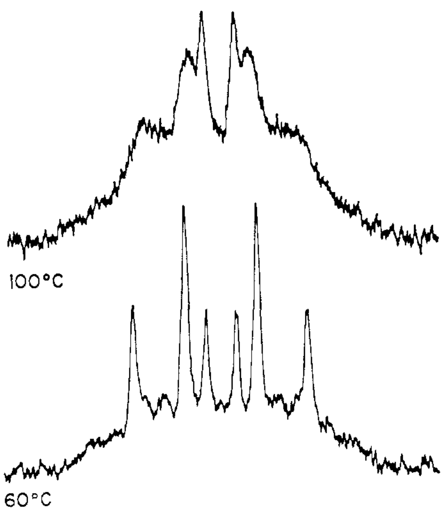

Figure 3. Temperature dependence of the 220-MHz ^1H hydride spectrum of $H_2Ru[C_6H_5P(C_2H_5)_2]_4$. The barrier for the related $H_2Ru[C_6H_5P(CH_3)_2]_4$ complex is higher, ostensibly because of less significant ligand–ligand repulsions.

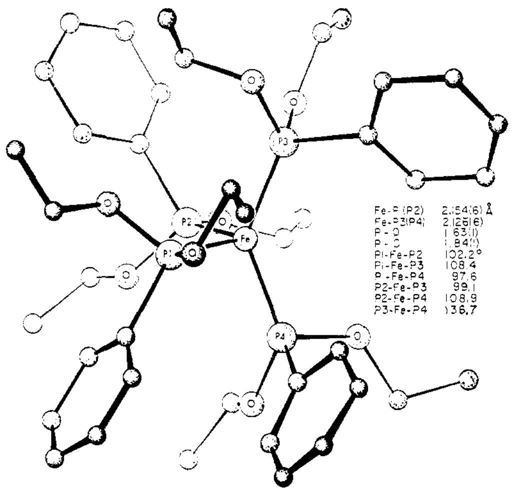

Figure 4. Structure of $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$. The hydride hydrogen atoms are presumed to be vicinal as indicated by their *trans* influence on the Fe–P(1) and Fe–P(2) bond distances. The shortest nonhydrogen contacts between atoms on different phosphorus atoms involve oxygen contacts with methylene or benzene carbon atoms.

spin system) which are unaffected by permutations of the phosphorus spins. The iron dihydrides have similar rearrangement barriers, although complex **5**, in which the ligand has the smallest cone angle,[3] appears to have the highest barrier. Complex **2**, which is the only member of the series existing in both *cis* and *trans* forms, possesses a spectral temperature dependence (Figure 2) differing markedly from those of **1**, **3**, and **4–6**. The salient features of the spectra are a low-temperature quintet and a triplet of doublets diagnostic of the *trans* and *cis* forms, respectively, and the collapse to the high-temperature quintet *without* retention of any sharp features.

The ruthenium complexes synthesized and examined are set forth in Table I. Complex **13** has been prepared previously and its low-temperature hydride spectrum explained by a *cis* structure.[4] All new complexes except **10** display low-temperature spectra similar to that of **13** and are assigned *cis* structures. Complex **10**, like its iron analog, exists as both *cis* and *trans* isomers in solution.

Figure 3 shows the 60 and 100° hydride spectra of **12**. Broadening of the low-temperature spectrum is not observed for any of the ruthenium hydrides below 60°. In fact, the fast exchange limit, which should be a 1:4:6:4:1 quintet, has not been detected for any Ru complexes owing to their thermal instability and the high temperatures (>150°) which are required. The rearrangement barriers are all qualitatively higher than those for the iron set. It should be noted that the sharp features attributable to the $|M\ \alpha\alpha\alpha\alpha\rangle \rightarrow |M'\ \alpha\alpha\alpha\alpha\rangle$ transitions remain distinct, and because of differences in signs and magnitudes of coupling constants are now the inner lines of the low-temperature spectrum and the outer lines of the high-temperature quintet.

The crystal structure of $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$ was solved from 3900 pieces of single-crystal data collected on an automatic diffractometer using Mo Kα radiation. Crystals are triclinic, space group $P\bar{1}$, with cell dimensions of a = 11.786 (8), b = 17.491 (12), c = 11.970 (8) Å, α = 90.20 (3), β = 114.97 (9), and γ = 85.03 (3)°. The molecule (Figure 4) has no imposed or idealized molecular symmetry. The iron–phosphorus geometry is nearly midway between that expected for octahedral and tetrahedral phosphorus disposition, with the rms angular deviation favoring the tetrahedral geometry.

We had tentatively proposed that the mechanism of the polytopal rearrangement in these metal dihydrides comprises vibrational population of a pseudotetrahedral ML_4 state with hydride tunneling of face and edge positions. Our new data are consistent with this proposal. The X-ray determination shows that the complex is, in fact, distorted in the manner proposed earlier.[1] Furthermore, if the LL nonbonding repulsions provide some driving force for the rearrangement, those complexes based on the smaller metal atom and bulkier ligands should have lower barriers. This is the experimental observation. In contrast, if a trigonal twist mechanism were primarily responsible for the rearrangement, steric arguments would suggest that the complexes with the larger metal and the more compact ligands have the lower barriers.[5]

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(3) C. A. Tolman, *J. Amer. Chem. Soc.*, in press.

(4) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 7, 546 (1968).

(5) The nmr spectra of compounds such as $H_2Ru(NCC_6H_5)[P(C_6H_5)_3]_3$, $H_2OsCO[P(C_6H_5)_3]_3$, and $H_3Ir[C_6H_5P(C_2H_5)_2]_3$ have been examined and show no evidence for rapid intramolecular rearrangement. On purely steric grounds we would expect these to be relatively nonrigid if a trigonal twist were operative.

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Received March 30, 1970

Intramolecular Exchange and "Thermal" Decoupling in $B_3H_8^-$ Compounds

Sir:

During an investigation of the apparent discrepancy between the crystal structure of the $B_3H_8^-$ anion (I)[1]

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(1) C. R. Peters and C. E. Nordman, *J. Amer. Chem. Soc.*, 82, 5758 (1960).

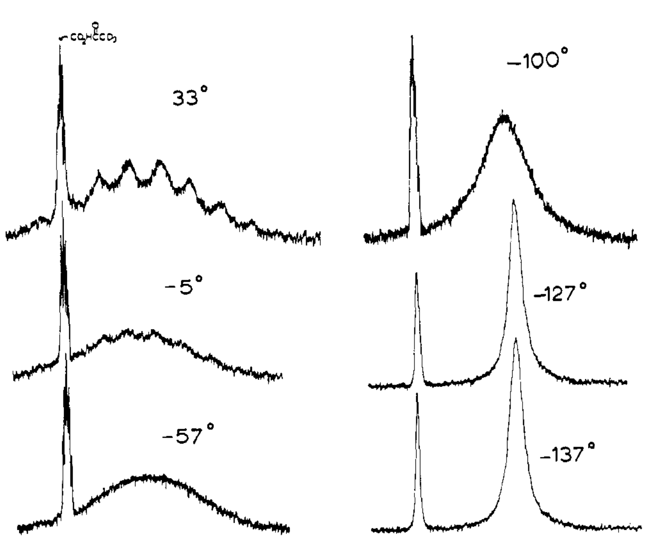


Figure 1. The pmr spectrum (60 MHz) of TlB_3H_8 in 50% CD_3OD/50% CD_3COCD_3 as a function of temperature.

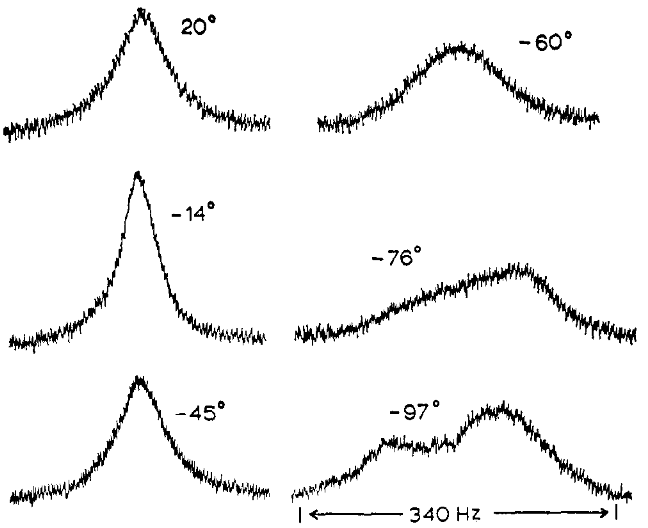
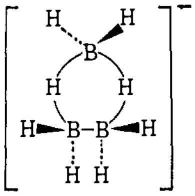


Figure 2. The pmr spectrum (60 MHz) of the B_3H_8 protons of $[(C_6H_5)_3P]_2CuB_3H_8$ as a function of temperature.

and the solution nmr spectrum[2] of I, which indicates all borons coupled equivalently to all hydrogens,[3] we investigated the temperature dependence of the pmr spectrum (60 MHz) of TlB_3H_8, $(CH_3)_4NB_3H_8$, and $[(C_6H_5)_3P]_2CuB_3H_8$. This report concerns the observation of a dramatic effect of temperature on the boron-hydrogen spin-spin splitting in $B_3H_8^-$ due to quadrupole-induced ^{11}B and ^{10}B relaxation, as well as fluxional behavior which shows a significant dependence on cation.

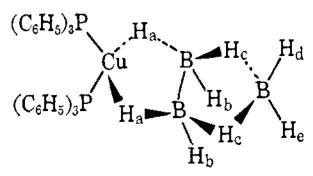


I

Examination of the pmr spectrum (60 MHz) of TlB_3H_8 in 50% CD_3OD/50% CD_3COCD_3 (v/v) at room temperature revealed a typical ten-line multiplet (Figure 1) (two outer peaks lost in noise) reflecting coupling of the hydrogens to three *equivalent* ^{11}B nuclei ($I = {}^3/_2$). Lowering the temperature slightly caused a coalescence of the spin-spin splitting pattern (Figure 1), but at substantially lower temperature (−127°, Figure 1) the spectrum has resharpened into a constant-shape one-line spectrum ($W_{1/2} \sim 10$ Hz). No evidence for any other $B_3H_8^-$ resonances was obtained at high signal amplification by sweeping 20 ppm to low and high field of the singlet observed at −127°. This behavior would seem to be best rationalized by more effective quadrupole-induced ^{11}B and ^{10}B relaxation at lower temperatures (slower molecular motions), effectively decoupling boron from hydrogen. The sharpening of the spectrum at low temperatures is inconsistent with intramolecular exchange processes which would be expected to be slower at low temperatures, giving a more complicated spectrum. It is evident that the one-line spectrum observed at −127° is still inconsistent with a static form for I in solution, and that intramolecular scrambling is rapid on the pmr time scale even at −137°.

The $(CH_3)_4NB_3H_8$ exhibited exactly analogous behavior in 50% CD_3OD/50% CD_3COCD_3 and 50% $(CD_3)_2NCDO$/50% CD_3COCD_3, indicating no significant effect of solvent or cation.

However, examination of the pmr spectrum (60 MHz) of the B_3H_8 hydrogens of $[(C_6H_5)_3P]_2CuB_3H_8$ (II)[4] (50% $CDCl_3$/50% CH_2Cl_2 (v/v) as solvent) at 20° revealed a broad resonance (Figure 2) with no boron-hydrogen coupling evident. This lack of resolution of the boron-hydrogen coupling is in contrast to TlB_3H_8 and $(CH_3)_4NB_3H_8$. For all of the spectra used in this study, it was assured that the CH_2Cl_2 resonance was Lorentzian in order to avoid the ambiguities associated with asymmetry of line shapes. When the sample temperature was lowered to *ca.* −14°, the B_3H_8 pmr signal *sharpened* to a significantly greater degree than at 20° (Figure 2). This behavior strongly suggests the intervention of quadrupole-induced ^{10}B and ^{11}B spin relaxation ("thermal" decoupling), but again is in contrast to TlB_3H_8 and $(CH_3)_4NB_3H_8$, in which the sharpening of the B_3H_8 pmr peaks is not observed until *ca.* −100°. This difference in behavior may be the result of slowed molecular motion due to the greater size of the Cu compound or to a higher barrier to intramolecular exchange. At lower temperatures (Figure 2), the pmr spectrum of the B_3H_8 protons of II broadened again, but in an asymmetric fashion, strongly suggesting the slowing of a rate process, *e.g.*, pseudorotation, on the pmr time scale. At −93°, the spectrum consists of at least two broad overlapping resonances, clearly indicating hydrogens in different environments (Figure 2). Although



II

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(2) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 81, 4496 (1959). W. N. Lipscomb's suggestion of pseudorotation is cited as a private communication in this reference.

(3) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, 1, 117 (1959).

(4) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 3, 1475 (1964).

each individual resonance is not resolved, the spectrum is consistent with a series of *three* different types of terminal hydrogens (H_b, H_d, and H_e in II) giving the relatively more broad downfield portion of the spectrum,[5] and only *two* different types of bridging hydrogens (H_a, H_c in II) giving the more narrow upfield resonance (Figure 2). Using this rationalization, it is assumed that thermal boron–hydrogen decoupling is effective below −14°. The shape of the B_3H_8 pmr signal did not change from −93 to −108°, at which temperature crystallization occurred. Subsequent examination of the 100-MHz pmr spectrum of II at −90° revealed five separate resonances consistent with effective thermal decoupling and slow (on the pmr time scale) intramolecular exchange.

The implication in the above results is clear and should be useful in determining structure and studying fluxional behavior in boron compounds. By selection of the appropriate temperature, boron–hydrogen coupling can be eliminated providing a greatly simplified spectrum. In most instances, the pmr spectra of boron compounds are ambiguous, owing to chemical shifts and coupling constants of approximately the same magnitude. Although quadrupole-induced ^{11}B and ^{10}B spin relaxation has not been recognized previously, the effect of the ^{14}N quadrupole has been observed in pyrrolidine hydrochloride[6] and nitrogen trifluoride.[7]

The above data provide unequivocal evidence for a slowed rate process on the pmr time scale in $[(C_6H_5)_3P]_2CuB_3H_8$, in contrast to TlB_3H_8 and $(CH_3)_4NB_3H_8$, which display rapid equilibration on the pmr time scale even at −137°. The dramatic effect on the barrier to intramolecular exchange can be ascribed to the covalently bonded copper(I).

We are continuing our investigations of fluxional behavior in $B_3H_8^-$ adducts, especially with respect to the identity of the metals and ligands.

Acknowledgment. H. B. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and C. H. B. to Research Corporation for support of this research.

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(5) D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 1438 (1970).

(6) J. D. Roberts, *ibid.*, **78**, 4495 (1956).

(7) E. L. Muetterties and W. D. Phillips, *ibid.*, 81, 1084 (1959).

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Intramolecular Rearrangements in Asymmetric Rhodium(I) Diolefin Complexes

Sir:

The temperature dependence of the proton nmr (pmr) spectra of several monoolefin complexes of rhodium(I)[1] and platinum(II)[2] has been interpreted in terms of an intramolecular mechanism involving rotation of the coordinated olefin. Another kind of fluxional behavior has been described[3] for molecules of the type[4] [(NOR)MLX] or [(COD)MLX], in which the nonequivalent protons of the coordinated diolefin become averaged with increasing temperature on the pmr time scale.[5] A kinetic analysis[3] of these reactions reveals them to be complex, with ligand dissociation and intermolecular exchange processes predominating. As described in the present report, the interpretation of pmr data in such systems has been considerably simplified by the synthesis and study of compounds containing an asymmetric, bidentate anion (usually S–DBM) and a diolefin coordinated to a transition metal. The general approach is analogous to that described elsewhere[6] for related metal π-allyl complexes.

The compounds[4] (NOR)Rh(S–DBM), (NOR)Rh(DBM), (COD)Rh(S–DBM), and (COD)Rh(DBM) were prepared by allowing the thallium salt[6b] of DBM or S–DBM to react with the appropriate [(diolefin)$RhCl]_2$ dimer.[7,8] The pmr spectra at 40° of these complexes are summarized in Table I. The chemical shift values of the H_A protons in both (NOR)Rh(S–DBM) and (COD)Rh(S–DBM) occur 0.60–0.80 ppm downfield from those of the H_B protons. Protons H_A are therefore assigned to the olefin group *trans* to the sulfur atom.[9] A solution of (COD)Rh(S–DBM) in $o\text{-}C_6H_4Cl_2$ was heated with no significant change in the pmr spectrum up to 155°, when the sample decomposed. In the same solvent, however, the H_A and H_B resonances of (NOR)Rh(S–DBM) symmetrically broadened with increasing temperature and finally collapsed into a single line at τ 5.80 ppm above 118° (Figure 1a,b). The process was found to be reversible with temperature.

Table I. Chemical Shift Values[a] in Various Solvents at 40°

Compound[b]	H_A	H_B	Bridge-head	Meth-ylene	Solvent
(NOR)Rh(S–DBM)	5.25	5.85	6.20	8.55	$CDCl_3$
(NOR)Rh(S–DBM)	5.50	6.10	6.50	8.80	$o\text{-}C_6H_4Cl_2$
(NOR)Rh(S–DBM)	5.40	6.10	6.10	8.45	C_6F_5Br
(NOR)Rh(S–DBM)	5.50	6.10	6.50	8.80	C_6H_5Cl
(NOR)Rh(DBM)	5.95	5.95	6.20	8.75	$CDCl_3$
(NOR)Rh(DBM)	6.10	6.10	6.50	8.95	C_6H_5Cl
(COD)Rh(S–DBM)	5.05	5.85		7.4–8.2	$CDCl_3$
(COD)Rh(S–DBM)	5.25	5.85		7.8–8.5	$o\text{-}C_6H_4Cl_2$
(COD)Rh(DBM)	5.75	5.75		7.3–8.3	$CDCl_3$
NOR	4.45	4.45	6.65	8.10	$o\text{-}C_6H_4Cl_2$

[a] τ, ppm. [b] See ref 4 for abbreviations.

A study of the concentration dependence of the collapse of H_A and H_B a few degrees above the coalescence temperature was carried out in C_6F_5Br, chosen to reduce

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(1) (a) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964); (b) R. Cramer, *ibid.*, **89**, 5377 (1967); (c) R. Cramer, J. B. Kline, and J. D. Roberts, *ibid.*, **91**, 2519 (1969).

(2) C. E. Halloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., A*, 53 (1969).

(3) (a) P. W. N. M. van Leeuwen, K. Vrieze, and A. P. Praat, *J. Organometal. Chem.*, 20, 277 (1969); (b) K. Vrieze, H. C. Volger, and A. P. Praat, *ibid.*, **15**, 447 (1968); (c) K. Vrieze, P. W. N. M. van Leeuwen, and H. C. Volger, *Inorg. Chim. Acta*, **3**, 109 (1969), and references cited therein.

(4) Abbreviations: NOR = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene); COD = cycloocta-1,5-diene; S–DBM = monothiodibenzoylmethane anion, DBM = dibenzoylmethane anion; M = metal (Rh, Ir, etc.); X = halide; L = group V donor ligand (R_3P, R_3As).

(5) (a) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965); (b) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(6) (a) S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, **91**, 2504 (1969); (b) S. J. Lippard and S. M. Morehouse, in preparation.

(7) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(8) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 3178 (1959).

(9) Assuming a *trans* influence S > O[6a] similar to P > Cl, this choice is in agreement with the assignment[10] of [(diolefin)RhLX] pmr spectra, but cannot be regarded as absolute at the present time.[6b]

(10) K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometal. Chem.*, **14**, 185 (1968).