alkylphosphine vibrations are based on data compiled by Corbridge[6] and by Beattie and Collis.[7] The Ti–P stretching vibration for $TiCl_4 \cdot P(C_6H_5)_3$ was assigned to a 463-cm^{-1} band.[8] This vibration occurs between 410 and 320 cm^{-1} for the $TiCl_3$–alkylphosphine adducts. The frequency of the Ti–P stretch decreases as the size of the phosphine molecule increases. For each of the alkylphosphine complexes a second strong band 15–35 cm^{-1} below the Ti–P stretch shows a similar decrease in frequency with increasing ligand size. This band is probably due to a complex Ti–Cl, Ti–P vibration. The methylphosphine adducts show a third band in the 335–295-cm^{-1} region which is most probably a Ti–Cl stretching vibration.

TABLE II

SUMMARY OF VISIBLE SPECTRA FOR TITANIUM(III) CHLORIDE–ALKYLPHOSPHINE ADDUCTS IN TOLUENE AT ROOM TEMPERATURE

Phosphine	Phosphine: $TiCl_3$ mole ratio	Soln color	λ_1, nm	λ_2, nm
$(CH_3)PH_2$	3	Yellow-brown	497 ($\epsilon \sim 35$)	
$(CH_3)_2PH$	3	Blue-green	565^a	660^a
$(CH_3)_3P$	3	Yellow-brown	570^b	650^b
$(C_2H_5)_3P$	3	Green-brown	470^c	610^c

[a] Relative band intensity $A_{565}:A_{660} = 1.0$. [b] Relative band intensity $A_{570}:A_{650} = 1.2$–1.3. [c] Relative band intensity $A_{470}:A_{610} = 1.1$.

TABLE III

INFRARED SPECTRAL ASSIGNMENTS FOR TITANIUM(III) CHLORIDE–ALKYLPHOSPHINE ADDUCTS (CM^{-1})

Assignment	$(CH_3)PH_2$	$(CH_3)_2PH$	$(CH_3)_3P$	$(C_2H_5)_3P$
C–H asym def	1415 m	1420 m	1425 s	1410 s
	1300 sh			
C–H sym def	1295 m	1298 m	1305 s	1270 m, br
	1265 m	1285 m	1290 s	
	1090 sh	1095 w	1090 w	1100 s, br
H–P–C def	1075 s			
CH_3 rock				1050 vs
	995 m	1000 sh		
H–P–C def		985 vs		
CH_3 rock	965 vs	955 vs	955 vs	965 m
	855 w	840 m	840 w	870 s, br
	805 w	790 w	785 w	
	755 w	745 m		
P–C str	720 s	730 m	735 s	765 vs, br
C–C str				740 sh
Ti–P str	410 s	375 vs	370 vs	320 vs
	400 s, sh			
Ti–Cl or Ti–P str	375 s	350 s	340 s	305 vs
Ti–Cl str	335 s	312 s	295 m	
	298 s			

An X-ray crystallographic study of single crystals of $TiCl_3 \cdot 2PH(CH_3)_2$ is in progress.

Acknowledgment.—The financial support of the National Science Foundation, Grant GP-11526, the assistance of Dr. Peter Nassiff with epr measurements, and the assistance of Mr. Thomas Ballintine with molecular weight measurements are gratefully acknowledged.

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[6] D. E. C. Corbridge, *Top. Phosphorus Chem.*, **6**, 323, 345 (1969).

[7] I. R. Beattie and R. Collis, *J. Chem. Soc. A*, 43 (1969).

[8] A. D. Westland and L. Westland, *Can. J. Chem.*, **43**, 426 (1965).

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Intramolecular Rearrangement Reactions of Tris(*N*-methyl-*N*-benzyldithiocarbamato)-iron(IV) Tetrafluoroborate by Proton Magnetic Resonance

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The determination of mechanisms for intramolecular metal-centered rearrangement reactions of tris-chelate complexes has always been an important problem in inorganic chemistry.[1] Recent interest has been sparked by the use of dynamic nmr (dnmr) spectroscopy in the elucidation of such mechanisms. Several reviews of this topic have recently appeared.[2] The majority of the dnmr investigations have dealt with diamagnetic tris-bidentate-chelate complexes of trivalent metals such as Al, Ga, In, and Co.[3–9] In some of these cases mechanisms of isomerization reactions were sought by computer analysis of complex coalescence patterns.[3,5] The analyses were elegantly performed and in one case a unique mechanism was derived.[3] Paramagnetic complexes which manifest the isotropic shift phenomenon offer the added advantage of nonlinearly magnifying chemical shift differences between similar but magnetically nonequivalent nuclei.[10] Several dnmr investigations on paramagnetic tris-chelate systems have appeared[11–15] and in three cases mechanistic information was inferred.[11a,13,14] In these cases a computer analysis was unnecessary in determining the mechanism because all nonequivalent nuclei were resolved and the isomerization pathway was elucidated from the coalescence pattern alone.

We report here the first dnmr investigation of a tris-chelate complex of iron in the "IV" formal oxidation state: tris(*N*-methyl-*N*-benzyldithiocarbamato)-iron tetrafluoroborate, $[Fe(MeBz(dtc))_3]BF_4$ (I). This complex was prepared by air oxidation of $Fe(MeBz(dtc))_3$ (II) in the presence of BF_3. Pasek and Straub[16] recently reported this oxidation and characterized a series of compounds as cationic "iron(IV)"

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 300–334.

[2] (a) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971); (b) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, in press.

[3] S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 6411 (1972).

[4] S. S. Eaton and R. H. Holm, *ibid.*, **93**, 4913 (1971).

[5] J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

[6] B. Jurado and C. S. Springer, Jr., *Chem. Commun.*, 85 (1971).

[7] E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **91**, 4420 (1969).

[8] J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).

[9] R. C. Fay and T. S. Piper, *ibid.*, **3**, 348 (1964).

[10] R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).

[11] (a) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971); (b) L. H. Pignolet and R. H. Holm, *ibid.*, **92**, 1791 (1970).

[12] J. G. Gordon, II, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, **5**, 381 (1971).

[13] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *Inorg. Chem.*, **11**, 99 (1972).

[14] M. C. Palazzotto and L. H. Pignolet, *J. Chem. Soc., Chem. Commun.*, 6 (1972).

[15] G. N. La Mar, *J. Amer. Chem. Soc.*, **92**, 1806 (1970).

[16] E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

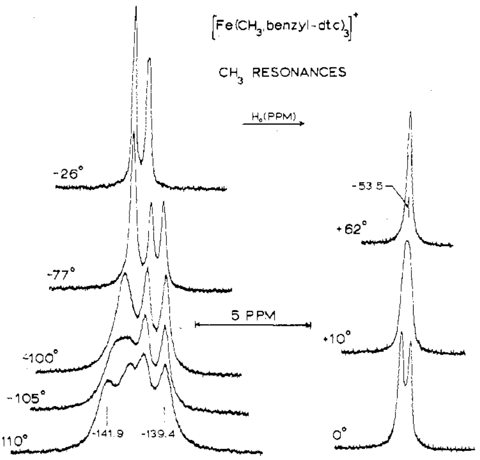


Figure 1.—Dnmr spectra of the methyl resonances of [Fe-(MeBz(dtc))$_3$]BF$_4$ in CD$_2$Cl$_2$ solution. Chemical shifts are in ppm relative to CHDCl$_2$ internal standard.

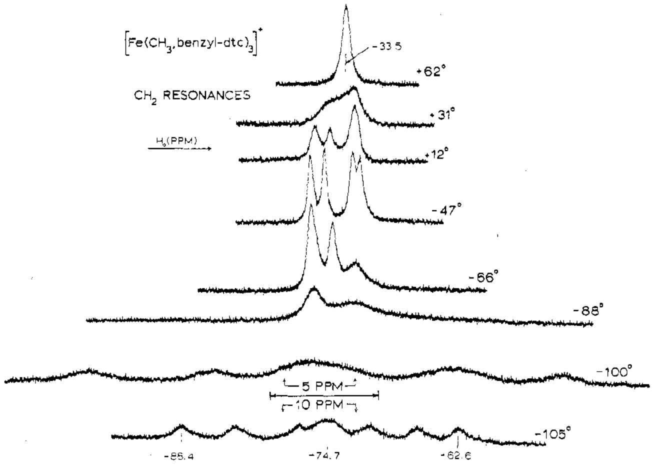


Figure 2.—Dnmr spectra of the methylene resonances of [Fe-(MeBz(dtc))$_3$]BF$_4$ in CD$_2$Cl$_2$ solution. Chemical shifts are in ppm relative to CHDCl$_2$ internal standard.

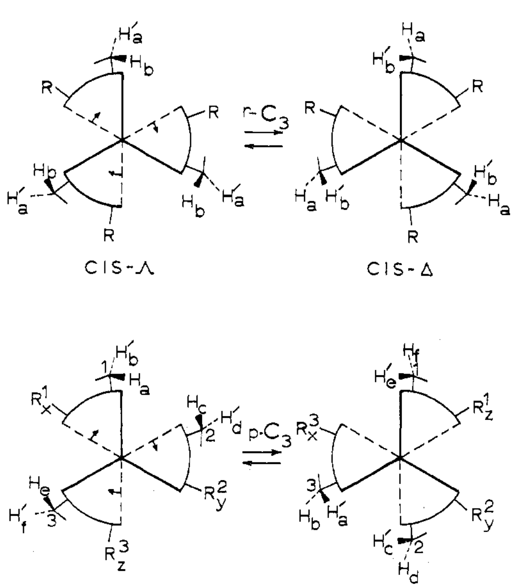
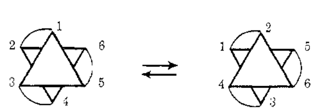


Figure 3.—Inversion of the cis-Λ and trans-Λ isomers of [Fe-(MeBz(dtc))$_3$]BF$_4$ proceeding by a trigonal twist about the real C_3 and pseudo C_3 axes, respectively. R refers to the methyl group and H refers to the methylene protons. Numbers and primes refer to substituent groups while letters refer to magnetic environments.

complexes with two unpaired electrons. Compound I is consistent with this formulation and has magnetic moments in solid state (23°) and CH$_2$Cl$_2$ solution (30°) of μ = 3.01 and 3.02 BM, respectively. We classify these complexes as tris chelates because the one-electron oxidation of Fe(Et$_2$dtc)$_3$ to Fe(Et$_2$dtc)$_3^+$ in DMF is reversible ($E_{1/2}$ = +0.423 V *vs.* sce)[17] and the dnmr and infrared spectra of I are extremely similar to those of II (*vide infra*). Several X-ray structure determinations have shown the Fe(dtc)$_3$ complexes to be true tris chelates.[18]

The dnmr spectra of the methyl and methylene resonances of I in CD$_2$Cl$_2$ solution are shown in Figures 1 and 2, respectively. Both figures clearly show two distinct kinetic processes. Exchange broadening due to the low-temperature process (LTP) is complete at −77 and −47° in Figures 1 and 2, respectively, whereas the high-temperature process (HTP) is complete at +62°. The coalescence pattern of the *N*-methyl group is similar to that of Fe(MePh(dtc))$_3$ (III), which has previously been analyzed.[14] The LTP of III has been assigned as a metal-centered rearrangement and the HTP as an S$_2$C–N bond rotation or a mixture of other isomerization mechanisms.[14] These assignments are entirely consistent with the dnmr of I. The mechanism for the metal-centered rearrangement of I is intramolecular[19] and is a process which does not interconvert the cis, C, and trans, T, isomers because the four *N*-methyl environments (one from C and three from T[20]) are not simultaneously scrambled. The *N*-methyl coalescence pattern has been analyzed for III and is consistent with a nonbond-breaking trigonal-twist mechanism.[14,21] This pathway is illustrated in Figure 3 for the C-Λ and T-Λ isomers. Note that the (R = methyl) environments X and Z in the T isomer are averaged whereas the T-Y and the C environments are not.

Eaton, *et al.*,[3] and Musher[22] have recently carried out a complete permutational analysis for M(AB)$_3$ type complexes. This analysis shows that the *N*-methyl coalescence pattern is *only* consistent with two rearrangement pathways: (i) a trigonal-twist mechanism (Eaton's A$_6$) or (ii) a rearrangement which results in *no* C-T or Λ-Δ isomerization but which does scramble two of the T environments (Eaton's A$_2$).[3] Pathway (ii) is illustrated by eq 1.[23]



(1)

The coalescence pattern of the methylene group shown in Figure 2 unambiguously distinguishes between these two pathways. The trigonal-twist mechanism illustrated in Figure 3 predicts fast-exchange environ-

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[17] G. S. Patterson and R. H. Holm, submitted for publication.

[18] P. C. Healy and A. H. White, *Chem. Commun.*, 1446 (1971).

[19] Ligand exchange has been examined by mixing two different "iron(IV)" (dtc)$_3$ complexes together and is slow on the nmr time scale at temperatures where the HTP is fast.

[20] The C and T populations are statistical within experimental error making assignment impossible.

[21] The trigonal-twist mechanism is visualized as a twisting motion about the real or pseudo C_3 axes of the C and T isomers, respectively, proceeding through a trigonal-prismatic transition state.

[22] J. Musher, private communication.

[23] The transition-state geometry pictured for this mechanism is distorted hexagonal planar and is considered stereochemically encumbered.

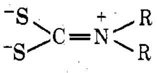
mental scramblings shown for the T isomer by eq 2,

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

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



IV

stretching frequencies also show a 42-cm^{-1} increase on going from "iron(III)" to "iron(IV)."[27]

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]

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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, $F_2PPF_2 \cdot BH_3$

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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.