mation of the reference isomer to a polytopal isomer which offers a pathway for hydrogen atom interchange. Only deformations requiring relatively minor motion of the heavy atom ligands are invoked. This leads to monocapped trans and cis octahedral intermediates, *via* the deformations pictured in Figure 2d and e. A tricapped tetrahedral intermediate is unlikely because of the relatively large heavy atom motions required to reach it. The pathways for hydrogen motion and the implied permutational isomerization reactions are given beneath the intermediate polytopal isomers in Figure 2.

In the trans octahedral intermediate the capping hydrogen moves from one polytope face to another, as in the tetrahedral tunneling mechanism.[18] In the cis octahedral intermediate concerted rotation of H_5, H_6, and H_7 is possible for $ReH_3(dppe)(PPh_3)_2$ and $ReH_3(dpae)(PPh_3)_2$ but is blocked by the CH_2CH_2 bridges in $ReH_3(dppe)_2$ and $ReH_3(dpae)_2$. The lower barrier in $ReH_3(dpae)(PPh_3)_2$ may be due to the accessibility of this mechanism without initial deformation. Further work is in progress.

[18] See ref 8a and the references cited therein.

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Nonrigid Stereochemistry in Eight-Coordinate Pentahydridorhenium Complexes

Sir:

This communication reports the observation of slow-exchange limit nmr spectra for the stereochemically nonrigid eight-coordinate complexes $ReH_5(P(C_6H_5)_2C_2H_5)_3$[1] and $ReH_5(As(C_6H_5)_2C_2H_5)_3$.[2] The results are of interest because three distinct fluxional processes are frozen out between +30 and −135° and because of the information they provide about magnetic equivalence of the hydride protons in the rigid form of the molecules. Also, this represents only the second instance in which slow-exchange limit nmr spectra have been detected for nonrigid eight-coordinate complexes, the first examples being $MoH_4(P(C_6H_5)_2CH_3)_4$ and $MoH_4(P(C_6H_5)_2C_2H_5)_4$ and the corresponding tungsten complexes.[3]

Figure 1 shows the hydride region 100-MHz ^1H nmr spectrum of $ReH_5(As(C_6H_5)_2C_2H_5)_3$ at several temperatures. At −135° the spectrum consists of four resonances: τ 15.96, 16.42, 17.26, and 19.54; the intensities correspond respectively to 1, 2, 1, and 1 protons. On raising the temperature, the τ 16.42 and 19.54 absorptions coalesce to a single band at about the same position as the τ 17.26 band. The coalescence is complete by −90° when the spectrum consists of a composite absorption of intensity 4 protons at τ 17.39 and a band of intensity 1 proton at τ 16.00. Above −90°, the τ 16.00 resonance coalesces with the intensity 1 component of the τ 17.39 composite absorption (*i.e.*, the τ 17.26 resonance) to give at −60° a band of intensity 2 protons at τ 16.67, while the remaining intensity 3 band is now at τ 17.34. Further increase in the temperature above −60° results in coalescence of the τ 16.67 and 17.34 bands to give a single resonance of intensity 5 protons at τ 16.90 (+30°).

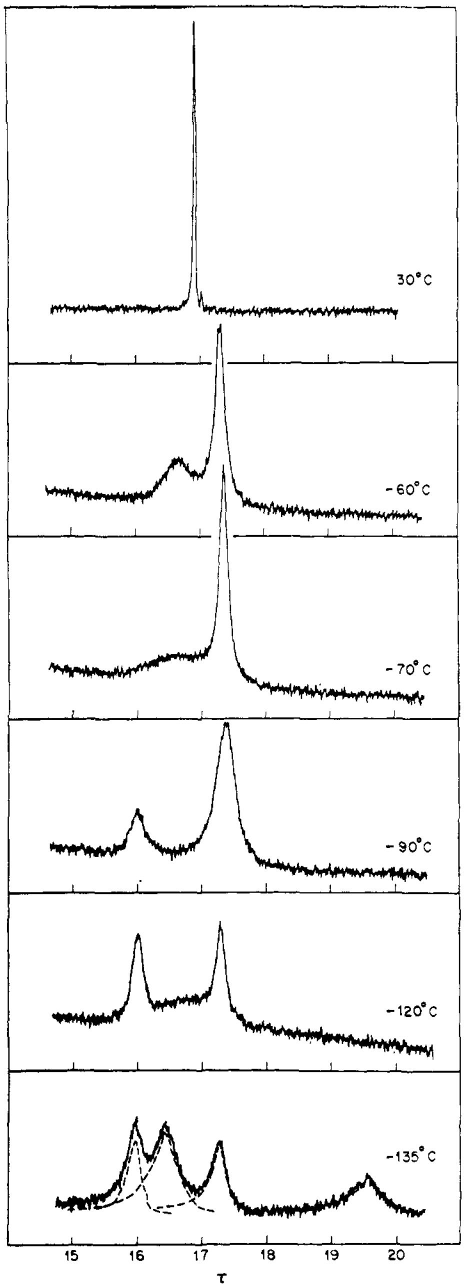

Figure 1. Hydride region 100-MHz ^1H nmr spectra of $ReH_5(As(C_6H_5)_2C_2H_5)_3$ in 2:1 CF_2Cl_2–$CHFCl_2$ with TMS internal reference at several temperatures.

The spectrum of $ReH_5(P(C_6H_5)_2C_2H_5)_3$, observed with ^{31}P–^1H heteronuclear spin decoupling, has a temperature dependence qualitatively similar to that of the arsenic complex. Without decoupling, the spectrum is a quartet at +30° and the quartet structure is visible down to ∼−50°. At lower temperatures, when exchange has been slowed sufficiently that nonequivalent hydrogen atoms may be distinguished, the line widths are considerably greater than in the decoupled spectra, but multiplet structure could not be seen.

Below −135°, down to ∼−155°, the lowest tem-

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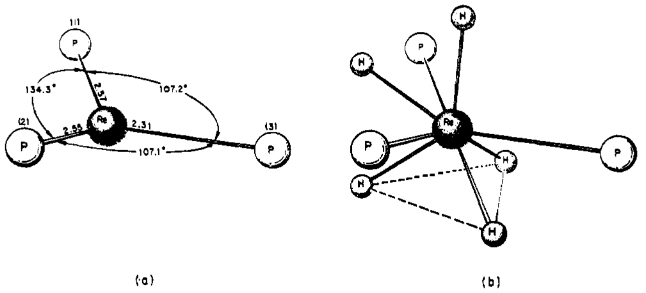

Figure 2. (a) Phosphorus atom coordination to rhenium in $ReH_5(P(C_6H_5)_3)_3$. (b) Proposed coordination geometry for $ReH_5(MR_3)_3$ (M = P, As). The structure has C_s point group symmetry and may be viewed as a distorted dodecahedron, a distorted truncated octahedron, or a distorted bicapped octahedron.

perature studied, the spectra of both the phosphine and arsine complex show a uniform broadening of all components. This very low-temperature broadening is probably due to increased viscosity of the sample solutions; there is no evidence of further collapse of the intensity two component of the spectra (*i.e.*, of the τ 16.42 absorption) over and above the general broadening. The low-temperature spectra show clearly that three of the five hydride protons in the rigid molecule are magnetically nonequivalent, while the remaining two appear to be equivalent.[4] Although we consider it unlikely, the possibility remains that the equivalence of two of the hydride protons is not a characteristic of the rigid molecule but results from rapid interchange by a process that is not slowed even at $\sim -155°$.

In order to obtain information about the solid-state geometry of the pentahydride complexes, a partial determination of the crystal structure of $ReH_5(P(C_6H_5)_3)_3$[1] was carried out. A full determination, with usual reliability, was precluded due to the extensive radiation damage suffered by the crystals in Mo Kα X-ray beams.

The crystal is monoclinic,[5] with lattice constants $a = 13.62 \pm 0.02$, $b = 33.14 \pm 0.04$, and $c = 9.92 \pm 0.02$ Å with $\beta = 92.3 \pm 0.1°$. The space group is $P2_1/n$, with four formulas per unit cell and a calculated density of 1.45 g cm^{-3}. Approximate coordinates for the heavy atoms, obtained from solution of the three-dimensional Patterson function, are shown in Table I.

Table I. Approximate Coordinates for the Heavy Atoms in $ReH_5(P(C_6H_5)_3)_3$

Atom	*x*	*y*	*z*
Re	0.303	0.604	0.199
P(1)	0.167	0.563	0.307
P(2)	0.487	0.612	0.247
P(3)	0.235	0.673	0.151

The corresponding bond lengths are Re–P(1) = 2.57, Re–P(2) = 2.55, and Re–P(3) = 2.51 Å; the interatomic distances are P(1)–P(2) = 4.71, P(1)–P(3) = 4.08, and P(2)–P(3) = 4.06 Å. Bond angles are P(1)–Re–P(2) = 134.3°, P(1)–Re–P(3) = 107.2°, and P(2)–Re–P(3) = 107.1°. Figure 2a illustrates the arrangement of the phosphorus atoms about the rhenium atom; the latter lies 0.49 Å out of the phosphorus atom plane.

Models of the different polyhedra that have been suggested for eight coordination[6,7] were constructed using the measured bond angles and distances and assuming an Re–H distance of ~1.7 Å.[8] The observed pattern of hydride proton equivalence (1, 1, 1, 2) may be accounted for by geometries based on the dodecahedron, truncated octahedron and bicapped octahedron with caps on adjacent faces. The structures derived from these polyhedra all have C_s point group symmetry and differ from each other only by small hydrogen atom displacements; they are exemplified by Figure 2b.

It does not appear worthwhile, at this stage, to speculate about the mechanism of the fluxional behavior of $ReH_5(MR_3)_3$ complexes. However, we note that three distinct mechanisms are required to account for the temperature dependence of the nmr spectra; a number of possibilities are evident from the proposed structure. Further work on these systems is in progress.

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[4] The presence of two isomers, both of which are fluxional *and* rapidly interconvert at the highest temperature, is excluded by the observed temperature dependence of the spectra.

[5] $ReH_5(P(C_6H_5)_3)_3$ may be obtained in three different crystalline modifications (α, β, and γ), all of which give the same molecular species in solution. The α form, studied here, results when the complex is crystallized from CS_2–petroleum ether (1:4) at 2°: A. P. Ginsberg, to be submitted for publication.

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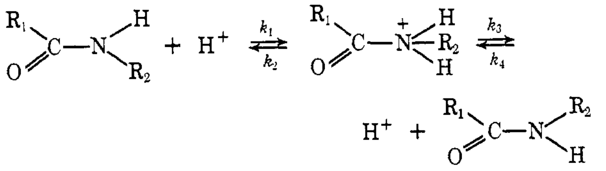
Predominant N-Bound Hydrogen Exchange *via* O-Protonated Amide[1]

Sir:

The generally accepted mechanism for both acid-catalyzed cis–trans isomerization and exchange of nitrogen-bound hydrogens in amides is *via* an N-protonated intermediate (eq 1).[2] General acid catalysis



(1)

has been observed,[3] consistent with the first step as rate limiting. Hydronium ion is the only general acid catalyst considered here. Assuming a low steady-state concentration of the N-protonated species, the second-order rate constant for hydrogen exchange of an N-monosubstituted amide is given by $k_N = k_1/2$. Favoring of the trans isomer and occurrence of the exchange process in most cases precludes observation of isomerization in monosubstituted amides by proton

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