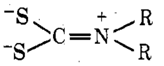
mental scramblings shown for the T isomer by eq 2,

$$\underset{\text{trans }\Lambda}{\begin{bmatrix}1\text{-a}\\1'\text{-b}\\2\text{-c}\\2'\text{-d}\\3\text{-e}\\3'\text{-f}\end{bmatrix}} \overset{\text{pseudo } C_3}{\rightleftarrows} \underset{\text{trans }\Delta}{\begin{bmatrix}1\text{-f}\\1'\text{-e}\\2\text{-d}\\2'\text{-c}\\3\text{-b}\\3'\text{-a}\end{bmatrix}} \qquad (2)$$

where numbers and primed numbers designate methylene protons and letters designate the different environments. *All* six methylene resonances from the T isomer will coalesce into three (pairwise averagings a–f, b–e, and c–d) and the two C resonances (a and b) will coalesce into one. This predicts eight resonances for the slow-exchange limit which will *all* simultaneously coalesce into four resonances in the fast-exchange limit. A similar analysis for pathway (ii) predicts that of the eight resonances observed in the slow-exchange limit, only two pairs will coalesce during exchange broadening.[24] Therefore, four resonances are unaffected by mechanism (ii). Figure 2, which shows eight peaks coalescing into four at −47°, is completely consistent with the trigonal-twist pathway. The LTP of I is unambiguously assigned as the rearrangement mode given by the trigonal-twist mechanism.

The same coalescence pattern has been observed for the methylene resonances of II in CD_2Cl_2 solution unambiguously establishing the trigonal-twist mechanism for this "Fe(III)" complex as well.[25] These mechanistic determinations are the only ones reported to date on tris-chelate complexes where direct dnmr evidence, without a complex computer analysis, has led to a unique result. A trigonal-twist mechanism has also been determined for $Fe(dtc)_2(S_2C_2R_2)$ complexes where $R = CF_3$ or CN by direct dnmr evidence; however, in these complexes pathway (ii) could not be definitely eliminated but was considered unreasonable because of steric considerations.[11,13] The present work supports this assignment.

The HTP is consistent with any mechanism which randomly scrambles all C and T environments. We have assigned this as S_2C–N bond rotation because of a comparison of the dnmr spectra to those of the corresponding "iron(III)" dtc complex. The barrier to the HTP is significantly greater in the cationic "iron(IV)" complexes which is consistent with an increased stabilization of resonance structure IV.[16,26] Infrared C–N stretching frequencies also show a 42-cm^{-1} increase on going from "iron(III)" to "iron(IV)."[27]



IV

Kinetic parameters for the trigonal twist cannot accurately be measured because the LTP was not completely frozen out. Approximate coalescence lifetimes indicate that the metal-centered rearrangement is faster for I than for II. Work on this aspect is currently in progress.

Experimental Section

Compound II was prepared by standard means and characterized by elemental analysis and nmr. Compound I was synthesized by bubbling BF_3 through a benzene solution of II for *ca.* 30 sec in a plastic beaker open to the air[16] and was was collected as a black oil which was purified several times by extracting with methylene chloride and oiling out by adding benzene. *Anal.* Calcd for $C_{27}H_{30}BF_4N_3S_6Fe$: C, 44.33; H, 4.13; N, 5.74. Found: C, 44.54; H, 3.94; N, 5.38. Infrared (KBr disk) bands in 1600–650-cm^{-1} region: 1539 vs, 1494 w, 1453 m, 1436 m, 1403 s, 1350 m, 1331 sh, 1300 vw, 1725 w, 1244 m, 1202 m, 1089 s, b, 1035 sh, 999 w, 950 sh, 925 sh, 878 w, 834 w, 811 vw, 753 m, 739 m, 701 s, 675 sh.

Nmr spectra were recorded on a Varian XL-100-15 spectrometer equipped with a variable-temperature probe. Temperatures were monitored by a thermocouple mounted in a nmr tube. Solid magnetic moments were measured by the Faraday method and solution moments were determined by the method of Evans.[28]

Acknowledgment.—We thank the Research Corp., the donors of the Petroleum Research Fund, and the University of Minnesota Graduate School for support of this work. We also acknowledge useful discussions with R. H. Holm and J. Musher.

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[24] Note that mechanism (ii) cannot scramble the diastereotopic methylene environments because this pathway does not result in inversion of configuration.

[25] L. H. Pignolet, B. L. Edgar, D. J. Duffy, and M. C. Palazzotto, in preparation.

[26] Detailed kinetic line shape analysis is in progress.

[27] This assignment is the opposite to the one made in ref 14. In light of this new result we also assign the HTP for III to S_2C–N bond rotation.

(28) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

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The Phosphorus–Phosphorus Bond. IV. A Temperature-Dependent Nuclear Magnetic Resonance Investigation of Tetrafluorodiphosphine–Borane, $F_2PPF_2 \cdot BH_3$

BY H. LESLIE HODGES AND R. W. RUDOLPH*

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The original characterization of tetrafluorodiphosphine–monoborane, $F_2PPF_2 \cdot BH_3$, suggested that rapid exchange of the BH_3 moiety between phosphorus atoms might be occurring since no P–B coupling was observed in the ^{11}B nmr spectrum.[1] In a recent report of the bisborane adduct, $H_3B \cdot F_2PPF_2 \cdot BH_3$, Paine and Parry suggest that there is no oscillation of the BH_3 group between phosphorus sites in the monoborane adduct.[2] In this note we present evidence which rules out both intramolecular and intermolecular borane exchange for the $F_2PPF_2 \cdot BH_3$ molecule from −100 to 0°.

It is clear from the present study that P–B coupling was not observed in the original investigation because spectra were not determined above −80°.[3] As shown in Figure 1, the 1:3:3:1 quartet of the ^{11}B spectrum first begins to sharpen considerably around −60°; incipient P–B coupling appears near −30° and is evident on each member of the quartet by 0°. The disappearance of P–B coupling might be consistent with intermolecular exchange of the BH_3 group, but not in this case, since the observed temperature dependence is opposite to that predicted. In the slow-exchange limit (low temperatures) the lifetime of the P–B bond would predictably be long and P–B coupling would be

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(1) K. W. Morse and R. W. Parry, *J. Amer. Chem. Soc.*, **89**, 172 (1967).

(2) R. T. Paine and R. W. Parry, *Inorg. Chem.*, **11**, 210 (1972).

(3) K. D. W. Morse, Ph.D. Dissertation, University of Michigan, 1966.

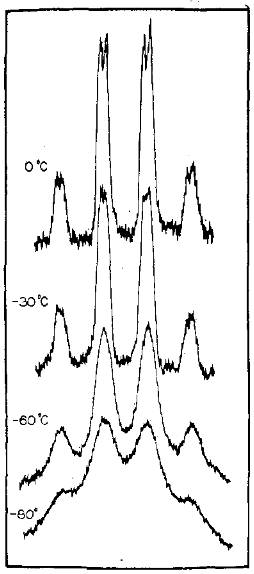

Figure 1.—The ^{11}B nmr spectra of $F_2PPF_2 \cdot BH_3$ as a function of temperature. The 1:3:3:1 quartet is centered 2.34 ppm from $(C_2H_5)_2O \cdot BF_3$ (external standard). Because of the quadrupolar broadening effects discussed in the text, the B–H coupling appeared to increase in magnitude with increasing temperature (95 at −80°, 101 at −60°, 104 at −30°, and 105 Hz at 0°). The P–B coupling is 13 Hz.

observable[4] in the absence of other effects. In the subject case the "other effect" responsible for loss of P–B spin–spin coupling is probably rapid spin-lattice relaxation induced by the quadrupolar boron nucleus. Recent detailed studies have shown a similar "thermal decoupling"[5] or "wash-out"[6] of B–H spin–spin coupling in various boron hydrides as the temperature is lowered. We also observe the loss of B–H coupling in $F_2PPF_2 \cdot BH_3$ at low temperatures which again points to the presence of a relaxation effect associated with boron and mitigates further against BH_3 exchange.

It should be noted that the observation of the P–B spin–spin doublet at "high temperatures" also rules out the alternative possibility of intramolecular borane exchange between the two phosphorus bonding sites in F_2PPF_2 regardless of the presence of quadrupolar relaxation. In the slow-exchange limit an intramolecular mechanism would maintain coupling with only one phosphorus atom giving rise to a doublet for the P–B coupling. In the rapid-exchange limit, spin–spin coupling with both phosphorus sites would be equal and a 1:2:1 triplet would be predicted for the P–B coupling feature of the boron spectrum. Since only doublet P–B coupling features are observed, and then only at "high temperatures," intramolecular borane exchange is slow in the temperature range of this study.

Fluorine nmr spectra give no evidence for either inter- or intramolecular exchange. For instance, mixtures of F_2PPF_2 and $F_2PPF_2 \cdot BH_3$ showed only the unshifted superpositioning of the component spectra. A $CFCl_3$ solution of $F_2PPF_2 \cdot BH_3$ (20 mol %) showed two distinct fluorine environments which were separated by 6.7 ± 0.2 ppm in the 0 to −100° temperature range.

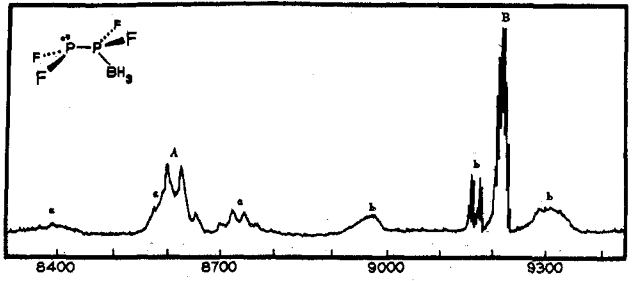

Figure 2.—The ^{19}F nmr downfield half-spectrum of $F_2PPF_2 \cdot BH_3$ (20 mol %) at −45° in $CFCl_3$. The peaks labeled with A and a constitute the half-spectrum of the PF_2 group coordinated to BH_3 as evidence by the breadth of peak A (quadrupolar broadening) and the magnitude of $^3J_{HF}$ = 26 Hz (1:3:3:1 quartet). By comparison, the half-spectrum of the uncoordinated PF_2 group is much sharper (peaks B and b) and B has a much smaller $^4J_{HF}$ = 4 Hz. Both half-spectra show $^3J_{FF}$ = 8 Hz. The result is a 1:3:3:1 quartet of 1:2:1 triplets for A, and because $^3J_{FF}$ is twice $^4J_{HF}$, overlap gives a 1:3:5:7:7:5:3:1 octet for B. The magnitudes of and relative signs of $^2J_{PF}$ and $^1J_{PF}$ are hidden in the second-order features of the spectrum (satellite peaks a and b). The entire spectrum can be generated quite well by reflection of the half-spectra through their midpoints at 9218 and 9798 Hz, respectively. The frequency scale represents hertz upfield from a $CFCl_3$ internal standard.

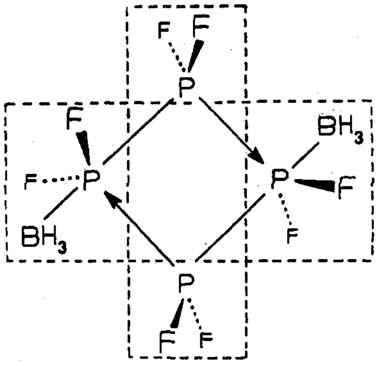

Figure 3.—A possible dimeric form of $F_2PPF_2 \cdot BH_3$. The dotted lines outline the portions of the molecule which are potential XX′AA′X″X‴ spin systems for P and F.

Although the spectra provide no evidence for rapid BH_3 exchange, they show several most interesting temperature-dependent features which are the subject of further investigation. The multiplet patterns are reminiscent of two overlapping XX′AA′X″X‴ spin systems (Figure 2), each similar in many respects to that found for F_2PPF_2.[7] Since a second-order spin system would not be anticipated for monomeric $F_2PPF_2 \cdot BH_3$, we explored the possibility of dimeric or other aggregate molecules in solution.[8] For instance, the dimer shown in Figure 3 might give two second-order spin systems. However, we now discount the possibility of a dimeric molecule on the basis of both low-temperature molecular weight studies in $CFCl_3$ and calculated nmr spectra. The ^{19}F (and ^{31}P) spectra are second order by virtue of the accidentally coincident chemical shifts for the two phosphorus environments. This unusual chemical shift feature was observed in the

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[4] For example, see typical $^1J_{PB}$ values in R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, **93**, 6821 (1971); A. H. Cowley and M. C. Damasco, *ibid.*, **93**, 6815 (1971).

[5] C. H. Bushweller, H. Beall, M. Grace, W. J. Dewkett, and H. S. Bilofsky, *ibid.*, **93**, 2145 (1971).

[6] T. J. Marks and L. A. Shimp, *ibid.*, **94**, 1542 (1972).

[7] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *ibid.*, **88**, 3729 (1966); F. A. Johnson and R. W. Rudolph, *J. Chem. Phys.*, **47**, 5449 (1967); R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, **92**, 1195 (1970).

[8] H. L. Hodges and R. W. Rudolph, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

^{31}P spectra and when taken into account leads to satisfactory calculated ^{19}F spectra.[9]

Experimental Section

Tetrafluorodiphosphine-Borane, $F_2PPF_2\cdot BH_3$.—It was found that when $F_2PPF_2\cdot BH_3$ was prepared by the method of Morse and Parry[1] using a twofold excess of B_2H_6, the product was always contaminated by a small amount of the bis adduct, $H_3B\cdot F_2PPF_2\cdot BH_3$, recently characterized by Paine and Parry.[2] The bis adduct was not easily removed by fractional distillation, and appeared to facilitate decomposition of the $F_2PPF_2\cdot BH_3$ in the liquid state. The best yields of the desired mono adduct were obtained when only a slight excess of B_2H_6 was used. In a typical run, 3.50 mmol of F_2PPF_2[10] and 1.88 mmol of B_2H_6 were condensed together at −196° in a 1000-ml reaction bulb, which was then allowed to warm slowly to 25°. After 12 hr the volatile products were collected at −196° and purified by passing through traps held at −97 and −196°. A 2.45 mmol sample of $F_2PPF_2\cdot BH_3$ (70% yield based on F_2PPF_2) was recovered from the −97° trap. The −196° trap contained unreacted B_2H_6, PF_3, and $PF_3\cdot BH_3$. The products were characterized by their infrared spectra. A small amount of unidentified, nonvolatile, pyrophoric yellow oil remained in the reaction bulb.

Spectra.—Known amounts of purified $CFCl_3$ and $F_2PPF_2\cdot BH_3$ were measured out as gases, condensed into nmr tubes, and the samples then sealed off *in vacuo*. Spectra were obtained in the −100 to 0° temperature range on a Varian instrument operating at 100, 94.1, 40.4, and 32.1 MHz for ^1H, ^{19}F, ^{31}P, and ^{11}B, respectively. The ^{19}F spectra were run with $CFCl_3$ as an internal lock signal. Spectra for the other nuclei were calibrated with audio side bands of known frequency.

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[9] The main features of the spectra can be fit with the computer program LAOCN3 [No. 111, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.] if H–F and B–F coupling features are neglected so that the system reduces to six spins. A comprehensive investigation of the fluorine spectra, including simplification by spin-decoupling, temperature dependence, and concentration dependence, is under further investigation.

[10] L. C. Centofanti and R. W. Rudolph, *Inorg. Syn.*, **12**, 282 (1969).

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Formation of Chlorine Dioxide by the Electrolytic Oxidation of Perchlorate Anion[1,2]

BY GARY E. GLASS*[3] AND ROBERT WEST

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Early studies using the electrolytic technique to produce radical chemical species employed perchlorate salts as electrolytes.[4,5] Oxidative electrolysis of those solutions yielded transient esr signals which were assigned to the perchlorate radical.[4,5] In this note we report the identification of chlorine dioxide by low-temperature esr and uv spectra as the reaction product resulting from the electrolytic oxidation of perchlorate salts in ethereal solutions.

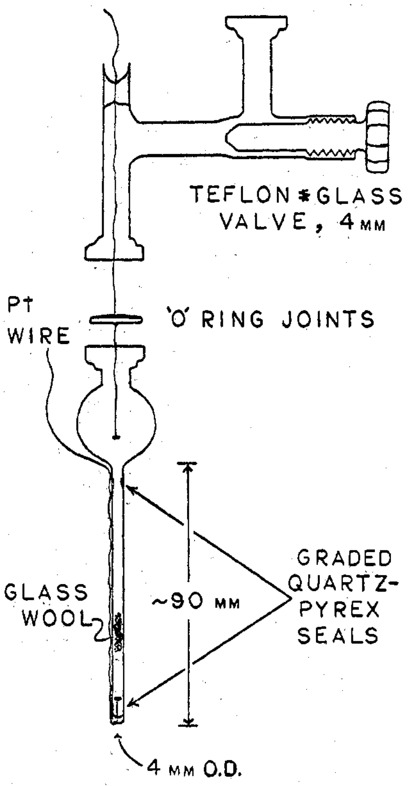

Figure 1.—Electrolytic cell for variable-temperature esr and electronic spectral measurements.

Experimental Section

Electrolysis Cell.—Electrolysis was carried out directly in the esr cavity or in the light path using the cell shown in Figure 1. The cell design allows both variable temperature esr and electronic spectral measurements to be made on either the anodic or cathodic compartments. Several milligrams of electrolyte, sodium perchlorate, or tetra-*n*-butylammonium perchlorate was placed in the mixing bulb and the cell assembled with a brass clamp. The electrolytic cell was then evacuated to $<10^{-4}$ Torr and solvent, tetrahydrofuran, dimethyl ether, or tetrahydrofuran–dimethoxyethane distilled into the mixing bulb. The glass wool plug separates the two electrolysis chambers and prevents connection. The cell was kept at constant temperature in a quartz dewar insert attached to a Varian V-4557 variable-temperature controller. The electrolysis cell is operated at a constant current, 0–40 μA, using a simple voltage divider, 300 V battery, and a microammeter.

Esr Spectra.—A Varian V-4502-13 spectrometer utilizing 100 kc modulation was used to observe the esr spectra. A dual cavity was used with a water solution of peroxylaminedisulfonate anion to record simultaneously spectral *g*-value calibrations. *g* values are believed accurate to ±0.00004 G. Coupling constants were determined on an X-Y recorder calibrated using tetracene radical cation and values reported by Carter and Vincow.[6] Line-sharpened spectra were obtained using the method according to Glarum[7] by adding partial third-derivative character to the first-derivative signal. This technique significantly decreased the amount of overlap in the recorded spectra and allowed more accurate determination of line positions.

Electronic Spectra.—A Cary 14 spectrometer was modified so that the quartz dewar insert attached to a Varian variable-temperature accessory could be inserted into the light path of the sample compartment.

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[1] Presented at the 157th National American Chemical Society Meeting, Minneapolis, Minn., April 1969.

[2] This work was supported by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. AF-AFOSR 1061-66.

[3] Author to whom correspondence should be addressed at the National Water Quality Laboratory, Duluth, Minn. 55804.

[4] A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959); *J. Amer. Chem. Soc.*, **82**, 2671 (1960).

[5] G. Cauquis and D. Serve, *C. R. Acad. Sci.*, **262**, 1516 (1966).

[6] M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 292 (1967).

[7] S. H. Glarum, *Rev. Sci. Instrum.*, **36**, 771 (1965).