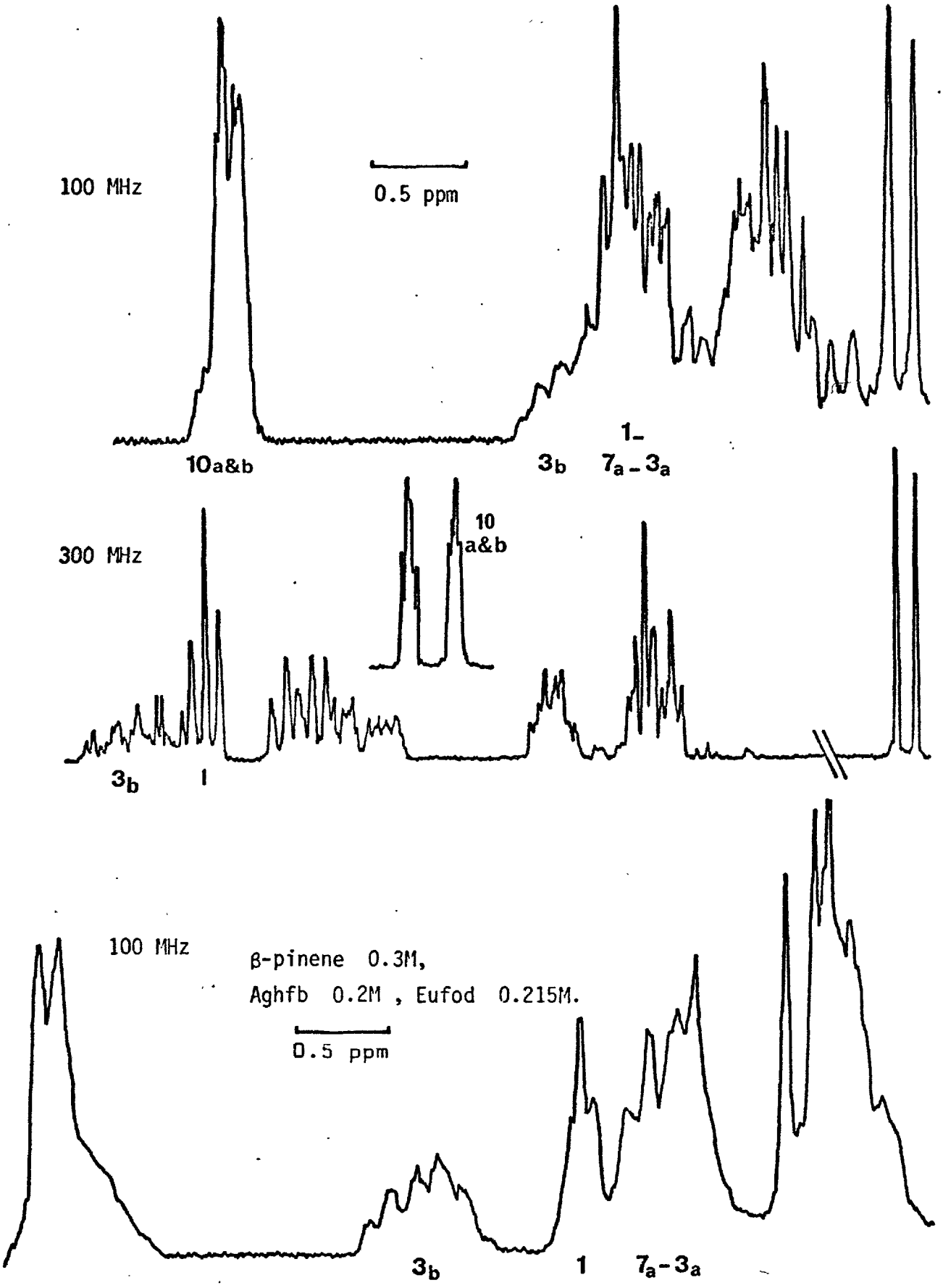


Fig. 11 Nmr spectra of β-pinene and of the β-pinene-Aghfb-Eufod system in CCl_4 . T = 35°C . Ref. TMS.

The olefinic protons 10a and 10b are shifted downfield by nearly 1ppm. Significant information can be obtained concerning the geometry of the complex. The large shifts of protons 3b and 7b (1.27 and 1.02ppm respectively) indicate that the silver complexes the olefin from above the double bond (as indicated in fig. 10).

Other systems : chiral OML

Optically active LSR have been widely used to distinguish between enantiomers.[55] In the best conditions (strong donor substrates), induced shifts are smaller than those obtained with the non-chiral shift reagents. In addition, the chiral centre on the LSR (camphorato group) is far-removed from the chiral centre of the substrate so the chiral splitting obtained is not very big.

However, if the silver salt were chiral instead of the LSR, such a system should be more effective than the active LSR - non-active silver salt system since the chiral centre is much closer to the olefin and $Ln(fod)_3$, which could then be used, is a more powerful shift reagent.

Two optically-active salts have been investigated : silver 1-pentafluorophenylethanesulphonate and silver d-10-camphorsulphonate. Neither were soluble under the required conditions. Silver salts of stronger sulphonic acids might be more suitable, e.g. silver (d or l)-1-phenyl-2,2,2-trifluoroethanesulphonate.

2) Attempts to obtain OML systems with other transition metals

In an attempt to obtain more efficient OML systems, square-planar rhodium(I) complexes were regarded as very promising. $Rh^{I}(CO)_2$ β-diketonates were used for glc separation of olefins by Gil Av and Schurig[56] who stated that the interaction between the olefin and the rhodium diketonate (forming a five-coordinate complex) is far stronger than in the case of silver salts. Dicarbonyl-Rh^{I}-3-trifluoroacetyl-camphorate, claimed to be the most efficient, was prepared and purified by sublimation. However ir spectroscopy has not shown the slightest sign of complexation under conditions which would be used for nmr studies.

The ir spectra of solutions in which the olefin : Rh-diketonate ratio was varied were compared to the spectrum of the diketonate without olefin : the ν_{co} stretching bands ($2090cm^{-1}$ and $2023cm^{-1}$) remained unchanged both in position and intensity even when the diketonate was dissolved in pure olefin. These operations were repeated with a sample provided by Johnson, Matthey Ltd. with the same results.

The most likely explanation for Gil Av and Schurig's observations is that there is an interaction between the olefin, the rhodium complex and the adsorbant used to pack the glc column.

Further attempts to complex olefins with square planar transition metal compounds were equally unsuccessful : they included $(CO)_2Rh^{I}acac$, $CORh^{I}Cl(PPhEt_2)_2$, $COIr^{I}Cl(PPh_3)_2$, $COIr^{I}Cl(PMe_3)_2$ - some complexes with ligands forming stronger

adducts with LSR (such as OH, OR, F, CN) : $OHRh^{I}CO(PPh_3)_2$, $FIr^{I}(CO)(PPh_3)_2$, - complexes of the type $ClRh^{I}(CO)_2X$ where X = picolinate, 8-oxyquinolate, salicylaldoxime, pyrimidine, 2-pyridinealdoxime.

Diacetato Pd^{II}-olefin complexes were insoluble and $PdCl_2(PhCN)_2$ also reacted with olefins but the corresponding adducts precipitated in $CDCl_3$ or CCl_4.

The tetraphenylarsonium analogue of Zeise's salt : $[PtCl_3C_2H_4]^-[AsPh_4]^+$ complexed slightly with LSR in $CDCl_3$ but when olefin was added no exchange with the complexed ethylene could be observed.

Conclusions

OML systems containing a silver salt such as Aghfb have proved very versatile : a wide variety of olefins has been successfully investigated : from n-hexene to sterically hindered α-pinene or camphene; downfield europium-induced shifts of olefinic protons range from 0.6ppm (α-pinene) to 1.6ppm (n-hexene). However the induced shifts observed for olefins are smaller than those normally obtained with other substrates.[2] Shifts could be greatly enhanced if the olefin-lanthanum distance was reduced. More effective shift reagents for olefins should be found with suitable OH, F or CN complexes of transition metals.

CHAPTER II

DNMR STUDY

OF MONOAMINE-LSR SYSTEMS

Kinetics and conformational aspects of shift reagent-monoamine systems are discussed in this chapter. Monoamines were chosen for their versatility and strong donor properties :

- amines are strong donors, they form stable adducts with lanthanide β-diketonates and large induced shifts are obtained. Intermolecular exchange between "free" and complexed amine has been slowed down[34] thus enabling a study of the bound substrate.

- amines are versatile : a simple synthesis enables the study of a wide range of different amines. An increase in the bulk of the substituents on the nitrogen affects the stoïchiometry of the adduct and the kinetics of substrate exchange.

Rates of nitrogen inversion are usually too fast to be measured by dnmr processes : techniques such as infra-red, microwave and ultrasonic absorption[57] spectroscopy have been used to calculate low-energy inversion barriers such as those in NH_3 (5.78 $kcalmol^{-1}$),[58] methylamine (4.83 $kcalmol^{-1}$),[59] or dimethylamine (4.4 $kcalmol^{-1}$).[60] However, dnmr has proved useful when inversion barriers are in the 5 to 25 $kcalmol^{-1}$ range (61-63) although, at the lower end of this range, it has not always been clear whether the barriers measured are those of nitrogen inversion or of hindered rotation about the C-N bonds.[64]

Amine protonation in concentrated acid solution has been used as another method of measuring rates of nitrogen

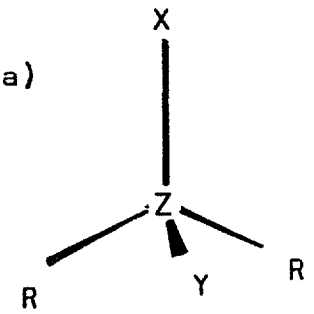
inversion by nmr (Saunders,[65] Robinson.)[66] This technique can only be used in aqueous or polar solvents.

Co-ordination of amines to transition metals raises considerably the pyramidal inversion barrier : stable invertomers such as $\left[Co(dien)_2\right]^{3+}$ have been isolated.[67] Nitrogen inversion is slow on an nmr time-scale in substitued Ni^{II} chelates.[68]

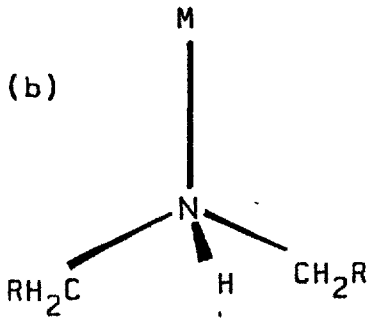
Fast N inversion presumably means that the life-time of the complexed amine in solution is short. Consequently, N inversion can be used as a probe to study intermolecular exchange : resonance splitting due to the presence of a chiral or prochiral nitrogen indicates that intermolecular exchange is slow (or that the free to complexed amine ratio is very ~~big~~ small as in the protonation experiment mentioned above.)[65]

Magnetic nonequivalence, diastereotopicity

(a)



(b)



The centre Z of a tetrahedral assembly such as (a) is called a "prochiral centre" if, by replacing one of the identical ligands R by a different ligand, Z becomes a chiral centre (cf. Hanson,[69] Jennings.)[70]

The nmr spectrum of compound (b) can show two distinct signals for the methylene protons if nitrogen inversion has been slowed down even

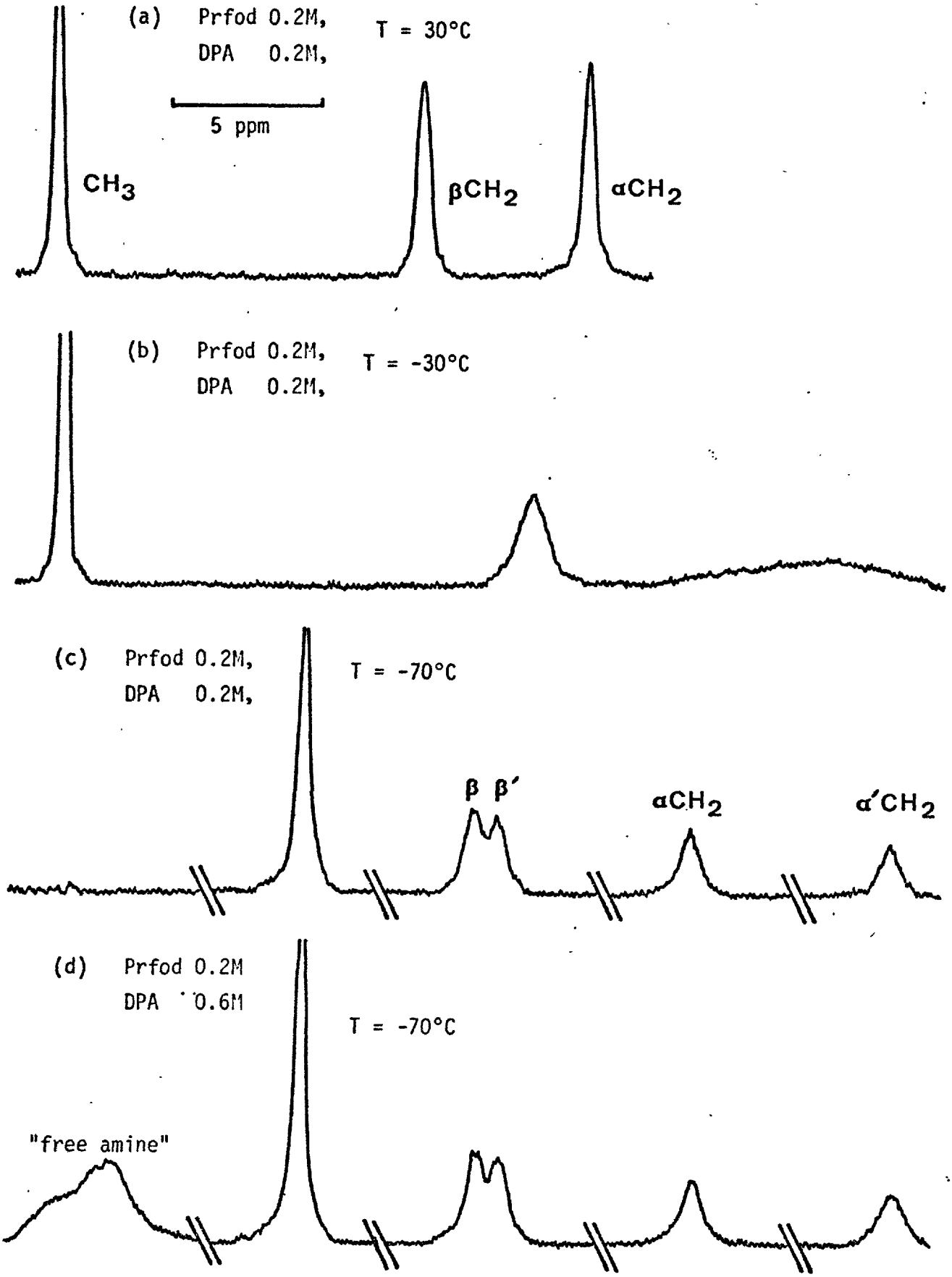
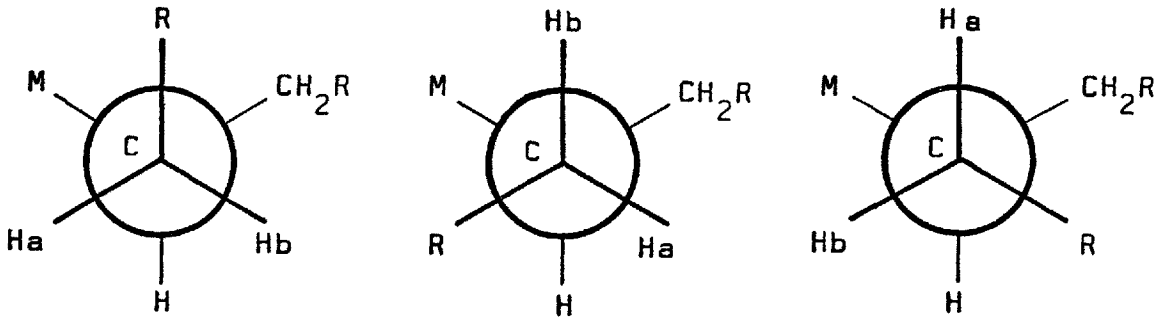


Fig. 12 60 MHz spectra of the $Pr(fod\text{-}d_9)_3$-DPA system in $C_6D_5CD_3$.

if rotation about the N—CH_2 bond is rapid.

Figure 13

Newman projections of a prochiral amine as seen down the methylene-nitrogen bond.



(I) (II) (III)

Ha and Hb cannot be exchanged without nitrogen inversion. The environment of Ha in rotamer (I) is not the same as that of Hb in rotamer (II) nor of Hb in rotamer (III) : in rotamer (I), Ha "sees" H partly overshadowed by Hb but in rotamer (III), Hb "sees" H partly overshadowed by R. Even when rapid rotation averages out their successive positions, Ha and Hb, or any other geminal group in the same position, are said to be magnetically nonequivalent or diastereotopic, and will (except by accident) have different chemical shifts.

Determination of solvation numbers and study of intermolecular exchanges.

Solvation numbers in LSR-amine systems can usually be measured in the low temperature nmr spectra of solutions containing an excess of amine.[34] However the presence of free substrate often considerably increases intermolecular exchange rates. The study of solutions containing an excess of reagent was often advantageous for obtaining solvation numbers and slowing down nitrogen inversion.

SPECTRA INTERPRETATION

1) Secondary amines

a) Di-n-propylamine (DPA) and N-methyl-n-propylamine (MPA).

Bound chemical shifts can be found in table 9.

Prfod-DPA

The room temperature spectra of $Pr(d_9fod)_3$-DPA solutions (fig. 12a) show three peaks : α-CH_2 at high-field, β-CH_2 and γ-CH_3 at low field. As expected the shifts vary with the LSR : amine ratio. As the solution is gradually cooled, the α- and β-CH_2 peaks broaden (fig. 12b). At -70°C, complete diastereotopic splitting is observed (fig. 12c).

At low temperature, the spectrum of a solution containing an excess of amine (fig. 12d) displays distinct signals for free and complexed substrate. Integration of these signals indicates that the species present is predominantly a 1:2 adduct. No other resonances appear either at low or at high

Table 9

'Bound' chemical shifts of Ln(d_9-fod)$_3$ complexes of dipropylamine and N-methylpropylamine.*

Ln S n	α'CH_2	αCH_2	β'CH_2	βCH_2	γCH_3	T°C
Pr DPA 2	50.8	43.0	30.4		11.6	-40
	56.0	45.7	31.8		12.2	-50
	59.8	47.9	34.3	33.6	13.3	-60
	63.2	49.5	36.2	35.4	13.9	-70
	67.1	51.2	38.5	37.6	14.9	-78
Eu DPA 1	22.8	17.8	14.9		5.6	-30
	26.0	20.9	16.7		6.2	-50
	27.2	22.5	17.0		6.5	-60
	28.7	24.4	17.6		6.6	-70
	29.5	25.3	18.1		6.7	-75
Eu DPA 2	29.6	22.6	19.9		7.1	-50
	32.2	23.4	23.7		8.2	-70
	32.6	24.9	24.5		8.5	-75

Ln S n	αCH_3	α'CH_2	αCH_2	β'CH_2 & βCH_2	γCH_3	T°C
Pr MPA 2	47.3	52.1	47.6	28.6 27.2	12.0	-50
	51.3 50.5	56.1 55.7	49.9	30.2 29.2 28.5	12.7	-60
	54.1 53.0	59.7 58.7	51.9	31.5 30.3 30.1	13.4 13.1	-70

Ln S n	αCH_3	α'CH_2	αCH_2	βCH_2	γCH_3	T°C
Eu MPA 2	28.1	32.6	29.1	18.5 16.9	7.4	-50
	30.1	35.3 34.0	31.3 30.2	20.5 17.9	8.0	-60
	31.4	38.4 36.6	33.1 31.4	21.5 19.0	8.6	-70
Eu MPA 1	27.9	—	—	—	—	-50
	29.4	—	—	—	6.7	-60
	31.0	—	—	—	6.9	-70

* Shifts in ppm; LSR = 0.2M in d_8-toluene.

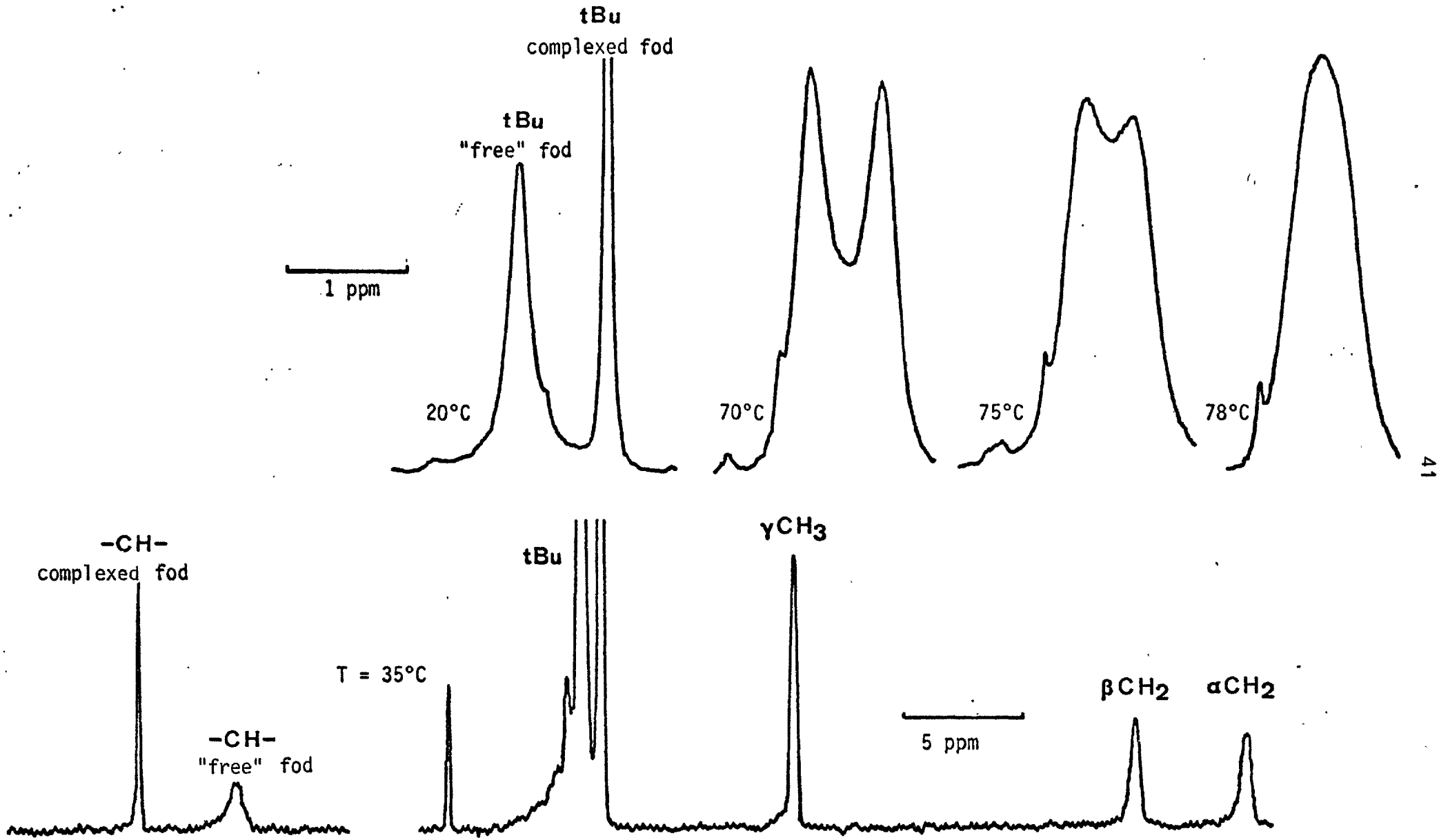


Fig. 14 Spectra of a $Pr(fod)_3$- (0.2M) DPA (0.1M) solution. $CD_3C_6D_5$.

LSR to amine ratios.

Above 0°C, solutions containing 2eq. of undeuterated $Pr(fod)_3$ and 1eq. of DPA give two sets of resonances corresponding to free and complexed $Pr(fod)_3$ (fig. 14). These peaks were assigned by varying the LSR:substrate ratio. Contrasted with the low temperature measurements, there is evidence from integration of the fod methine and tBu resonances for a significant proportion of a 1:1 complex. The free fod signals are broad at 35°C and collapse near 0°C (owing to dimerization or trimerization). The complexed fod signals are sharp at room temperature but coalesce with their free counterparts at ca. 80°C (fig. 14).

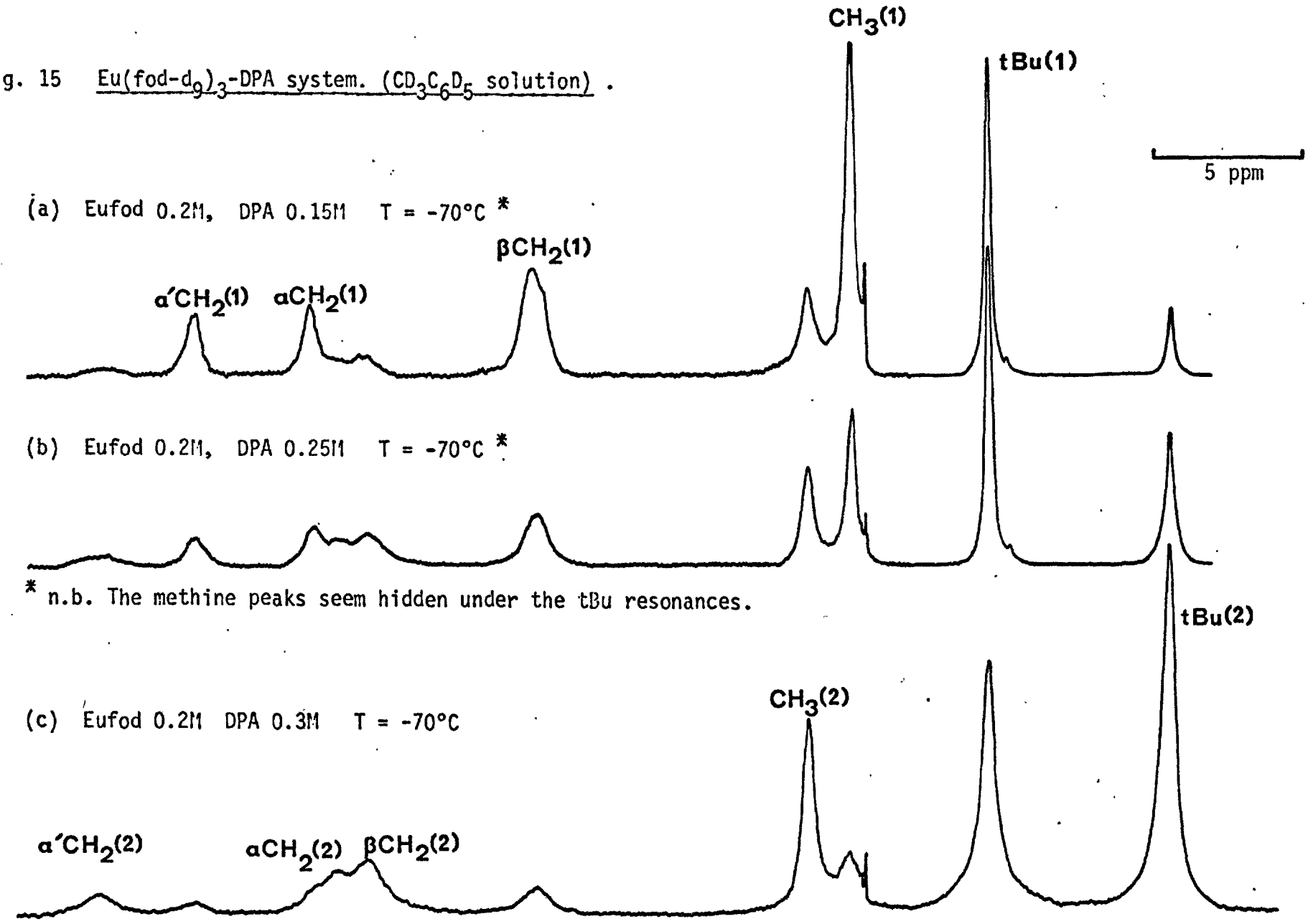
Eufod-DPA

Unlike the analogous praseodymium system, Eufod-DPA solutions with different LSR:amine ratios have different low temperature spectra (see spectra 15a, 15b & 15c) where these ratios are respectively 1:1, 1:1.25 and 1:1.5).

The spectra are interpretated as the superimposed resonances of RS and RS_2 adducts.

The room temperature resonances of free and complexed fod nearly coincide. However, they can be distinguished from each other as the free peak is broad owing to dimerization or polymerization and the complexed peak is sharp. They have roughly the same area (as measured by integration) in an equimolar LSR and amine solution. This indicates that the solution now contains predominantly RS-type adducts.

Fig. 15 Eu(fod-d_9)$_3$-DPA system. ($CD_3C_6D_5$ solution) .



Prfod-MPA

The spectral pattern of this system (spectra 16a & 16b) is complicated by the resonance of the N-methyl group : the resulting difficulty in interpretation was overcome by studying the $N-CD_3$ complex (spectrum 16c). Solutions containing a known excess of amine show that mainly 1:2 adducts are formed at low temperature. This is confirmed by the low temperature splitting of the $\gamma-CH_3$ and $N-CH_3$ groups owing to the formation of diastereoisomers in approximately equal abundance.[71] The α-methylene resonance pattern consists of one peak from the meso or racemic adduct (CH_2 in figure 16b) and two peaks of half intensity ($\alpha'CH_2$) from the other diasteroisomer. In one of the diastereoisomers the methylene protons are accidentally equivalent. It was not possible to assign each peak individually.

Eufod-MDPA

Low temperature spectra (fig. 17) give evidence of the formation of an RS_2 adduct but the small resonance between the γ-methyl peak and the deuterotoluene peak can be attributed to an RS adduct. The presence of meso and racemic isomers together with magnetic nonequivalence (due to the proximity of the chiral nitrogen) account for the four -methylene resonances.

b) Piperidine

Bound chemical shifts for the $Eu(d_9-fod)_3$- and $Pr(d_9-fod)_3$-piperidine systems are listed in table 10. All three CH_2 signals split as the temperature is lowered

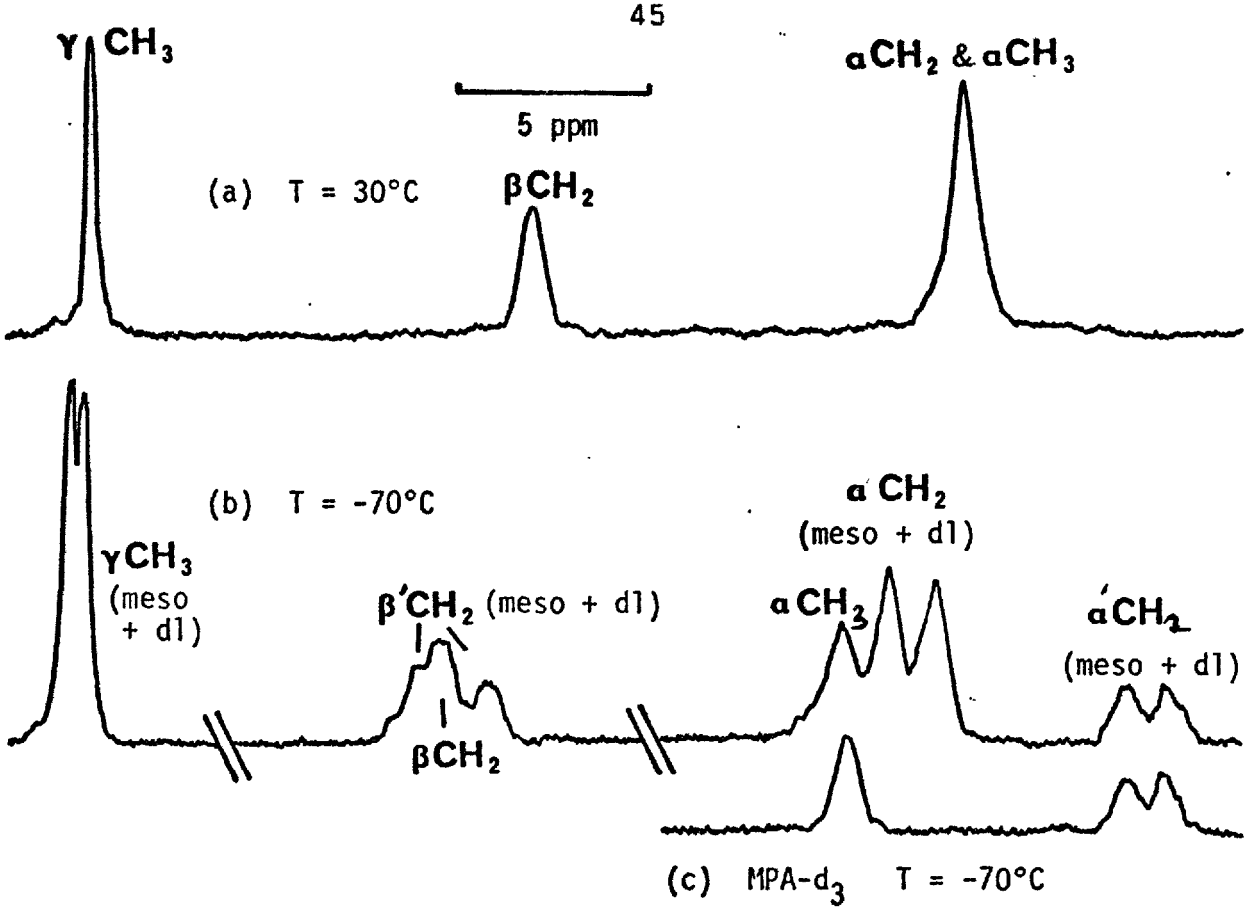


Fig. 16 Pr(fod-d_9)$_3$- (0.2M) MPA (0.2M) system in $CD_3C_6D_5$.

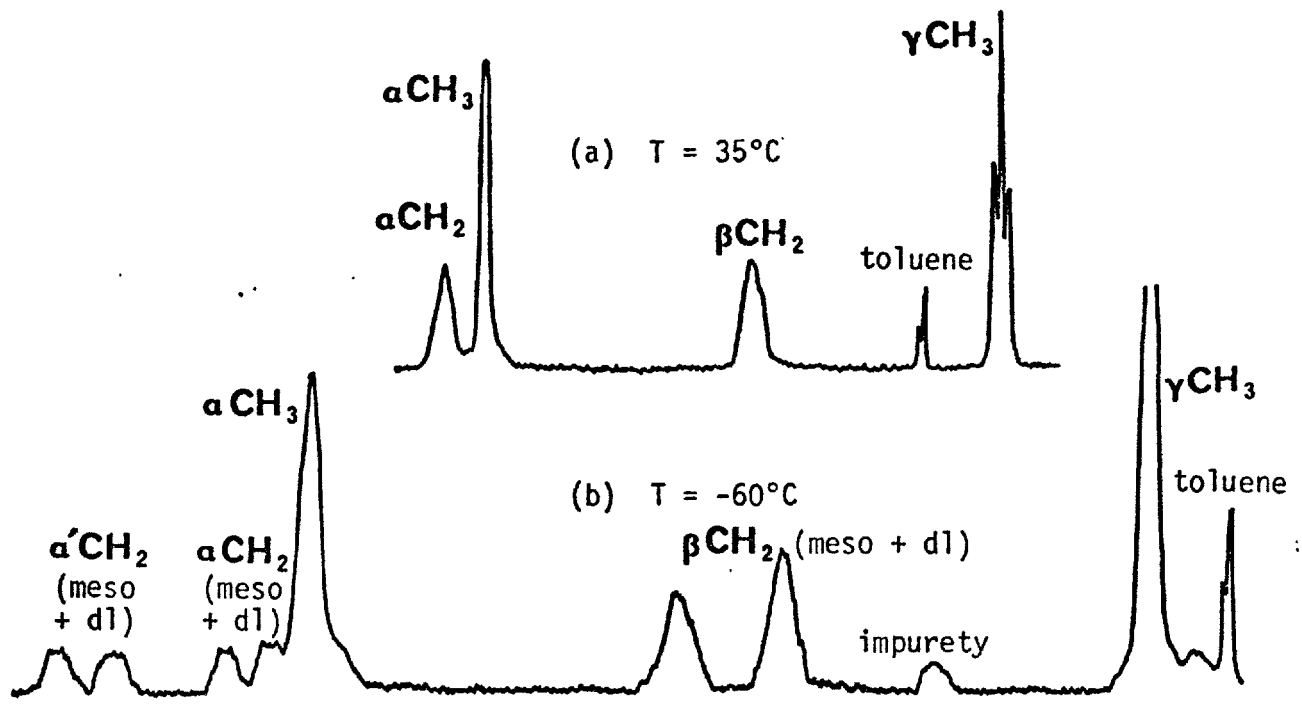


Fig. 17 Eu(fod-d_9)$_3$- (0.2M) MPA (0.3M) system in $CD_3C_6D_5$.

Table 10

'Bound' chemical shifts for Lnfod-piperidine systems.*

T°C	Piperidine - $Eu(d_9\text{-fod})_3$					
	α'	α	β'	β	γ'	γ
-50	-35.5	-31.0	-14.7	-7.6	-13.1	-9.6
-55	-36.7	-32.1	-15.3	-8.0	-13.5	-10.0
-60	-37.8	-32.9	-15.7	-8.2	-14.0	-10.2
-70	-40.4	-34.9	-16.6	-8.8	-14.8	-10.8
-75	-41.7	-36.0	-17.0	-9.2	-15.2	-11.1
-80	-43.2	-37.2	-17.7	-9.6	-15.8	-11.4
-85	-44.8	-38.5	-18.3	-10.0	-16.4	-11.9
-90	-46.4	-39.7	-18.9	-10.3	-17.0	-12.2

T°C	Piperidine - $Pr(d_9\text{-fod})_3$					
	α'	α	β'	β	γ'	γ
-20	38.7	43.2	14.7	22.6	13.7	17.1
-30	40.4	45.3	15.1	24.3	14.4	18.3
-50	42	ca. 45	ca. 15	26.1	ca. 15	18.8

* 0.2M solutions in d_8-toluene; shifts in ppm.

but the coalescence temperature and, consequently, the exchange life-time τ vary as more amine is added to the solution (T_c = -7°C, τ= 0.86 ms for [Prfod]/ [piperidine] = 2; T_c = -30°C, τ= 0.41 ms for [Prfod]/ [piperidine] = 1).

The solvation number of the adducts were not directly measured at low temperature for intermolecular exchange cannot be slowed down. The spectra of solutions containing more than 2 eq. of amine for 1 eq. of LSR display no resonances for uncomplexed amine. However there is evidence of the simultaneous presence of 1:1 and 1:2 adducts in the room temperature spectra of solutions containing 1 eq. of undeuterated $Pr(fod)_3$ and 0.5 to 1 eq. of piperidine; distinct resonances for the tBu and methine protons can be observed (τ = 1.7 ms at 80°C).

c) Other amines : diethylamine (DEA) and N-methyl-t-butylamine (MTA)

The same techniques as those previously described show that intermolecular exchange is slowed down at low temperature in the Prfod-MTA system (table 11) and in the Prfod-DEA system when DEA is not in excess.

The adducts present in the solution at low temperature are mainly of the RS_2 type.

Table 11

$Pr(d_9\text{-fod})_3$-MTA bound chemical shifts (ppm, $CD_3C_6D_5$ sol.)

T(°C)	-20	-40	-50	-60	-70
CH_3	43.3	50.8	54.0	57.1	ca. 59
tBu	27.0	30.3	32.1	33.4	35.1

2) Tertiary amines

a) Acyclic amines

A diastereotopic splitting of the methylene resonances is observed in low temperature spectra of Eufod-MDEA (N-methyldiethylamine), coalescence is obtained at -5°C ($\tau \simeq 1.5$ ms). The methylene resonances also split in the spectra of Eufod-MEPA (N,N-methylethylpropylamine).

Nitrogen inversion (and consequently intermolecular exchange) has therefore been slowed down in these two systems. However there is no splitting of the MEPA methyl groups which would reveal the presence of RS_2 diastereoisomers. The usual techniques (room temperature integration of undeuterated fod peaks and low temperature integration of free and complexed amine in excess-amine solutions) show that the adduct stoïchiometry is entirely 1:1. An appreciable broadening of signals is observed when the LSR to amine ratio is varied from 1:0.75 to 1:1 and even more so in a 1:1.5 solution : the intermolecular exchange rate increases as more substrate is added to the solution.

In the Eufod-DMTA system (N,N-dimethyl-tertiobutylamine), where steric interactions are important because of the bulk of the tBu group and the small europium radius, the rate for intermolecular exchange is slower than in the other amines. Dissociation of the adduct is significant even in solutions containing a low amine to LSR ratio.

An apparent equilibrium constant can be calculated (see appendix III) if reagent dimerization is not taken

into account. $K_1 = [RS][R]^{-1}[S]^{-1} = 3.8 \pm 0.5\ mol^{-1}$.

Neither nitrogen inversion nor intermolecular exchange could be slowed down in Prfod-MDEA and in Prfod-DMPA (N,N-dimethylpropylamine). Exchange is fast at room temperature and signals flatten out as the temperature is lowered.

The room temperature spectrum of a solution 0.2M in Prfod and 0.1M in MDPA (N-methyldipropylamine) displays resonances for R (or R_2) and RS species. Integration of the undeuterated fod peaks indicates 1:1 stoïchiometry; the tBu peaks coalesce at 77°C (τ = 2.9 ms). At 40°C single resonances are observed for the α- and β- methylene protons : nitrogen inversion is fast on an nmr time-scale. Furthermore, the coalescence temperatures vary with the Prfod : MDPA ratio (T_c = 35°C, 25°C and 15°C for R:S = 4, 2 and 1.3 respectively).

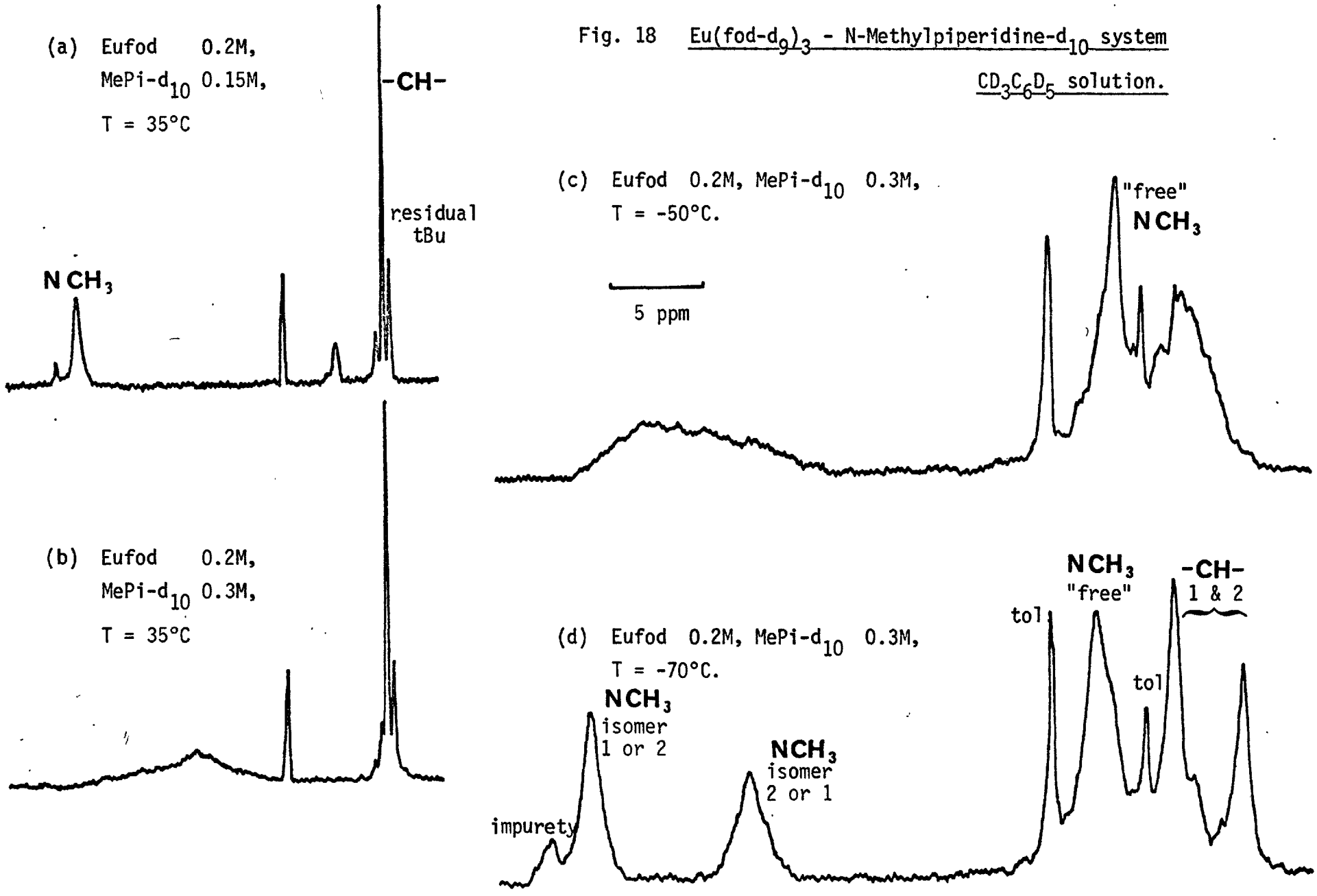
b) Cyclic amines : Eufod-MePi (N-methylpiperidine)

Owing to its great complexity, the low temperature nmr spectrum of the Eu(d_9-fod)$_3$-MePi system could not be interpreted.

The analogous MePi-d_{10} (N-methyldecadeuteropiperidine) room temperature spectrum is very simple (fig. 18a). As the temperature is lowered, the methyl resonance broadens and finally splits in two thus suggesting the presence of two adducts. Integration of the methyl peaks at various temperatures and R:S ratios indicates that the two species are equally populated (within experimental error).

Fig. 18 Eu(fod-d_9)$_3$ - N-Methylpiperidine-d_{10} system

$CD_3C_6D_5$ solution.



Intermolecular exchange and ring inversion are both slow on an nmr time-scale at -70°C (fig. 18d). At -50°C (fig. 18c) the free amine resonance is quite sharp showing that intermolecular exchange is slow. However, the resonance pattern of the complexed amine indicates that ring inversion is moderately fast. The room temperature spectrum of a solution containing an excess of Eufod (fig. 18a) displays a single sharp peak arising from the averaged equatorial and axial methyl resonances whereas the analogous peak in a solution containing an excess of substrate (fig. 18b) is very broad owing to intermolecular exchange between free and complexed amine.

The stoïchiometry of the adduct was determined as 1:1 by integration of the free and complexed substrate resonances in the low temperature spectrum of a solution containing an excess of MePi-d_{10}.

The methyl resonances coalesce at ca.-48°C(τ = 0.65 ms) (fig. 18a).

INTERPRETATION OF RESULTS

The variety of LSR-amine systems studied in this chapter yields useful information on how steric interactions between reagent and substrate will effect the stability and stoïchiometry of the adducts formed. Although such systems cannot be reduced to simple mathematical models, attempts have been made to calculate rough values of kinetic and equilibrium constants in order to have an idea of the adduct-formation mechanism.

1) Stoichiometry and stability of LSR-amine adducts

a) Tertiary amines form 1:1 complexes only, with both Prfod and Eufod. The steric requirements of a tertiary amine, even as small an amine as Et_3N, cf. Evans & Wyatt,[34] are quite large.

A bulky amine such as DMTA also forms a 1:1 adduct with Eufod but appreciable dissociation takes place even in a solution containing an excess of shift reagent. DMPA is less sterically demanding since no measurable dissociation is observed in a solution containing equimolar quantities of Eufod and amine.

b) Secondary amines have smaller steric requirements than their tertiary counterparts. They usually form 1:2 adducts with Prfod and also with Eufod when the amine is not too bulky (as in the case of DEA and MPA). The greater tendency of Prfod to form 1:2 complexes can be attributed to the larger size of the Pr^{3+} ion. When the amine contains two bulky groups (eg. DPA), there can be a marked preference for 1:1 adduct formation with Eufod (K_2/K_1 = 0.01 to 0.05 in the Eufod-DPA system; see appendix III for calculations). The Eufod-DPA system contradicts all predictions since induced shifts of the 1:2 adducts are greater than those for the 1:1 adduct. These predictions were based on the mean Ln-proton distances that should be greater in a 1:2 adduct than in a 1:1 adduct,[72] or on the average values of θ.[34] The directions of the magnetic axes of the systems are presumably such that the

averaged δ values are smaller in the 1:2 than in the 1:1 adduct.

2) Proposed mechanisms

Chemical shift nonequivalence in the resonances of diastereotopic groups is a very useful probe for intermolecular exchange studies : the method can be used at any S:R ratio whereas other methods require an excess of either substrate or reagent.

However, great care must be taken in interpreting spectral results : ambiguity seems to appear in the Prfod-MDPA system where the spectra recorded between 40°C and 70°C each display two distinct sets of fod peaks (free and complexed fod in a solution containing an excess of shift reagent) and nonequivalence of the methylene protons only appears at lower temperature. This can be explained (see below) by the fact that the mechanisms involved are not necessarily the same for Lnfod exchange and for the presence of diastereotopic splitting.

a) Tertiary amines

Both dissociative and associative mechanisms were found for the substrate exchange processes in the Eufod- and Prfod-triethylamine systems.[34]

An associative mechanism involving an eight-coordinate transition state can explain the apparent ambiguity mentioned above in the Prfod-MDPA system for $R/S \leqslant 1$:

$$RS + S^* \rightleftharpoons RSS^* \rightleftharpoons RS^* + S$$

Catalytic amounts of free substrate[73] can cause a scrambling of the free and complexed MDPA resonances due to

ligand exchange and rapid N inversion in the free amine while the reagent spectrum still displays signals corresponding to free (R or R_2) and complexed (RS) forms. The collapse of these signals involves the dissociative mechanism $RS \rightleftharpoons R + S$. If this interpretation is correct, T_c should increase steadily as the LSR to amine ratio is increased : this is in fact observed (cf. p.49). The limit for T_c should be the coalescence temperature of the fod peaks (77°C) but this could not be observed experimentally.

b) Secondary amines

The two main equilibria involving reagent and substrate are the following :

((1)) $R + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RS$; $K_1 = k_1/k_{-1}$.

((2)) $RS + S \rightleftharpoons RS_2$; K_2.

Exchange involving equilibrium ((1)) is usually slow on an nmr time-scale at room temperature : coalescence of the free and complexed fod peaks occurring at high temperatures (75 to 80°C). This indicates that either k_1 or k_{-1} is small; K_1 is known to be large hence k_{-1} is small.

Nitrogen inversion is normally fast at room temperature : it is concomitant with amine exchange through equilibrium ((2)), for inversion can only occur when either equilibrium ((1)) or ((2)) is fast, and equilibrium ((2)) is always found to be faster than ((1)).

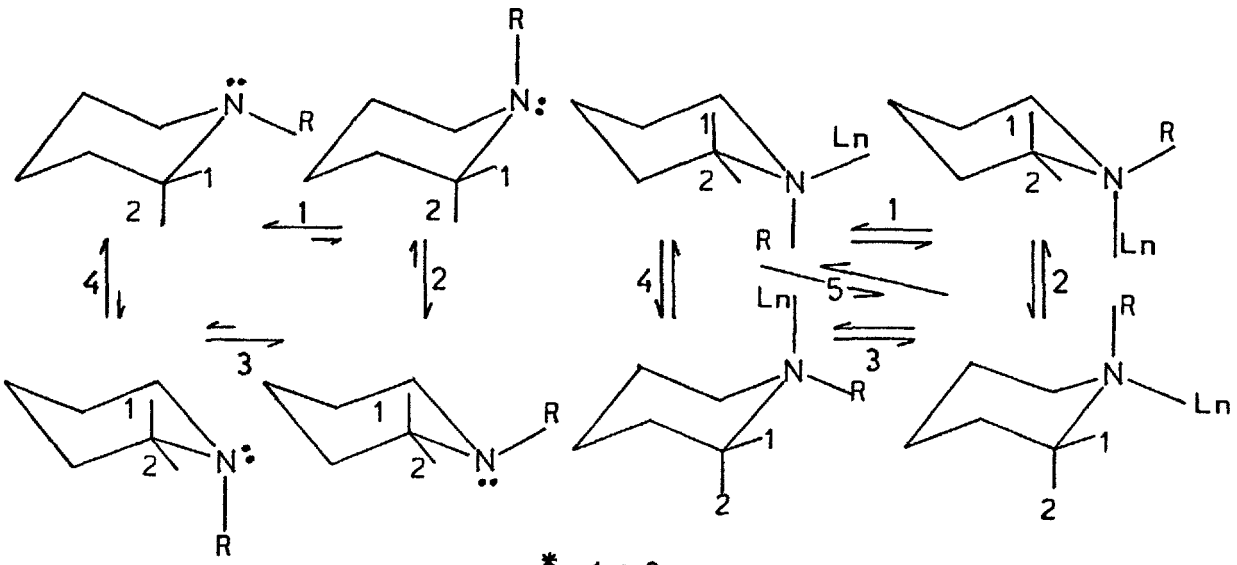
Exchange rates increase as more free substrate is present in solution. This is an indication of an appreciable contribution of the associative mechanism described in equilibrium ((2)).

c) Cyclic amines

The following diagrams illustrate the various exchange processes in free and complexed piperidine (R = H) and N-methyl-piperidine (R = Me). Ln = LSR ; H_1 and H_2 are two distinct α-protons.

Fig. 19a : Free amine.

Fig. 19b : Amine - LSR system.*



* 1 & 3 involve N—Ln bond breaking

- Piperidine

If it is assumed that nitrogen inversion does not occur whilst the amine is complexed (see earlier discussion) and that the equatorial-lanthanide adduct is favoured over the axial-lanthanide adduct, the only possible types of exchange in a piperidine-LSR adduct, are those listed in the following table.

Table 12

Exchanges in an LSR-piperidine system.

exchange type	intermolecular exchange	ring inversion	H_1 , H_2	equilibria involved
A	slow	slow	2 signals*	—
B	slow	fast	2 signals	2&4
C	fast	slow	2 signals	1&3
D	fast	fast	1 signal	1,2,3&4

* Two small sets of resonances would theoretically also be expected for the protons of the unfavoured axial-Ln complex.

Like the other secondary amine-LSR systems studied in this chapter, intermolecular exchange ((1)) : $R + S \rightleftharpoons RS$ is slow at room temperature. Intermolecular exchange ((2)) : $RS + S \rightleftharpoons RS_2$ could not be slowed down in solutions containing more than 2 eq. of amine and 1 eq. of LSR. The nmr spectra of solutions containing 1 eq. of shift reagent and 0.5 to 2 eq. of amine gave no indication as to whether equilibrium ((2)) had in fact been slowed down.

Room temperature spectra of Eufod- or Prfod-piperidine solutions display single resonances for both protons H_1 and H_2 (fig. 19). The data listed in table 12 indicate that intermolecular exchange and ring inversion are both fast according to situation D. The adduct behaves as if it were following equilibrium process 5 (see fig. 19b).

Table 13

Kinetic data for Prfod-piperidine solutions

Coalescence of the β-CH_2 resonance

[R]:[S]	T_c	$\lvert\delta_{ax} - \delta_{eq}\rvert$	τ_c (ms)	$\tau_{-62.5°C}$ (ms)
1:1 (a)	-5°C	261 Hz	0.86	580 (c)
1:2 (a)	-30°C	543 Hz	0.41	14 (c)
0 (b)	-62.5°C	32.4 Hz	15	15

(a) data concerning the coalescence of the βCH_2 resonance; d_8-toluene solutions.

(b) from (74), data concerning the coalescence of the αCH_2 resonances; d_4-methanol solution.

(c) estimated (see appendix I).

Life-times at the coalescence temperature (T_c) are given by the expression $\tau_c = 1/\pi\sqrt{2}\left|\delta_{ax}-\delta_{eq}\right|$ (see appendix I), where $\left|\delta_{ax}-\delta_{eq}\right|$ is the absolute difference in shifts between the axial and equatorial β-CH_2 protons.

The figures listed in the table indicate that in the solution containing 1eq. of LSR and 1 eq. of piperidine, the coalescence observed at -30°C corresponds to a mechanism involving fast N—Ln bond rupture followed by ring inversion in the free amine and subsequent complexation. In the equimolar solution, the β-CH_2 protons coalesce at a higher temperature. The smaller apparent rate of ring inversion

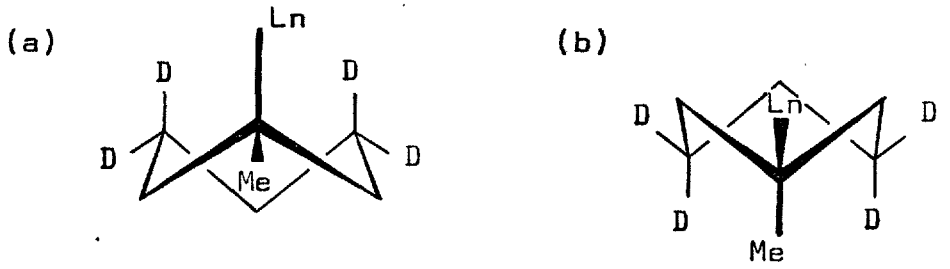
(τ = 0.86 ms for the 1:1 solution and an estimated 0.05 ms for the 1:2 solution at -5°C) is presumably due to the smaller molar ratio of free to complexed substrate (cf. the protonation experiments[65] mentioned earlier).

In the presence of an excess of Prfod, intermolecular exchange is slower than ring inversion. Adding more substrate to the solution increases the intermolecular exchange rate. In the presence of more than 2 eq. of amine and 1 eq. of Prfod, separate signals for free and complexed amine could not be seen even at low temperature.

N-Methylpiperidine

At low temperature, the nmr spectra of Prfod-MePi-d_{10} solutions indicate, somewhat surprisingly, that conformers (a) and (b) have approximately equal populations. (see p.49)

Fig. 20 Chair conformations of the Eufod-MePi-d_{10} adduct



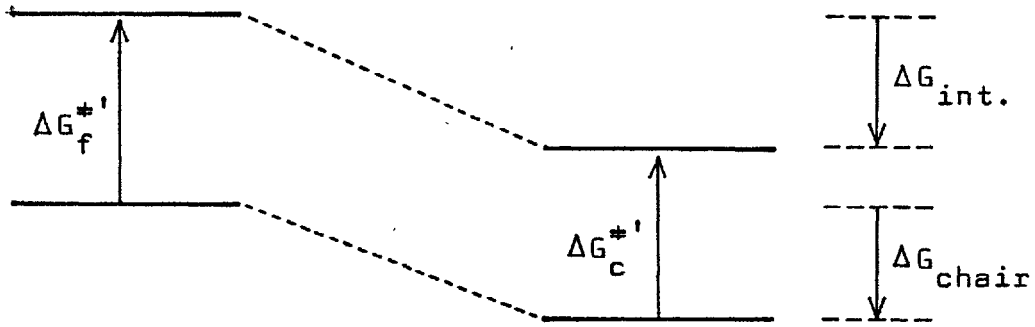
The Eufod and methyl groups have comparable steric requirements in the complex : although the Eufod moiety has a larger bulk than the methyl group, the N-Eu distance (ca. 2.6 Å) is nearly twice the N-CH_3 distance (1.47 Å).

Since intermolecular exchange is much slower than ring inversion, the activation energy of the latter process could

be calculated from the observed coalescence of the methyl resonances. As expected, the coalescence temperature was virtually independent of the R/S ratio. The value so obtained ($\Delta G_c^{\ddagger}$ = 10.1 ± 0.1 kcalmol^{-1} at -48°C) is substantially smaller than that of the free substrate ($\Delta G_f^{\ddagger}$ = 12.1 kcalmol^{-1} at -28°C).(74)

Fig. 21 illustrates the fact that stabilization by lanthanide complexation is greater for the ring inversion intermediate ($\Delta G_{int.}$) than for either of the two ground state conformations (ΔG_{chair}).

Fig. 21 Energy diagrams of the Eufod-MePi system.



n.b. the energies $\Delta G_f^{\ddagger}$ and $\Delta G_c^{\ddagger}$ are for the overall chair-chair ring inversion processes. If a single intermediate exists and two barriers of equal energies are crossed in the ring inversion process,

$\Delta G^{\ddagger'}_{(\text{chair to intermediate})} = \Delta G^{\ddagger}_{(\text{chair-chair})} - RT\ln 2$.

At -50°C, $RT\ln 2$ = 0.3 kcalmol^{-1}.(75)

This stabilization of the transition state of the amine relative to the ground (chair form) state could arise from steric effects or electronic effects (an increase in the donor properties of the amine).

d) Interpretation of chemical shift nonequivalence

The use of diasterotopic splitting to obtain conformational information can be hazardous because of the great number of geometrical parameters involved in the calculation of ϑ and r values (see introduction) in complicated systems.(76)

An attempt to describe the likely conformations of Prfod- and Eufod-amine complexes will nevertheless be made by means of qualitative arguments.

Figure 22 and 23 represent the three staggered positions that can be interconverted by a $2\pi/3$ rotation about the CH_2—N bond. The expected primary and secondary effects (effects concerning H_a, H_b and $H_{a'}$, $H_{b'}$, respectively) are listed in the following table :

Table 14

Diastereotopic effects in Lnfod-RDPA adducts.

effect	a	b	c
Primary	$\delta H_a > \delta H_b$	$\delta H_a = \delta H_b$	$\delta H_a < \delta H_b$
Secondary	$\delta H_{a'} > \delta H_{b'}$	$\delta H_{a'} = \delta H_{b'}$	$\delta H_{a'} < \delta H_{b'}$

In conformation a proton H_a is closer to the lanthanide than is H_b, hence $\delta H_a > \delta H_b$. The secondary effect can

Figure 22

RDPA-Ln(fod)$_3$ complex : Newman projections down a CH_2—N bond (R = H, CH_3).

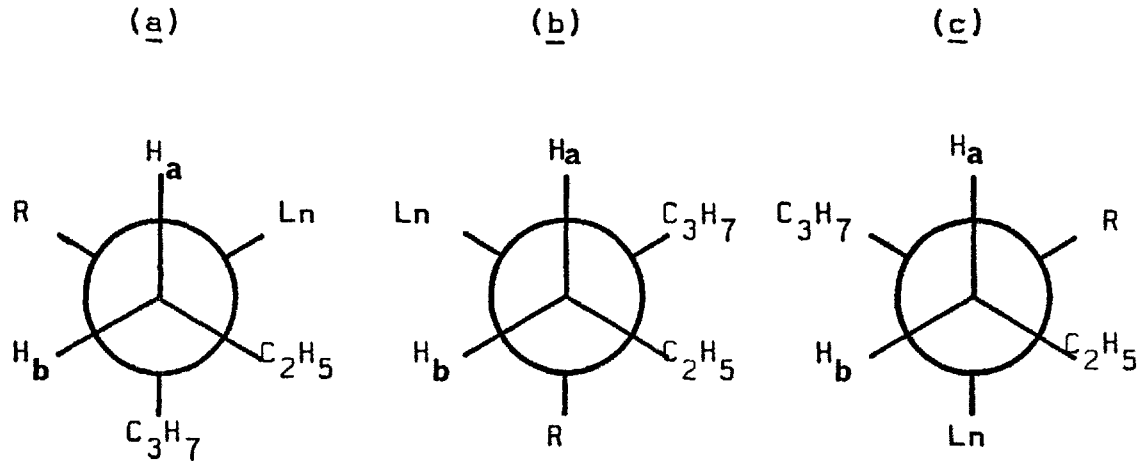
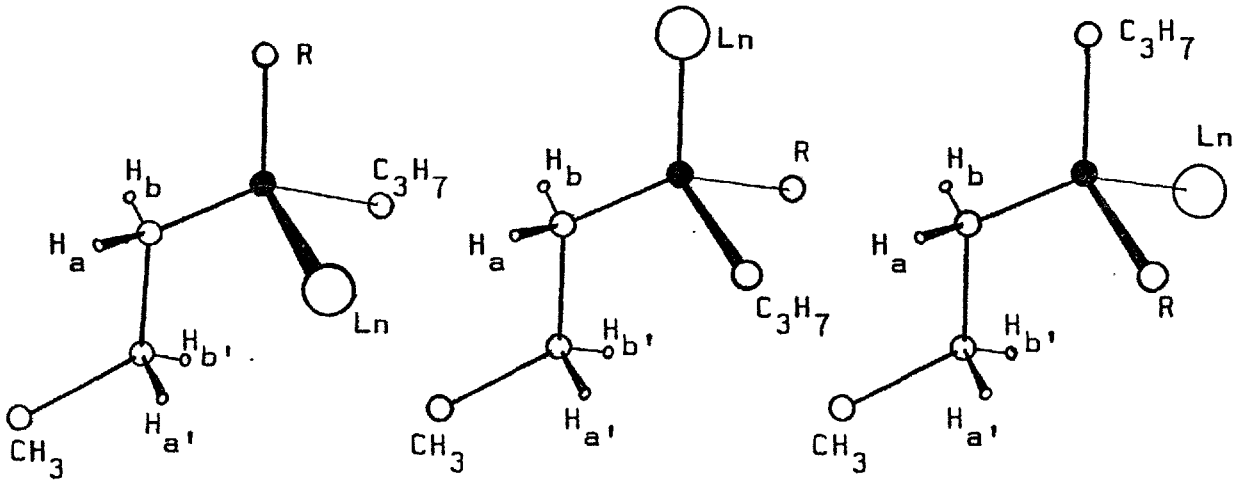


Figure 23

RDPA-Ln(fod)$_3$ complex.



$\delta H_a > \delta H_b$ $\quad$ $\delta H_a = \delta H_b$ $\quad$ $\delta H_a < \delta H_b$

$\delta H_{a'} > \delta H_{b'}$ $\quad$ $\delta H_{a'} = \delta H_{b'}$ $\quad$ $\delta H_{a'} < \delta H_{b'}$

be deduced from figures 23 a, b, c representing the most favourable (least sterically demanding) position of the β-carbon tetrahedral system, which is the one where the methyl group lies in a plane bissecting the (CH_a, CH_b) angle.

Although rotation about the C—C and C—N bonds is rapid, some conformations are more stable than others, and hence more populated. The magnitude of the resulting chemical shift will depend on the relative populations of the various conformations although it may be noted (see p.38) that even if the conformers were equally populated, there would still be an 'intrinsic' nonequivalence.(70)

DPA.

Rotamer (a) (fig. 22) should be the least stable as there are two interactions between bulky groups (C_2H_5 is "between" C_3H_7 and Ln). Rotamers (b) and (c) can be considered as approximately equivalent on first analysis. The populations of the two rotamers will presumably depend on the relative sizes of the LSR and the n-propyl group.

Table 15 lists the values of the chemical shift differences $\Delta = |\delta H_a - \delta H_b|$ and of $\zeta = \Delta / \bar{\delta}$ where $\bar{\delta}$ is the average chemical shift $\frac{1}{2} |H_a + H_b|$. ζ is a measure of the relative chemical shift nonequivalence of H_a and H_b since it takes account of the temperature dependence of lanthanide induced shifts. The corresponding values for protons H_a' and H_b' are also listed.

Table 15

Primary and secondary diastereotopic effects in LSR-amine complexes.*

Lnfod:amine	T°C	δH_a^{**}	δH_b^{**}	ζ	$\delta H_{a'}^{**}$	$\delta H_{b'}^{**}$	ζ'
Prfod:DPA 1:2	-40	50.8	43.0	0.166	—	—	—
	-50	56.0	45.7	0.202	—	—	—
	-60	59.8	47.9	0.221	34.3	33.6	0.021
	-70	63.2	49.5	0.243	36.2	35.4	0.022
	-78	67.1	51.2	0.269	38.5	37.6	0.024
Eufod:DPA 1:1	-30	22.8	17.8	0.24_6	no secondary effect.		
	-50	26.0	20.9	0.21_7			
	-60	27.2	22.5	0.18_9			
	-70	28.7	24.4	0.16_2			
	-75	29.5	25.3	0.15_3			
Eufod:DPA 1:2	-50	29.6	22.6	0.26_8	no secondary effect.		
	-70	32.2	23.4	0.31_7			
	-75	32.6	24.9	0.26_7			
Prfod:MDPA 1:1	-40	42.4	44.7	0.05_3	26.1	30.2	0.14_6
	-50	44.0	45.7	0.04_0	25.6	30.0	0.15_8
	-60	46.0	49.4	0.07_1	26.3	31.2	0.17_0
	-70	51.2	54.0	0.05_3	27.6	33.2	0.18_4

* δ and ζ are defined on p.62 ; deuterotoluene solutions.

** ppm.

As the temperature is lowered, ζ increases in the Prfod$(DPA)_2$ complex, where conformation (c) is presumably preferred, ζ decreases in Eufod(DPA) and no trend is observed in Eufod$(DPA)_2$.

These results are consistent with the fact that the Eu—N bond is presumably shorter than the Pr—N bond, (by ca. 0.1 Å), hence interactions between the C_2H_5 group and the europium fod moiety are greater than those in the analogous praseodymium system.

Secondary effects (nonequivalence of H_a' and H_b' are smaller than primary effects : ζ' is only one-tenth of ζ in the Prfod-DPA adduct. No secondary effect was observed in the europium adduct.

Prfod-MDPA

The populations of the three rotamers should be approximately equivalent with perhaps a slight preference to conformation (b) where the n-propyl group is staggered between H_a and H_b. Overall ζ values are substantially smaller than in the analogous DPA adduct. No definite trend was observed in the temperature-dependency of ζ : this can be partly attributed to the low precision in the measurement of small chemical shift differences.

Large values of ζ' cannot only be explained in terms of proximity of the diasterotopic protons to the lanthanide; the ϑ angles between the Ln-H axes and the magnetic axis of the complex should also be taken into account.

CHAPTER III

DIAMINO CHELATES OF LANTHANIDE SHIFT REAGENTS

Diaminoalkanes have long been known as powerful chelating agents. Metal complexes with ethylenediamine and substituted ethylenediamines have played an important part in the development of inorganic conformational analysis.[77]

This chapter describes the dnmr study of conformational exchanges in substituted en chelates of $Ln(fod)_3$, (Ln = Pr mainly,[78] but also Eu and Yb). Longer chain diamines and NN'-dimethylpiperazine have also been investigated. The various dynamic processes in diamino-chelates can be listed as follow :

-a) complete dissociation involving the cleavage of both Ln—N bonds. The slowing down of this process can be evidenced by the presence of distinct resonances for the free and complexed species.

-b) the rupture of a single Ln—N bond leads to racemization of the chelate through nitrogen inversion followed by rotation about the C—C and C—N bonds and ring closure.

-c) chelate ring inversion : this process involves no bond breaking, hence no racemization of the chiral (or prochiral) centres.

-d) intramolecular rearrangements of the various chelate rings. This low-energy process can cause an overall

broadening of the nmr spectrum at low temperature.

GEOMETRY OF DIAMINO CHELATES

1) five membered rings

It has now been firmly established by X-ray and ir spectroscopy that ethylenediamine and substituted ethylenediamine chelate rings adopt a puckered conformation in the solid state.[79] Nmr studies of paramagnetic complexes[80] have shown that such a conformation is also adopted in solution.

Figure 25 shows the ethylenediamine chelate ring in a "λ" configuration[79a] and figure 26 shows its enantiomeric "δ" configuration.

Nmr studies of the Ni^{II} dimethylethylenediamine (DMen) complex in aqueous solution by Reilley[68] show that two geometric isomers are present : an optically active dl form and an inactive meso form as illustrated in fig. 24.

Fig. 24 Conformations of DMen chelates.

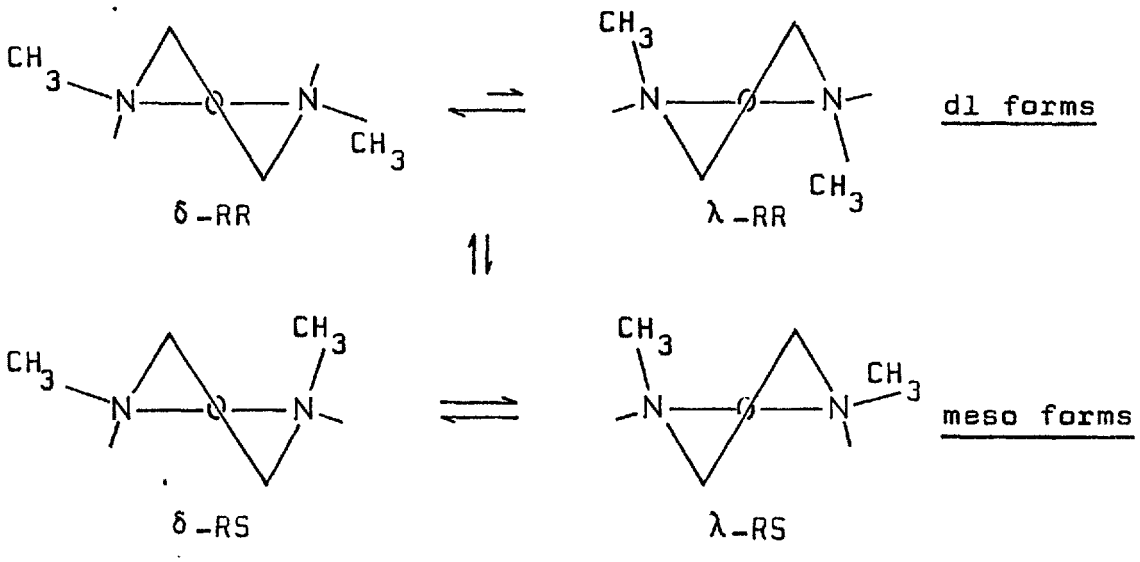


Fig. 25 Symmetric skew five-membered chelate ring λ configuration. From (79a).

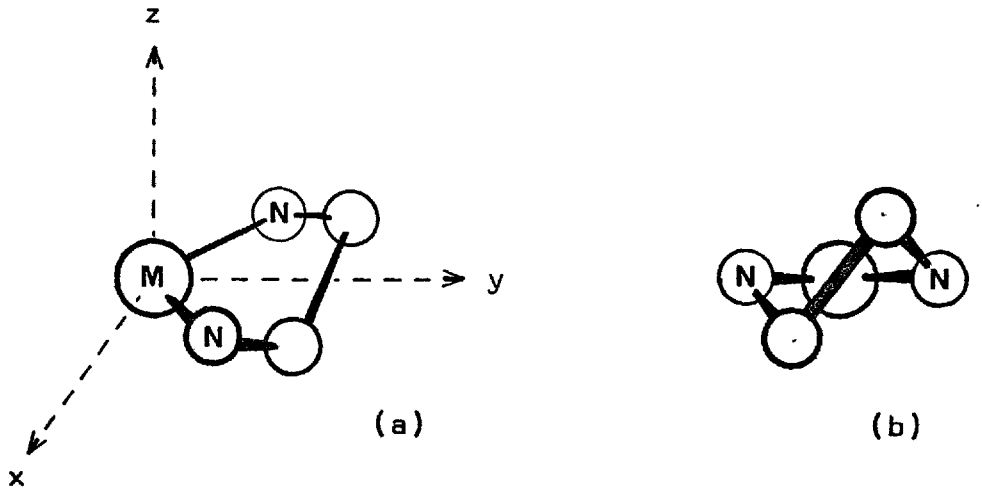


Fig. 26 δ configuration.

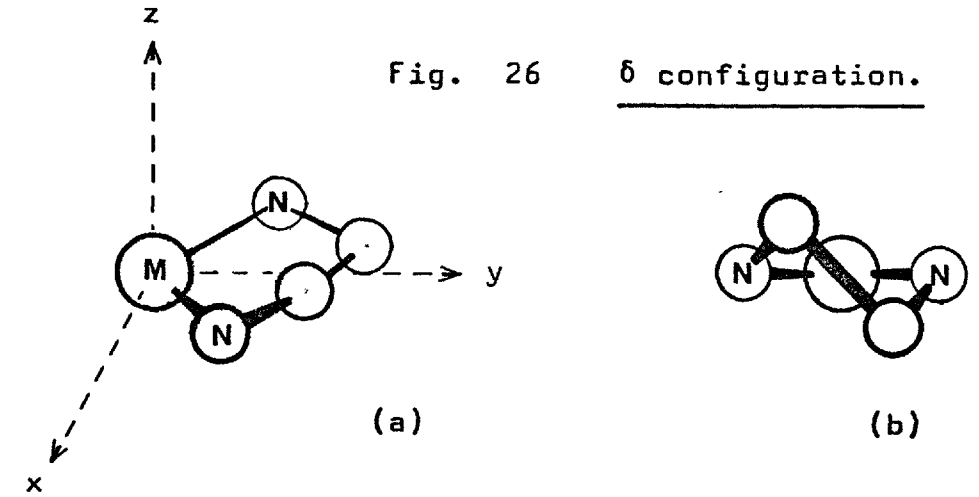
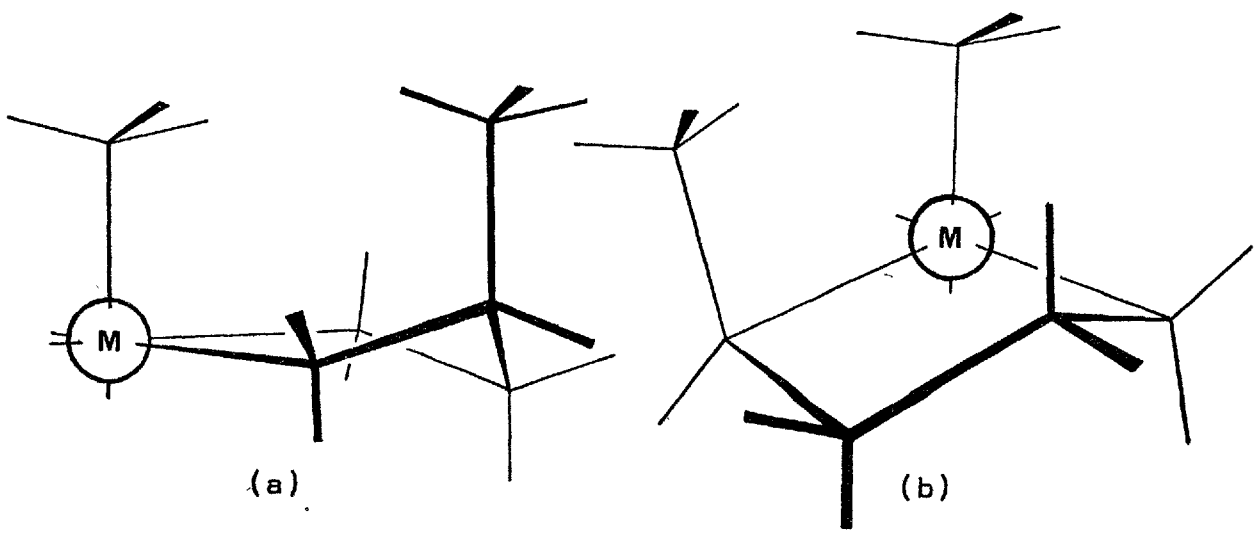


Fig. 27 Axial orientation of the substituent in a C-substituted (a) and N-substituted (b) ethylenediamine complex. From (79a).



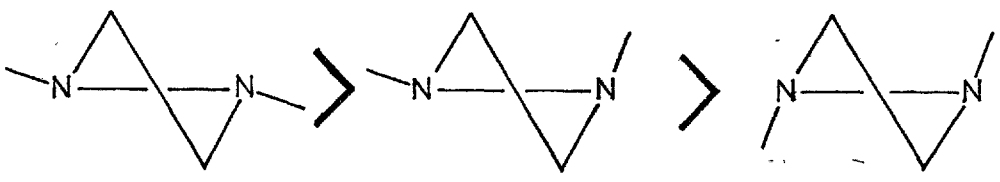
δ-RR and its enantiomer λ-SS have identical nmr spectra as do λ-RR and δ-SS (neither λ-SS nor δ-SS have been represented above). The two enantiomeric meso forms also have identical nmr spectra.

Three distinct species are found in aqueous solutions of Ni^{II} 2,3-diaminobutane two nonidentical racemic forms and one meso form.[81]

Unfortunately ring inversion is fast on an nmr time-scale in these systems; aqueous solutions cannot be cooled down sufficiently to enable observation of slow inversion of the chelate ring (see also ref.[82] for $Ni^{II}(en)_3$).

However barriers to ring inversion have been calculated (ca. 6kcalmol^{-1} for Ni^{II} ethylenediamine complexes[77b] and conformational preferences have been determined by indirect methods.

Through-space interactions between two ring substituents or between a substituent and the rest of the complex (as in fig. 27) can stabilize a particular conformation. The preferred conformation will normally be that having as many substituents as possible in an equatorial position.[68] The order of preference for a DMen chelate will be :



Reilley[68] found the percentage of racemic form to be 58% for an aqueous solution of $\left[Ni^{II}(DMen) \right]^{2+}$. He also estimated the percentages of diequatorial (47%) and diaxial (11%) species.

2) Piperazine adducts.

Stable chelates of N N'-dimethylpiperazine (DMp) have been reported with metals such as Pd^{II}, Pt^{II}, Ir^{I}.[83] An early X-ray determination gives evidence that the piperazine ring is in the boat conformation in $Pd^{II}Cl_2(DMp)$.[84] A recent complete molecular structure of a lithio-carbene complex containing a DMp chelating system confirms the boat conformation. The metal to nitrogen bond lengths are 2.00 Å in the palladous complex and 2.24 Å in the lithium complex.[85]

3) Other chelate rings.

The six-membered chelate ring formed by 1,3-diaminopropane (tn) has not been studied as intensely as its five-membered counterpart. However, theory[86] and experimental methods,[87] indicate that a slightly-flattened chair form is the most stable conformation. The calculated barrier to inversion of a chair form with a metal to nitrogen bond length of 2 Å is ca.7 $kcalmol^{-1}$.

Seven-membered chelate rings are little known, they do not form as readily as the six- or five-membered rings : the chelate effect tends to decrease with increasing ring size.[88]

SPECTRAL INTERPRETATION FOR $Ln(fod)_3$ DIAMINO CHELATES.

1) Prfod-substituted ethylenediamine systems.

a) N N N'N'-Tetramethylethylenediamine (TMen).

The room-temperature spectrum of $Pr(d_9\text{-fod})_3$ (TMen) (fig. 28a) displays two major peaks, one from the methyls and the other from the ring methylenes. The small resonance upfield from the toluene signals arises from the residual protons of the fod-d_9 tBu groups. The fod methine signal which is not displayed in fig. 28a is at higher field.

As the temperature is lowered, the two main peaks broaden and at -60°C, two sets of resonances can be observed in fig. 28b : the high-field methyl resonance was attributed to the equatorial position in a 5-membered puckered ring by analogy with the $Pr(fod)_3$-DMen spectra (see later). Similarly the high-field methylene resonance was attributed to the equatorial protons by analogy with the Prfod-TMpn spectra (see later).

At -30°C, the spectrum of a solution containing an excess of TMen displays separate peaks due to free and complexed amine. However the spectrum of the complexed amine shows that intramolecular exchange between the axial and equatorial methyl groups and methylene protons is still fast whilst intermolecular exchange has been slowed down. It is clear that TMen forms a bidentate complex for if it were monodentate, intermolecular exchange and methyl (or methylene proton exchange would be isochronous.

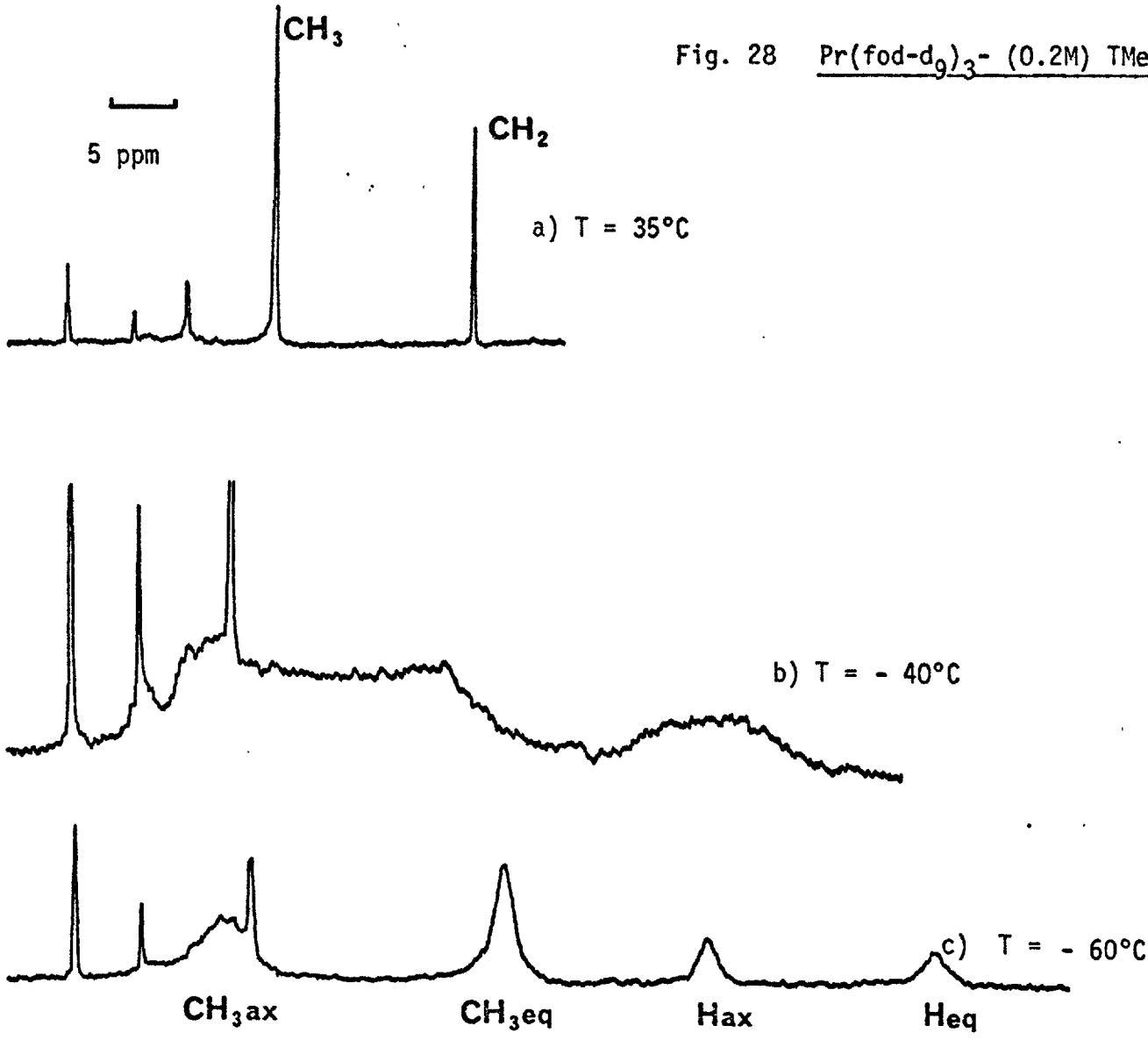


Fig. 28 Pr(fod-d_9)$_3$- (0.2M) TMen (0.2M) system in $CD_3C_6D_5$.

SPECTRAL INTERPRETATION FOR $Ln(fod)_3$ DIAMINO CHELATES.

1) Prfod-substituted ethylenediamine systems.

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Table 16

Bound chemical shifts of Prfod-TMen.* (ppm)

T°C	CH_{3eq}	CH_{3ax}	H_{ax}	H_{eq}
-50	24.8	5.7	38.4	52.5
-60	26.2	6.1	41.1	57.5
-70	27.6	6.0	45.1	62.9

Table 17

Prfod-TEen chemical shifts.*

T°C	CH_3(1) or (2)	CH_3(2) or (1)	H_a**	H_b**
-25	17.0	26.6	36.3	41.1
-30	17.2	28.0	36.9	43.3
-35	17.5	28.2	38.6	44.6
-40	18.0	29.2	40.6	—
-45	18.7	30.0	40.9	—

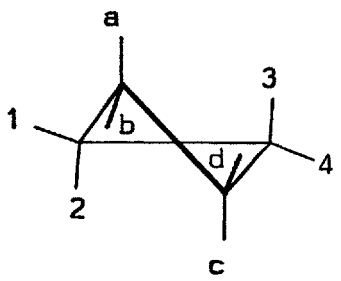


Table 18

Prfod-TMpn chemical shifts.*

T°C	2 or 3	3 or 2	1 or 4	4 or 1	CH_3(b)	H_a	H_c	H_d
35	1.9	2.9	17.6	21.8	12.2	28.1	26.1	19.5
25	2.0	3.0	18.5	22.8	12.9	30.1	27.9	20.7
20	2.0	3.0	18.9	23.3	13.4	31.1	28.7	21.4
0	2.3	3.2	20.8	25.9	15.2	36.0	33.2	24.6
-20	3.0	3.5	22.6	28.3	17.3	41.5	38.1	28.3
-40	4.1	4.1	25.3	31.8	20.5	50.0	45.5	33.8
-50	4.5	4.5	26.1	33.0	21.8	53.9	49.0	36.4
-60	ca. 4.9	ca. 4.9	27.3	34.5	23.6	59.0	53.4	39.7
-70	—	—	28.2	35.9	25.3	ca. 64	57.8	43.0

(1,2,3,4,b = CH_3)

*Average values for various LSR/amine ratios; d_8-toluene solutions.

**Most likely assignments.

Integration of the free and complexed amine peaks at low temperatures and of the free and complexed undeuterated fod peaks at room temperature (in a solution containing 2 eq. of Prfod and 1 eq. of TMen) indicate a 1:1 stoïchiometry for the complex.

Since substrate exchange is much slower than ring inversion, it is possible to calculate the barrier to ring inversion at the coalescence temperature of the methyl resonances ($\Delta G^{\ddagger}$ = 10.11 kcalmol^{-1} at -36°C) or at the coalescence temperature of the methylene resonances ($\Delta G^{\ddagger}$ = 10.07 kcalmol^{-1} at -38°C).

Bound chemical shifts for the Prfod-TMen complex are listed in table 16.

b) N N N'N'-tetramethyl-1,2-diaminopropane (TMpn)

The resonance pattern of a Pr(d_9-fod)$_3$-TMpn solution does not vary much in the +35°C to -60°C temperature range. A 20°C spectrum (fig. 29a) displays five signals from the methyl groups and three signals from the ring protons.

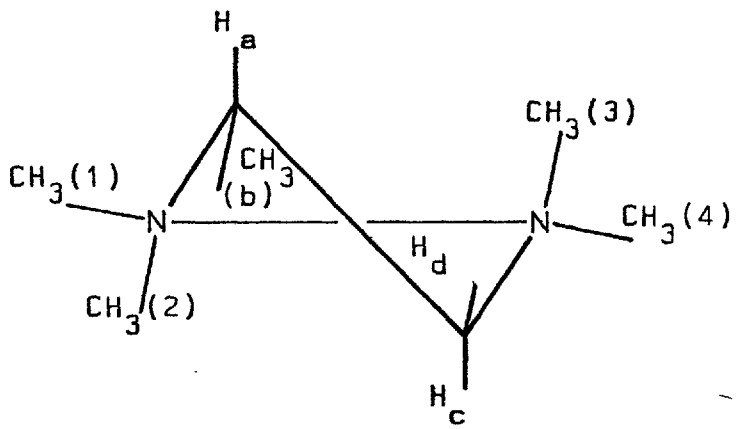
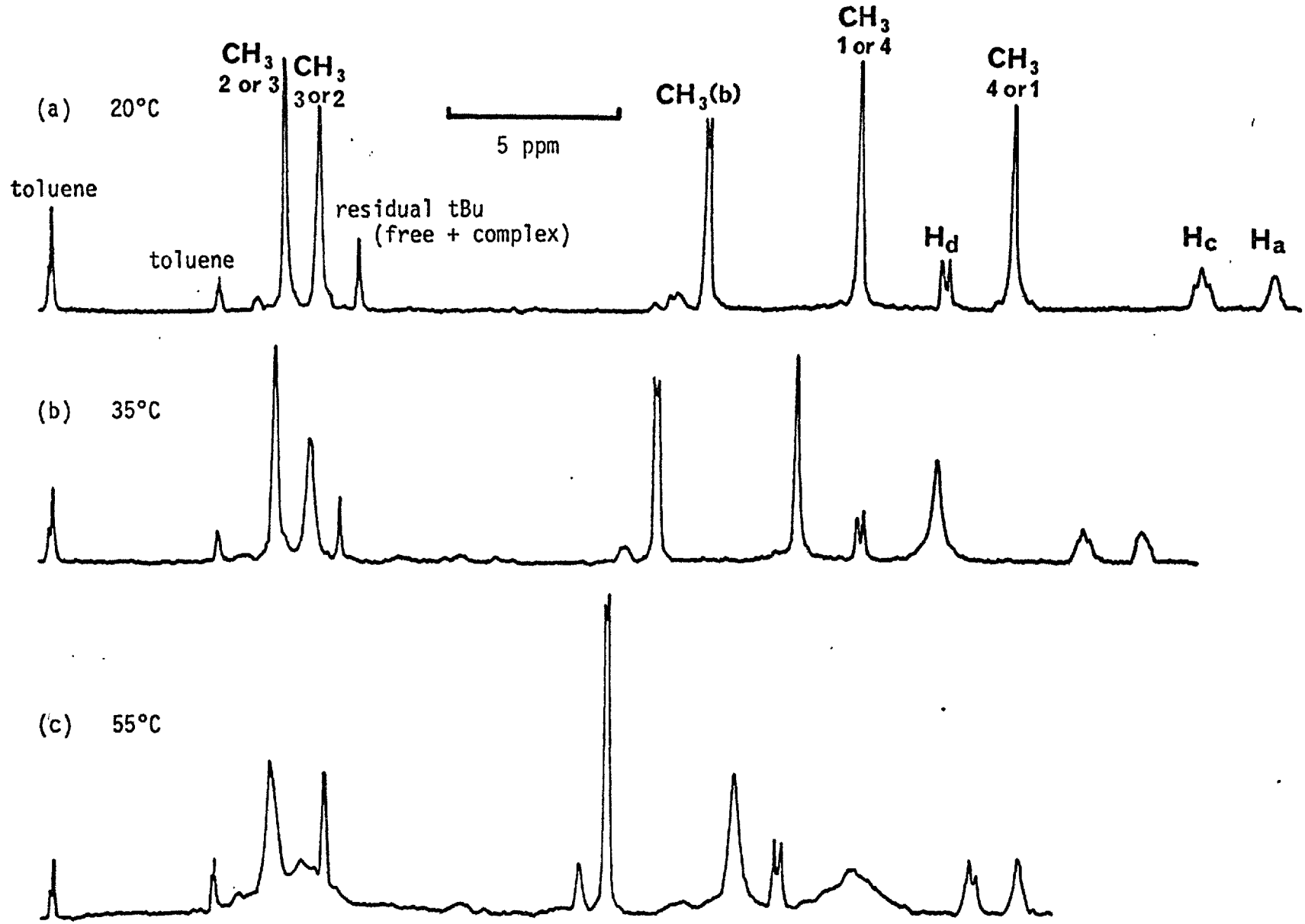


Fig. 29 Pr(fod-d_9)$_3$- (0.2M) TMpn (0.15M) solution in $CD_3C_6D_5$.



One of the methyl resonances, that with a doublet structure could immediately be assigned to the $CH_3(b)$ protons coupled with H_a. Assignment of the ring proton resonances could also be made on the basis of the spin-spin splitting pattern (as in $Co^{III}(pn)_3$).[89] The resonance with a doublet structure is that of H_d strongly coupled with H_c ($^2J_{c-d}$ ca. 12 Hz). The triplet structure of the resonance of H_c arises from spin coupling with both H_d and H_a with $^2J_{c-d} \simeq {}^2J_{c-a}$. The higher-field resonance is that of H_a which is highly split; the fine structure cannot be seen owing to a short relaxation time.

The two lower-field methyl resonances are attributed to the axial $CH_3(2)$ and $CH_3(3)$ by analogy with the Prfod-DMen spectrum (see p.78). The N-methyl resonances cannot be assigned unambiguously. However, the two peaks that start broadening at +35°C (fig. 29b) are likely to be the resonances of methyl groups substituted on the same nitrogen atom. At +55°C (fig. 29c) the other two methyl resonances start broadening. An interpretation is given on p.90. Figure 29a incorporates these assignments.

The expected 1:1 stoïchiometry of the Prfod-TMpn complex was determined by the usual methods. The room-temperature spectrum of a solution containing 1eq. of TMpn and 2eq. of undeuterated Prfod displays two signals of equal intensity arising from the tBu protons of the free (R or R_2) and complexed (RS) fod. These signals coalesce at 110°C ($\tau = 3.4$ ms).

The spectra of solutions containing an excess of amine show that intermolecular exchange is slowed down at low temperatures as witnessed by the simultaneous presence of free and complexed amine resonances.

Table 19 illustrates the variation of the width of the complexed CH_3(b) group (in the slow exchange region) when the LSR to amine ratio is varied and when the solution is diluted :

Table 19

Variations of substrate line width with R/S and dilution.*

$[TMpn]_o/[Prfod]_o$	$[TMpn]_o$	CH_3(b) width
1	0.3 mole	110 Hz
	0.375 "	150 Hz
1.25	0.188 "	90 Hz
	0.094 "	60 Hz

↓ dilution

* d_8-toluene solution at 5°C.

These results indicate that the exchange rate increases as more amine is added to the solution and that the rate decreases when the solution is diluted.

Bound chemical shifts of TMpn are listed in table 18.

c) N N'-Dimethylethylenediamine (DMen)

Three peaks are observed in the +65°C spectrum of a $Pr(d_9\text{-fod})_3$-DMen solution (spectrum 30a) : they are the resonances of the ring protons, the N-H and N-CH_3 protons. The fod resonances, i.e. methine groups and residual tBu protons

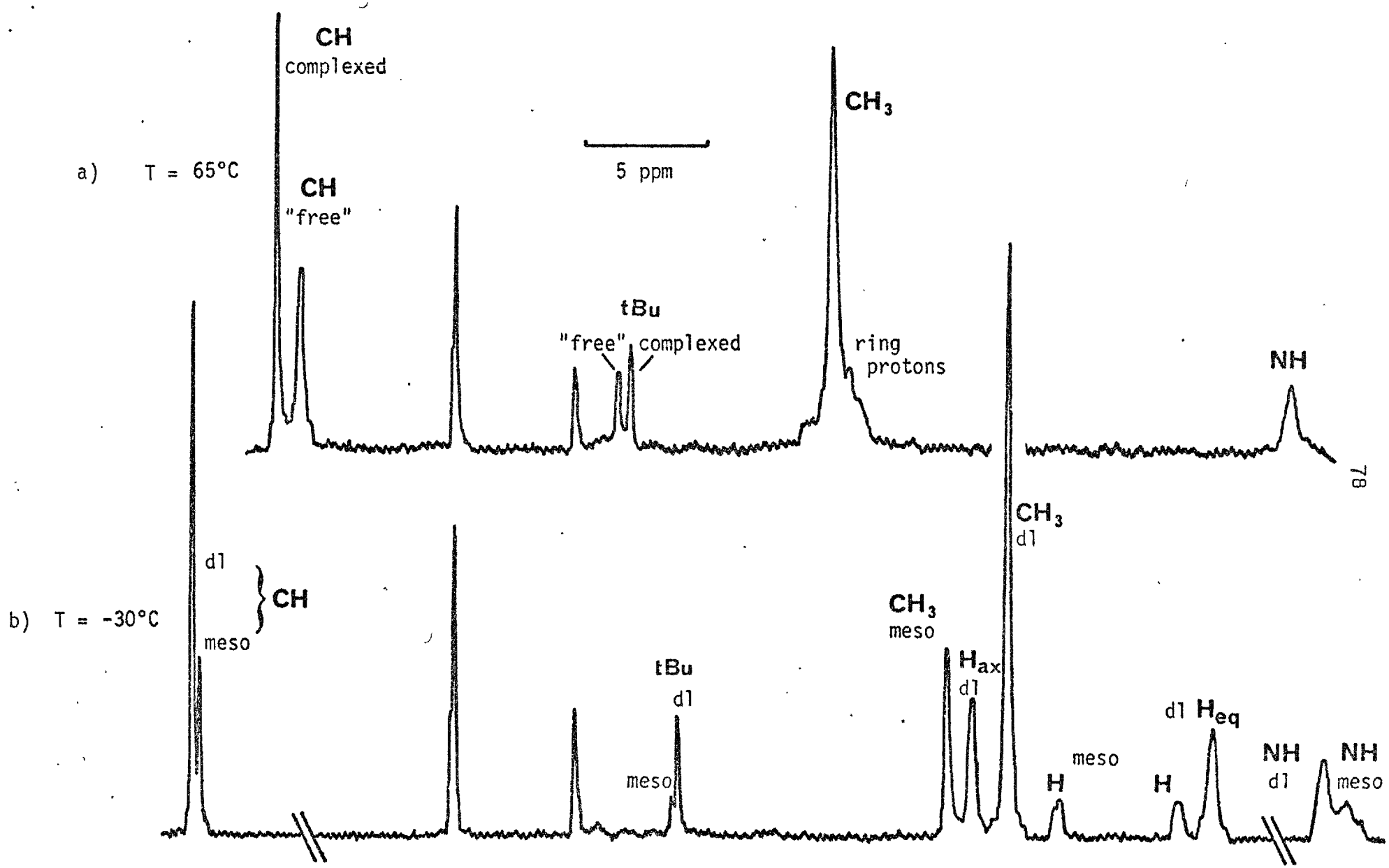


Fig. 30 $Pr(fod\text{-}d_9)_3$- (0.2M) DMen (0.1M) system in $CD_3C_6D_5$.

of free and complexed $Pr(fod)_3$ indicate that the adduct has a 1:1 stoïchiometry.

At -30°C (see spectrum 30b), intermolecular exchange is slow. The complexed fod peaks are each split into two peaks in a 1:3 ratio. Note : the free fod peaks are so broad, at -30°C, that they cannot be seen. Thus two species are present in solution in a 1:3 ratio and this accounts for the complicated spectral pattern. These two species can be assumed to be the meso and racemic conformations. As discussed previously, the meso form is expected to be slightly less stable than the racemic form, and accordingly, the more intense set of resonances is attributed to the dl form (see fig. 30b). Eight peaks are observed in the -20°C spectrum. A likely assignment was made possible by integration of the various peaks and by comparison with the analogous TMpn spectrum. The largest peak was attributed to the equatorial methyl groups from the racemic isomer. Four resonances were attributed to the racemic form and four to the meso conformers which undergo rapid interconversion, otherwise additional resonances would be observed.

All resonances are sharp down to -70°C (a slight broadening of the meso resonances is however noticed), but at -80°C, reagent and substrate resonances become very broad.

In presence of excess amine, intermolecular exchange could not be slowed sufficiently to enable observation of distinct free and complexed DMen resonances although it is clear from the observation of meso and racemic forms at low

LSR/amine ratios that intermolecular exchange is slow.

Bound chemical shifts are listed in table 20a.

d) N N N'N'-Tetraethylethylenediamine (TEen)

Intermolecular exchange is fast at 35°C in a $Pr(d_9fod)_3$-TEen solution (cf. fig. 31a), but it is slowed down at 0°C (fig. 31b). At this temperature diastereotopic nonequivalence is observed for the CH_2(ex) protons. The coalescence temperature for this diastereotopic splitting (T = 15°C in an equimolar solution) varies little with the R/S ratio. Ring inversion is however still fast as shown by the single methyl and ring methylene resonances.

At lower temperatures these signals broaden and at -25°C each split into axial and equatorial resonances.

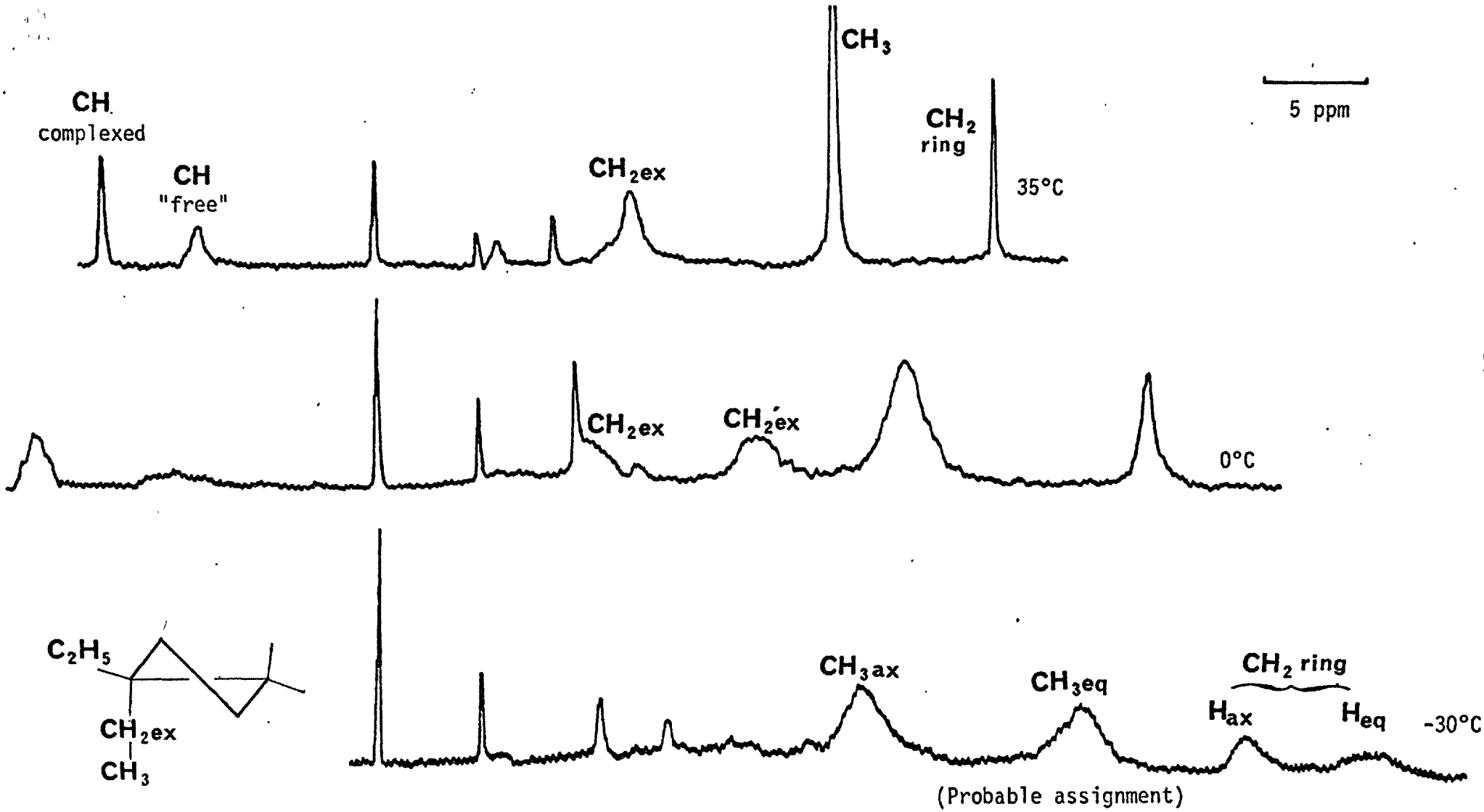
A further splitting of the CH_2(ex) resonances is expected but the four resulting peaks are presumably too broad to be observed and are lost in the noise background (fig. 31c). Coalescence of the methyl resonances is obtained at -13°C ($\Delta G^{\ddagger}$ = 11.5 $kcalmol^{-1}$).

Below -45°C, all resonances broaden; the entire spectrum is practically "flat" at -55°C and eventually a new pattern of resonances appears at -70°C but assignment is not possible.

In a solution 0.2M in LSR and 0.3M in TEen, coalescence of the free and complexed substrate signals is observed at 15°C.

All bound chemical shifts are listed in table 17.

Fig. 31 $Pr(fod\text{-}d_9)_3$- (0.2M) TEen (0.1M) system in $CD_3C_6D_5$.



2) Six-membered ring systems with Prfod

Intermolecular exchange in a solution containing 1eq. of Prfod and 1.25eq. of N N N'N'-tetramethyl-1,3-diaminopropane (TMtn) is slow on an nmr time-scale at -40°C. However three resonances are observed at that temperature which indicate that the amine is bidentate and that ring inversion is fast. Separation of the methyl resonances into axial and equatorial signals is just observed at -85°C ($\Delta G^{\ddagger} \simeq 9$ kcalmol^{-1} at -60°C) but the signals are very broad.

3) Eufod chelates

a) en, DMen, TMen

Europium fod chelates of ethylenediamine and its N-methylated derivatives have been studied at various LSR/amine ratios.

In all three systems, en-, DMen- and TMen-Eufod, the only adduct observed in solution has a 1:1 stoïchiometry : all room-temperature spectra of solutions containing 1eq. of amine for 2eq. of Eufod, show free fod resonances and complexed fod resonances of equal intensities.

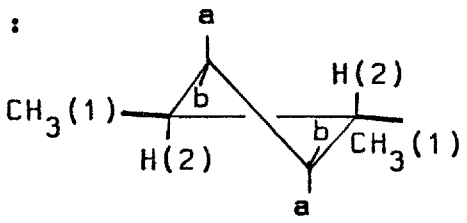
Exchange between free and complexed DMen or TMen can be slowed down below -20°C, whereas the same exchange with en as substrate is rapid at -70°C.

Ring inversion of the TMen and en chelates could not be slowed down sufficiently, even at -70°C, for a barrier to be estimated. Only one conformer, the dl form most probably, is observed in DMen-Eufod solutions (see table 20b).

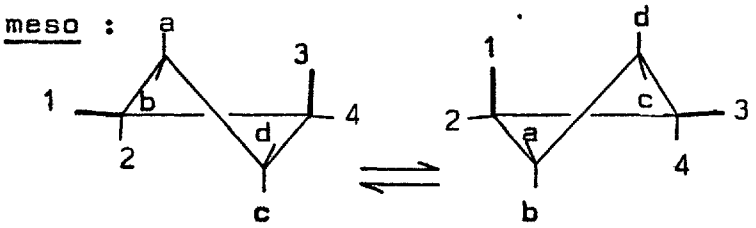
Table 20

Bound chemical shifts of DMen chelates . (ppm)

dl :



meso :



a) Prfod-DMen (d_8-toluene solution).*

	dl				meso			
T°C	$CH_3(1)$	H(2)	H(a)	H(b)	1&3	2&4	a&d or b&c	b&c or a&d
-10	16.5	44.7	14.0	22.6	13.4	46.1	17.4	20.9
-20	17.1	46.0	15.2	24.3	14.2	47.9	18.2	22.4
-30	17.6	50.3	16.4	26.1	15.0	50.9	19.5	24.8
-50	19.3	59.6	19.9	31.3	17.5	57.9	22.4	28.7
-60	19.9	64.6	21.9	34.1	18.6	61.4	24.5	30.9
-70	20.9	—	24.4	37.6	ca. 21	—	26.8	34.1

(2,4,a,b,c,d = H; 1,3 = CH_3)

b) Eufod-DMen (d_8-toluene solution).**

T°C	$CH_3(1)$	H(2)	H(a) or H(b)	H(b) or H(a)
0	-7.2	+10.8	ca.-2.0	ca.-1.0
-30	-9.6	+11.6	ca.-1.7	ca.-0.9
-40	-11.0	+13.0	ca.-1.7	ca.-1.0
-50	-12.0	+13.2	ca.-1.7	ca.-1.5
-60	-13.6	+14.2	ca.-1.7	ca.-1.7

dl

* Average values for various LSR/amine ratios; LSR = 0.2M .

** LSR/amine = 1; LSR = 0.2M .

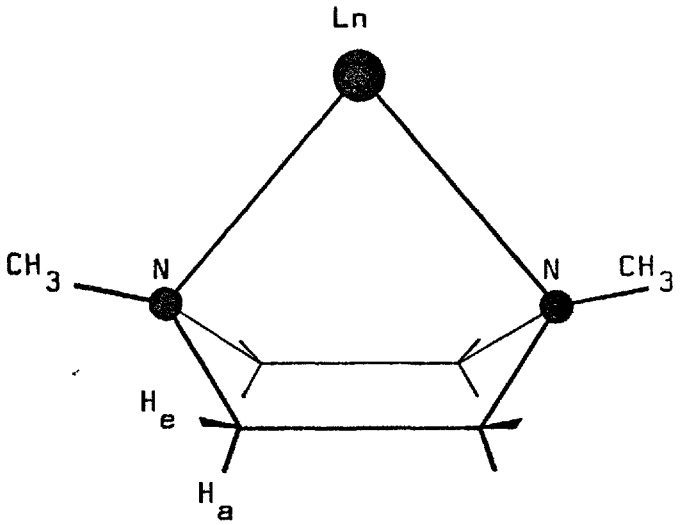
Unfortunately, intense line-broadening prevents precise measurements to be done below -40°C in the DMen and TMen solutions.

b) NNN'N'-Tetramethyl-1,4-butanediamine.

There is no evidence of slow substrate exchange whatever the LSR/amine concentration ratio even at -80°C.

4) NN'-dimethylpiperazine chelates (DMp).

The room temperature spectra of the three systems $Ln(d_9\text{-fod})_3$-DMp (Ln = Pr, Eu, Yb) each display three signals (fig. 32a) which can be attributed to the methyl groups, pseudo-equatorial and pseudo-axial ring protons of a boat-form chelate. The two latter resonances could not be individually assigned. It can be noted that in the limit of a slow exchange, a monodentate would display four resonances or more in its nmr spectrum.



The room temperature spectra of solutions containing excess Lnfod (Ln = Eu, Pr) also displayed distinct resonances for free and complexed LSR. Separate resonances for free and complexed are also observed at 35°C $(Ln = Eu)_3$ in-

Fig. 32 Equimolar (0.2M) solution of $Pr(fod\text{-}d_9)_3$ and DMp. $CD_3C_6D_5$.

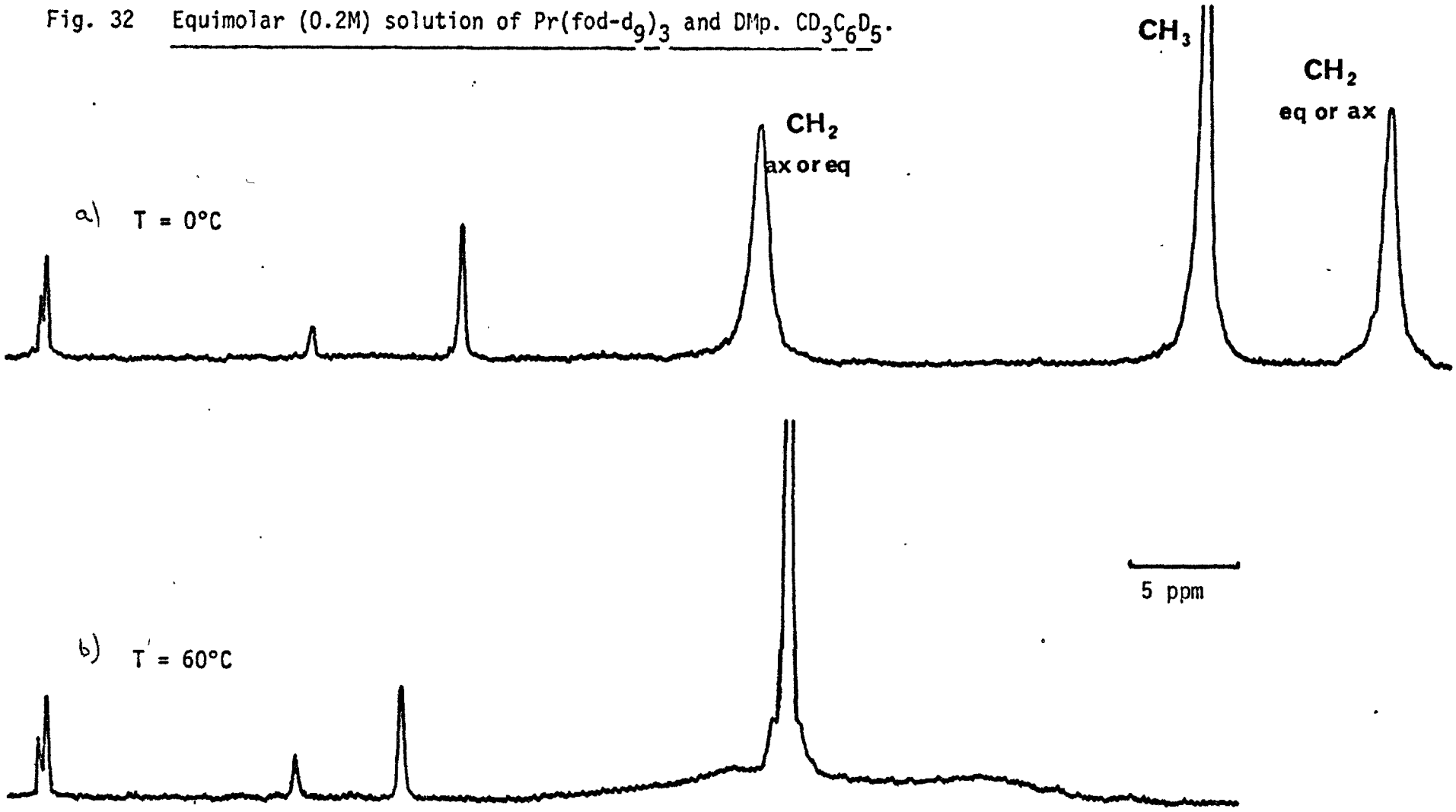


Table 21

Bound chemical shifts of dimethylpiperazine-Ln(fod)$_3$.*

	Eu(fod)$_3$			Pr(fod)$_3$			Yb(fod)$_3$		
T°C	CH_3	H_a or H_e	H_e or H_a	CH_3	H_a or H_e	H_e or H_a	CH_3	H_a or H_e	H_e or H_a
60	2.4	-7.7	-3.0	—	—	—	—	—	—
45	2.4	-8.3	-3.5	—	—	—	—	—	—
35	2.5	-8.5	-3.9	11.7	7.8	16.3	—	—	—
20	2.6	-9.2	-4.4	—	—	—	—	—	—
0	2.6	-9.9	-5.3	16.5	8.3	20.1	9.0	0.4	12.3
-15	—	—	—	18.9	8.1	21.7	10.2	0.4	13.6
-30	2.6	-11.3	-6.8	22.0	8.1	23.6	—	—	—
-60	2.2	-12.5	-8.5	—	—	—	—	—	—
-70	2.0	-13.0	-9.1	34.5	7.0	30.7	—	—	—
-80	<1.8	-13.4	-9.1	38.4	6.3	32.7	—	—	—

* Average values (in ppm) for various DMp/LSR ratios; d_8-toluene solutions.

dicating that intermolecular exchange is slow at room temperature. At +60°C (fig. 32b) single resonances are observed for the methyls and for the methylene protons signifying rapid intermolecular exchange.

A broadening of the substrate resonances is observed in the slow exchange region when the molar ratio $[DMp]/[Eufod]$ is increased. The width at half-height of the low-field ring proton is respectively 20, 60 and 80 Hz in a solution 0.2M in Eufod and 0.1, 0.2 and 0.3M in DMp at 35°C.

Coalescence of the ring proton resonances as a result of intermolecular exchange is obtained at $T_c \simeq +60°C$ ($\tau = 1.3ms$) for a solution 0.2M in Eufod and 0.1M in amine.

In the Ybfod-DMp system, resonances below -15°C were extremely broad.

Bound chemical shifts are listed in table 21.

DISCUSSION

1) Ring inversion

As mentioned earlier, ring inversion in five-membered metal chelates is normally fast on an nmr time scale.[77,78]

The results obtained in the present work show clearly that ring inversion can be slowed down in $Pr(fod)_3$-TMen and $Pr(fod)_3$-TEen.

Theoretical calculations[80a] show that an increase in the metal to nitrogen bond length will increase ring puckering thus raising the barrier to ring inversion.

Table 22

Barrier to ring inversion of an isolated ethylenediamine ring as a function of the M–N bond length

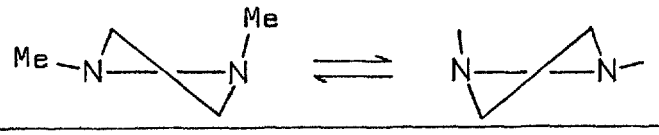
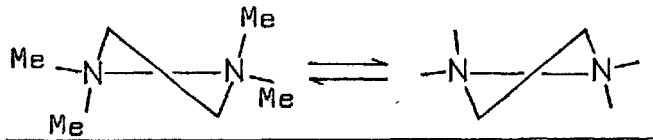
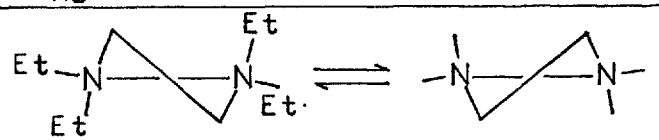
M–N (Å)	2.0	2.1	2.2	2.3
$\Delta G^{\ddagger}$ ($kcal.mol^{-1}$)	4.2	4.8	5.2	5.6

data calculated from (80a).

The range of distances listed in table 22 is appropriate for complexes of the first and second transition series (Ni^{II}, Co^{III}, Rh^{III}). These results would indicate that the ethylenediamine chelates of lanthanides are much more suitable for a dnmr study since longer M–N bond lengths would increase the barrier to ring inversion (Eu–N = 2.6 to 2.65 Å,(27, 90) Pr–N ca.2.7 Å (estimated)).

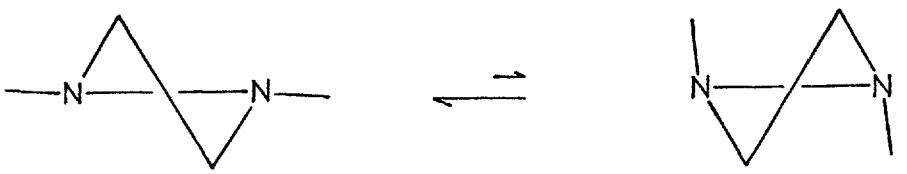
Table 23

Barriers to ring inversion for N-substituted ethylenediamine Prfod chelates.

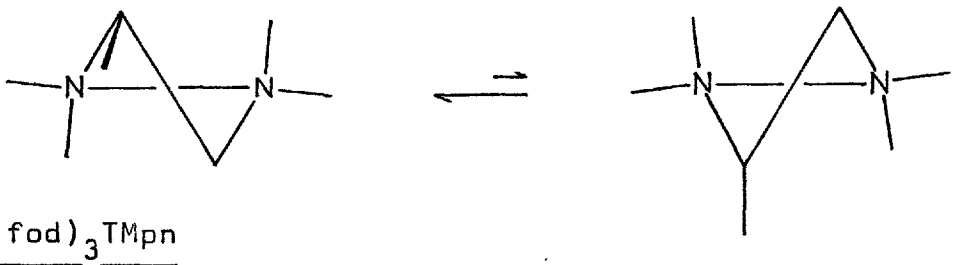
Exchange	T_c	$\Delta G^{\ddagger}$ ($kcalmol^{-1}$)
	not slowed down	< 8.5
	-38°C	10.1
	-13°C	11.5

A further factor responsible for raising the barrier to ring inversion is presumably the presence of substituents on the nitrogen as illustrated by table 23. Bulky substituents would destabilize the $\delta \rightleftharpoons \lambda$ quasi-planar transition state owing to repulsive interactions between the various groups. This is in agreement with the greater barrier to ring inversion in $Pr(fod)_3$-TEen than in $Pr(fod)_3$-TMen, and also to the fact that ring inversion could not be slowed down in Prfod(DMen,RS).

Ring inversion could not be studied in the two complexes below :



$Pr(fod)_3$(DMen,RR)



$Pr(fod)_3$TMpn

In both cases, one conformation is greatly preferred over the other. The nmr spectrum of the two conformers exchanging rapidly is practically identical to that of the most favoured conformer.

The barrier to ring inversion in six-membered chelates

has been estimated by Gollogly and Hawkins[87] as 7 kcal.mol^{-1} for chair-type conformations with metal to nitrogen bond lengths of 2.0 Å .

An increase in bond length together with bulky substituents on the nitrogen atoms also appears to raise the barrier to ring inversion. The experimental value $\Delta G^{\ddagger}$ was found to be approximately 9 kcal-mol^{-1} at -70°C.

No fluxional behaviour (observable by nmr spectroscopy) is permitted in the rigid cage-like chelate Pr(fod)$_3$DMp other than those involving Ln—N bond breaking.

2) Exchanges involving Ln—N bond breaking

In all the compounds studied in this work, substrate exchange is slow at room-temperature in solutions where the shift reagent to amine molar ratio is $\geqslant 1$. Separate peaks for free and complexed fod protons (methine and tBu groups) are observed and coalesce at higher temperature (T_c = 78°C, τ = 2 ms for Prfod-TEen; T_c = 110°C, τ = 3.4 ms for Prfod-TMpn).

The nmr spectra of Prfod-TEen in the presence of excess Prfod illustrate the fact that single Ln—N bond breaking, and exchange through the rupture of both Ln—N bonds are different processes. A probable further example of this distinction is the Prfod-DMen complex where, for T > 55°C, exchange between the meso and dl isomers is rapid in a solution containing an excess of LSR, while substrate exchange is slow as witnessed by the separate free and complexed fod signals. Single-bond breaking is also very likely in Prfod-TMpn. At 20°C, four distinct signals are observed for

the N–CH_3 resonances : nitrogen inversion is slow. As the temperature is raised, two of these resonances (one axial and one equatorial methyl presumably attached to the same nitrogen atom) start broadening and coalesce before the other two. As a result of the asymetry introduced by the C–CH_3 group, one pair of methyls interchanges more rapidly than the other pair. A plausible mechanism is that initially one Pr–N bond is broken. Inversion of the nitrogen atom, rotation about the C–N bond followed by ring closure will interchange $CH_3(1)$ and $CH_3(2)$ or $CH_3(3)$ and $CH_3(4)$.

In Prfod-TMen there is no chiral probe (as in DMen) nor prochiral probe (as in TEen) which would yield information on the origin of the splitting of the methyl and methylene resonances. In the spectral interpretation the splitting was attributed to a slowing down of ring inversion. However there are two other possible interpretations : a process involving rupture of one of the Pr–N bonds or an intramolecular rearrangement in the eight-co-ordinate complex. The latter mechanism is likely to be fast at -40°C since the complexed fod methine and tBu resonances are sharp and not split. However a slowing down of intramolecular rearrangement is probably the reason for the additional broadening of the split CH_3 and CH_2 resonances together with the fod resonances below -60°C. It is likely that the process slowed down at -40°C is ring inversion, for bond-breaking occurs at substantially higher temperatures in the analogous TMpn and TEen chelates.

3) Stability and exchange mechanisms

Like the corresponding monoamine adducts, the LSR diamine complexes are very stable : solutions containing equimolar quantities of shift reagent and diamine show no sign of dissociation. Substrate exchange can be slow up to high temperatures (75°C to 110°C).

An excess of amine can increase the intermolecular exchange rates and lead to a broadening of resonances in the slow exchange region and a lowering of the coalescence temperature.

Intermolecular exchange rates in solutions containing an excess of substrate tend to decrease with increasing bulk of the amine.

Table 24

Coalescence temperatures for intermolecular exchange in $Pr(d_9\text{-fod})_3$-amine solutions containing an excess of substrate

Amine	T_c	$\left[\text{Amine}\right] / \left[\text{LSR}\right]$
DMen	<-60°C	1.5
TMen	0°C	1.5
TMpn	ca. +15°C	1.25
TEen	+15°C	1.5

Two associative mechanisms can be put forward to explain this behaviour, and these are illustrated in fig. 33.

Fig. 33a Mechanism a.*

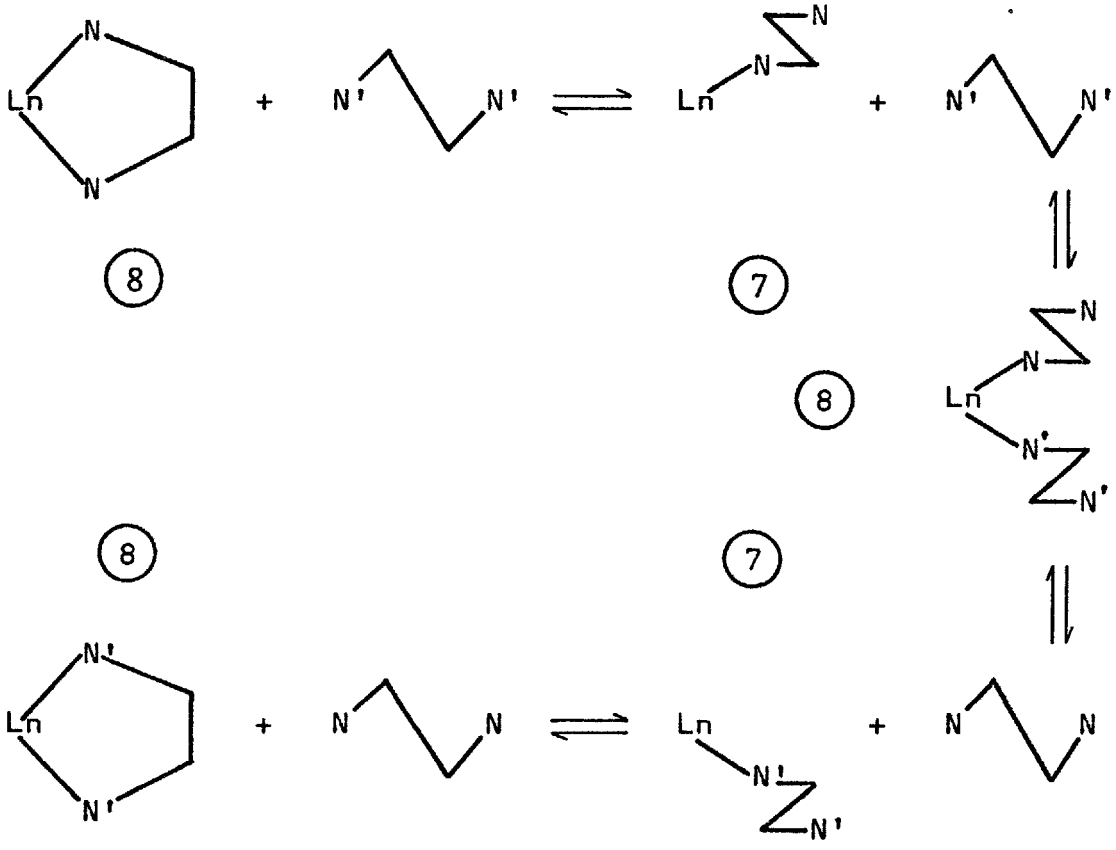
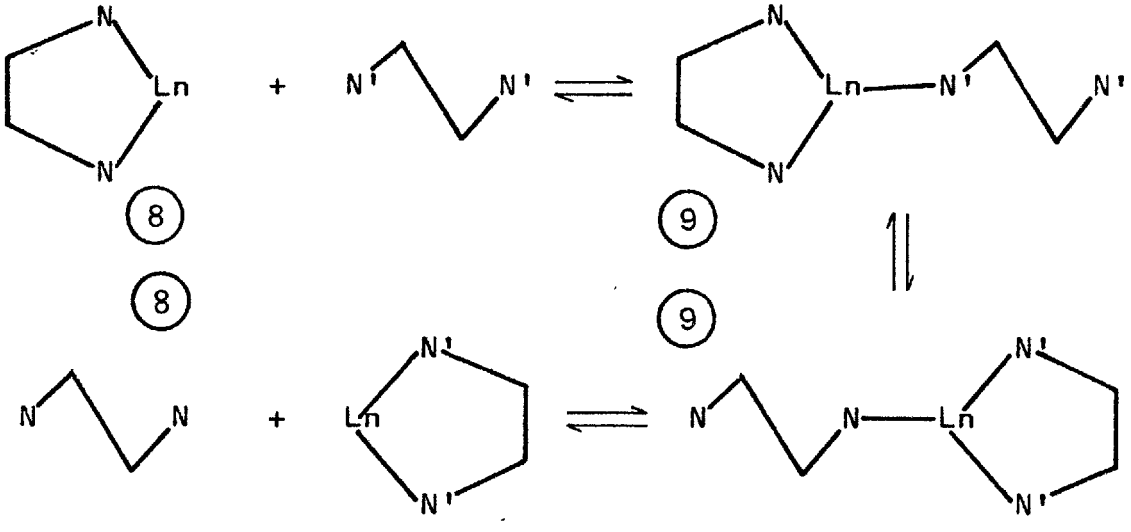


Fig. 33b Mechanism b.*



* The figures in circles are the Ln co-ordination numbers.

In the Prfod-TMpn system, the coalescence of the N-methyl resonances occurs at high temperatures ($T_c \cong 80°C$): this process is much slower than the ligand exchange that causes a scrambling of the substrate resonances in presence of excess amine ($T_c \cong 15°C$). The opening of the chelate ring in an 8-co-ordinate species (as in mechanism a) is a process too slow to be considered.

Ligand exchange in presence of excess amine is more likely to occur according to mechanism b where ring opening (in the 9-co-ordinate species) should be a fast process. The steric requirements of the latter mechanism are greater than those of mechanism a hence the greater increase of intermolecular exchange rates in the less bulky DMen (table 24).

4) Intramolecular rearrangements

The overall broadening of the chelate and fod resonances which is observed at the lower temperature range is presumably due to the slowing down of the intramolecular rearrangements in the 8-co-ordinate complexes. These could occur either by one-ended bond rupture processes of the β-diketonate rings or by "twist" processes.[91] Since, as shown above, bond breaking of the amine chelate rings occur at much higher temperatures, the "twist" mechanism seems more likely.

The broadening is dependent on the bulk of the substrate, that is to say on the steric interactions between

the various chelate rings.[76, 83]

Substantial resonance broadening is observed in low temperature (-80°C) spectra of Eufod complexes of TMen and DMen and Prfod complexes of TMen, DMen and TMpn. But with Prfod-TEen solutions, an overall broadening of the nmr spectrum occurs at a much higher temperature (-50°C) and a new resonance pattern starts appearing at -70°C. The solution could not be cooled below -80°C where poor resolution and crystallization prevents spectral interpretation.

EXPERIMENTAL

Silver salts : Silver heptafluorobutyrate and d-10-camphorsulphonate.

Slightly less than 1 eq. of the corresponding acid was added to a stirred suspension in water of freshly prepared silver oxide. The solution was filtered and water was evaporated at 50°C under vacuum. The silver salts were vacuum-dried and stored over Linde 3Å molecular sieves for at least 48 hours before use.

Silver 1-pentafluorophenylethane-sulphonate.

1-Chloro-1-pentafluorophenylethane was obtained from 1-pentafluorophenylethanol following the method described in [92]. The chloro- compound was converted to sodium 1-pentafluorophenylethanesulphonate.[93]

A concentrated solution of the sodium salt (approx. 4.10^{-2} mole) was passed through an ion-exchange column packed with 80ml. of Permutit "Zeo-Karb"225 (SRC 13) previously rinsed with 400ml. of normal HCl. The resulting solution was evaporated, reacted with freshly prepared silver carbonate and treated as described above.

Silver fluoride

as in [94].

Transition metal complexes :

Biscarbonyl Rh^{I}(β-diketonate)

390 mg of $[Rh(CO)_2Cl]_2$ were dissolved in 10 ml. of benzene and 1 eq. of Tl^{I}(β-diketonate) in 35 ml. of benzene was added. The resulting solution was filtered and partially evaporated. The rhodium^{I} β-diketonate was crystallized from petroleum ether and dried under vacuum.

Di-μ-chlorotetrakis(carbonyl)dirhodium^{I} was prepared from hydrated rhodium trichloride[95] and the thallium^{I} β-diketonateswere prepared as in[96].

$RhCl_3,nH_2O$ and a sample of $(CO)_2Rh^{I}$facam were provided by Johnson, Matthey, Ltd. The latter complex was also synthetized independently from the β-diketone (provided by Dr. J. N. Tucker).

Complexes with anionic chelating ligands : as in [97].

These compounds comprise $(CO)_2Rh^{I}Cl$(picolinate), (8-oxyquinolate), (salicyladoximate) and (pyridinealdoximate).

Other complexes :

$OHRh^{I}(CO)(PPh_3)_2$	(98)
$ClIr^{I}(CO)(PMe_3)_2$	(99)
$ClIr^{I}(CO)(PPh_3)_2$	(99)
$FIr^{I}(CO)(PPh_3)_2$	(100)
$FRh^{I}(CO)(PPh_3)_2$	(100)
$ClRh^{I}(CO)(PPhEt_2)_2$	(100)
$[Rh^{I}(Cl)(C_2H_4)_2]_2$	(101)
$Rh^{I}(C_2H_4)_2$acac	(101)

Amines

Common amines were obtained commercially and purified as below. Where necessary, monoalkylation of primary amines was carried out following the method described in [102], and complete methylation of primary or secondary amines as in [103]. The methods were modified as follows : the alkylated amine hydrochloride was evaporated to near dryness, cooled in an ice bath, and a saturated aqueous solution of KOH was slowly added. The salted-out amine was separated from the KOH-KCl slurry by centrifugation, dried over KOH pellets, then over molecular sieves and finally distilled under an inert atmosphere. The tertiary amines were distilled over sodium to destroy traces of secondary amines. All amines were stored over 3Å molecular sieve under argon.

1-Methylpiperidine-d_{10} (MePi-d_{10})

Pyridine-d_5 was deuterated by sodium in C_2H_5OD following the directions given for undeuterated piperidine.[104] After steam-distillation, the solution of deuterated piperidine was neutralised to pH7 with N HCl and evaporated to dryness on a rotary evaporator. The piperidine-d_{10} hydrochloride was treated with a solution of sodium formate, formic acid and formaldehyde and methylation was carried out as described above.

Shift Reagents

Lanthanide shift reagents, obtained from Nuclear Magnetic Resonance, Ltd., were always dehydrated before

use by heating to ca.100°C under vacuum (mercury diffusion pump) for at least three hours.

Preparation of nmr solutions

The nmr tube was dried in an oven and flushed with argon. The solutions were made up in a dry bag in the tube itself. The tube was sealed with a rubber serum cap through which liquid substrates were introduced with a syringe.

Olefin - silver salt - LSR solutions

Typically, to 0.09 mmole of shift reagent and 0.09 mmole of silver salt in an nmr tube, were added approximately 0.4 ml of a carbon tetrachloride solution containing 1% TMS and 1.5 eq. of olefin. The resulting suspension was shaken and warmed until all the solid had dissolved. If necessary, more olefin was added.

Amine - LSR solutions

Shift reagent, solvent (d_8-toluene) and amine were introduced into an nmr tube as above. Concentration studies were carried out by successive injections of 0.25, 0.5 or 1 eq. of substrate.

nmr runs

Variable temperature nmr spectra were recorded on a 60 MHz Perkin-Elmer R12B spectrometer. Room temperature spectra were recorded on 100 MHz Perkin-Elmer R14 or Varian HA100 spectrometers.

Temperature calibration was periodically carried out on a methanol sample.[105]

A P P E N D I X

I CALCULATION OF KINETIC PARAMETERS

A comprehensive study of theoretical and practical aspects of time-dependent nmr can be found in [106].

The following kinetic parameters can be calculated from the nmr spectra of a nucleus or a group of nuclei exchanging between two equally populated sites.

— The mean life time for exchange at the coalescence temperature (T_c) is given by the following expression :[75b]

$$\tau_c = 1/2^{\frac{1}{2}}\pi\Delta_c \qquad ((1))$$

Δ_c is the chemical shift difference (expressed in Hz) between the two nuclei; it is calculated at the coalescence temperature by linear extrapolation of a plot of log Δ against log T.

— The rate constant :

$$k = 1/2\tau_c = \pi\Delta_c/2^{\frac{1}{2}} \qquad ((2))$$

(For unequal populations in the two exchanging sites see [107].

— An accurate value for $\Delta G^{\ddagger}$, the free energy of activation, can be obtained at the coalescence temperature by substituting equation ((2)) in Eyring's equation

yielding equation ((3)) :

$$e^{-\Delta G^{\ddagger}/RT} = h\Delta_c/2^{\frac{1}{2}}kT_c \qquad ((3))$$

(The constants h, k and R have their usual meaning.)

An approximation for the variations of τ with T can be calculated from equations ((1)) and ((3)) if it is assumed that $\Delta S^{\ddagger}$ is zero.

$$-\Delta G^{\ddagger} = RT_c \ln(\pi h\Delta_c/2^{\frac{1}{2}}kT_c)$$

$$= RT_c \ln(h/2kT_c\tau_c)$$

$$RT_c \ln(h/2kT_c\tau_c) = RT\ln(h/2kT\tau)$$

$$(h/2kT_c\tau_c)^{T_c/T} = h/2kT\tau$$

$$\tau = T^{-1}(T_c\tau_c)^{T_c/T}(h/2k)^{(1-T_c/T)}$$

II OVERLAP OF TWO NMR SIGNALS

Calculation of the chemical shift difference $\Delta\nu_{real}$ between two overlapping Lorentzian signals :

Fig. 34a: f_1 & f_2

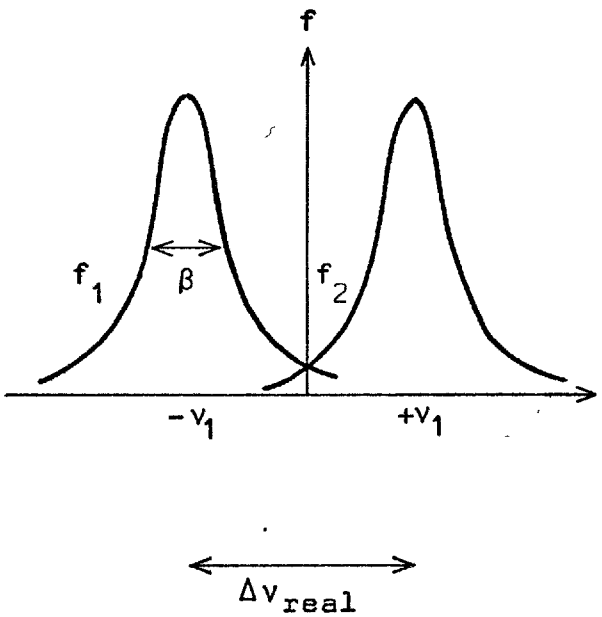
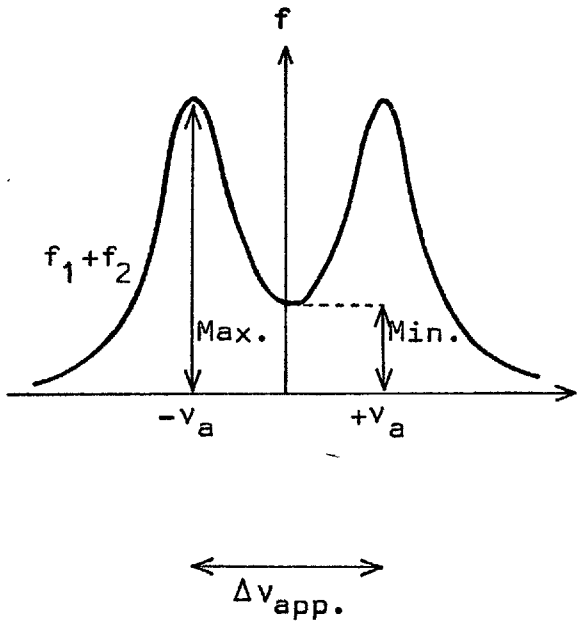


Fig. 34b: $f_1 + f_2$



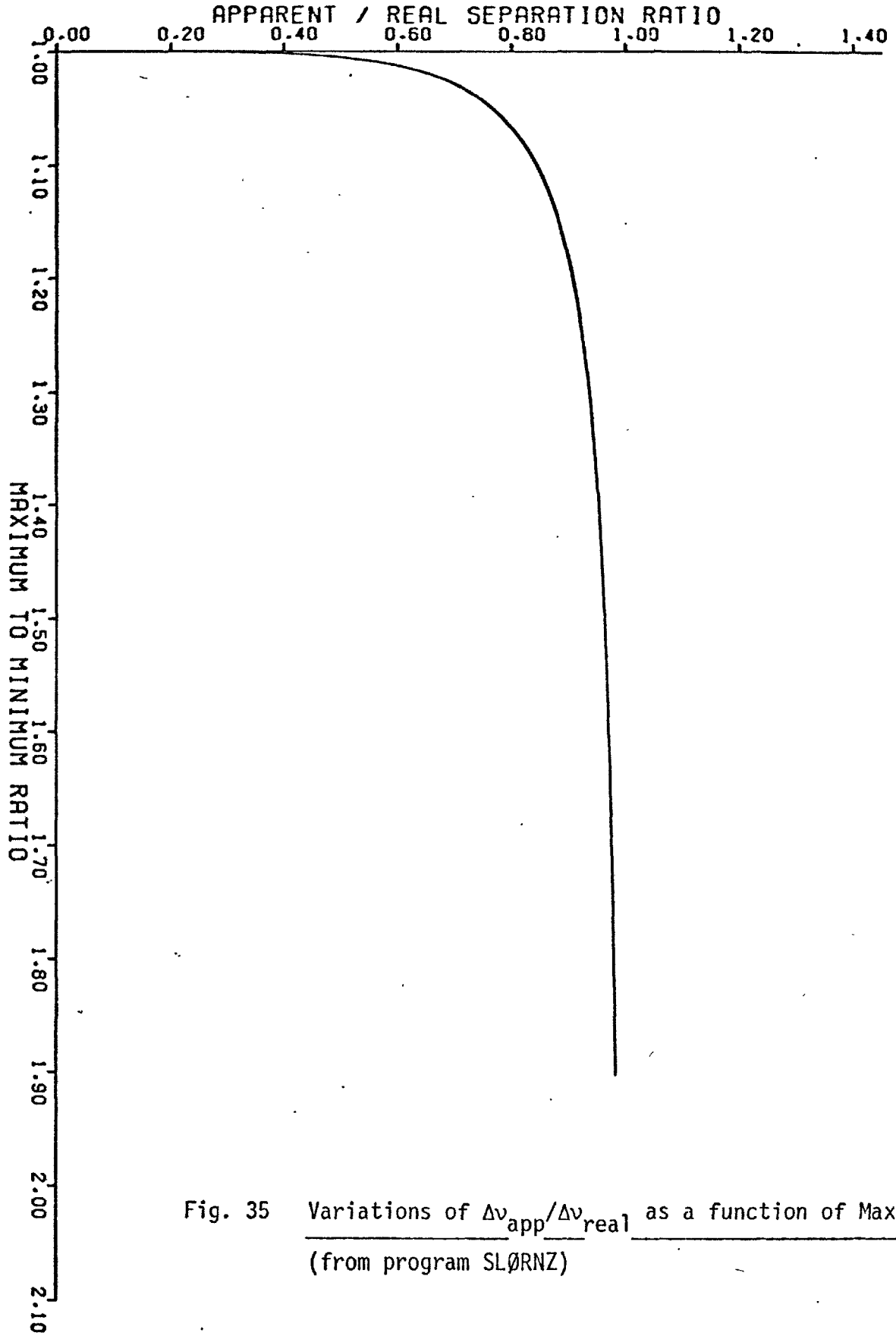


Fig. 35 Variations of $\Delta\nu_{app}/\Delta\nu_{real}$ as a function of Max/Min. (from program SLØRNZ)

$$f_1 = 1/\left[1 + \beta(\nu+\nu_1)^2\right]$$

$$f_2 = 1/\left[1 + \beta(\nu-\nu_1)^2\right]$$

$$d(f_1+f_2)/d\nu = (-2\beta/D^2)\Phi$$

$$D = \left[1 + \beta(\nu-\nu_1)^2\right]\left[1 + \beta(\nu+\nu_1)^2\right]$$

$$\Phi = \left[1 + \beta(\nu+\nu_1)^2\right]^2(\nu-\nu_1) + \left[1 + \beta(\nu-\nu_1)^2\right]^2(\nu+\nu_1)$$

$$= 2\nu\left[\beta^2\nu^4 + 2\beta(\beta\nu_1^2+1)\nu^2 - 3\beta^2\nu_1^4 - 2\beta\nu_1^2 + 1\right]$$

$$\Phi(\pm\nu_a) = 0 \quad \text{and} \quad \Phi(0) = 0$$

$$\nu_a = \pm\left[-(\nu_1^2+\beta^{-1}) + 2\nu_1(\nu_1^2+\beta^{-1})^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

if $\beta = 1$:

$$\nu_a = \pm\left[-(\nu_1^2+1) + 2\nu_1(\nu_1^2+1)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

Fig. 35 shows the variations of

$$\nu_a/\nu_1 = \Delta\nu_{app}/\Delta\nu_{real}$$

as a function of Max/Min (Program SLØRNZ).

III CALCULATION OF AN EQUILIBRIUM CONSTANT

1) one equilibrium involved

$$R + S \rightleftharpoons RS, \quad K = [RS]/[R][S]$$

$$[R_o] = r$$

$$[S_o] = s$$

$$[RS] = sx$$

$$[S] = s(1 - x)$$

$$[R] = r - sx$$

If dimerization of R ($2R \rightleftharpoons R_2$) is neglected :

$$K = x/(r-sx)(1-x)$$

2) two equilibria involved

$$R + S \rightleftharpoons RS \quad K_1 = [RS]/[R][S]$$

$$RS + S \rightleftharpoons RS_2 \qquad K_2 = [RS_2]/[RS][S]$$

$$[R_o] = r = [R] + [RS] + [RS_2]$$

$$[S_o] = s = [S] + [RS] + 2[RS_2]$$

$$K = K_2/K_1 = [RS_2][R]/[RS]^{-2}$$

If $[S]$ is small (ie. $[S] \ll 2[R]$ if K_1 and K_2 are large) :

$$[RS_2] = s/2 - [RS]/2$$

$$[R] = r - [RS] - [RS_2] = r - s/2 - [RS]/2$$

$$K = s(2r - s)(2[RS])^{-2} - r(2[RS])^{-1} + 1/4$$

$$\underline{K = (2r/s - 1)\rho^2 + (r/s - 1)\rho}$$

with $\rho = [RS_2]/[RS]$

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