fluorine bond. The rhodium compound $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh) has also been found to undergo a variety of oxidative-addition reactions with iodine compounds of the type RI (R = I, CF_3, C_2F_5, n-C_3F_7, and n-C_7F_{15}) to give the oxidative-addition products of general structure III as listed in Table I. These reactions appear to be the first examples of oxidative-addition reactions of metal–trifluorophosphine complexes. Similar oxidative-addition reactions have been recently reported for the iridium carbonyl derivative $(CH_3)_5C_5Ir(CO)_2$.[13]

Table I. Oxidative-Addition Reactions of $(CH_3)_5C_5Rh(PF_3)_2$[a]

Reactant	Product[b]	Color	Mp, °C	Yield, %
I_2	$Me_5C_5Rh(PF_3)I_2$	Deep red	Dec >275	95
CF_3I	$Me_5C_5Rh(PF_3)(CF_3)I$	Orange-brown	Dec >200	72
C_2F_5I	$Me_5C_5Rh(PF_3)(C_2F_5)I$	Red-brown	230–231	76
n-C_3F_7I	$Me_5C_5Rh(PF_3)(n\text{-}C_3F_7)I$	Deep red	147–149	77
n-$C_7F_{15}I$	$Me_5C_5Rh(PF_3)(n\text{-}C_7F_{15})I$	Orange	86–88	62

[a] These reactions were all carried out at room temperature in benzene solution using a large excess of the iodine compound. [b] All of these products were characterized by correct analyses for five elements and infrared spectra and nmr spectra (proton and fluorine).

Various metal carbonyl halides also react with $Ni(PF_3)_4$ in boiling toluene to form metal–trifluorophosphine complexes,[14] sometimes with dehalogenation. Thus $Mn(CO)_5Br$ reacts with $Ni(PF_3)_4$ to give a mixture of $Mn_2(CO)_{10-x}(PF_3)_x$ (x = 0, 1, or 2) derivatives with removal of the bromine atom. Under appropriate conditions a reasonably pure sample of the known[15] compound $Mn_2(CO)_8(PF_3)_2$ could be isolated. Reaction of the rhenium analog $Re(CO)_5Br$ with excess $Ni(PF_3)_4$ gives a 25% yield of white $Re(CO)_3(PF_3)_2Br$, mp 40-41°, with retention of the bromine atom. Reaction of $C_5H_5Fe(CO)_2I$ with excess $Ni(PF_3)_4$ gives a 77% yield of brown $C_5H_5Fe(CO)(PF_3)I$, mp 102–103°. Reaction of $C_5H_5Mo(CO)_3Cl$ with $Ni(PF_3)_4$ results in dechlorination to give either dark red $(C_5H_5)_2Mo_2(CO)_5PF_3$, mp 159–160° dec, or dark red $[C_5H_5Mo(CO)_2PF_3]_2$, decomposing at ~175°, depending upon the reaction conditions.

The nickel compound $Ni(PF_3)_4$ can also be used as a source of trifluorophosphine in reactions with halogen-free metal complexes. Thus, the σ-methylmetal derivatives $CH_3M(CO)_3C_5H_5$ (M = Mo and W) react with $Ni(PF_3)_4$ in boiling toluene to give the yellow derivatives $CH_3M(CO)_2(PF_3)C_5H_5$ (IV, M = Mo and W).[14]

Further details on the compounds described here and closely related ones will be described in future publications.

Acknowledgment. The authors are indebted to the National Institute of Medical Sciences for partial support of this work under Grant No. GM-14664-03.

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Stereochemical Nonrigidity in an Eight-Coordinate Complex

Sir:

We wish to report the first characterization of stereochemical nonrigidity in an eight-coordinate complex. Magnetic equivalence of ligand nuclei in eight-coordinate complexes has been a general observation.[1-6] In some instances, the magnetic equivalence has been ascribed to a rapid intramolecular rearrangement, and various stylized mechanisms have been considered.[1-3] However, in no case has the limiting, slow-exchange nmr spectrum been detected.

In the present communication we give data for the limiting fast- and slow-exchange ^1H and ^{31}P nmr spectra for complexes of the form $MoH_4(PR_3)_4$.[7] Figure 1 shows the 90-MHz ^1H nmr spectrum for the hydride protons of $MoH_4[P(C_6H_5)_2CH_3]_4$[7] at three temperatures. Figure 2 shows the 36.4-MHz ^{31}P nmr spectrum (with selective decoupling of the ligand protons) for the same complex at two temperatures; it is a 1:4:6:4:1 quintet in the high-temperature limit, confirming the presence of four hydride hydrogens in the molecule. Similar ^1H nmr spectra were obtained for the complex $MoH_4[P(C_6H_5)_2C_2H_5]_4$.[7] For both complexes, the ^1H hydride spectral patterns are independent of the spectrometer frequency in the low-temperature limit, as shown by experiments at 220 MHz. Thus the hydride hydrogens are chemically equivalent in the "rigid" state of the molecules.

Figure 1 illustrates the broadening of the central three lines of the high-temperature quintet as the temperature is lowered; similar behavior was observed in the ^{31}P spectrum, and in both cases the two outer lines remain sharp down to the low-temperature limit, a feature characteristic of intramolecular rearrangements in systems of this type.[8,9]

Preliminary work has been done on the analysis of the low-temperature limit spectra assuming a T_d model of two interpenetrating H_4 and P_4 tetrahedra. The model has an AA′A″A‴XX′X″X‴ spin system with two independent P–H coupling constants, a P–P coupling constant, and an H–H coupling constant. From the high-temperature limit spectrum, the sum

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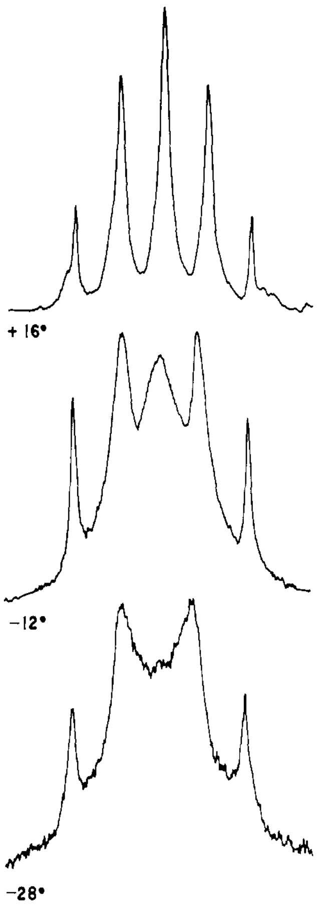

Figure 1. Temperature dependence of the 90-MHz ^1H nmr spectrum for the hydride protons of $MoH_4[P(C_6H_5)_2CH_3]_4$ in CD_2Cl_2. The averaged P–H coupling constant is 32 Hz.

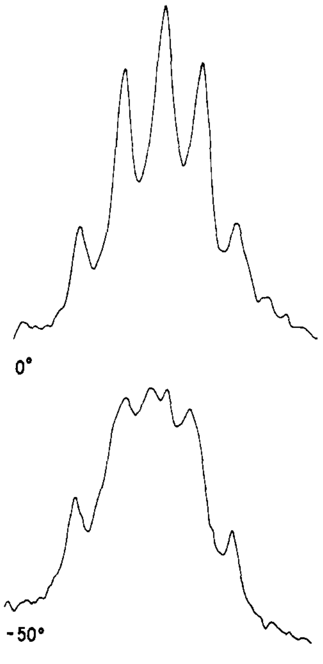

Figure 2. Temperature dependence of the 36.4-MHz ^{31}P nmr spectrum of $MoH_4[P(C_6H_5)_2CH_3]_4$ in CH_2Cl_2. The spectrum is extensively time averaged and the ligand aromatic protons are selectively decoupled.

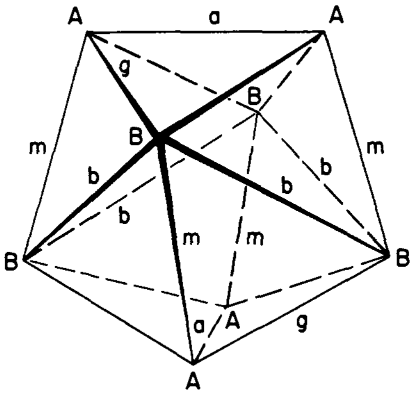

Figure 3. Trigonal dodecahedral geometry in eight-coordination. The hydride hydrogens are assumed to be in the A sites. The notation and diagram are due to Hoard and Silverton, ref 11.

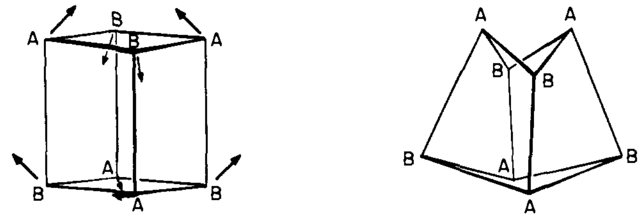

Figure 4. The breathing motion relating the T_d and D_{2d} structures of an H_4ML_4 complex.

of the P–H couplings is ~128 Hz. Best fits to date have been obtained with the cis P–H couplings ~38 Hz and the trans coupling ~14 Hz (both couplings having the same sign). The fits are, however, very sensitive to the values of J_{PP} and J_{HH}, making accurate reproduction of the experimental spectra rather difficult. It appears that with relatively small values of J_{PP} and J_{HH}, depending on the relative magnitudes of J_{PH} cis and J_{PH} trans, virtual coupling effects could lead to regular quintet spectra even in the low-temperature limit. For the two molecules considered here, J_{PP} and J_{HH} must be small.

A T_d structure (1) based on two interpenetrating tetrahedra is not the only possible idealized geometry in which there would be chemically equivalent sets of hydrogen and of phosphorus nuclei.[10] Alternatives are (2) a cube with four hydrogen atoms on a common face, (3) a square antiprism with four hydrogens on a common face, and (4) a square antiprism with trans phosphorus and trans hydrogens on each square face. All other possible geometries with chemically equivalent phosphorus and chemically equivalent hydrogen nuclei involve symmetrical distortions from these idealized structures. Structures based on (2) and (3) are unattractive on electronic and steric grounds.

Hoard and Silverton[11] in a classic paper have noted that in an MX_4Y_4 species a dodecahedral geometry is favored relative to a square antiprism if the two sets of nuclei are significantly different either electronically or sterically. They further note that smaller donor atoms should go to the A sites. This model is depicted in Figure 3. It is, in fact, a symmetry-reduced version of the two regular interpenetrating tetrahedra model of T_d symmetry (1). The tetrahedron based on the A sites is elongated to give a D_{2d} substructure and that based on the B sites is similarly compressed. These T_d

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(10) For discussion of possible idealized geometries for eight-coordinate structures, see ref 1–3 and especially ref 11.

(11) See J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963), for notational considerations and a definitive discussion of the relative stabilities of idealized geometries in eight-coordination.

and D_{2d} versions are related by a relatively simple breathing motion[11] shown in Figure 4. We suggest that a T_d ground state will be favored for phosphine or phosphite ligands where steric crowding is important. Diffraction data will be obtained for exemplary species to establish the solid-state geometries. It should be noted that the above-mentioned breathing motion may well be so rapid that the true limiting slow-exchange nmr spectra would not be obtained for a D_{2d} species.

Earlier we discussed[9,10,12,13] for H_xML_4 molecules a novel rearrangement mechanism which comprised an approach to a near regular tetrahedral ML_4 substructure in the ground or transition state, with concomitant hydrogen atom traverse of the ML_4 tetrahedral faces. This mechanism, given the trivial label of "tetrahedral tunneling," was demonstrated for six-[8,10,13] and suggested for five-coordinate[12] complexes. We anticipated that this same mechanism would also be operative in some seven (H_3ML_4) and eight (H_4ML_4) classes with the exchange barrier being higher in the latter case because hydrogen atom motion must be concerted. We propose that the H_4MoL_4 phosphine complexes have a D_{2d} tetrahedral or near regular tetrahedral MoP_4 substructure and that intramolecular rearrangement comprises a concerted hydrogen atom traverse of the tetrahedral faces. From an analysis of the molecular permutation group,[13] we find that there are four basic permutational sets plus the identity set which are potentially distinguishable on the basis of nmr line-shape studies. Simple physical mechanisms involving largely hydrogen motion would be pairwise exchange of the hydrogens, a concerted motion of three hydrogens, or a concerted motion of all four hydrogens. As yet we have not established whether mechanistic information can be qualitatively or quantitatively inferred from an analysis of the nmr line shapes, but of the possible mechanistic sets we believe that the most realistic one involves predominantly a concerted motion of three of the hydrogen nuclei.

We are presently attempting to obtain a more complete analysis of the low-temperature limit nmr data and mechanistic information from the line-shape data. Additionally, we are examining analogous eight-coordinate molybdenum and tungsten complexes to see whether the steric or electronic character of the ligand can have a profound effect upon the barrier to intramolecular rearrangement. Preliminary information for the complex $MoH_4[P(OC_2H_5)_2C_6H_5]_4$ has established that its nmr characteristics are qualitatively different from those of the above-described phosphine complexes. A full report on this study of stereochemically nonrigid eight-coordinate complexes will be presented shortly.

Acknowledgment. We are indebted to Mr. William Peet and Dr. D. H. Gerlach for substantial assistance in the preparation of these complexes.

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N-Fluoro-2,6-dimethylpiperidines. Conformational Behavior as Observed by ^{19}F Nuclear Magnetic Resonance

Sir:

Nitrogen inversions in amines are known to be fast, but generally get slower if nitrogen is substituted by at least one electronegative atom, such as oxygen or chlorine.[1] In recent work, nitrogen inversion in cyclic *N*-chloroamines was studied[2] and the authors concluded that for *N*-chloropiperidine, nitrogen inversion may be excluded as the rate-determining process; on the other hand they stated that "the observation of only one AB spectrum (for the α protons in *N*-chloropiperidine-*3,3,5,5-d*$_4$ at −40°) can be explained either by the presence of only one conformer, presumably with chlorine equatorial, or by a superposition of the AB spectra from the two conformers."[2]

It appears, therefore, that the proton nmr is not very satisfactory in this case as no clear demonstration can be drawn. It seemed interesting to us to use *N*-fluoro compounds for solving problems such as "six-membered ring reversal, *vs.* nitrogen inversion," this for two reasons: one is that fluorine will decrease as much as possible the rate of inversion of nitrogen; the other is that it will be easy to observe this nucleus by ^{19}F nmr technique with which large spectral differences between conformers are expected.[3]

We prepared separately the two *N*-fluoro derivatives of *cis*- and *trans*-2,6-dimethylpiperidine according to the expected reaction.[4] According to a described

$$2R_2NH + FClO_3 \longrightarrow R_2NF + R_2NH_2^+ClO_3^-$$

procedure, 2,6-dimethylpyridine was hydrogenated into *cis*- and *trans*-2,6-dimethylpiperidine which were separated on a spinning band column:[5] cis, bp 64° (100 mm); trans, bp 71° (100 mm). The fluorination can be carried out either in ether or in $CFCl_3$ solution (100 ml) at low temperature (between −60 and −20°) by an excess of perchloryl fluoride ($FClO_3$) diluted in nitrogen (15% vol). By this procedure 3.3 g of the *cis*-2,6-dimethylpiperidine (0.03 mol) gave 2.4 g of chlorate (0.0122 mol) which precipitated; from the solution the expected *N*-fluoro cis derivative was isolated by evaporation of the solvent at low temperature: a viscous oil, not distillable, but rather stable at room temperature; mass spectrum m^+/e M = 131 (0.09), M − CH_3 = 116 (1), M − NF = 98 (0.62).

Anal. Calcd for $C_7H_{14}NF$: C, 64.08; H, 10.75; N, 10.67; F, 14.48. Found: C, 63.48; H, 11.4; N, 10.38; F, 11.5.

By the same procedure 2 g of *trans*-2,6-dimethylpiperidine (0.018 mol) gave 1.57 g of chlorate (0.008 mol) which precipitated; from the solution the expected *N*-fluoro trans derivative was isolated by evaporation of the solvent at low temperature: a viscous oil, not distillable, and rather unstable at room temperature; it may be kept for a long time under nitrogen at −70°; mass spectrum m^+/e M = 131 (0.12), M − CH_3 = 116 (1), M − NF = 98 (0.65).

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