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Preliminary communication

Stereochemical assignment of a silanol complex by use of a lanthanide shift reagent

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SUMMARY

A paramagnetic lanthanide shift reagent, [Eu(DPM)$_3$], was used in the stereochemical assignment of (1-*exo*-hydroxy-1-*endo*-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)(π-cyclopentadienyl)cobalt.

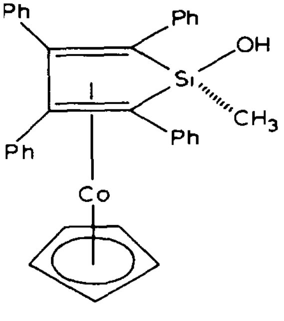
Although lanthanide shift reagents have been used extensively in the stereochemical determinations[1], no application to an organosilicon function has been reported. A silanol complex (I)[2] obtained from (1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)-(π-cyclopentadienyl)cobalt has an exceptionally stable hydroxyl function, and it has been suggested that compounds having hydroxyl functions may form relatively strong complexes with paramagnetic lanthanide complexes[3]. Therefore, we expected that shift reagents could be used to determine the stereochemistry of (I), in which the position of the hydroxyl group was not certain. Foreman and Leppard[4] have recently reported the first application of a shift reagent to some iron complexes.

Table 1 summarizes the experimental results of chemical shifts determination of

TABLE 1

DATA OF CHEMICAL SHIFTS IN $CDCl_3$

Relative concentration [Eu(DPM)$_3$]/[I]	*δ(Si–Me) (ΔH)*	*δ(π-Cp) (ΔH')*
0	1.05 (0.00)	4.73 (0.00)
7 002 × 10^{-2}	1 55 (0 50)	4.87 (0.14)
1.827 × 10^{-1}	2.17 (1 12)	5.05 (0.32)
2.801 × 10^{-1}	2 72 (1 67)	5.22 (0 49)
3 714 × 10^{-1}	3.13 (2.08)	5.35 (0.62)
5 085 × 10^{-1}	3.83 (2.78)	5.56 (0.83)



(I)

(I) in the presence of tris(dipivalomethanato)europium, $\mathrm{Eu(DPM)_3}$.

Good straight lines are obtained by plotting the induced shift ΔH (and $\Delta H'$) *vs.* molar ratio, $[\mathrm{Eu(DPM)_3}]/[\mathrm{I}]$ ($= X$), in deuterochloroform solution. For Si–Me protons:

$$\Delta H = 5.17_8\ X + 0.16_7 \quad \text{(correlation coefficient = 0.999)} \qquad \text{(i)}$$

For cyclopentadienyl protons:

$$\Delta H' = 1.57_5\ X + 0.034_9 \quad \text{(correlation coefficient = 0.999)} \qquad \text{(ii)}$$

Approximate induced shifts for these protons can be obtained by extrapolation of equations (i) and (ii) to a point where the molar ratio X is unity. Therefore, we get $(\Delta H(\text{Si–Me})/\Delta H(\pi\text{-Cp})\ (X = 1) = (5.34_5/1.61_0) = 3.32$.

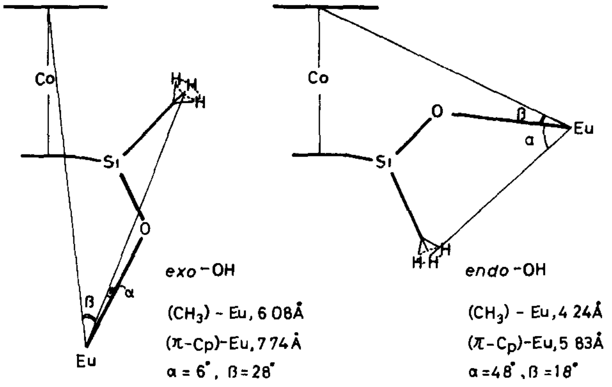


Fig. 1 Models of *exo* and *endo* isomers for calculation of the pseudocontact shifts. The following parameters are used: C(π-Cp)–C(π-Cp) (1.46 Å) [6], C=C (1.36 Å) [6], C–C (1.53 Å) [6], π-Cp–Co (1.67 Å) [6], (cyclopentadiene)–Co (1.68 Å) [6], Si–C (1 87 Å) [5], Si–O (1.63 Å) [5], C–H (1.09 Å) [5], ∠ EuOSi (128°) [7] and Eu–O (3.0 Å) [7].

The pseudocontact shift is well known to be proportional to the geometric factor given in equation (iii)

$$\Delta H_i = k(3\cos^2\theta_i - 1)/r_i^3 \qquad \text{(iii)}$$

where r_i is the distance of vector between the paramagnetic metal ion and the *i*th proton, and θ_i is the angle between the vector and the principal molecular axis. The compilation of data on bond distances[1,3,5–7] and inspection of molecular models provided models for *exo*- and *endo*-hydroxyl complexes as shown in Fig. 1.

The calculated ratios of pseudocontact shifts for models of *exo*- and *endo*-hydroxyl complexes are 3.01 and 0.52, respectively. The value for the *exo*-hydroxyl model is closely to the observed value of 3.32. Although the models chosen for calculations can be varied somewhat, the data clearly indicate the structure of (I) to be (1-*exo*-hydroxy-1-*endo*-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)(π-cyclopentadienyl)cobalt.

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