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.

(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-$C_6H_4Cl_2$ 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-$C_6H_4Cl_2$
(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-$C_6H_4Cl_2$
(COD)Rh(DBM)	5.75	5.75		7.3–8.3	$CDCl_3$
NOR	4.45	4.45	6.65	8.10	o-$C_6H_4Cl_2$

[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

(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).

the noise level due to solvent proton resonances at low sample concentrations. The spectra were identical over a tenfold concentration range.[11] Measurement of $\tau(H_A)^{-1}$ and $\tau(H_B)^{-1}$ in the slow-exchange[12] region also showed them to be independent of concentration.

In order to eliminate reaction 1 as a possible route for

$$\text{(NOR)Rh(S–DBM)} \rightleftharpoons \text{Rh(S–DBM)} + \text{NOR} \qquad (1)$$

effecting the *cis–trans* exchange of H_A and H_B, an o-$C_6H_4Cl_2$ solution 0.11 *M* in (NOR)Rh(S–DBM) and 0.11 *M* in free norbornadiene was prepared. The sample was heated to 139°, at which temperature the olefinic protons H_A and H_B had collapsed to a single peak. The olefinic protons of NOR did not average in. The peaks assigned to the bridgehead and methylene protons of complex and free ligand (see Table I) had only broadened slightly, indicating that exchange with free norbornadiene proceeds at a rate much slower than *cis–trans* exchange. The process was reversible with temperature. In a similar experiment, (NOR)-Rh(S–DBM) and (NOR)Rh(DBM) were mixed in approximately equal proportions in chlorobenzene. The pmr spectrum of this mixture at 98° contained a broad peak at 5.80 ppm, the average of H_A and H_B in this solvent, and a peak due to the olefinic protons of (NOR)Rh(DBM) at 6.10 ppm, which retained its fine structure. Reaction 2 therefore appears to be an unlikely pathway for exchange of H_A and H_B.[13] Another reason for regarding eq 2 as an unlikely pathway for the

$$\text{(NOR)Rh(S–DBM)} \rightleftharpoons \text{(NOR)Rh}^{+} + \text{S–DBM}^{-} \qquad (2)$$

averaging process is the apparent insensitivity of the activation energy to the solvent polarity. Arrhenius plots of the inverse mean lifetime for exchange, computed[2,12] both below and above the coalescence temperature,[14] gave values for E_a of 18.6 ± 1.8 kcal/mol ($\log A = 12.4 \pm 1.0$) in o-dichlorobenzene solution and 19.7 ± 1.3 kcal/mol ($\log A = 13.2 \pm 0.6$) in nitrobenzene.

Among the possible remaining mechanisms[15] consistent with the above experimental data are (1) dissociation of one end of either NOR or S–DBM to form a trigonal planar intermediate, followed by attack of the uncoordinated end of the ligand to re-form the complex;[3a] (2) nucleophilic attack of a solvent molecule to form a five-coordinate intermediate which undergoes one or more polytopal rearrangements[16] before losing solvent to re-form the complex;[17] and (3) a planar–tetrahedral–planar "twist".[19] The second process has frequently been postulated to explain the kinetic behavior of various [(diolefin)RhLX] systems.[3,10] The absence of any marked solvent dependence of the activation energy[22] might appear to make it a somewhat less attractive alternative in the present case. It does have the virtue, however, of providing a rationale for the nonfluxional character of (COD)Rh(S–DBM) since, in a related study,[23] (NOR)RhCl(PPh$_3$) was found to form five-coordinated species more readily than (COD)RhCl(PPh$_3$).

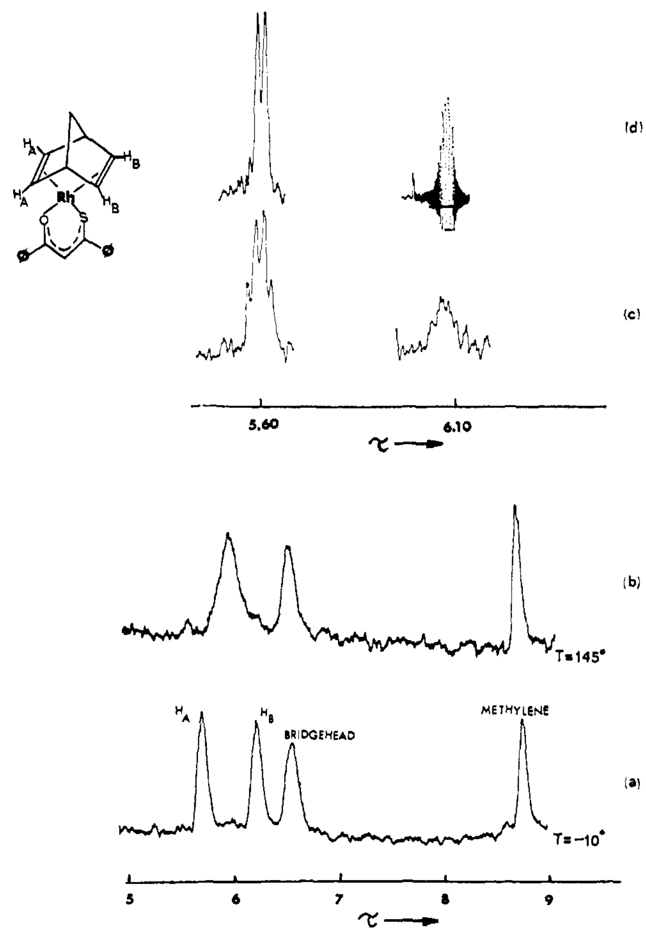

Figure 1. Proton nmr spectra of (NOR)Rh(S-DBM), (a) and (b) in o-dichlorobenzene, (c) in DMSO-d_6 at 40°, (d) with spin decoupling of bridgehead protons in DMSO-d_6 at 40°.

In a parallel series of experiments, the pmr spectra of (NOR)Rh(S–DBM) and (COD)Rh(S–DBM) in dimethyl sulfoxide-d_6 solutions were recorded. In both cases protons H_A and H_B had averaged at 40° (Figure 1c). Spin decoupling of the bridgehead protons in (NOR)Rh(S–DBM) resulted in a sharp doublet for the H_A–H_B averaged resonance due to the ^{103}Rh coupling (J_{Rh-H} = 1 Hz.; Figure 1d). The rearrangement there-

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[11] Assuming an activation energy of 19 kcal mol^{-1} (*vide infra*), a tenfold decrease in concentration would produce a spectrum equivalent to that of the concentrated sample 33° lower in temperature, if $\tau(H_A)^{-1}$ were proportional to the complex concentration.

[12] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966), and references cited therein.

[13] This argument is predicated on the assumption that DBM would be at least as kinetically labile as S–DBM.

[14] More accurate values for the lifetimes, and thus the activation energies, are being obtained by computer simulation of the temperature dependence of the pmr spectra, and will be reported at a later date.

[15] Although the actual spatial relationships of the metal and ligand atoms in the three mechanisms cited here are very similar, one can distinguish them by the different coordination numbers of the rhodium species involved in the rate-determining step.

[16] E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 4115 (1969).

[17] The geometry commonly postulated for solvent attack on a planar molecule, in which the incoming ligand occupies an equatorial coordination site in the transition state,[18] would not average H_A and H_B without one or more polytopal rearrangements of the resulting intermediate.

[18] See, for example, C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 19.

[19] Recently a tetrahedral intermediate was considered as a possibility for a thermal *cis–trans* rearrangement in a Pt(II) complex.[20] Planar (S = 0)–tetrahedral (S = 1) equilibria are known to occur in certain bis-chelate complexes of Co(II) and Ni(II).[21]

[20] R. Ellis, T. A. Weil, and M. Orchin, *J. Amer. Chem. Soc.*, **92**, 1078 (1970).

[21] D. H. Gerlach and R. H. Holm, *ibid.*, **91**, 3457 (1969), and references cited therein.

[22] The relatively large errors in the present E_a values make it impossible at present to distinguish small differences in the two solvents.[14]

[23] K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometal. Chem.*, **15**, 195 (1968).

fore must be intramolecular. Rapid *cis–trans* exchange was also observed in deuteriochloroform solutions of (NOR)Rh(S-DBM) to which varying amounts of DMSO were added. Careful line-shape measurements at −36° indicated the rearrangement to be first order in added DMSO. It thus may be concluded that in the presence of the donor molecule DMSO, either as a solvent or added ligand, the intramolecular rearrangement of (diolefin)Rh(S-DBM) complexes proceeds *via* a five-coordinate intermediate. On the basis of the present evidence, however, it is not possible to distinguish among mechanisms 1, 2, and 3 in the solvents which are, at best, poor nucleophiles.

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Addition Reactions on Coordinated Olefinic Ligands. III. *trans* Addition of a Nucleophile to a Platinum(II) Coordinated Simple Olefin

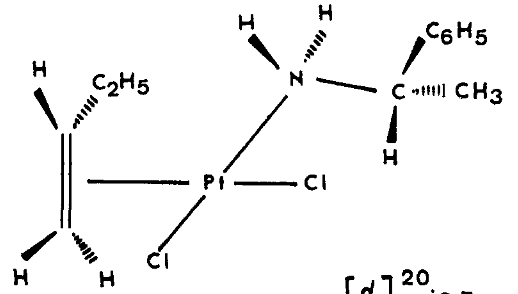
Sir:

It is well known[1] that coordination to platinum-group metals yields simple unsaturated hydrocarbons susceptible to attack by nucleophiles. Studies of the mechanism of this type of reactions have been carried out, mainly on catalytic systems.[2] Noncatalytic processes have also been reported and observations on the mechanism presented[3] in some cases. A double role has been generally attributed to the metal,[4] which is assumed to activate *both* the unsaturated substrate and the nucleophile, *via* coordination.

In fact, kinetic results[5] for the oxidative hydrolysis of simple olefins are consistent with *cis* addition to the unsaturated ligand of a precoordinated nucleophile. Furthermore, the presence of the nucleophile as a ligand in a rearranging intermediate is in accord with the general observation, recently pointed out,[6] that coordination should assist a reaction in which a nucleophilic reagent attacks a ligand.

On the other hand, no coordination of the nucleophile is involved when the reacting substrate is a diene complex: the stereochemical pattern of some of the reactions has been investigated[7] and the *exo* configuration[8] of the reaction products gave unambiguous evidence for a *trans*-addition mechanism. This difference in behavior between diene and simple olefin complexes has been discussed[9,10] on steric grounds.

It has been shown[11,12] in a previous study on the reactivity of coordinated olefins that stable alkyl derivatives are formed upon addition of ammonia and amines to Pd(II) and Pt(II) diene complexes and monoolefin Pt(II) complexes. It has been found[11] that the reaction of an amine with a diene complex involves a *trans* addition, which utilizes the same steric pathway as the nucleophilic attacks quoted in ref 7. In the present investigation we examined the analogous reaction of diethylamine and ammonia with a resolved diastereoisomeric complex of a prochiral α olefin,[13] *i.e.*, of a substrate in which only one of the two nonsuperimposable faces of the unsaturated ligand is coordinated to the metal.



I $[\alpha]^{20}_{D}$ +2.7 c 0.1, acetone

The complex, (+)-*cis*-dichloro[(*S*)-1-butene][(*S*)-α-methylbenzylamine]platinum(II), $[\alpha]^{20}\text{D}$ +2.7° (*c* 0.1, acetone), was prepared by a procedure similar to that described[13] for the analogous propylene complex and resolved by consecutive fractional crystallization from acetone until constant rotation was obtained.

Anal. Calcd for $C_{12}H_{19}NCl_2Pt$: C, 32.51; N, 3.16; Pt, 44.01. Found: C, 32.72; N, 3.19; Pt, 44.32.

Assignment of the absolute configuration to the coordinated 1-butene has been made on the basis of a previous X-ray analysis[14] on an analogous diastereoisomeric complex and of the CD spectrum of I, which is reported in Figure 1. More precisely the assignment was made on the basis of the sign of the 27,000-cm^{-1} band, which has been correlated[15] to the configuration of the coordinated olefin.[16] The reaction of diethyl-

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[1] See, as early reports (a) J. Smidt, W. Hafner, R. Jira, and J. Sedlmeier, *Angew. Chem.*, **71**, 176 (1959); (b) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); (c) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961); (d) J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

[2] See, for a review, J. Halpern, *Advan. Chem. Ser.*, No. **70**, 1 (1968).

[3] (a) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961); (b) E. W. Stern, *ibid.*, 111 (1963); (c) J. Tsuji and K. Ohno, *Advan. Chem. Ser.*, No. **70**, 155 (1968), and references therein; for hydride attack on an iron π complex, see M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

[4] This is certainly the case in the reactions which involve a *cis* ligand insertion mechanism, see P. Cossee, *Recl. Trav. Chim. Pays-Bas*, **85**, 1151 (1966).

[5] For a review, see P. M. Henry, *Advan. Chem. Ser.*, No. **70**, 126 (1968).

[6] M. M. Jones, "Ligand Reactivity and Catalysis," Academic Press, New York, N. Y., 1968, pp 84–85.

[7] (a) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966); (b) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967); (c) L. I. Dahl and W. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965); (d) W. A. Whitla, H. M. Powell, and M. L. Venanzi, *Chem. Commun.*, 310 (1966); (e) J. K. Stille and D. B. Fox, *Inorg. Nucl. Chem. Lett.*, **5**, 157 (1969).

[8] Only in one case has a *cis* addition been reported, see C. B. Anderson and B. J. Burreson, *Chem. Ind.* (London), 620 (1967).

[9] B. L. Shaw, *Chem. Commun.*, 464 (1968).

[10] F. R. Hartley, *Nature*, **223**, 615 (1969).

[11] R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **91**, 3874 (1969), part I in the series.

[12] A. Panunzi, A. De Renzi, R. Palumbo, and G. Paiaro, *ibid.*, **91**, 3879 (1969), part II in the series.

[13] A. Panunzi and G. Paiaro, *ibid.*, **88**, 4843 (1966), and literature cited therein.

[14] E. Benedetti, P. Corradini, and C. Pedone, *J. Organometal. Chem.*, **18**, 203 (1969).

[15] (a) P. Corradini, G. Paiaro, A. Panunzi, S. F. Mason, and G. H. Searle, *J. Amer. Chem. Soc.*, **88**, 2863 (1966); (b) E. Premuzic and A. I. Scott, *Chem. Commun.*, 1078 (1967); (c) A. D. Wrixon, E. Premuzic, and A. I. Scott, *ibid.*, 639 (1968); (d) A. I. Scott and A. D. Wrixon, *ibid.*, 1184 (1969).

[16] Data from a X-ray analysis on the complex I confirm the absolute