Nuclear Magnetic Resonance Studies of Lanthanoid Complexes. Part 2.[1] Adducts of Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)-praseodymium and -europium with Unidentate Secondary and Tertiary Amines

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Proton resonance spectra are reported for the title complexes [Pr(fod)$_3$] and [Eu(fod)$_3$] with a variety of secondary and tertiary amines. At low temperatures both substrate exchange and nitrogen inversion are slow on a proton-resonance time scale. Secondary amines form both 1 : 1 and 2 : 1 adducts, but tertiary amines give 1 : 1 adducts only. In the 2 : 1 adducts of NHMePr^n, *meso* and *rac* isomers, in approximately equal abundance, can be distinguished. In the 1 : 1 adduct of *N*-methylpiperidine with [Eu(fod)$_3$], axial and equatorial isomers are present in approximately equal amounts.

In Part 1 [1] of this series, ^{1}H n.m.r. spectra were reported for a variety of lanthanoid shift reagents with a number of different, strongly co-ordinating, substrates. At low temperatures, substrate exchange was slow on a proton-resonance time scale. Two main equilibria, (1) and (2), were involved. However, in some cases, no 2 : 1 adducts were formed.

$$R + S \rightleftharpoons RS \quad K_1 = [RS]/[R][S] \qquad (1)$$

$$RS + S \rightleftharpoons RS_2 \quad K_2 = [RS_2]/[RS][S] \qquad (2)$$

The present work is concerned with complexes of [Pr(fod)$_3$] and [Eu(fod)$_3$] with a variety of secondary and tertiary amines (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate). These substrates were chosen for a number of reasons. They are readily available, and form quite stable adducts in which substrate exchange can normally be slowed down at low temperatures. It was also anticipated that, in the absence of substrate exchange, nitrogen inversion would also be slow on a proton-resonance time scale. In simple free amines, nitrogen inversion is quite fast. Although nitrogen inversion has been studied by dynamic n.m.r., in a number of cases (normally below —100 °C) it is not always clear whether the process involved is nitrogen inversion, or hindered rotation about the C–N bonds.[2]

It is well established that co-ordination of amines to transition metals very considerably increases the barrier to nitrogen inversion, and stable invertomers of complexes such as [Co(dien)$_2$]$^{3+}$ (dien = diethylenetriamine) have been isolated.[3] Nitrogen inversion is also slow on a proton-resonance time scale in chelated nickel(II) complexes containing substituted ethylenediamines.[4]

In a number of experiments an excess of the lanthanoid shift reagent was used, and its Bu^t and methine resonances were also studied. Under these conditions, not only could additional structural and kinetic information be obtained but also the rate of substrate exchange was markedly reduced.

EXPERIMENTAL

Handling techniques were as described previously.[1] Common amines were obtained commercially and purified as below. Where necessary, monoalkylation of primary amines was carried out using the method described in ref. 5, and complete methylation of primary or secondary amines as in ref. 6. The secondary amines were shaken with K[OH] pellets, further dried over Linde 3A molecular sieves, and finally distilled in an inert atmosphere. The tertiary amines were distilled from sodium. All the amines were stored over molecular sieves under argon.

*Perdeuterio-*N*-methylpiperidine.*— Perdeuteriopyridine was deuteriated by sodium in C_2H_5OD following the directions given for the preparation of undeuteriated piperidine.[7] The steam distillate was adjusted to pH 7 with hydrochloric acid, and evaporated to dryness on a rotary evaporator. The resulting perdeuteriopiperidine hydrochloride was treated with sodium formate, formic acid, and formaldehyde, and methylation was carried out as above.

The ^{1}H n.m.r. spectra were obtained at 60 MHz on a Perkin-Elmer R12B spectrometer using perdeuteriotoluene as the solvent. The variable-temperature probe was calibrated as previously.[1]

RESULTS

Secondary Amines.—[Pr(fod)$_3$]–NHPr$^n_2$. Figure 1 shows n.m.r. spectra for the [Pr([^{2}H$_9$]fod)$_3$]–NHPr$^n_2$ system. At room temperature, three resonances are observed corresponding to the α-CH_2, β-CH_2, and CH_3 protons. As the temperature is decreased the α-CH_2 and β-CH_2 peaks broaden, and finally, at −60 °C and below, both split into two separate resonances. This shows that nitrogen inversion in the amine has been slowed down on an n.m.r. time scale, since in the absence of nitrogen inversion the α-CH_2 and β-CH_2 protons are diastereotopic (*cf.* ref. 8). At low temperatures the spectrum of a solution containing an excess of amine [Figure 1(*d*)] displays distinct signals for free and complexed substrate. Integration of these signals shows that the species present is a 2 : 1 adduct. No other resonances could be detected, even at moderately low amine : shift reagent ratios (≥0.8 : 1). Clearly, in this system, K_2 is appreciably greater than K_1. The ' bound ' chemical shifts for the 1 : 2 adduct are presented in the Table.

Above 0 °C, solutions containing 2 equivalents of [Pr(fod)$_3$] and 1 equivalent of NHPr$^n_2$ give two sets of resonances corresponding to free and complexed [Pr(fod)$_3$] (Figure 2) The peaks were assigned by varying the amine : shift reagent ratio. In contrast to the low-temperature measurements

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[2] J. B. Lambert, *Topics Stereochem.*, 1971, **6**, 19; C. H. Bushweller, W. G. Anderson, P. E. Stevenson, and J. W. O'Neil, *J. Amer. Chem. Soc.*, 1974, **96**, 3892.
[3] G. H. Searle and F. R. Keene, *Inorg. Chem.*, 1972, **11**, 1006.
[4] F. F. L. Ho and C. N. Reilley, *Analyt. Chem.*, 1969, **41**, 1835.
[5] S. Wawzonek, W. McKillip, and C. J. Peterson, *Org. Synth.*, 1964, **44**, 75.
[6] R. N. Icke, B. B. Wisegarver, and G. A. Alles, *Org. Synth.*, 1945, **25**, 89.
[7] A. Ladenburg, *Annalen*, 1888, **247**, 50.
[8] W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.

' Bound ' chemical shifts (p.p.m.) for $[Ln(fod)_3]\cdot nS$ adducts with secondary and tertiary amines. Shifts for Ln = Pr are to high field and for Ln = Eu are to low field

Ln	S	n	α-CH_2	α′-CH_2	$\frac{2(\alpha\text{-}CH_2 - \alpha'\text{-}CH_2)}{\alpha\text{-}CH_2 + \alpha'\text{-}CH_2}$	β-CH_2	β′-CH_2	γ-CH_3	θ_c/°C
Pr	$NHPr^n_2$	2	50.8	43.0	0.166	30.4		11.6	−40
			56.0	45.7	0.202	31.8		12.2	−50
			59.8	47.9	0.221	34.3	33.6	13.3	−60
			63.2	49.5	0.243	36.2	35.4	13.9	−70
			67.1	51.2	0.269	38.5	37.6	14.9	−78
Eu	$NHPr^n_2$	1	22.8	17.8	0.24_6	14.9		5.6	−30
			26.0	20.9	0.21_7	16.7		6.2	−50
			27.2	22.5	0.18_9	17.0		6.5	−60
			28.7	24.4	0.16_2	17.6		6.6	−70
			29.5	25.3	0.15_3	18.1		6.7	−75
		2	29.6	22.6	0.26_8	19.9		7.1	−50
			32.2	23.4	0.31_7	23.7		8.2	−70
			32.6	24.9	0.26_7	24.5		8.5	−75
			α-CH_3	α-CH_2	α′-CH_2	β-CH_2	β′-CH_2	γ-CH_3	
Pr	$NHMePr^n$	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
Eu	$NHMePr^n$	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
Pr	$NMePr^n_2$	1		44.7	42.4	26.1	30.2		−40
				44.0	45.7	25.6	30.0		−50
				46.0	49.4	26.3	31.2		−60
				51.2	54.0	27.6	33.2		−70
			α-CH_3	α-CH_2	α′-CH_2	β-CH_3			
Eu	$NMeEt_2$	1	37.6	31.0	28.1	11.0			−50
			39.8	32.8	29.8	11.3			−60
			41.8	34.9	31.3	11.4			−70

described above, integration of the methine and t-butyl resonances showed a significant proportion of a 1 : 1 adduct. This is not unexpected, in view of the higher temperatures, and the lower amine : shift reagent ratio. The free fod signals are broad at 35 °C, but collapse near 0 °C. This is presumably connected with the dimerization or trimerization of $[Ln(fod)_3]$ shift reagents which is known to occur in solution.[9] The complexed fod signals are sharp at room temperature, but coalesce with their free counterparts at *ca.* 80 °C. Clearly, exchange between R and RS is comparatively slow, much slower than between RS, RS_2, and S.

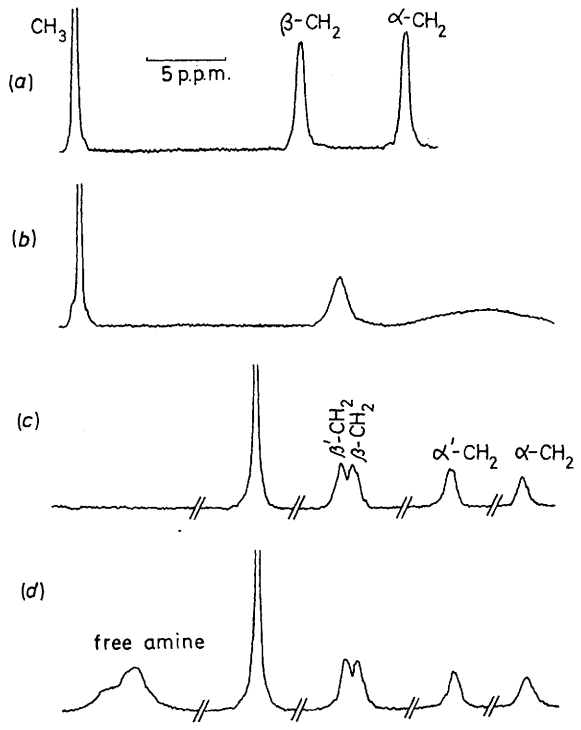

FIGURE 1 Hydrogen-1 n.m.r. spectra of a 0.20 mol dm^{-3} solution of $[Pr([^2H_9]fod)_3]$ and 0.20 mol dm^{-3} $NHPr^n_2$ at 30 (*a*), −30 (*b*), and −70 °C (*c*), and of 0.20 mol dm^{-3} $[Pr([^2H_9]fod)_3]$ and 0.60 mol dm^{-3} $NHPr^n_2$ at −70 °C (*d*)

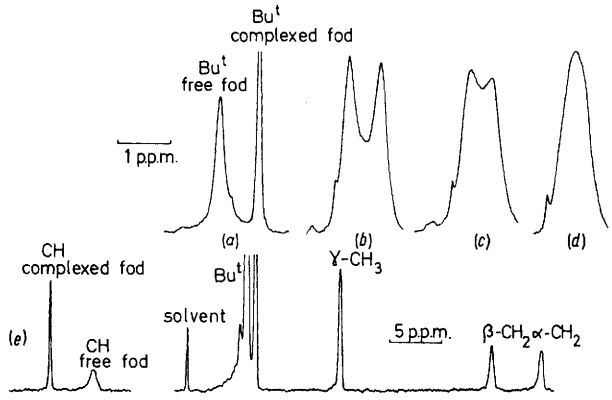

FIGURE 2 Hydrogen-1 n.m.r. spectra of a 0.20 mol dm^{-3} solution of $[Pr(fod)_3]$ and 0.1 mol dm^{-3} $NHPr^n_2$ at 20 (*a*), 70 (*b*), 75 (*c*), 80 (*d*), and 35 °C (*e*)

[Eu(fod)$_3$]–$NHPr^n_2$. A somewhat different behaviour is found in the corresponding $[Eu(fod)_3]$–$NHPr^n_2$ system at low temperatures (Figure 3). Peaks due to both the 1 : 1 and 2 : 1 adducts are observed and can be readily assigned as shown. The bound chemical shifts for both adducts are given in the Table. The value of K_2/K_1 is *ca.* 0.05 at −70 °C, where K_1 is an apparent equilibrium constant neglecting polymerization of the shift reagent.

The room-temperature resonances of free and complexed

[9] A. H. Bruder, S. R. Tanny, H. A. Rockefeller, and C. S. Springer, *Inorg. Chem.*, 1974, **13**, 880.

fod nearly coincide. However, they can be distinguished from each other since the free peak is broad as in the praseodymium system and the complexed peak is sharp. In a solution with an amine : shift reagent ratio of 0.5 : 1 the

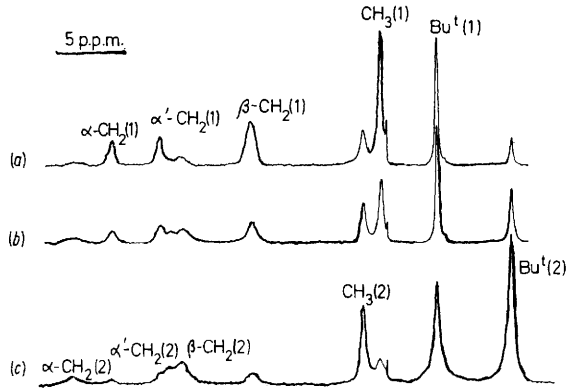

FIGURE 3 Hydrogen-1 n.m.r. spectra at −70 °C of 0.20 mol dm^{-3} [Eu(fod)$_3$] and 0.15 (*a*), 0.25 (*b*), and 0.30 mol dm^{-3} NHPr$^n_2$ (*c*)

resonances have approximately the same intensity, indicating that 1 : 1 adducts are predominantly formed under these conditions.

[Pr(fod)$_3$]- and [Eu(fod)$_3$]–NHMePr^n. In the absence of nitrogen inversion, NHMePr^n is chiral. In both these systems, 2 : 1 adducts are formed at low temperatures, and *meso* and *rac* isomers, in approximately equal abundance, can be distinguished (Figure 4). The spectrum of [Pr([^{2}H$_9$]-fod)$_3$]–NH(CD$_3$)Pr^n was also studied to help the assignment. Appreciable differences are observed in the two systems. With [Pr(fod)$_3$], but [notEu(fod)$_3$], separate α-CH$_3$ and γ-CH$_3$ resonances are observed for the *meso* and *rac* isomers. On the other hand, while both the diastereotopic α-CH$_2$ protons give separate *meso* and *rac* resonances in the [Pr(fod)$_3$] system, with [Eu(fod)$_3$] only one of the diastereotopic α-CH$_2$ resonances is found to be split. Two weak resonances in the [Eu(fod)$_3$] system indicate the presence of a small proportion of a 1 : 1 adduct.

Tertiary Amines.—[Eu(fod)$_3$]–NMeEt$_2$. At low temperatures, diastereotopic splitting of the methylene resonance is observed for [Eu(fod)$_3$]–NMeEt$_2$, showing that nitrogen inversion has been slowed down. In a solution 0.2 mol dm^{-3} in both components, coalescence of the CH$_2$ resonances occurs at −5 °C (τ 1.5 × 10^{-3} s). As the amine to shift reagent ratio is increased from 0.75 to 1.5 : 1 the rate of nitrogen inversion also increases markedly. Bound chemical shifts measured at lower temperatures are given in the Table. The usual techniques (low-temperature integration of free and complexed amine peaks in solutions containing an excess of amine, or room-temperature integration of fod resonances in solutions containing an excess of shift reagent) show that the adduct stoicheiometry is entirely 1 : 1. Similar diastereotopic splitting was also observed in the [Eu(fod)$_3$]–NMeEtPr^n system.

Neither nitrogen inversion nor intermolecular exchange could be slowed down in [Pr(fod)$_3$]–NMeEt$_2$ or –NMe$_2$Pr^n. Exchange is fast at room temperature and the signals merely flatten out as the temperature is decreased.

[Pr(fod)$_3$]–NMePr$^n_2$. At 40 °C the spectrum of a solution 0.2 mol dm^{-3} in [Pr(fod)$_3$] and 0.1 mol dm^{-3} in NMePr$^n_2$ shows separate resonances for free and complexed [Pr(fod)$_3$], and integration indicates 1 : 1 stoicheiometry. The resonances coalesce at 77 °C (τ 2.9 × 10^{-3} s). Nevertheless, at 40 °C, single resonances are observed for the α-CH$_2$ and β-CH$_2$ protons of the amine, and nitrogen inversion is rapid on a proton-resonance time scale. Diastereotopic splitting is, however, found at lower temperatures (Table). As before, the rate of nitrogen inversion increases with the amine : shift reagent ratio, coalescence temperatures being 35 (ratio 0.25), 25 (0.5), and 15 °C (0.77 : 1).

[Eu(fod)$_3$]–NMe$_2$Bu^t. For all the other tertiary amine systems studied, free amine resonances could not be detected at low temperatures in solutions with amine : shift reagent ratios $\leqslant$ 1. This shows that K_1 is quite large. However, with NMe$_2$Bu^t, a solution 0.15 mol dm^{-3} in amine and 0.2 mol dm^{-3} in [Eu(fod)$_3$] displayed distinct free amine signals at −10 °C and below. From integration of the free and complexed amine peaks at various amine : shift reagent ratios, K_1 = 3.8 ± 0.5 dm^3 mol^{-1} at −50 °C. This means that, at low temperatures, not only is dissociation of the 1 : 1 adduct slow, but so is its formation. The small K_1, and slow formation of the adduct, can be attributed to steric effects of the bulky t-butyl group. Presumably, in forming the adduct, a considerable rearrangement of the lanthanoid complex is required.

[Eu(fod)$_3$]–N-*methylpiperidine*. In free *N*-methylpiperidine (mpip) the conformer in which the methyl group is equatorial is greatly favoured. The most reliable value for

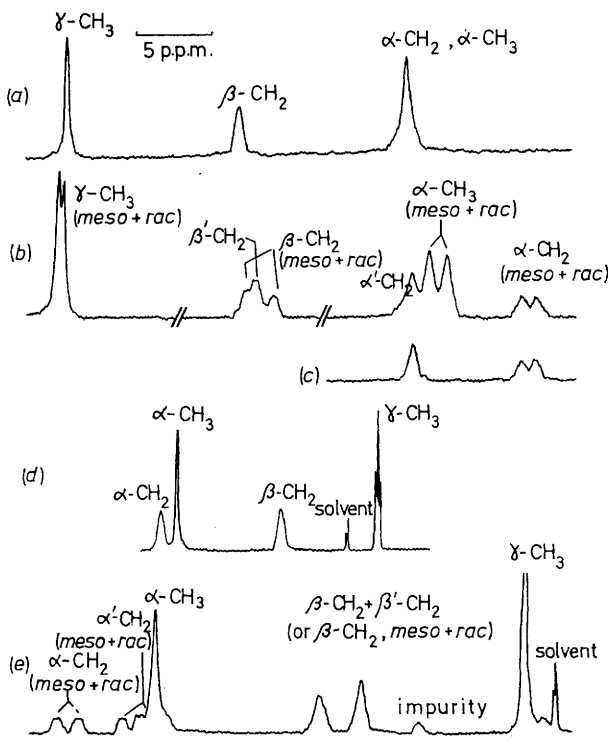

FIGURE 4 Hydrogen-1 n.m.r. spectra of a 0.20 mol dm^{-3} solution of [Pr([^{2}H$_9$]fod)$_3$] and 0.20 mol dm^{-3} NHMePr^n at 30 (*a*) and −70 °C (*b*), 0.20 mol dm^{-3} [Pr([^{2}H$_9$]fod)$_3$] and 0.20 mol dm^{-3} NH(CD$_3$)Pr^n at −70 °C (*c*), and 0.20 mol dm^{-3} [Eu([^{2}H$_9$]fod)$_3$] and 0.30 mol dm^{-3} NHMePr^n at 35 (*d*) and −60 °C (*e*)

the free-energy difference $\Delta G^\ominus$ between the axial and equatorial conformers is *ca.* 2.7 kcal mol^{-1} (cyclohexane, room temperature),* corresponding to an equilibrium constant

* Throughout this paper: 1 cal = 4.184 J.

of *ca.* 100.[10] Ring inversion, with concomitant nitrogen inversion, has been studied by dynamic n.m.r., and the barrier $\Delta G^{\ddagger}$ is 12.1 kcal mol^{-1} at −28 °C in methanol.[11] No information was obtained concerning nitrogen inversion alone, and, in view of the great predominance of one conformer, to do so would be very difficult.

Co-ordination of mpip to a lanthanoid shift reagent should appreciably stabilize the (CH_3) axial isomer. The ^{1}H n.m.r. spectrum of [Eu(fod)$_3$]–mpip at low temperatures was quite complicated, and mainly indicated that more than one isomer was present. Accordingly, the corresponding [Eu(fod)$_3$]–[$^2H_{10}$]mpip system was studied, and the results are shown in Figure 5. At 35 °C a solution containing an excess of [Eu-

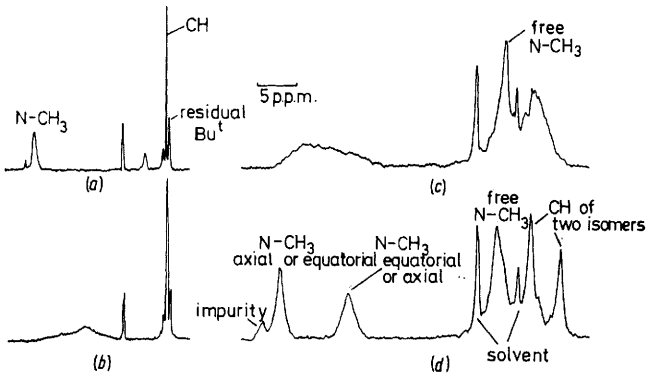

FIGURE 5 Hydrogen-1 n.m.r. spectra of 0.20 mol dm^{-3} [Eu([$^2H_9$]fod)$_3$] and 0.15 mol dm^{-3} [$^2H_{10}$]mpip at 35 °C (*a*), and of 0.20 mol dm^{-3} [Eu([$^2H_9$]fod)$_3$] and 0.30 mol dm^{-3} [$^2H_{10}$]mpip at 35 (*b*), −50 (*c*), and −70 °C (*d*)

([$^2H_9$]fod)$_3$] showed a single, fairly sharp, CH_3 resonance [5(*a*)]. In the presence of an excess of amine the resonance becomes very broad [5(*b*)], due to an intermediate rate of exchange between free and complexed amine. At −50 °C intermolecular exchange is slow, since the free CH_3 resonance is fairly sharp, but the co-ordinated CH_3 peak is broad [5(*c*)] as a result of ring inversion. Finally, at −70 °C, intermolecular exchange, ring inversion, and nitrogen inversion are all slow, and two separate CH_3 resonances [5(*d*)] appear for the 1 : 1 adduct. These correspond to the axial and equatorial isomers which are present in approximately equal amounts. (It is not possible to assign the peaks individually.) Clearly, in this context the effective bulk of [Eu(fod)$_3$] and of a CH_3 group are almost equal. Although the shift reagent is much larger than a CH_3 group, the Eu–N bond is much longer than the C–N bond (*ca.* 2.6 as compared with 1.47 Å). The coalescence temperature of the CH_3 resonances was −48 °C, and did not change on reducing the amine : shift reagent ratio. The barrier to ring inversion $\Delta G^{\ddagger}$ is 10.1 ± 0.1 kcal mol^{-1}, which is substantially smaller than in the free amine.

DISCUSSION

Stoicheiometry of the Adducts.—It was previously concluded [1] that, for strongly co-ordinating substrates, steric effects are very important in determining the stoicheiometry of adducts formed by lanthanoid shift reagents. This is borne out by the present results. Tertiary amines, which have large steric requirements close to the co-ordinating site, form 1 : 1 adducts only, while secondary amines give both 1 : 1 and 2 : 1 adducts. With secondary amines, [Pr(fod)$_3$] shows a greater tendency than [Eu(fod)$_3$] to form 2 : 1 adducts, presumably because of the larger size of the Pr^{3+} ion.

For the [Eu(fod)$_3$]–NHPr$^n_2$ system, the 'bound' chemical shifts are appreciably greater in the 2 : 1 adduct (Table). This is somewhat surprising. The mean Eu–H distances will be slightly greater in the 2 : 1 adduct,[12] and partial averaging of the angle factors might also be expected.[1] Presumably, the direction of the magnetic axes are such that the angle factors are more favourable in the 2 : 1 than in the 1 : 1 adduct.

Disastereotopic Splitting.—Some insight into the magnitude and temperature dependence of the diastereotopic splittings in α-CH_2 groups can be obtained by considering the three rotamers arising from rotation about the CH_2–N bond. These rotamers for adducts of NHPr$^n_2$ and NMePr$^n_2$ are represented in Figure 6. In rotamer (a), δ(H_a) should be considerably greater than δ(H_b), in rotamer (c) the inverse should be true, and in rotamer (b) δ(H_a) and δ(H_b) should be approximately equal. Even if all three rotamers were equally populated, there would, of course, still be an *intrinsic* non-equivalence.[8]

Changes in the diastereotopic splitting with temperature will normally arise from two factors: the usual temperature dependence of lanthanoid-induced shifts,[1] and alterations in the relative populations of the three rotamers. The first factor can be eliminated by considering, not δ(H_a) − δ(H_b), but this difference divided by the mean chemical shift, *i.e.*, 2[δ(H_a) − δ(H_b)]/[δ(H_a) + δ(H_b)]. Values of this parameter for NHPr$^n_2$ adducts are given in the Table.

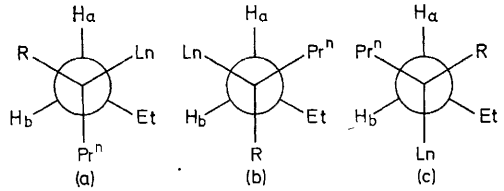

FIGURE 6 Rotamers arising from rotation about the CH_2–N bond for [Ln(fod)$_3$] complexes with NHPr$^n_2$ (R = H) and NMePr$^n_2$ (R = Me)

For NHPr$^n_2$ adducts, rotamer (a) should be less stable than (b) and (c), since three bulky groups {Et, Pr^n, and [Ln(fod)$_3$]} are adjacent. In the 2 : 1 praseodymium adduct the corrected diastereotopic splitting increases as the temperature decreases, suggesting that rotamer (c) is preferred. In the 1 : 1 [Eu(fod)$_3$]·NHPr$^n_2$ adduct the corrected diastereotopic splitting decreases as the temperature decreases, while with the 2 : 1 adduct there is little change. Since the Eu–N bond will be appreciably shorter than the Pr–N bond, interactions between the shift reagent and the ethyl group will be greater, and hence rotamer (b) should be more favoured (especially in the 1 : 1 adduct).

[10] F. A. L. Anet, I. Yavari, I. J. Ferguson, A. R. Katritzky, M. Moreno-Manas, and M. J. T. Robinson, *J.C.S. Chem. Comm.*, 1976, 399.

[11] J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Amer. Chem. Soc.*, 1967, **89**, 3761.

[12] B. L. Shapiro, 'Nuclear Magnetic Resonance Shift Reagents,' ed. R. E. Sievers, Academic Press, 1973, p. 236.

The α-CH_2 diastereotopic splittings are much less in the [Pr(fod)$_3$]·2 $NMePr^n_2$ adduct (Table). This can be easily understood, since replacing a hydrogen atom by a methyl group will presumably increase the relative stability of rotamer (a). In this system, the diastereotopic splittings of the β-CH_2 groups are much greater than those of the α-CH_2 groups.

Exchange Processes.—Three main exchange processes have been observed in the present work: (*i*) with excess of shift reagent, intermolecular exchange between free and complexed shift reagent; (*ii*) with excess of amine, intermolecular exchange between free and complexed amine; and (*iii*) nitrogen inversion in the amine, which can be studied at any amine : shift reagent ratio.

In solutions containing an excess of amine, slowing down of nitrogen inversion necessarily involves a slowing down of intermolecular amine exchange. With an excess of shift reagent, however, it is possible for intermolecular amine exchange to be fast and nitrogen inversion slow if the stability of the adduct(s) is sufficiently high (as in the room-temperature protonation technique introduced by Saunders and Yamada [13]). However, it seems likely that the rate-determining step for nitrogen inversion in these systems is normally intermolecular amine exchange.

Process (*i*), which involves dissociation of the RS adduct, is quite slow, typical coalescence temperatures being *ca.* 80 °C. It is not surprising that, in secondary amine systems, intermolecular amine exchange and nitrogen inversion are normally much faster. Both 1 : 1 and 2 : 1 adducts are present, and intermolecular exchange can involve the equilibrium $RS + S \rightleftharpoons RS_2$. Tertiary amines form 1 : 1 adducts only, but here also exchange of shift reagent is slower than amine exchange or ring inversion as exemplified by the [Pr(fod)$_3$]–$NMePr^n_2$ system. This can be attributed to an associative mechanism for substrate exchange [equation (3), *cf.* ref. 1]. In systems

$$RS + S^* \rightleftharpoons RSS^* \rightleftharpoons RS^* + S \qquad (3)$$

with an excess of shift reagent, presumably small amounts of S are produced by the equilibrium dissociation of the adduct.

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