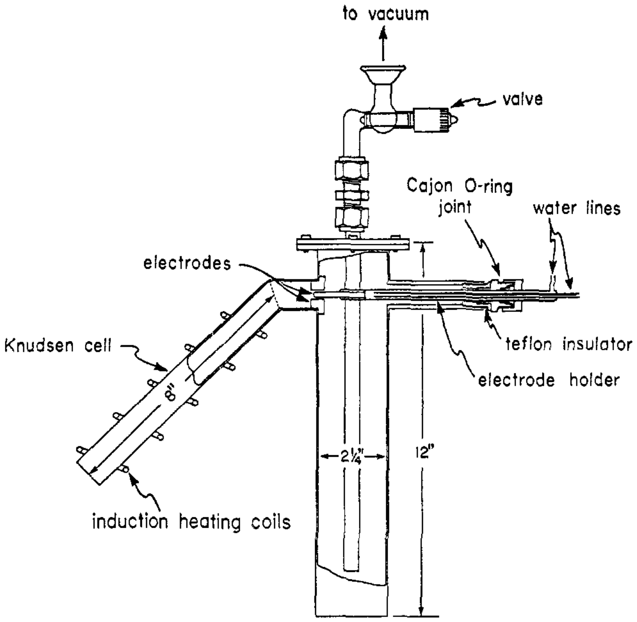

Figure 1.

was terminated. The extremely air- and moisture-sensitive products were handled with care under argon.

The products were hydrolyzed at 0°, passed through a trap at -30° to remove H_2O, and collected at -196°. The yield (gas measurement) of gaseous products averaged 11 mmol/45 min. The hydrolysis products were characterized using a high-resolution double-focusing C.E.C.-21-110B mass spectrometer at 70 eV. Parent ions were observed for CH_4^+ (16.03133), $C_2H_2^+$ (26.01671), $C_2H_4^+$ (28.03081), and $C_3H_4^+$ (40.03177). The principal product, C_3H_4, ranged from 40 to 65% of the volatile products. Percentage yields of other hydrocarbons were CH_4, 0–10%, and C_2H_2, 10–30%. The yield of C_2H_4 averaged 15%, but occasionally accounted for 45% of the volatile products. Spectroscopic quantities of several higher molecular weight products were also observed.

The principal product, C_3Li_4,[4] which is known to be soluble in THF, was then derivatized by adding $ClSi(Me_3)_3$ to a -78° THF solution of the reaction product and warmed while stirring over a 24-hr period. A white compound, $C_3(SiMe_3)_4$, was recovered and was characterized by its mass and nmr spectra. A parent ion was observed at 328 and a $(P - CH_3)^+$ peak occurred at 313 with the appropriate silicon isotopic distributions. The H^1 nmr spectrum of the compound in CCl_4 gave a singlet at τ 9.89 which is in agreement with the spectrum previously reported (τ 9.90) for $C_3(SiMe_3)_4$.[4]

Acknowledgment. We are grateful to the Advanced Research Project Agency and the National Science Foundation for support of this work. The authors thank Dr. Charles Hignite and Professor Klaus Biemann for the work in high-resolution mass spectroscopy.

(4) R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **91**, 6155 (1969); R. West, P. A. Carney, and I. C. Mineo, *ibid.*, **87**, 3788 (1965).

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Nuclear Magnetic Resonance Evidence for Stereochemical Rigidity in ML_5 Complexes

Sir:

We wish to report, for the first time, nmr evidence for stereochemical rigidity in an ML_5 complex, $\{Rh[P(OCH_3)_3]_5\}^+B(C_6H_5)_4^-$. All previous nmr investigations have indicated that the barriers to intramolecular rearrangement in ML_5 compounds are very low, resulting in a rapid exchange of the five ligands. Despite the large body of work concerned with rigidity in five coordination, attempts to observe the inequivalence of the ligands for any ML_5 species in solution (required by all reasonable structures), starting with the early nmr studies of PF_5,[1–3] have so far failed.

In molecules such as IF_5, the inequivalence of the fluorine ligands can be observed using nmr;[4] the barrier to rearrangement is large and the low-temperature limit spectra are not compatible with the idealized structures expected in five coordination (trigonal bipyramid or square pyramid). In accord with the Gillespie–Nyholm rules, we regard these molecules as effectively six-coordinate with the nonbonding electron pair acting as the sixth ligand. In other cases where inequivalence of the ligands can be observed using nmr (such as SbF_5), the molecules are not monomeric in solution.[5]

Confining our attention to group VIII transition metal complexes with d^8 configurations, we may note that a single resonance was observed in the natural abundance ${}^{13}C$ spectrum of $Fe(CO)_5$ at room temperature.[6] No change was observed in this spectrum on cooling a solution in ether.[7] We have observed that the ${}^{13}C$ nmr spectrum of a solution of $Fe(CO)_5$ in 90% chlorodifluoromethane–10% methylene chloride remains a sharp single line down to $\sim -170^\circ$. More recently we[8] have recorded the ${}^{19}F$ nmr spectra of $Fe(PF_3)_5$, $Ru(PF_3)_5$, and $Os(PF_3)_5$ down to -160° in chlorodifluoromethane. Again, all five ligands were observed to be equivalent on the nmr time scale.

Our observation that in $HM(PF_3)_4$ complexes the barrier decreases on going from the neutral species of the cobalt triad to the isoelectronic anions of the iron triad, and that there was a steady increase in barrier on going down a triad,[8,9] led us to believe that there would be a good chance of observing slow exchange limit nmr spectra for ML_5^+ cationic species of rhodium or iridium. Rhodium has the additional advantage that its nuclear spin $I = {}^1/_2$ and rhodium to phosphorus couplings are readily observed in ML_5^+ complexes where L is a trivalent phosphorus ligand. This ligand

(1) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(2) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

(3) Infrared, Raman, and electron diffraction methods show conclusively that PF_5 has a trigonal-bipyramidal D_{3h} structure.

(4) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **79**, 322 (1957).

(5) C. A. Hoffmann, B. E. Holder, and W. Jolly, *J. Phys. Chem.*, **62**, 364 (1958).

(6) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).

(7) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(8) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

(9) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *ibid.*, **93**, 1797 (1971).

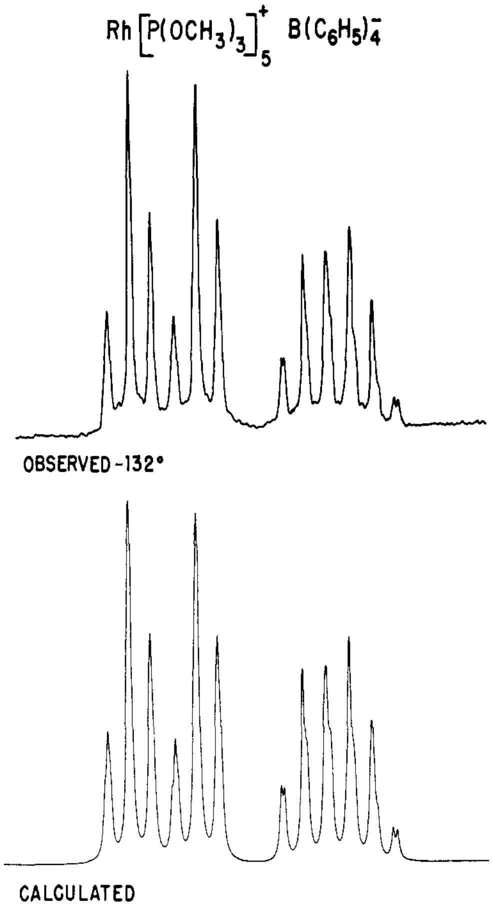
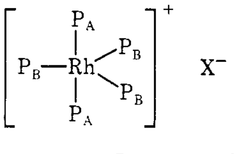


Figure 1. Low-temperature limit Fourier mode proton noise decoupled 36.43-MHz ^{31}P nmr spectrum of a solution of $\{Rh[P(OCH_3)_3]_5^+\}B(C_6H_5)_4^-$ in 10% methylene chloride-90% chlorodifluoromethane. The lower part of the figure is a computer simulation of the spectrum using a A_2B_3X model with the parameters given in the text. The right-hand side of the spectrum is to high field.

to metal coupling is useful in establishing the intramolecular nature of a rearrangement process.

The upper part of Figure 1 shows the low-temperature limit (−132°) ^1H noise-decoupled Fourier mode ^{31}P nmr spectrum of a solution of the complex $\{Rh[P(OCH_3)_3]_5\}^+B(C_6H_5)_4^-$ [10] in 90% $CHClF_2$–10% CD_2Cl_2 (used for the ^2H lock) recorded on our Bruker HFX 90/Digilab FTS 3 spectrometer. The lower part of the figure shows a computer simulation of the spectrum using an A_2B_3X model. The good fit between the observed and calculated spectra indicates that the structure in solution is



with the nmr parameters $J_{P_AP_B} = 67.5$ Hz, $J_{P_ARh} = 142$ Hz, $J_{P_BRh} = 207$ Hz, and $\delta_{P_AP_B} = -14.5$ ppm at −132°. The resonances assigned to the equatorial phosphorus nuclei lie to low field (the chemical shift difference is quite strongly temperature dependent, possibly due to an ion pairing equilibrium; the coupling constants, on the other hand, have no measurable temperature dependence). To first order the spectrum should consist of a doublet of triplets and a doublet of quartets; however, significant higher order effects can be seen in Figure 1 and these are accurately reproduced by the calculations. As the temperature is raised, the chemical shift separation decreases and the lines begin to broaden, indicating the onset of an exchange process (Figure 2). On further warming, the spectra become very broad and eventually, in the high temperature (fast exchange) limit, coalesce into a sharp doublet with a coupling constant of 189 Hz. This is equal to the weighted average of the low-temperature limit ^{31}P–^{103}Rh coupling constants. The maintenance of the

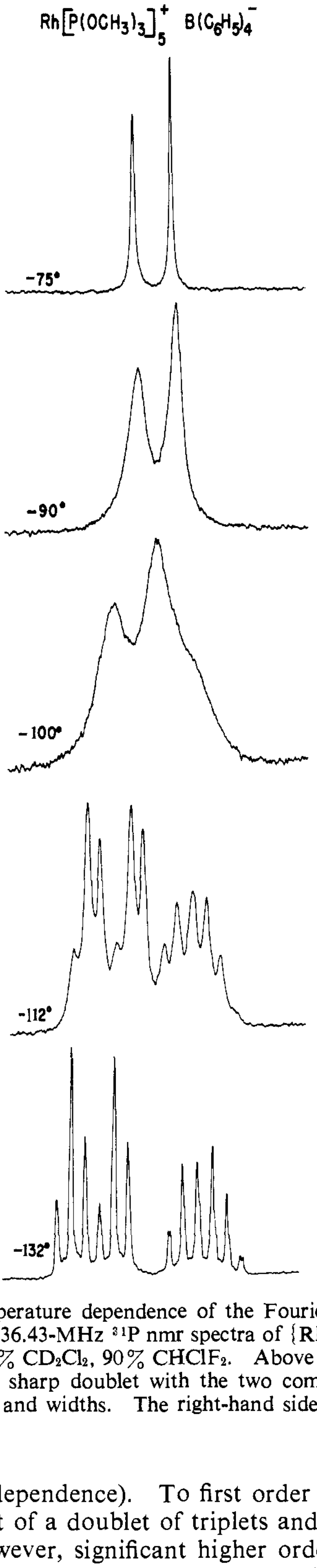


Figure 2. Temperature dependence of the Fourier mode proton noise-decoupled 36.43-MHz ^{31}P nmr spectra of $\{Rh[P(OCH_3)_3]_5^+\}B(C_6H_5)_4^-$ in 10% CD_2Cl_2, 90% $CHClF_2$. Above −75° the spectrum becomes a sharp doublet with the two components having equal intensities and widths. The right-hand sides of the spectra are to high field.

(10) L. M. Haines, *Inorg. Chem.*, **10**, 1685 (1971).

phosphorus–rhodium coupling at high temperatures indicates that the exchange process is intramolecular, and from an estimated exchange rate of 500 sec^{-1} at $-107°$ we obtain a free energy of activation, $\Delta G^{\ddagger}$, of 7.4 kcal mol^{-1}. The barrier is higher than anticipated and, as a result, the spectra show some evidence for inequivalence of the ligands at temperatures as high as ~ -50 to $\sim -70°$ (Figure 2). The possibility should not be overlooked that interactions with the counterion may contribute to the barrier, although any interaction of this type must be averaged rapidly on the nmr time scale even at very low temperatures. As noted above, however, for transition metal hydrides of the form HML_4 and HML_4^-, barriers for isoelectronic pairs are similar,[8] suggesting that the contribution from ion pairing is small. (The barriers are, in fact, smaller for the ionic species.)

For a D_{3h} ML_5 system, there are two possible types of temperature-dependent nmr line shapes[8] (three basic permutational sets[11] including the identity). One of these (which includes the Berry[12] process) involves the simultaneous exchange of the axial ligands with two of the equatorial ligands. The other involves single axial–equatorial exchanges. We are currently undertaking a complete density matrix line shape analysis[11] of these spectra in order to distinguish between these two possibilities.

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[11] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

[12] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

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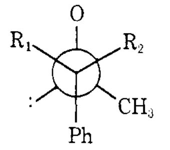
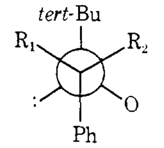
Kinetic Preference between the Diastereotopic Hydrogens in the Lithiation of Benzyl Methyl and Benzyl *tert*-Butyl Sulfoxides

Sir:

In previous communications[1] we have described the thermodynamic preference of one of the two diastereotopic lithio derivatives of benzyl methyl and benzyl *tert*-butyl sulfoxides by trapping the lithio derivatives (α-sulfinyl carbanions) with an excess of several reactive electrophiles (D_2O, acetone, CH_3I). In the case of benzyl methyl sulfoxide the isomer, **1**, having the *S*,*S*[2] configuration was preferred over the *R*,*S* isomer, **2**, by approximately 15:1 in THF at $-60°$, while for benzyl *tert*-butyl sulfoxide the preference of the *S*,*S* isomer **3** was so large that the presence of **4**, the *R*,*S* isomer, could not be detected by nmr analysis of the crude trapping products.[1b]

In view of the considerable work on the kinetic preference observed in the exchange of the diastereotopic hydrogens α to sulfoxides,[1,3] we would like to present our results on the relationship between the kinetic and thermodynamic preferences. In addition, Nishihata and Nishio[4] have reported isotope effects and selectivity factors in the lithiation of benzyl methyl[4a] and benzyl *tert*-butyl sulfoxides[4b] which differ significantly from ours.





1 (*S*,*S*), $R_1 = Li$; $R_2 = H$
2 (*R*,*S*), $R_1 = H$; $R_2 = Li$
5 (*S*,*S*), $R_1 = D$; $R_2 = H$
6 (*R*,*S*), $R_1 = H$; $R_2 = D$

3 (*S*,*S*), $R_1 = Li$; $R_2 = H$
4 (*R*,*S*), $R_1 = H$; $R_2 = Li$
9 (*S*,*S*), $R_1 = D$; $R_2 = H$

The kinetic preference for the removal of the diastereotopic hydrogens in benzyl methyl sulfoxide was determined using the method described by Eliel, *et al.*[5] Several samples of α-deuteriobenzyl methyl sulfoxide of known configuration[1] and isotope content were each treated with methyllithium at $-60°$ for 1 min and then quenched with excess CH_3I (eq 1). The α-methylbenzyl methyl sulfoxides, **7** and **8**, thus obtained were examined for deuterium content by nmr[6] (see Table I).

$$\mathbf{5} + \mathbf{6} \xrightarrow{CH_3Li} \mathbf{1} + \mathbf{2} \xrightarrow{CH_3I} \underset{\mathbf{7}}{PhCH(CH_3)S(O)CH_3} + \underset{\mathbf{8}}{PhCD(CH_3)S(O)CH_3} \quad (1)$$

Table I. Reaction of $PhCHDS(O)CH_3$ with CH_3Li followed by CH_3I

Starting materials[a]		Products[6]	
% **5**	% **6**	% **7**	% **8**
92	8	39	61
53	47	30	70
6	94	20	80

[a] Ratios were measured in DMSO-d_6 solution using a Varian HA-100 spectrometer equipped with deuterium decoupling; error ±5%.

Appropriate corrections for the presence of nondeuterated and dideuterated sulfoxides, as determined from mass spectra, were made.

The isotope effect[7] ($IE = k_H/k_D$) and the selectivity factor ($S = k_{H_S}/k_{H_R}$) were calculated using the equations[8] $\mathbf{7}/\mathbf{8} = N_5(S/IE) + N_6/S \times IE$ and $\mathbf{8}/\mathbf{7} = N_5(IE/S) + N_6(S \times IE)$; N_5 and N_6 = mole fractions of **5** and **6**, respectively.

The solution of these equations gives an isotope effect of 2.5 ± 0.4 and a selectivity factor 1.7 ± 0.3.[9]

The magnitude of the isotope effect is reasonable for

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[1] (a) T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, *Can. J. Chem.*, **48**, 2148 (1970); (b) T. Durst, R. Viau, and M. R. McClory, *J. Amer. Chem. Soc.*, **93**, 3077 (1971).

[2] Although we were working with racemic mixtures, all formulas are presented and discussed in terms of the sulfur chirality as *S*.

[3] (a) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Amer. Chem. Soc.*, **94**, 8795 (1972), and references therein; (b) A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *ibid.*, **87**, 5498 (1965); (c) J. E. Baldwin, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 1415 (1969); (d) M. Bullock, J. W. M. Scott, and P. D. Golding, *ibid.*, 168 (1967); (e) M. Nishio, *ibid.*, 562 (1968).

[4] (a) K. Nishihata and M. Nishio, *J. Chem. Soc., Perkin Trans. 2*, in press; (b) M. Nishio, *Tetrahedron Lett.*, 4839 (1972).

[5] E. L. Eliel, A. A. Abatjoglou, and A. A. Hartmann, *J. Amer. Chem. Soc.*, **94**, 4786 (1972).

[6] Carried out on a Varian HA-100 spectrometer by comparison of the integrals due to $CHCH_3$ (d) and $CDCH_3$ (s) during deuterium decoupling.

[7] It is assumed that the isotope effects for the *pro-S* and *pro-R* hydrogens are approximately equal, *cf.* Eliel, *et al.*[5]

[8] D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, **75**, 6011 (1953).

[9] These values contrast with those obtained by Nishihata and Nishio[4a] who reported IE = 7 and *S* = 0.66 for the reaction of **5** and **6** with *n*-BuLi in THF at $-70°$. A selectivity factor <1 is highly unlikely since it implies that the less stable carbanion **2** is formed more readily than the more stable carbanion **1**.