Table I. Representative Product Yields From the Charge-Transfer Photochemistry of $Rh(NH_3)_5I^{2+}$[a]

Primary absorbing species	$10^3 \times$ [Rh(III)], *M*	$[I^-]$,[b] *M*	*N*[c]	ϕ_t[d]	ϕ_{NH_3}	Range of $10^4 \times I_a$, einsteins l.$^{-1}$ min^{-1}
$Rh(NH_3)_5I^{2+}$	2.0	0	3	0.035 ± 0.006	0.29 ± 0.03	5–6
	1.0[e]	0	3	0.025 ± 0.006	0.27 ± 0.02	2–5
	1.0	0	2	*f*	0.32 ± 0.03	0.33
	1.0	1.0×10^{-3}	2	0.15 ± 0.02	0.16 ± 0.01	2–3
I^-[g]	1.0	0.10	8	0.44 ± 0.05[h]	0.4[h,i]	0.26–3.3

[a] 25°, pH 1 ($HClO_4$), except as indicated. [b] Initial concentration. [c] Number of determinations. [d] Yield of *trans*-$Rh(NH_3)_4I_2^+$. [e] pH 1–3. [f] Too small to detect. [g] At pH 3; rhodium(III) present initially as $Rh(NH_3)_5OH_2^{3+}$. [h] Quantum yields based on maximum yield of rhodium(II) formed from reaction of e_{aq}^- with $Rh(NH_3)_5OH_2^{3+}$, using 0.29 as the yield of solvated electrons (ref 10). [i] One determination.

$(NH_3)_5OH_2^{3+}$ (Table I), although there is no *net* photooxidation of I^- in these cases.

Flash photolysis of $Rh(NH_3)_5I^{2+}$ in iodide-free solutions produces no detectable transient (the high-intensity transitions of I atoms lie in the far-uv), but when small amounts of I^- are present in bulk solution a transient (λ_{max} 380 nm) identified as I_2^- is observed. This transient is also observed on flashing I^- in solutions containing $Rh(NH_3)_5OH_2^{3+}$. The I_2^- transient (regardless of the absorbing species) is shorter lived (*i.e.*, has about seven-tenths the characteristic lifetime of I_2^-) under conditions which produce rhodium(II) than when rhodium(II) is absent.

By placing filter solutions between the flash lamps and the sample solution we have been able to demonstrate (Table II) that the I_2^- transient is produced only when the charge-transfer-to-metal (CTTM) bands are irradiated. The relative redox yield is highest (at least 30%) when the σ CTTM band is irradiated. The photochemical changes which do occur on irradiating other spectral regions have not yet been fully characterized.

Table II. Wavelength Dependence of Transient Yields in Flash Photolysis of $Rh(NH_3)_5I^{2+}$

Wavelength region irradiated,[a] nm	Type of absorption bands[b]	$([I_2^-] + [I])$[c] $\times 10^7$, *M*	% redox[d]
230–250	CTTM (σ)	10.6	30
250–270	CTTM ($\pi + \sigma$)	3.0	7
270–320	CTTM ($\pi + \sigma$)	0.6	0.6
320 and longer	d–d + CTTM (π)	<0.1	<0.1

[a] Filter solutions were used to eliminate the shorter wavelength spectral regions. Product yields are actually differences in yields obtained using the succession of filter solutions. [b] See ref 6. [c] [I] obtained from the observed I_2^- yields and the reported formation constant for $I + I^- \rightleftarrows I_2^-$ (ref 7). [d] $([I_2^-] + [I])$ divided by the observed decrease in $[Rh(NH_3)_5I^{2+}]$. Spectral changes indicate large changes in $[Rh(NH_3)_5I^{2+}]$ for every region irradiated.

These observations demonstrate that photoreduction is an important process in photochemistry of rhodium(III). The net product yields (and the transient decay kinetics) are compatible with facile recombination reactions, provided the five ammonia ligands of the rhodium(II) produced are not all equivalent; *i.e.*, that rhodium(II) is tetragonally distorted to the extent that four ammines have relatively long coordinated lifetimes. Thus, the three basic steps in the charge-transfer photochemistry may be represented as follows.[13] For photoreduction (a) with $Rh(NH_3)_5I^{2+}$ as the absorbing species

$$Rh(NH_3)_5I^{2+} + h\nu \longrightarrow Rh(NH_3)_4^{2+} + NH_3 + I \qquad (\phi I_a)$$

or (b) with I^- as the absorbing species[10,11]

$$I^- + h\nu \longrightarrow I + e_{aq}^-$$

followed by

$$e_{aq}^- + RH(NH_3)_5OH_2^{3+} \longrightarrow Rh(NH_3)_4^{2+} + NH_3$$

for complexation

$$I + I^- \rightleftarrows I_2^-$$

and for recombination

$$Rh(NH_3)_4^{2+} + I_2^- \longrightarrow trans\text{-}Rh(NH_3)_4I_2^+$$

or

$$Rh(NH_3)_4^{2+} + I + H_2O \longrightarrow Rh(NH_3)_4OH_2I^{2+}$$

Although I_2^- is clearly very reactive toward $Rh(NH_3)_4^{2+}$, it is not at all evident that both iodide ligands of *trans*-$Rh(NH_3)_4I_2^+$ originated in I_2^-.

This work demonstrates that photoredox behavior is important in the photochemistry of rhodium(III). It appears that the principal differences between the photochemistry of cobalt(III) and rhodium(III) are the higher product yields[14,15] on irradiation of d–d absorption bands and the higher energy of charge-transfer transitions of the latter complexes, together with some differences in the chemical behavior of cobalt(II) and rhodium(II).

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[13] Note that this mechanistic discussion is based on the observed *bulk* radicals. We are not yet in a position to propose a detailed mechanism for the formation of these bulk radicals. The mechanism is proposed for the redox steps only.

[14] By analogy with what seems to be generally the case for cobalt(III), d–d irradiation would not be expected to result in photoredox behavior in rhodium(III) complexes.

[15] It should be noted that few investigators have bothered to look for ammonia in the photochemistry of cobalt(III) complexes, so even this difference may not be entirely general.

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Paramagnetic Induced Shifts in the Proton Magnetic Resonance Spectra of Alcohols Using Tris(dipivalomethanato)europium(III)

Sir:

The initial discovery by Hinckley[1] of the effectiveness of the dipyridine adduct of the rare earth complex tris(dipivalomethanato)europium(III) [Eu(DPM)$_3$·2py]

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, 91, 5160 (1969).

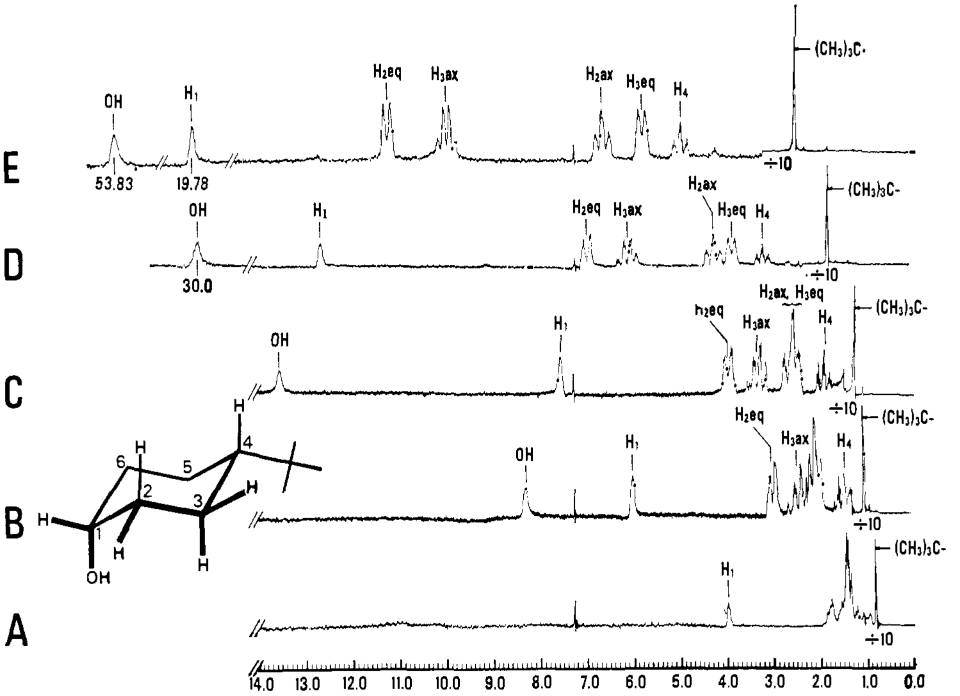

Figure 1. 100-MHz pmr spectra of *cis*-4-*tert*-butylcyclohexanol (20 mg, 1.28 × 10^{-4} mol) in $CDCl_3$ (0.4 ml) containing various amounts of $Eu(DPM)_3$: A, 0.0 mg; B, 10.3 mg; C, 16.0 mg; D, 33.1; E, 60.2 mg.

as a shift reagent, followed by the findings of Sanders and Williams[2] of the even more remarkable shifting ability of the corresponding pyridine-free complex $Eu(DPM)_3$, has prompted us to investigate further the effect of $Eu(DPM)_3$[3,4] on the chemical-shift behavior of protons in four model compounds, namely, *trans*- (**1**) and *cis*- (**2**) 4-*tert*-butylcyclohexanols, isoborneol (**3**), and borneol (**4**).

In the absence of polar solutes, $Eu(DPM)_3$ exhibits a solubility of approximately 20 mg/0.5 ml in $CDCl_3$ and the *tert*-butyl protons of the complex give rise to a broad singlet centered at *ca.* 0.59 ppm on the low-field side of TMS. However, upon addition of 20 mg of any one of the alcohols studied, an approximately fourfold increase in the solubility of $Eu(DPM)_3$ is noted, permitting the dissolution of an equimolar amount of $Eu(DPM)_3$ ($\simeq$90 mg), and the *tert*-butyl signal of the complex is shifted to the high-field side of TMS ($\delta \simeq -0.72$). These observations, and the fact that the spectra of the parent deoxy derivatives of compounds **1**–**4** are unaffected by addition of any amount of $Eu(DPM)_3$, show that specific coordination of metal complex to solute occurs through the agency of hydroxyl lone-pair electrons and can be best rationalized in terms of a change in the coordination geometry of $Eu(DPM)_3$ upon association.[5–7]

The effect on the resonance positions of the different protons in **2** upon addition of increasing amounts of $Eu(DPM)_3$ is shown in Figures 1 and 2 which are typical of the behavior of the four solutes studied. In the absence of $Eu(DPM)_3$ (Figure 1A), only H_1 and the *tert*-butyl protons are readily assignable. Increasing the amount of $Eu(DPM)_3$, however, increasingly resolves the spectrum of **2** such that, at a molar ratio of complex to solute of 0.7, the spectrum of **2** becomes first order (see Figure 1E). Proton assignments shown were based on observed splitting patterns and confirmed by decoupling at 100 MHz. Figure 2 demonstrates the linearity[8] of the chemical shift on metal ion concentration, in accord with earlier findings,[1] and shows that shifts for all solute protons are in the same direction, *i.e.*, to lower field values.

Approximate deuteriochloroform resonance positions for the various protons of **2** can be obtained by simple extrapolation of the least-squares concentration lines to their origin (see Figure 2). Accordingly, if resulting δ_{CDCl_3} values for the different protons are subtracted from corresponding values obtained by extrapolating in the opposite direction to a point where the molar ratio of complex to solute is one ($n = 1$), a paramagnetic induced shift for different solute protons is determined,[9] and is defined as $\Delta_{Eu} = \delta_{CDCl_3} - \delta^{n=1}_{Eu(DPM)_3}$. The

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(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(3) $Eu(DPM)_3$ used in this study was obtained from Ventron Alfa Inorganics, Inc., Beverly, Mass.

(4) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965).

(5) Because of a sufficiently large ionic radius to accommodate attached ligands and the availability of vacant 5d, 6s, and 6p orbitals to accommodate electron pairs donated by Lewis bases, rare earth ions can exhibit eightfold or even greater coordination.[6,7]

(6) C. Brecher, H. Samelson, and A. Lempicki, *J. Chem. Phys.*, **42**, 1081 (1965).

(7) G. H. Frost, F. A. Hart, C. Heath, and M. B. Hursthouse, *Chem. Commun.*, 1421 (1969).

(8) Slight deviations from linearity occur at low $Eu(DPM)_3$ concentrations (see plot for H_{1eq} in Figure 2) which give rise to some differences between δ_{obsd} and δ_{extrap}. However, since differences between these two values are never greater than approximately 2% of their corresponding Δ_{Eu} value, these differences are of little consequence to correlations presented later. Possible origins of such deviations from linearity will be discussed in a future full paper.

(9) We realize that at $n = 1$, the saturation point in the association (*i.e.*, the point where δ is independent of metal concentration changes) has not been achieved. To reach this point would require either the addition of more $Eu(DPM)_3$ to the solution, which is not possible for solubility reasons, or a reduction in the amount of solute present. From our own observations on the interdependency of $Eu(DPM)_3$ solubility on solute concentration, we find that a solute concentration of

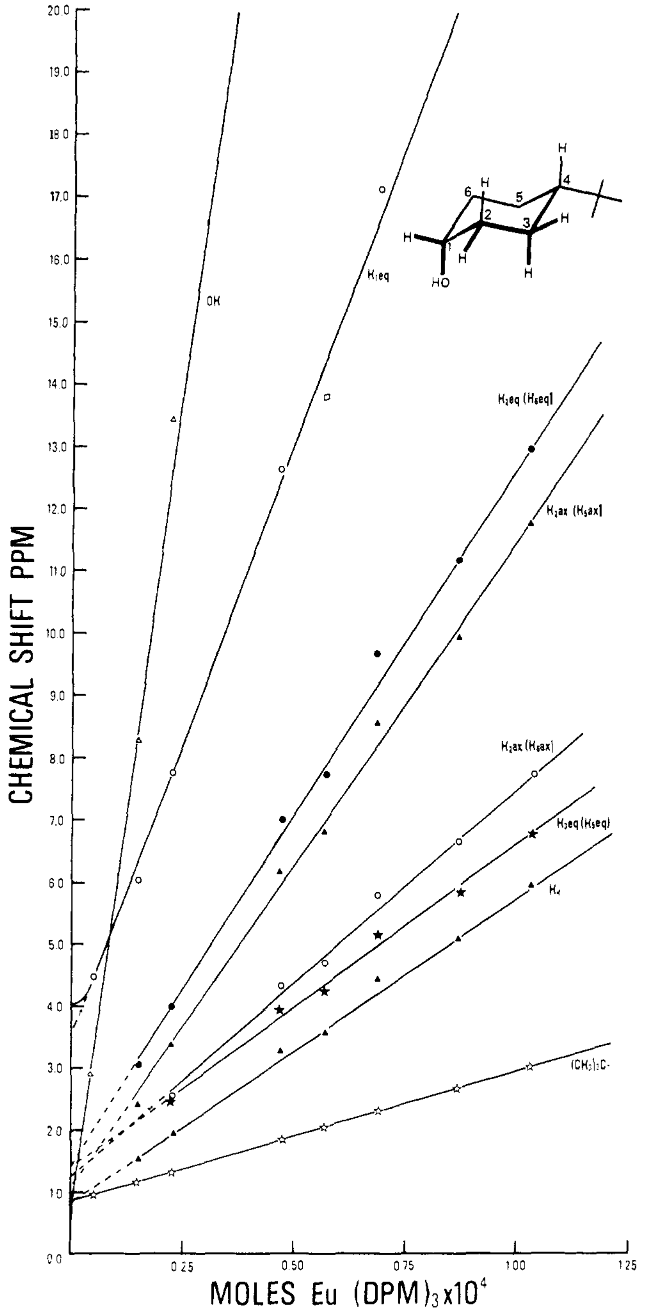

Figure 2. Variation in the chemical shift for the different protons of *cis*-4-butylcyclohexanol (1.28 × 10^{-4} mol in 0.4 ml of $CDCl_3$) with increasing concentration of $Eu(DPM)_3$. Straight lines shown are least-squares derived.

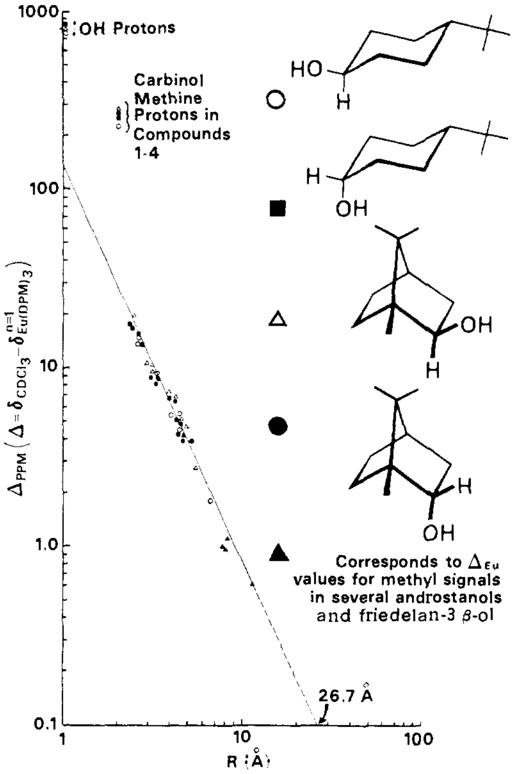

Figure 3. Plot of Δ_{Eu} *vs*. *R*, the vector distance between the proton in question and the hydroxyl oxygen. The straight line shown is derived from least-squares analysis of all plotted points except those corresponding to the carbinol methine and OH protons.

distinct advantage of this method is that it allows the estimation of Δ_{Eu} values not only for protons whose resonances are evident in their normal spectra, but also for protons whose resonances are not. Δ_{Eu} values determined by this procedure for all assignable protons in compounds **1-4** are recorded in Table I.

The following paramagnetic shift-structure relationships are noted from Table I, for protons occupying different spatial locations with respect to the hydroxyl function. (1) Protons located *geminally* to an OH function give rise to Δ_{Eu} values of −21.7 to −26.7 ppm. (2) Protons located *vicinally* to an OH function experience deshielding effects which range from −8.8 to −19.2 ppm. The extent of deshielding appears to be dependent upon the magnitude of the dihedral angle, θ, between the OH function and the proton under consideration. Thus, for $\theta \simeq$ 3-5°, Δ_{Eu} = −16.7 to −19.2 ppm; for $\theta \simeq$ 60°, Δ_{Eu} = −13.6 to −14.9 ppm; for $\theta \simeq$ 122°, Δ_{Eu} = −8.8 to −9.3 ppm; and for θ = 180°, Δ_{Eu} = −8.2 ppm. (3) Protons located 1,3 diaxially to an OH function give rise to Δ_{Eu} values ranging from −13.6 to −17.5 ppm.

A plot on logarithmic axes (see Figure 3) of Δ_{Eu} *vs.* vector distances[10] *R* for all protons in **1-4** (except the OH and carbinol methine protons) as well as for the methyl signals in several androstanols and friedelan-3β-ol gives a straight line (least-squares analysis gives correlation coefficient = 0.992) with a slope of −2.2. Since the pseudocontact term[11-13] is expected to be the main contributor to the paramagnetic shift as-

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approximately 1.0 mg/0.5 ml is necessary to reach this point. Poor signal-to-noise levels at these concentrations make such measurements generally unfeasible, even with the use of a CAT, since spectral regions spanning more than 20 ppm would have to be recorded. Fourier transform pmr will undoubtedly eliminate this problem.

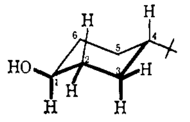
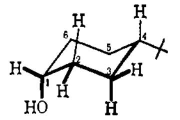
(10) *R* is the vector distance between the hydroxyl oxygen atom and the proton(s) in question. Although some error is involved in defining *R* as such, we have done so in order to eliminate the uncertainty, and in many instances, the impossibility (due to uncertain conformational preferences of the OH function and/or the bound europium complex) of defining the precise location of the coordinated europium ion.

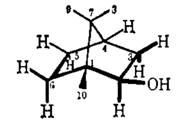
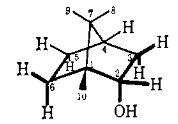
(11) The pseudocontact term[12,13] for axially symmetric complexes in which $\tau \ll T_1$ is given as $\Delta\nu/\nu = -3/5\epsilon f(g)[(3\cos^2\chi - 1)/R^3]$ where ϵ and $f(g)$ are constants characteristic of the metal under consideration and are defined elsewhere.[12] The term in brackets is the geometric factor which is dependent upon both the vector distance *R* from the metal ion to the proton and the angle θ which defines the position of the proton in the symmetry coordinates of the metal ion.

(12) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 29, 1361 (1958).

(13) G. N. La Mar, *ibid.*, 43, 1085 (1965).

Table I. $\Delta_{Eu}{}^{a}$ Values (ppm) Recorded for the Different Protons and Methyl Groups in Compounds **1-4**

Compd		OH	H_1	H_{2eq} (H_{6eq})	H_{2ax} (H_{6ax})	H_{3eq} (H_{5eq})	H_{3ax} (H_{5ax})	H_4	*tert*-Butyl
 **1**	Δ_{Eu}	−78.7	−21.7	−13.6	−14.7	−4.4	−5.4	−5.4	−1.8
	R^{b}	0.97	2.09	2.65	2.62	4.52	4.05	4.48	6.73
 **2**	Δ_{Eu}	−81.7	−24.7	−14.9	−8.2	−6.7	−13.6	−6.5	−2.8
	R	0.97	2.08	2.65	3.33	3.92	2.65	4.25	5.60

Compd		OH	H_2	H_{3exo}	H_{3endo}	H_4	H_{5exo}	H_{6exo}	H_{6endo}	8-CH_3	9-CH_3	10-CH_3
 **3**	Δ_{Eu}	−78.4	−26.7	−19.2	−9.3	−6.7		−5.1	−7.2	−11.0	−4.7	−10.5
	R	0.97	2.08	2.52	3.16	4.24		4.54	3.88	3.0	4.9	3.1
 **4**	Δ_{Eu}	−81.2	−25.5	−8.8	−16.7	−5.1	−5.1		−17.5	−4.4	−4.0	−8.6
	R	0.97	2.07	3.16	2.49	4.39	4.50		2.43	4.5	5.2	3.4

[a] $\Delta_{Eu} = \delta_{CDCl_3} - \delta^{n=1}_{Eu(DPM)_3}$, *i.e.*, the difference in resonance position for a given solute proton when dissolved in inert $CDCl_3$ from that when an equimolar amount of $Eu(DPM)_3$ is present in the same solvent. Δ_{Eu} values reported in the table are valid only for $CDCl_3$ solutions of the complex and are expected to be accurate to within ±2%. [b] For a methyl group R is taken as the distance from the center of the circle of rotation of the methyl protons to the hydroxyl oxygen atom. Values reported for R were determined from the Westheimer method for calculating nonbonded atomic distances (for a discussion of the method, see N. L. Allinger, *et al.*, *J. Amer. Chem. Soc.*, **91,** 337 (1969)).

sociated with europium,[14] this empirically derived slope value is unexpected since a $1/R^3$ dependency for the pseudocontact shift is well established.[12,13] We believe this discrepancy to be a consequence of either error involved in the measurement[10] of R and/or in the neglect of angular variables manifest in the pseudocontact term.[11] Thus, contrary to the cholesterol system studied by Hinckley,[1] where angular variables do not vary significantly from one proton to the next, compounds **1-4** present a variety of different angular situations between the coordinated metal ion and various solute protons. These points are presently being investigated and will be reported in a future paper. The fact that points for the carbinol methine and OH protons do not fall within the normal range of scatter (see Figure 3) suggests sizable contact contributions to the shifts of these protons. Extrapolation of the least-squares line to the origin reveals that even for distances of up to 26.7 Å from the site of coordination a sizable paramagnetic shift (*ca.* 0.1 ppm) is to be expected. It is important to emphasize that the distance-shift relationship shown in Figure 3 is valid only for deuteriochloroform solutions in which the molar ratio of solute-metal complex is one and for solutes containing only one function, *i.e.*, a hydroxyl function.

Acknowledgments. The authors are indebted to Professor N. L. Allinger for furnishing the Westheimer calculated internuclear distances used in this study.

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(14) D. R. Eaton, *J. Amer. Chem. Soc.*, **87,** 3097 (1965); F. A. Hart, J. E. Newberry, and D. Shaw, *Nature* (*London*), **216,** 261 (1967); J. Reuben and D. Fiat, *Chem. Commun.*, 729 (1967).

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Tris(dipivalomethanato)europium(III). A Shift Reagent for Use in the Proton Magnetic Resonance Analysis of Steroids and Terpenoids

Sir:

The usefulness of nuclear magnetic resonance in the study of hydrocarbon-like compounds has been severely limited by insufficient resolution. Although this deficiency has been partially overcome by the development of higher frequency spectrometers (220 MHz), the situation still remains unsatisfactory since considerable structural information usually remains buried in a featureless methylene-methine envelope common to such systems. The discovery by Hinckley[1]

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(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91,** 5160 (1969).