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

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Dynamic n.m.r. spectra have been obtained for adducts of the title complex [Pr(fod)$_3$] with substituted ethylenediamines. Four exchange processes have been characterized or observed: (*i*) intermolecular exchange; (*ii*) ring opening; (*iii*) ring inversion; and (*iv*) intramolecular rearrangement(s) of the eight-co-ordinate complex. Barriers to ring inversion are reported. For the *NN'*-dimethylethylenediamine adduct, DL and *meso* isomers are present in a 3.0 : 1 ratio.

THE present work is mainly concerned with the dynamic proton-resonance spectroscopy of systems comprising [Pr(fod)$_3$] with various substituted ethylenediamines (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate). In these systems 1 : 1 complexes are formed which contain a five-membered chelate ring. There are four likely exchange processes and all four have been characterized or observed: (*i*) intermolecular substrate exchange, involving rupture of both Pr–N bonds; (*ii*) the rupture of a single Pr–N bond, normally followed by N inversion, bond rotation, and ring closure; (*iii*) inversion of the puckered five-membered chelate ring; and (*iv*) intramolecular rearrangement of the four chelate rings in the eight-co-ordinate complex. The first process is, fortunately, normally the slowest, especially in the presence of excess of [Pr(fod)$_3$]. Previous n.m.r. studies on eight-co-ordinate complexes suggest that the process (*iv*) is likely to be comparatively fast.[1,3]

It is now well established, from *X*-ray studies and other evidence,[4,5] that in metal complexes of ethylenediamine (en) and substituted ethylenediamines the five-membered chelate ring is puckered. Such a ring is chiral, and exists in two enantiomeric configurations, λ and δ. Although there have been many proton-resonance studies of complexes of this type, in the great majority of cases, ring inversion has been fast on an n.m.r. time scale. However, in spite of this limitation, Ho and Reilley [6,7] were able to obtain valuable information from the proton-resonance spectra of complexes of Ni^{II} with ethylenediamine and substituted ethylenediamines.

EXPERIMENTAL

The handling techniques and purification of reagents were as described previously.[1] The proton-resonance spectra were obtained at 60 MHz on a Perkin-Elmer R12B spectrometer, using [$^2H_8$]toluene as solvent.

In the calculations of $\Delta G^‡$, the values of δ at the coalescence temperatures were obtained from extrapolations of linear plots of log δ against log T, using data measured at below the coalescence temperature.

RESULTS AND DISCUSSION

[Pr([$^2H_9$]fod)$_3$]-NNN'N'-*Tetramethylethylenediamine* (*tmen*).—At 35 °C, for a solution equimolar in both components, two peaks are observed for tmen, corresponding to the methyl protons and the ring methylene protons [Figure 1(*a*)]. As the temperature is decreased these peaks broaden and finally at −60 °C both split into two resonances [Figure 1(*c*)]. At −30 °C a solution containing an excess of tmen gives separate resonances for the free and complexed amine. Intermolecular exchange has thus been slowed down, although the first exchange process is still comparatively fast. Integration of the free and complexed amine peaks at low temperatures and also of the free and complexed fod peaks at room temperature {in a solution containing 2 equiv. of [Pr(fod)$_3$] and 1 equiv. of tmen} shows that a 1 : 1 complex is formed, which is clearly chelated.

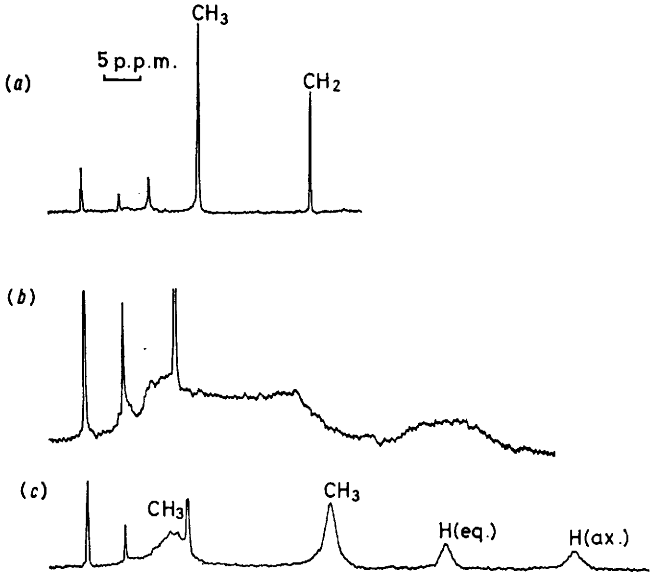

FIGURE 1 Hydrogen-1 n.m.r. spectra of a solution of 0.20 mol dm^{-3} [Pr([$^2H_9$]fod)$_3$] and 0.20 mol dm^{-3} tmen at 35 (*a*), −40 (*b*), and −60 °C (*c*). The other resonances are due to residual H$^+$ in the solvent and the [$^2H_9$]fod. The fod methine signal is at higher field and is not displayed

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[1] Part 2, D. F. Evans and G. C. de Villardi, *J.C.S. Dalton*, 1977, 2256.

[2] For a preliminary account see D. F. Evans and G. C. de Villardi, *J.C.S. Chem. Comm.*, 1976, 7.

[3] E. L. Muetterties, *Inorg. Chem.*, 1973, **12**, 1963.

[4] C. J. Hawkins, 'Absolute Configurations of Metal Complexes,' Wiley-Interscience, New York, 1971.

[5] L. J. De Hayes and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1505.

[6] F. F-L. Ho and C. N. Reilley, *Analyt. Chem.*, 1969, **41**, 1835.

[7] F. F-L. Ho and C. N. Reilley, *Analyt. Chem.*, 1970, **42**, 600.

The intramolecular exchange observed could conceivably arise from one of the processes (*ii*)—(*iv*) described above. However, the results obtained for other substituted ethylenediamines (see below) leave little doubt that ring inversion, (*iii*), is involved. Since substrate exchange is much slower than ring inversion, it is possible to calculate the barrier to ring inversion, $\Delta G^{\ddagger}$, from either the coalescence temperature of the methyl resonances (10.11 kcal mol^{-1} at −36 °C) or the coalescence temperature of the methylene resonances (10.07 kcal mol^{-1} at −38 °C).*

TABLE 1

' Bound ' chemical shifts (p.p.m.) for [Ln(fod)$_3$] complexes with bidentate amines. Shifts to high field are positive

Ln	Amine	CH_3(eq. or ax.)	CH_3(ax. or eq.)	H(eq.)	H(ax.)					θ_c/°C
Pr	tmen	24.8	5.7	38.4	52.5					−50
		26.2	6.1	41.1	57.5					−60
		27.6	6.0	45.1	62.9					−70
		CH_3(N)				CH_3(C)	H_a	H_c	H_d	
Pr	tmpn	1.9	2.9	17.6	21.8	12.2	28.1	26.1	19.5	35
		2.3	3.2	20.8	25.9	15.2	36.0	33.2	24.6	0
		3.0	3.5	22.6	28.3	17.3	41.5	38.1	28.3	−20
		4.5	4.5	26.1	33.0	21.8	53.9	49.0	36.4	−50
		DL				*meso*				
		CH_3	NH	H	H	CH_3	NH	H	H	
Pr	dmen	16.5	44.7	14.0	22.6	13.4	46.1	17.4	20.9	−10
		17.6	50.3	16.4	26.1	15.0	50.9	19.5	24.8	−30
		19.9	64.6	21.9	34.1	18.6	61.4	24.5	30.9	−60
		CH_3	H(ax. or eq.)	H(eq. or ax.)						
Pr	dmp	11.7	7.8	16.3						35
		16.5	8.3	20.1						0
		22.0	8.1	23.6						−30
		34.5	7.0	30.7						−70
Eu	dmp	2.5	$-8._5$	$-3._9$						35
		$2._6$	$-9._9$	$-5._3$						0
		$2._6$	$-11._3$	−6.8						−30
		2.0	$-13._0$	$-9._1$						−70
Yb	dmp	9.0	0.4	12.3						0
		10.2	0.4	13.6						−15

The assignment of the ring methylene protons [Figure 1(*c*)] is based on that for the tetramethylpropylene-1,2-diamine system (see below). ' Bound ' chemical shifts are presented in Table 1.

[Pr([$^2H_9$]fod)$_3$]-NNN'N'-*Tetramethylpropylene*-1,2-*diamine* (*tmpn*).—It is well established, on both experimental and theoretical grounds,[4-6] that in metal complexes of propylene-1,2-diamine and *N*-substituted propylene-1,2-diamines the CMe group greatly prefers an equatorial position [Figure 2(*a*)]. The proton-resonance spectrum of the [Pr([$^2H_9$]fod)$_3$]-tmpn system at 20 °C shows separate resonances for the 4CH_3(N) groups, the CH_3(C) group (a doublet due to splitting by H_b), and the three ring protons (Figure 3). The spin–spin splitting observed for the latter confirms that the CMe group is predominantly equatorial, and leads to the assignment shown (*cf*. refs. 8 and 9). H_d gives a doublet split by H_c [$J(H^cH^d)$ *ca*. 12 Hz]; the small *gauche* splitting $J(H^aH^c)$ is not resolved. H_c gives a triplet split approximately equally by H_d and H_b, while for H_a the expected extensive splitting cannot be observed due to slight paramagnetic broadening.

This spectrum does not change greatly in the range 20 to −60 °C, probably because the conformation with the CH_3(C) group equatorial is so greatly favoured. Thus, no information can be obtained concerning ring inversion. However, on increasing the temperature a different type of exchange process is observed. One pair of CH_3(N) resonances starts to broaden at *ca*. 35 °C,

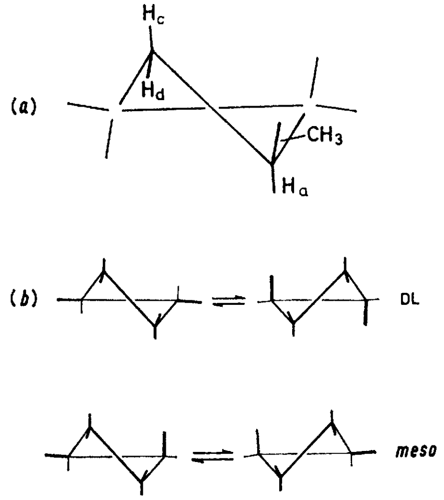

FIGURE 2 (*a*) The preferred conformation for a tmpn chelate ring (*R*δ). (*b*) The DL and *meso* isomers of a dmen adduct

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* Throughout this paper: 1 cal = 4.184 J.

[8] J. L. Sudmeier, G. L. Blackmar, C. H. Bradley, and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1971, **94**, 757.

[9] S. Sano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1969, **42**, 3184.

and the other pair at 55 °C. At 85 °C both pairs of methyl resonances coalesce to a very broad band, but the rest of the spectrum remains sharp.

The process involved is presumably an interchange of pairs of CH_3 groups attached to the same nitrogen atom. This involves rupture of one Pr–N bond, inversion at the nitrogen atom, rotation about the C–N bond, and ring closure. It is clear that one pair of CH_3 groups is interconverting more rapidly than the other. At 55 °C the respective lifetimes τ are 0.004 and 0.017 s. These lifetimes represent a lower limit to the rate of ring opening, since ring closure may occur before nitrogen inversion has taken place.

The expected 1 : 1 stoicheiometry of the $[Pr(fod)_3]$–tmpn complex was confirmed by the usual methods. A solution 0.2 mol dm^{-3} in $[Pr(fod)_3]$ and 0.1 mol dm^{-3} in tmpn displays two signals of equal intensity for the t-butyl resonances of the free and complexed $[Pr(fod)_3]$. These resonances coalesce at 110 °C (τ 3.4 × 10^{-3} s), indicating that the complex is very stable. The ' bound ' chemical shifts are given in Table 1.

$[Pr([^2H_9]fod)_3]$–NNN′N′-*Tetraethylethylenediamine* (*teen*).—In this complex it is possible to distinguish unambiguously between a one-ended opening of the chelate ring and ring inversion. In a chelate structure the CH_2 protons of the ethyl groups are diastereotopic. This diastereotopicity can be removed by opening of the chelate ring (with subsequent bond rotation and ring closure) but not by ring inversion. At 35 °C (Figure 4) single resonances are observed for the CH_2 ring protons, the CH_2 protons of the ethyl groups, and the CH_3 protons. As the temperature is decreased the CH_2(Et) resonance broadens and at 0 °C complete diastereotopic splitting is observed. The CH_3 and CH_2(ring) resonances have not split, showing that ring opening is now slow on an proton-resonance time scale, but ring inversion is still comparatively fast. The coalescence temperature of the two CH_2(Et) resonances is 20 °C (τ $5._5$ × 10^{-4} s) and is virtually independent of the shift reagent : amine ratio, provided this is >1.0 : 1. The resonances of free and complexed fod CH coalesce at 78 °C. Both these observations confirm that the process involved is ring opening, and not intermolecular exchange.

As the temperature is decreased further ring inversion is slowed down, and, at −30 °C, separate axial and equatorial resonances are observed for the CH_3 groups and the ring CH_2 protons. The CH_2(Et) protons should give a double doublet, but the expected resonances are presumably lost in the background. The CH_3 resonances coalesce at −13 °C ($\Delta G^‡$ 11.5 ± 0.2 kcal mol^{-1}).

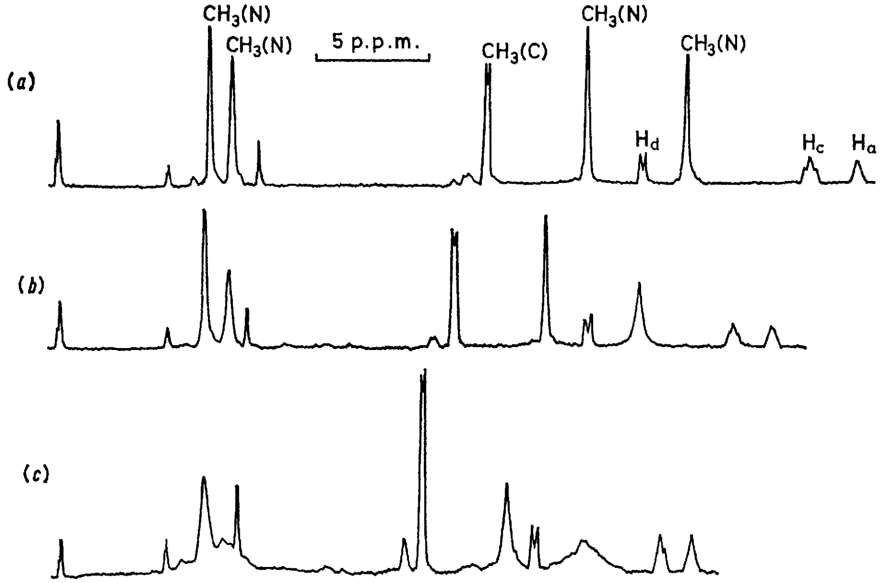

FIGURE 3 Hydrogen-1 n.m.r. spectra of a solution of 0.20 mol dm^{-3} $[Pr([^2H_9]fod)_3]$ and 0.15 mol dm^{-3} tmpn at 20 (*a*), 35 (*b*), and 55 °C (*c*)

Below −45 °C, all the resonances broaden (including those of the fod protons); the entire spectrum is practically flat at −55 °C, and finally a new pattern of resonances appears at −70 °C. This presumably represents a slowing down of intramolecular rearrangements in the eight-co-ordinate complex, which probably involve some form of twist mechanism.[3] Unfortunately, the resonances are fairly broad, and the spectrum is too complex to be interpreted.

As usual, intermolecular exchange was faster in the presence of excess of substrate. In a solution 0.2 mol dm^{-3} in $[Pr([^2H_9]fod)_3]$ and 0.3 mol dm^{-3} in teen, coalescence of the resonances of free and complexed substrate is observed at *ca.* 15 °C.

$[Pr([^2H_9]fod)_3]$–NN′-*Dimethylethylenediamine* (*dmen*).—In metal complexes of dmen the chelate ring can exist in DL and *meso* forms [6] [Figure 2(*b*)]. The preference of a CH_3(N) group to be equatorial is, however, much less marked than that of a CH_3(C) group.[5] At 65 °C a solution 0.1 mol dm^{-3} in [Pr([$^2H_9$]fod)$_3$] and 0.1 mol dm^{-3} in dmen gives the spectrum shown in Figure 5. Exchange between the DL and *meso* forms is fast on an n.m.r. scale (probably *via* a ring-opening mechanism). At −30 °C, however, two isomers are clearly present, in a 3.0 : 1 ratio. Ring inversion is still fast (certainly for the *meso* form) since further splitting of the CH_3 resonances is not observed. The greater splitting of the ring CH_2 resonances for the more abundant isomer indicates that this is the DL form [*cf.* Figure 2(*b*) and ref. 6]. The DL : *meso* ratio of 3.0 : 1 can be compared with that for [Ni(dmen)]$^{2+}$ (1.4 : 1) [6] and for [PtCl$_2$(dmen)] (1 : 1).[10]

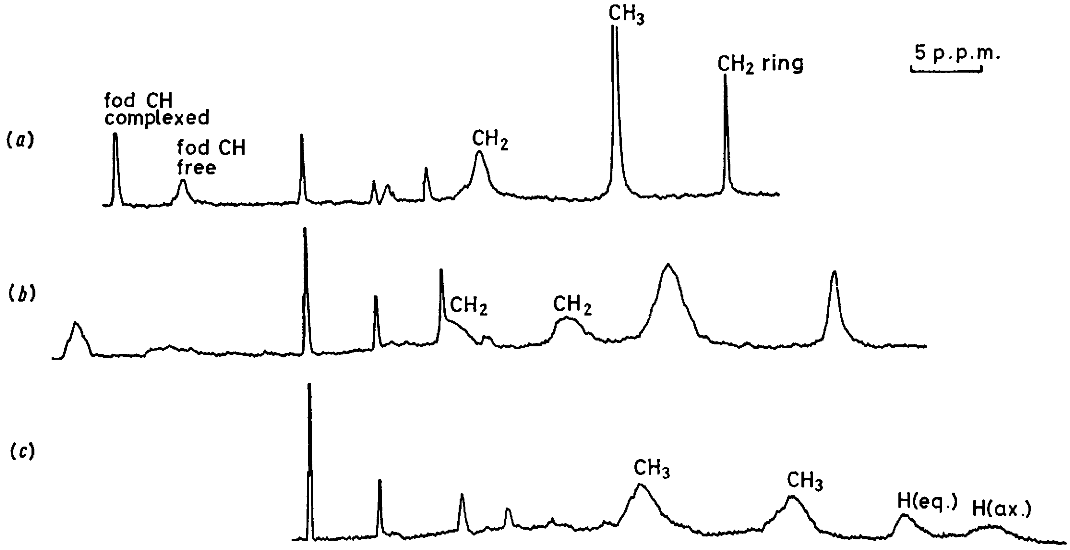

FIGURE 4 Hydrogen-1 n.m.r. spectra of a solution of 0.20 mol dm^{-3} [Pr([$^2H_9$]fod)$_3$] and 0.10 mol dm^{-3} teen at 35 (*a*), 0 (*b*), and −30 °C (*c*)

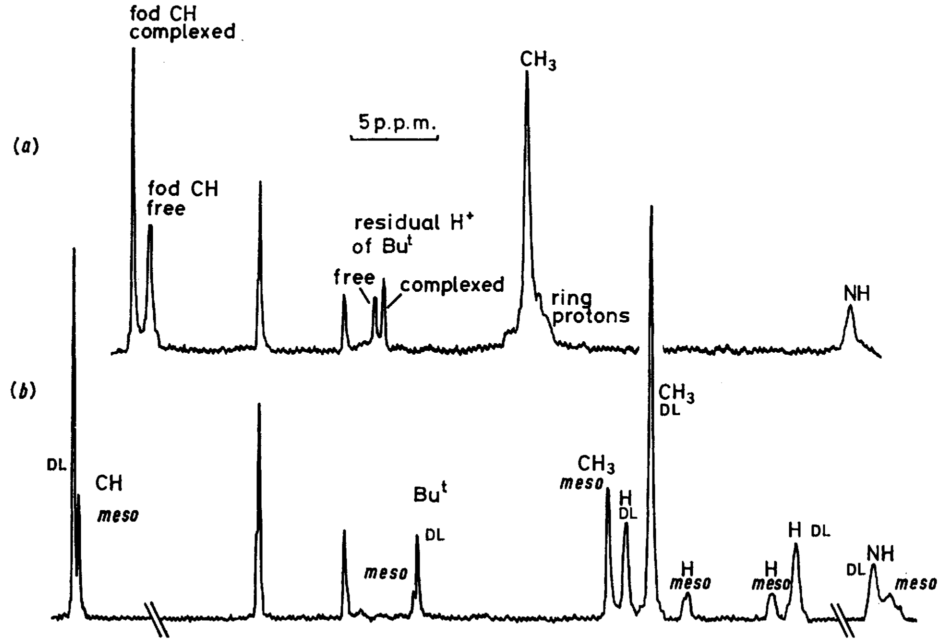

FIGURE 5 Hydrogen-1 n.m.r. spectra of a solution of 0.20 mol dm^{-3} [Pr([$^2H_9$]fod)$_3$] and 0.10 mol dm^{-3} dmen at 65 (*a*) and −30 °C (*b*). The methine signal of free fod cannot be observed at −30 °C (*cf.* ref. 1)

Ring inversion in the *meso* and DL forms could not be slowed down even at −70 °C. At −80 °C both the [Pr([$^2H_9$]fod)$_3$] and the substrate resonances become very broad. In the presence of excess of amine it was also not possible to slow down intermolecular exchange to allow observation of distinct free and complexed dmen resonances. The presence of DL and *meso* forms at

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[10] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1975, **14**, 2768.

high shift reagent : amine ratios, however, shows that under these conditions intermolecular exchange is slow.

NN'-*Dimethylpiperazine* (*dmp*) *Chelate Complexes.*—It is known from *X*-ray studies that dmp can act as a bidentate ligand, a boat-form chelate ring being formed.[11,12] The room-temperature spectra of the systems $[Ln([^2H_9]fod)_3]$–dmp (Ln = Pr, Eu, or Yb) each display three signals in a 3 : 2 : 2 intensity ratio. These can be assigned to the methyl groups, and pseudo-axial and pseudo-equatorial ring protons of a boat-form chelate. (In the limit of slow exchange, a unidentate adduct would display at least four resonances.) The ' bound ' chemical shifts (Table 1) display some unusual features. Normally (although not invariably), high-field shifts are observed with β-diketonate shift reagents when Ln = Pr, and low-field shifts when Ln = Eu or Yb. In the dmp adducts, with $[Pr(fod)_3]$ the normal pattern is found, with $[Eu(fod)_3]$ the resonance of the methyl groups is shifted upfield, and with $[Yb(fod)_3]$ all the three resonances are shifted in the ' wrong ' direction. There are also marked differences in the temperature dependence of the ' bound ' chemical shifts. These anomalies probably reflect differences in the predominant structure(s) adopted by the three adducts, which may partly arise from the ' demanding ' nature of the chelate dmp ligand, together with changes in the ionic radius of the lanthanoid ion.

$[Pr([^2H_9]fod)_3]$–NNN'N'-*Tetramethylpropane*-1,3-*diamine* (*tmpd*).—In metal complexes of propane-1,3-diamine and substituted propane-1,3-diamines the six-membered ring normally adopts either a chair or a ' skew-boat ' conformation.[5] Intermolecular exchange in a solution 0.20 mol dm^{-3} in $[Pr([^2H_9]fod)_3]$ and 0.25 mol dm^{-3} in tmpd is slow on the n.m.r. time scale at −40 °C. Three resonances are observed for the complexed substrate at this temperature, indicating that the amine is bidentate and that ring inversion is fast. On further cooling, ring inversion is slowed down, and the methyl resonance splits into two broad bands at −85 °C. The ring-proton resonances could not be observed and are presumably lost in the background. The coalescence temperature of the CH_3 resonances is −60 °C, giving a value for the barrier to ring inversion, $\Delta G^\ddagger$, of *ca.* 9.0 kcal mol^{-1}.

$[Pr([^2H_9]fod)_3]$–NNN'N'-*Tetramethylbutane*-1,4-*diamine.*—Formation of a seven-membered chelate ring is rather unlikely, and in this system there is no evidence of slow substrate exchange (whatever the shift reagent : amine ratio) even at −80 °C.

Barriers to Ring Inversion.—The barriers to ring inversion found in this work are given in Table 2, together with values obtained for three tmen complexes by other workers. These barriers are, in general, much higher than theoretical estimates for ethylenediamine complexes of metals such as Co^{II}, Ni^{II}, and Rh^{III} (*ca.* 5 kcal mol^{-1}).[13] The difference is probably largely due to the bulky substituents on the nitrogen atoms. In agreement with this, for the $[Pr(fod)_3]$ complexes, $\Delta G^\ddagger$ increases in the order dmen < tmen < teen. A further factor for the complexes of Pr and Mo may be the large metal–nitrogen distances, which will tend to increase the extent of ring puckering.[2,14] However, comparisons between different metal complexes should be made with caution in view of the differing interactions between the chelate rings and the other ligands in the complex.

TABLE 2

Barriers to ring inversion, $\Delta G^\ddagger$/kcal mol^{-1}

Complex	$\Delta G^\ddagger$	θ_c/°C
$[Pr(fod)_3(dmen)]$	$\leqslant 8.5$	
$[Pr(fod)_3(tmen)]$	10.1 ± 0.1	−37
$[Pr(fod)_3(teen)]$	11.5 ± 0.2	−13
$[Pr(fod)_3(tmpd)]$	*ca.* 9.0	−60
$[Mo(CO)_4(tmen)]$ [14]	10.36 [a]	−65
$[Co\{tmen(NO)_2\}]^+$ [b]	8.8	−90
$[Zn(tmen)Cl_2]$ [b]	8.9	−90

[a] $\Delta H^\ddagger = 9.92 \pm 0.45$ kcal mol^{-1}, $\Delta S^\ddagger = -2.1 \pm 2.2$ cal K^{-1} mol^{-1}. [b] K. J. Caulton, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 533.

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[14] C. J. Hawkins, R. M. Peachey, and C. L. Szoredi, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 881.