The rate-determining step of the Ramberg–Bäcklund rearrangement[15] and related cyclopropane forming addition–eliminations[16] may present such cases. In the former reaction an intramolecular S_N2 displacement leads to episulfone formation, with the less stable product preferentially formed. Here again reasonable alternative rationalizations have been proposed.[15,17]

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(14) Several such reactions have been discussed by M. Schlosser, who stresses a fundamental contrathermodynamic trend in carbon-carbon linking reactions: *Bull. Soc. Chim. Fr.*, 455 (1971); *Top. Stereochem.*, **5**, 1 (1970).

(15) N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966). Reviewed by F. G. Bordwell in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, p 271, and by L. A. Paquette in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, p 121.

(16) L. L. McCoy, *J. Amer. Chem. Soc.*, **80**, 6568 (1960); **82**, 6416 (1962); **84**, 2246 (1964); M. Mousseron, R. Fraise, R. Jacquier, and G. Bonavent, *C. R. Acad. Sci.*, **248**, 1465 (1959).

(17) L. A. Paquette, *Accounts Chem. Res.*, 1, 211 (1968); D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 253

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A Direct Proton Magnetic Resonance Study of Hydrogen Bond Formation of Organic Lewis Acids with Triethylamine

Sir:

The concept of the hydrogen bond has been widely applied to many chemical and biological systems, and consequently it has been the object of extensive discussion and review.[1] Several workers recently determined thermodynamic quantities for hydrogen bond formation in numerous Lewis acid–base mixtures by calorimetric,[2–7] infrared,[2,3,5,6,8–10] and fluorine-19 nmr[9–12] techniques. The enthalpies and equilibrium constants for hydrogen bond formation which they measured now provide a more quantitative basis for discussion of this process. For other acid–base systems, it has been demonstrated in these laboratories that at temperatures in the range of −100°, ligand and proton exchange can be slowed sufficiently to permit the observation of separate pmr signals for bulk ligand and ligand molecules bound to diamagnetic cations[13–15] and the boron trihalides.[16–18] We have extended this method to acid–base systems in dilute solution and now wish to report the direct observation of a pmr signal for hydrogen nuclei involved in a hydrogen bond. This contrasts with the usual chemical shift studies of exchange averaged pmr signals.

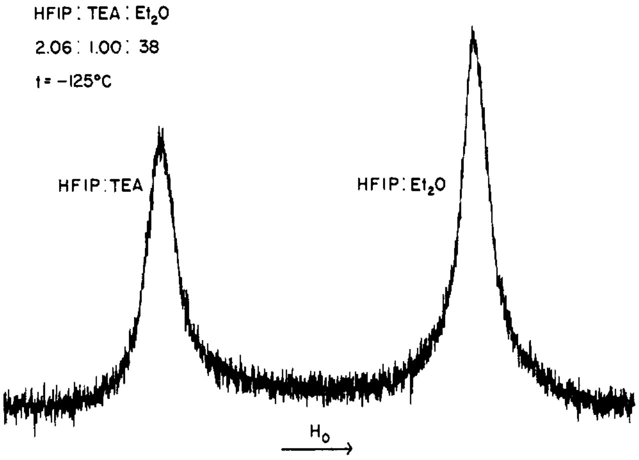

Figure 1. The proton magnetic resonance spectrum of the hydroxyl group of 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) in a mixture of this compound with triethylamine (TEA) in excess diethyl ether (Et_2O). The spectrum was recorded on a Varian HA-100 nmr spectrometer. The species responsible for the signals and the mole ratios of all components are shown in the diagram.

The alcohol portion of the room temperature pmr spectrum of a 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP)–triethylamine (TEA) mixture in a large excess of ether consists of a hydroxyl group singlet positioned ~7 ppm downfield from TMS and a multiple pattern for the 2-carbon hydrogen, split by the six fluorine neighbors. As the sample is cooled, the hydroxyl signal shifts far downfield, broadens extensively, even disappearing into the base line, and below −110°, it separates into two distinct peaks. The hydroxyl group signals for one of these mixtures, recorded at −125° on a Varian HA-100 spectrometer, are shown in Figure 1. Analogous spectra were obtained with all solutions listed in Table I. Since the presence of water is precluded by the drying and purification procedures,[19] the two signals in Figure 1 can be attributed to the hy-

(1) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960.

(2) E. M. Arnett, T. S. S. R. Murty, P. v. R. Schleyer, and L. Joris, *J. Amer. Chem. Soc.*, **89**, 5955 (1967).

(3) E. M. Arnett, L. Joris, E. Mitchell, T. S. A. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *ibid.*, **92**, 2365 (1970).

(4) E. M. Arnett and E. J. Mitchell, *ibid.*, **93**, 4052 (1971).

(5) K. F. Purcell, J. A. Stikeleather, and S. D. Brunk, *ibid.*, **91**, 4019 (1969).

(6) R. S. Drago, N. O'Bryan, and G. C. Vogel, *ibid.*, **92**, 3924 (1970).

(7) R. S. Drago, G. C. Vogel, and T. E. Needham, *ibid.*, **93**, 6014 (1971).

(8) D. F. DeTar and R. W. Novak, *ibid.*, **92**, 1361 (1970).

(9) J. Mitsky, L. Joris, and R. W. Taft, *ibid.*, **94**, 3442 (1972).

(10) R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *ibid.*, **91**, 4801 (1969).

(11) D. Gurka, R. W. Taft, L. Joris, and P. v. R. Schleyer, *ibid.*, **89**, 5957 (1967).

(12) D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969).

(13) A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *J. Chem. Phys.*, **47**, 4951 (1967).

(14) A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *ibid.*, **48**, 3705 (1968).

(15) A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *Inorg. Chem.*, **10**, 2552 (1971).

(16) A. Fratiello, T. P. Onak, and R. E. Schuster, *J. Amer. Chem. Soc.*, 90, 1194 (1968).

(17) A. Fratiello and R. E. Schuster, *Inorg. Chem.*, 11, 11 (1972).

(18) A. Fratiello and R. E. Schuster, *J. Org. Chem.*, 37, 2237 (1972).

(19) PFP was sublimed, the other reagents were dried over CaH_2 or $CaSO_4$, and all samples were prepared *in vacuo*.

Table I. Proton Magnetic Resonance Chemical Shift, Integration, and Kinetic Data for Lewis Acid–Base Hydrogen-Bond Complexes

Mole ratios		OH, δ, ppm[b]		Complex mole ratio	$\Delta H^{\ddagger}$,
Acid:base:solvent[a]	T, °C	Coordinated	Bulk[c]	Acid:base	kcal/mol
HFIP:TEA:Me$_2$O					
2.10:1.00:37	−135	12.85	10.80	0.9:1.0	14
HFIP:TEA:Et$_2$O					
3.10:1.00:13	−120	12.96	9.35	1.0:1.0	
2.71:1.00:29	−125	12.55	9.14	1.1:1.0	
2.06:1.00:38	−125	12.65	9.15	1.0:1.0	18
PFP:TEA:Et$_2$O					
1.95:1.00:34	−130	12.20	9.17	1.1:1.0	
2.02:1.00:39	−125	12.11	9.30	1.0:1.0	

[a] HFIP = 1,1,1,3,3,3-hexafluoroisopropyl alcohol; TEA = triethylamine; Me$_2$O = dimethyl ether; Et$_2$O = diethyl ether; PFP = *p*-fluorophenol. [b] Chemical shifts were measured with respect to internal TMS. [c] The hydroxyl group signals arising from the TEA and ether adducts of the acids are designated as "coordinated" and "bulk" signals, respectively.

droxyl group of HFIP molecules in different electronic environments.

The pmr concentration and area results of Table I indicate that the low-field signal in Figure 1 (and in analogous spectra for the other acid–base combinations listed) is due to the alcohol–TEA adduct and that at higher field arises from the remaining alcohol molecules hydrogen bonded to the ether. As seen in Table I signal areas showed that 1:1 complexes were formed in each system. At 1:1 mole ratios of Lewis acid to TEA, only the low-field signal was observed and at higher mole ratios the additional "bulk" proton signal became apparent. The calorimetric and spectroscopic studies of these systems indicate that at +25° complex formation is not complete,[2,3,5,11,12] but using their thermodynamic data, the equilibrium constants at −125° would be increased by several orders of magnitude. Thus, complete complexing of the base would be expected in these solutions.

Using only pmr methods, it has not been possible to determine whether the TEA–acid adduct in these systems is a hydrogen-bonded complex, $B\cdots HA$, or an ion pair, $BH^{+}\cdots A^{-}$, resulting from complete proton transfer. The absence of N–H spin coupling could result from quadrupole relaxation, and it is not sufficient to rule out a proton-transfer process. For comparison to solutions of Table I, attempts were made to generate an R_3NH^{+} cation in solution by dissolution of trialkylammonium salts or by the protonation of TEA with trichloroacetic acid. The fact that these attempts were unsuccessful because of solubility limitations may itself be evidence that the dominant process observed in the soluble systems of this study is hydrogen bonding.

Recent ir and calorimetric data on TEA interactions with HFIP and PFP, in solvents of low dielectric constant, have been interpreted in terms of hydrogen bonding.[2,3,5,7,10–12] Extensions of these ir measurements to mixtures of TEA with the much stronger acetic and benzoic acids[8] have led to a similar conclusion in contrast to earlier studies of these systems for which an ion-pairing mechanism was postulated.[20] Since none of these studies were carried out in ether, several ir experiments were made in these laboratories on HFIP–TEA mixtures in this solvent, at concentrations comparable to those shown in Table I.

The infrared spectra were recorded on a Beckman IR-12 double-beam grating spectrophotometer using 0.015-mm, sealed KBr liquid cells. This short absorption path was necessary to avoid having the region in which the triethylammonium cation NH^{+} stretch absorbs (2700 cm^{-1}), obscured by solvent absorption. Under these conditions hydrogen-bonded OH and OD stretching bands were easily identifiable as broad, moderately intense features at 3260 and 2420 cm^{-1}, respectively. No features attributable to the NH^{+} stretching motion of the triethylammonium cation or the CO^{-} stretching motion of the hexafluoroisopropoxide anion were observed in these solutions. Thus, the infrared evidence indicates that hydrogen bonding is the dominant process in these HFIP–TEA mixtures at 25°.

Finally, the ^{19}F nmr method developed by Taft[9–12] for investigating acid–base interactions was applied to a study of the *p*-fluorophenol (PFP)–TEA combination in ether.[21] It has been demonstrated that the ^{19}F nucleus in PFP and other acids is an extremely sensitive probe to interactions at the hydroxyl functional group. For example, the formation of the *p*-fluorophenoxide ion in solution by complete proton transfer causes a ^{19}F nmr chemical shift displacement of 14 ppm from the position observed with PFP.[11] The much smaller ^{19}F chemical shifts ($\sim$2 ppm) exhibited by PFP in the presence of a variety of bases indicate that the hydroxyl proton is involved in weaker, hydrogen-bond interactions.[9–12] As applied to one of the combinations of this study, solutions containing TEA, PFP, and ethyl ether in 0.5:1:30 and 1:1:30 mole ratios gave a ^{19}F chemical shift displacement of 0.8 and 1.3 ppm, respectively, at −110°, relative to 1:30 mole ratio mixture of PFP to ether.[21] These small shifts result from a hydrogen-bonding interaction with proton transfer possibly occurring only to a small extent, perhaps $\sim$10%. Since the concentration and temperature of the ^{19}F nmr measurements closely approximate those reported in Table I, the conclusion can be drawn that the proton nmr data also reflect a hydrogen-bonding process.

Although hampered by low signal intensities, the unknown contribution of viscosity broadening, and a small temperature range over which measurements could be made, approximate exchange data were obtained for HFIP–TEA in dimethyl ether and diethyl

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(20) G. M. Barrow and E. A. Yerger, *J. Amer. Chem. Soc.*, 76, 5211 (1954).

(21) The ^{19}F nmr measurements reported here were carried out by Professor R. W. Taft at the University of California, Irvine. The authors are grateful to Dr. Taft for these experimental results and for helpful discussions concerning this paper.

ether by the usual line width technique. The approximate activation enthalpies shown in Table I are similar to the 15–20 kcal/mol generally observed for ligand exchange from cation solvation shells[22–24] and larger than the 6–10 kcal/mol measured for proton exchange, for instance, in aqueous methylammonium ion,[25] $AlCl_3$,[24,26] and imidazolium ion[27] solutions.

Similar pmr spectral measurements have been possible for other systems, including acetic acid, diethylamine, and pyridines, and attempts are being made to expand this list still further.

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[22] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 40, 2686 (1964).

[23] A. Fratiello, D. P. Miller, and R. E. Schuster, *Mol. Phys.*, 12, 111 (1967).

[24] S. Thomas and W. L. Reynolds, *Inorg. Chem.*, **9**, 78 (1970).

[25] E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, 27, 630 (1957).

[26] D. W. Fong and E. Grunwald, *J. Amer. Chem. Soc.*, **91**, 2413 (1969).

[27] E. K. Ralph and E. Grunwald, *ibid.*, 91, 2422 (1969).

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A New Aromatic Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes[1]

Sir:

We have discovered a new type of metalated derivative formed in the reaction of $Ph_2P\text{-}C_6H_4\text{-}Mn(CO)_4$ (**1**)[2] with *cis*-$CH_3M(CO)_4L$ (M = Mn, L = PPh_3, **2**; M = Mn, L = CO, **3a**; M = Re, L = CO, **3b**). A solution of **1** (0.10 g, 0.23 mmol) and **2** (0.20 g, 0.45 mmol) in toluene (5 ml) is refluxed under nitrogen for 2 hr during which time the latter reagent is consumed as monitored by ir absorptions in the carbonyl-stretching region. The solvent is removed by water aspirator and the solids are redissolved in hexane for chromatography (silica gel, 20 mm diameter column, ×40 cm). Elution first with hexane and then with increasing quantities of added benzene up to 25% by volume reveals six bands of which the second proves to be a yellow-orange substance, air-stable in the solid, recrystallized from ether–hexane at −20°, $C_{44}H_{28}Mn_2O_8P_2$ (**4**).[3] The yield varies from 15 to 25% (based on **2**) depending on the reaction conditions.[4] The other products obtained are discussed below.

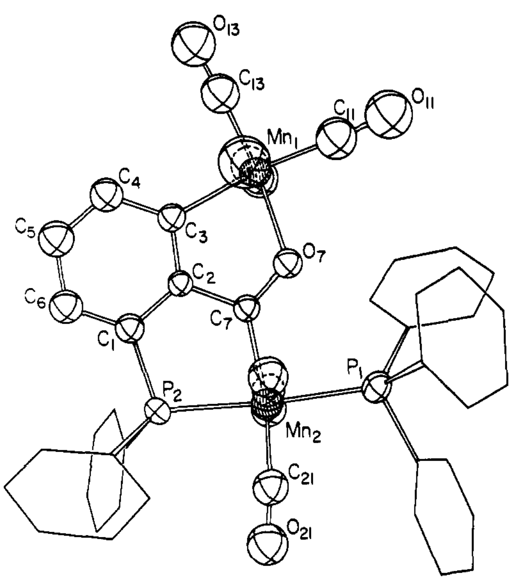

Figure 1. The structure of $Ph_2P\text{-}[C_6H_3(CO)(Mn(CO)_4)]\text{-}Mn(CO)_3PPh_3$ (**4**) projected onto the plane defined by Mn(1), Mn(2), and P(2). There are two axial CO groups, one above and one below each of the two Mn atoms, appearing greatly foreshortened in the present perspective. The bond angles and distances are within expected limits. Some selected values are given as follows: C(3)–Mn(1), 2.03 Å; Mn(1)–O(7), 2.05 Å; O(7)–C(7), 1.27 Å; C(7)–Mn(2), 2.03 Å; C(3)–Mn(1)–O(7), 80°; C(2)–C(7)–O(7), 112°; P(2)–Mn(2)–C(7), 82°.

A set of X-ray diffraction data was collected for a suitable crystal of **4**[5] on a Syntex $P\bar{1}$ automated diffractometer using graphite monochromated Mo Kα radiation. A θ–2θ scan was employed at a programmed rate varying from 2.4 to 24 deg/min from the weakest to the strongest reflections. Lorentz and polarization corrections were applied but no absorption corrections were required for the crystal of the dimension 0.18 × 0.22 × 0.24 mm for which the maximum effect on F due to absorption is ±3.5% (μ = 8 cm^{-1}). The structure was solved by the standard Patterson, Fourier, and difference-Fourier techniques. All 56 nonhydrogen atoms have been located. Least-squares refinement (in which thermal parameters for manganese and phosphorus were allowed to refine anisotropically) has resulted in a discrepancy index of R = 7.0% for 2518 independent nonzero reflections. Refinement is continuing.

The structure is shown in Figure 1. The coordination geometry around the manganese atoms is near-octahedral while that around the phosphorus atoms is tetrahedral. All of the labeled atoms form an extended coplanar system in which the deviation from the

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[1] Work supported by National Science Foundation (NSF) Grant No. 2367X2. Departmental instruments used in this work were supported as follows: nmr spectrometers, Varian A-60 and HA-100D, E. I. du Pont de Nemours and Co., Stauffer Chemical Co., Union Carbide Corp., and NSF Grants No. G20207 and GP 8223; Beckman IR-4, E. I. du Pont de Nemours and Co.; AEI MS9 mass spectrometer, NSF Grant No. GP 3672; Syntex $P\bar{1}$ automated diffractometer, NSF Grant No. GP 28248.

[2] (a) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **93**, 536 (1971); (b) R. Hoxmeier, Dissertation, University of California, Los Angeles, 1972.

[3] *Anal.* (Heather King, UCLA) Calcd: C, 61.68; H, 3.29. Found: C, 61.65; H, 3.46. Mass spectrum: Parent ion obsd *m/e* 856 (calcd 856). The first significant fragmentation ion at *m/e* 772 showing loss of three CO's followed by fragmentation ion peaks showing loss of four through eight CO's. Ir, metal carbonyl absorptions (hexane) (cm^{-1}): 2074 (m), 2024 (w), 1992 (vs), 1984 (s, shoulder), 1946 (vs), 1935 (vs), 1926 (shoulder).

[4] The formation of the new metalation product is favored in concentrated solution and in some cases optimized in the reaction of the molten solids at 140–150°.

[5] Crystals of **4** were found to belong to the centrosymmetric monoclinic space group C_2/c ($2/m$, no. 15), Z = 8. Unit cell data are a = 10.763 (2) Å, b = 34.713 (5) Å, c = 21.479 (3) Å, β = 92.93 (1)°, and V = 8014 Å^3; ρ_{obsd} = 1.44, ρ_{calcd} = 1.42.