Table IV. Theoretical (STO-3G) Energies of Degenerate Circumambulatory Rearrangement in the Homotropylium Cation (kcal mol^{-1})

Homotropylium (IV)	0
Eclipsed cycloheptatrienylcarbinyl (VI)	52
Bisected cycloheptatrienylcarbinyl (V)	55

mental lower bound (26 kcal mol^{-1}) placed on the process by Berson and Jenkins.[3] As was the case for the transition-state structures in the bicyclohexenyl degenerate rearrangement, both bisected and eclipsed forms of cycloheptatrienylcarbinyl (V and VI) show alternation of single and double bonds, much what one might expect from neutral planar cycloheptatriene.

Ex post facto it appears possible to rationalize the difference in activation energies for the two rearrangement processes primarily on account of the ground-state properties of the bicyclohexenyl and homotropylium carbocations. The former has a choice of being structured on the base of either the antiaromatic cyclopentadienyl cation or the classical (charge localized) cyclopentenyl ion. The lesser of the two evils is chosen, resulting in an ion not expecially stable, but resembling to a great extent the eventual transition state to circumambulatory rearrangement. The situation is different for homotropylium. Here the aromatic (charge localized) tropylium ion is the chosen base. Rearrangement *via* the classical cycloheptatrienylcarbinyl cation requires a significant change in geometry.

Acknowledgment. The author wishes to thank Professor J. A. Berson and Dr. J. A. Jenkins (Yale) for suggesting the application of *ab initio* theory to this problem, and for interesting exchanges of information during the course of the work, and Rousell Uclaf for their generous support.

Warren J. Hehre
Laboratoire de Chimie Theorique
Universite de Paris—Sud, Centre d'Orsay
91405 Orsay, France

Received August 14, 1972

Lanthanide Shift Reagents. X-Ray Structure of the Seven-Coordinate 3,3-Dimethylthietane 1-Oxide (1) Complex with Tris(dipivalomethanato)europium(III), Eu(dpm)$_3$·(1), and Its Implication on Pseudocontact Shift Calculations

Sir:

Exceptionally wide interest has been shown in the paramagnetic lanthanide shift reagents.[1] Their presence in solution often produces large isotropic shifts, which generally spread out the chemical shifts, frequently reducing the spectrum to first order, and thereby facilitating analysis. The Eu(III) and Pr(III) chelate complexes of 2,2,6,6-tetramethylheptane-3,5-dione and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione have proven to be the most popular shift reagents because of their favorable shift to line broadening characteristics.[1,2]

In addition to spectral simplification, there is evidence that the magnitudes of the shifts (and perhaps the line broadening as well)[3] can be interpreted in terms of the molecular geometry of the complex.[1] If this holds true, then the technique would be extremely important for the determination of molecular stereochemistry. In most cases it is clear that the shifts are a consequence of through-space dipolar interactions. The spatial dependence of the shifts for axially symmetric complexes is given by eq 1,[4] where ΔH_i is the change in field

$$\frac{\Delta H_i}{H} = f\left(g_{\parallel}, g_{\perp}, K, \frac{1}{T}\right)\frac{(3\cos^2\theta_i - 1)}{r_i^3} \qquad (1)$$

strength at nuclei i, r_i is the distance between the paramagnetic metal and nucleus i, and θ_i is the angle between the principal magnetic axis of the complex and the vector r_i.

In applying eq 1 to structural problems, a large number of authors have chosen to interpret the observed shifts using only an r^{-n} term.[2a] The exponent n has either been taken to be equal to 3 or adjusted to improve the fit between calculated and observed shifts. The distance r_i has been estimated in a number of ways. Some authors have chosen to set it equal to the distance between the site of coordination, Q, and nucleus i. Most have, however, estimated r_i by positioning the lantanide (Ln) at some predetermined distance from Q and calculating the Ln–(i) distance accordingly. Distances for Ln···Q ranging from the van der Waals radius of Q to roughly one and one-half times the sum of the covalent radii of Ln and Q have been employed. Usually this distance is adjusted to improve the fit of the calculated to the observed shifts.

There are a few examples in the literature where the full form of eq 1 has been used.[5] This generally results in fits which are significantly better[6] than those obtainable using only a distance parameter.

Several difficulties arise, however, when one attempts to use eq 1. The first is that in order to calculate a shift, it is necessary to average the calculated shifts over all orientations of the shift complex. The various conformations of the shift complex are unknown, as are their populations. A second difficulty is that the shift eq 1, strictly speaking, is only applicable to axially symmetric complexes.[7] Third, the angle θ_i is defined as the angle between the vector r_i and the principal magnetic axis. The location of this axis is unknown but has generally been taken along the Ln···Q axis.

---

[1] For a recent survey see W. De W. Horrocks, Jr., and J. P. Snipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

[2] D. R. Crump, J. K. M. Sanders, and S. H. Williams, *Tetrahedron Lett.*, 4419 (1970).

[3] C. D. Barry, A. C. T. North, J. A. Glasel, R. J. P. Williams, and A. V. Xavier, *Nature (London)*, **232**, 236 (1971).

[4] (a) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); (b) G. N. La Mar, W. De W. Horrocks, Jr., and L. C. Allen, *ibid.*, **41**, 2126 (1964); (c) G. N. La Mar, *ibid.*, **43**, 1085 (1965).

[5] (a) J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970); (b) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *ibid.*, 364 (1971); (c) S. Farid, A. Ateya, and M. Maggio, *ibid.*, 1285 (1971); (d) H. Huber and C. Pascual, *Helv. Chim. Acta*, **54**, 913 (1971); (e) M. R. Willcott, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972).

[6] Whether they are statistically better, considering the additional parameters adjusted, remains to be demonstrated: W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964.

[7] Clearly the generalized pseudocontact shift equation[4] could in principle be solved, but the complexity of the problem, we feel, makes such solutions impractical. In addition to R and θ, one would need to know the three principal g values and an additional angle. The geometry of the complex with respect to the magnetic axes would also need to be known in order to evaluate the shifts. In the case of a fluxional complex, the calculated shifts would have to be averaged over all molecular orientations.

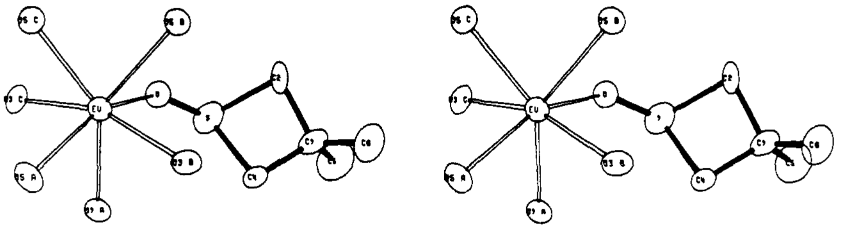


Figure 1. The 3,3-dimethylthietane 1-oxide–Eu(dpm)$_3$ adduct. This drawing constitutes a stereopair and is best seen with the aid of a hand viewer. The chelate rings which bridge oxygens A–A, B–B, and C–C have been omitted for clarity.

It is to the latter two difficulties that we wish to address this communication. A previous communication by Horrocks, *et al.*,[8] dealt with similar questions. They reported the crystallographic structure of the bis(4-picoline) adduct of Ho(dpm)$_3$. Significantly, they found that this eight-coordinate complex did not even approximate axial symmetry with respect to the two picoline molecules and that the N–Ho bond axes deviated *ca.* 20° from the likely principal magnetic axis. We wish to report an example of a seven-coordinate complex of 3,3-dimethylthietane 1-oxide (**1**) with Eu(dpm)$_3$, [Eu(dpm)$_3$·(**1**)] (**2**). This is of interest because of its 1:1 stoichiometry, lower coordination number, and the fact that it has been obtained on the more frequently used Eu(dpm)$_3$ shift reagent.

Complex **2** was obtained by recrystallization of Eu(dpm)$_3$ from acetonitrile containing excess sulfoxide **1**. It is an unstable white solid of mp 141–142° which belongs to the monoclinic space group $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14). The cell dimensions were found to be: a = 14.412 (6) Å; b = 20.23 (1) Å; c = 15.660 (8) Å; β = 98.55 (3)°; V = 4514.18 Å^3; Z = 4; d = 1.21 (found, 1.19 g/cc). A computer-controlled diffractometer using Mo Kα radiation was programmed to collect data in the 40–43° 2θ range. A total of 2890 reflections were used to solve the structure by heavy-atom and least squares refinement methods. Refinement of the data has converged to an R (based on F) of 0.052 using anisotropic temperature factors for all but two atoms.[9]

The coordination sphere, shown in Figure 1, conforms closely to a wedged octahedron with the sulfoxide oxygen occupying one of the four positions in the equatorial plane.[10] The Eu···O distances for the three heptanedionate ligands range from 2.32 to 2.37 Å while the Eu···O distance for the sulfoxide oxygen is 2.40 Å. The sulfoxide ring is puckered[11] by 35° and has the expected equatorial-oxygen conformation.[12]

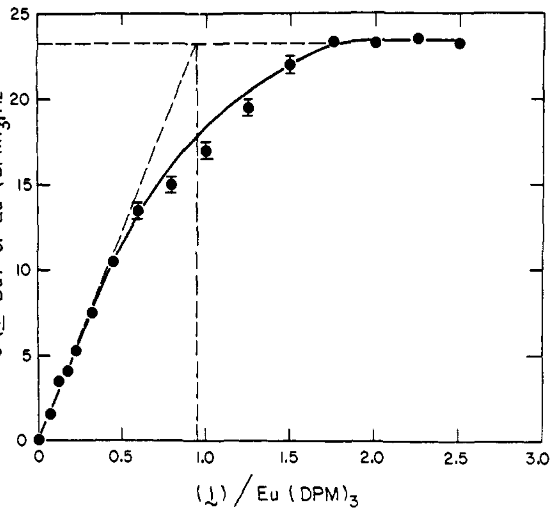


Figure 2. Plot of δ (chemical shift of *t*-Bu protons) *vs.* ratio of sulfoxide **1** to Eu(dpm)$_3$ in CDCl$_3$. Concentration of Eu(dpm)$_3$, 3.2 × 10^{-3} *M*.

It is significant to note that the sulfoxide lies in a position of lowest symmetry. Based on the usual reaction pathway,[13] the sulfoxide might have been expected to occupy one of the wedged positions, *cf.* O(5C) and O(5B) (Figure 1). One would have preferred it to occupy the axial position [O(3A)], since there it would experience the highest local symmetry. It is clear that this minimal condition must be satisfied to have coincidence of the Eu···O bond and the principal magnetic axis. Since one would expect our complex to make a significant contribution in solution,[14] one must seriously question the usual assumption of axial symmetry for shift reagent complexes in solution.

Since the conformations of sulfoxide **1** and its pmr spectrum have been carefully assigned and analyzed,[12,15] we decided to see whether it would have been possible to correctly assign the pmr spectrum using only Eu(dpm)$_3$ shift data. Making the usual assumptions about axial symmetry,[16] we find that we are able to fit[17] the

---

[8] W. De W. Horrocks, Jr., J. P. Snipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

[9] (a) Two C$_2$ carbons on different ligands consistently had nonpositive definite temperature factors, and consequently were refined isotropically. (b) Listings of structure factors, coordinates, and anisotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-8910. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

[10] *Cf.* (a) C. S. Erasmus and J. C. A. Boeyens, *J. Cryst. Mol. Struct.*, **1**, 83 (1971); (b) C. S. Erasmus and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **26**, 1843 (1970).

[11] S. Kumakuka, T. Shimozawa, Y. Ohnishi, and A. Ohno, *Tetrahedron*, 27, 767 (1971), and references therein.

[12] (a) C. R. Johnson and W. O. Siegel, *J. Amer. Chem. Soc.*, **91**, 2796 (1969); (b) W. O. Siegel and C. R. Johnson, *Tetrahedron*, **27**, 341 (1971), and references therein.

[13] (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 145; (b) N. S. Hush, *Aust. J. Chem.*, **15**, 378 (1962).

[14] (a) One might also wonder whether the 2:1 complex makes a significant contribution in solution, since this stoichiometry is commonly observed. We have measured the change in the chemical shifts of the *tert*-butyl resonances as a function of added sulfoxide **1**. These data are plotted in Figure 2 and clearly suggest that $K(1:1) \sim 3 \times 10^2$ mol $\gg K(2:1)$. (b) The intermolecular crystal packing forces are felt to be minimal because there are no intermolecular distances less than 3.1 A and only four between 3.1 and 3.5 Å. All of these are greater than the sum of the van der Waals radii.

[15] W. Wucherfpennig, *Tetrahedron Lett.*, 765 (1970).

[16] These calculations were performed in a manner analogous to that described by other workers, see ref 5.

shift data much better when we reverse the methyl assignments, Table I. This assignment is, however, clearly incorrect, and we must conclude that the apparent success, which many pseudocontact shift calculations have had, needs to be viewed with caution.

Table I. Eu(dpm)$_3$ Induced Shifts for Sulfoxide **1** in CDCl$_3$

	Protons				
	H$_{cis}$	H$_{trans}$	Me	Me	R,[c] %
Observed shifts	236	137	79	64	
Correct assignment[a]	222	138	77 (trans)	78 (cis)	6.21
Incorrect assignment[b]	234	133	83 (cis)	66 (trans)	2.25

[a] For the unshifted spectra δ[12,15] H$_{trans}$ > H$_{cis}$ > Me$_{cis}$ > Me$_{trans}$ while for spectra with [Eu(dpm)$_3$]/[**1**] > 0.15 δH$_{cis}$ > H$_{trans}$ > Me$_{trans}$ > Me$_{cis}$. [b] The methyl assignments are the reverse of the above. [c] R^2 = (calculated shift − observed shift)^2/(observed shift)^2; R (%) = 100R; calculated for the equatorial-oxygen conformation.[17]

(17) Since in solution 1 is known to exist in the equatorial-oxygen conformation,[12] and since this also is the conformation of the sulfoxide ring in the Eu(dpm)$_3$ adduct, we used the X-ray determined coordinates for these calculations. Fits with either assignment using a planar ring or a combination of equatorial and axial conformations were considerably poorer.

J. J. Uebel*
Department of Chemistry, University of New Hampshire
Durham, New Hampshire 03824

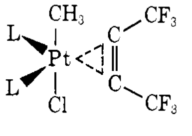
R. M. Wing
Department of Chemistry, University of California
Riverside, California 92502

Received April 4, 1972

Mechanism of the Insertion of an Acetylene into a Methylplatinum(II) Bond

Sir:

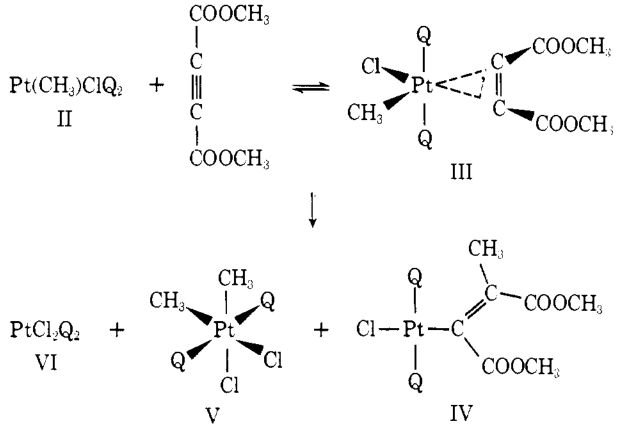
Initial coordination of an unsaturated molecule followed by insertion into a metal–hydrogen or metal–carbon bond is believed to form the basis of most metal-catalyzed hydrogenation and polymerization reactions of olefins and acetylenes.[1,2] The 1:1 adducts PtCl(CH$_3$)(CF$_3$C$\equiv$CCF$_3$)L$_2$, I,[3-6] where L = a *tert*-phosphine or arsine, formed in the methylplatinum insertion reaction of CF$_3$C$\equiv$CCF$_3$ with *trans*-PtCl(CH$_3$)L$_2$, present a rare[7] example of the isolation of a π intermediate.



However, further reaction of I in benzene led, in addition to the insertion product *trans*-PtCl{CCF$_3$=C(CH$_3$)CF$_3$}L$_2$ expected from an intramolecular rearrangement of I, to the formation of Pt(CF$_3$C$\equiv$CCF$_3$)L$_2$ and PtCl$_2$(CH$_3$)$_2$L$_2$.[4,5] The role played by the π complex I in these reactions remained uncertain.

We have now studied an analogous reaction between dimethyl acetylenedicarboxylate, CH$_3$OOCC$\equiv$CCOOCH$_3$, and *trans*-PtCl(CH$_3$){P(CH$_3$)$_2$C$_6$H$_5$}, II, in chloroform. Contrary to our expectations, we find that insertion into the platinum–methyl bond to give PtCl{CCOOCH$_3$=C(CH$_3$)COOCH$_3$}{P(CH$_3$)$_2$C$_6$H$_5$}$_2$, IV, does not proceed by a simple intramolecular rearrangement of the 1:1 adduct PtCl(CH$_3$)(CH$_3$OOCC$\equiv$CCOOCH$_3$){P(CH$_3$)$_2$C$_6$H$_5$}$_2$, III, but rather by a free-radical mechanism involving both II and III. Other products from this reaction are Pt(CH$_3$)$_2$Cl$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$, V, and PtCl$_2${P(CH$_3$)$_2$C$_6$H$_5$}$_2$, VI (see Scheme I).[8]

Scheme I



Q = P(CH$_3$)$_2$C$_6$H$_5$

We find that the reaction is very dependent on the particular sample of II. For some samples reaction proceeded as above (see Figure 1), but for others only the π complex III was formed, no insertion or disproportionation occurring over several weeks. Furthermore, addition of an "unreactive" solution to a "reactive" one immediately stopped the insertion and "disproportionation" reactions. On the other hand, these reactions occurred after addition of a small amount of the free-radical initiator C$_6$H$_5$COO$_2$OCC$_6$H$_5$ to an "unreactive" solution. This is illustrated in Figure 2 for an "unreactive" sample of II. These findings clearly show that the reaction proceeds by a free-radical mechanism. "Unreactive" samples of II must contain a trace of a radical scavenger (whose nature is unknown and which could not be removed by chromatography or recrystallization).

These reactions were followed by nmr spectroscopy (100 MHz). For a given concentration of radical initiator, the results are consistent with the rate law (1) for insertion.

$$\frac{d[\text{insertion}]}{dt} = k_{\text{ins}}[\text{PtClMeQ}_2][\text{PtClMeQ}_2(\text{acetylene})] \qquad (1)$$

---

(1) M. L. H. Green, "Organometallic Compounds," Vol. 11, Methuen, London, 1968, p 312.

(2) L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Polymer Reviews 12, Interscience, New York, N. Y., 1966.

(3) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970).

(4) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).

(5) H. C. Clark and R. J. Puddephatt, *ibid.*, 10, 18 (1971).

(6) B. R. Davies, N. C. Payne, and R. J. Puddephatt, *Can. J. Chem.*, **50**, 2276 (1972).

(7) For related π-coordinated intermediates, see H. A. Tayim and J. C. Bailar, *J. Amer. Chem. Soc.*, **89**, 4330 (1967), and W. H. Bradley and M. S. Frazer, *ibid.*, **91**, 3661 (1969).

(8) The stereochemistry of III (as shown in Scheme I) is deduced from the phosphinemethyl proton resonances of II which appear as overlapping triplets showing (i) the presence of mutually *trans*-phosphine ligands and (*ii*) the absence of a plane of symmetry within the P–Pt–P axis. Furthermore, we observed two well-separated methoxy proton resonances in III.