The Nature of the Fluorine Exchange Processes in Some Alkyl- and Dimethylaminofluorophosphoranes

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Abstract: The fluorine exchange processes in $(CH_3)_2PF_3$ (**1**), $(CH_3)_3PF_2$ (**2**), $(C_2H_5)_2PF_3$ (**3**), and $[(CH_3)_2N]_2PF_3$ (**4**) have been investigated by means of ^1H, ^{19}F, and ^{31}P dynamic NMR (DNMR) spectroscopy. When the experiments were conducted in Teflon or Kel-F cells, the exchange was found to be intramolecular. The earlier claim (T. A. Furtsch, D. S. Dierdorf, and A. H. Cowley, *J. Am. Chem. Soc.*, **92,** 5759 (1970)) that **1** and **2** undergo exchange via an intermolecular (bimolecular) process is therefore not valid. Regardless of the rigor of the purification of **1** and **2**, nonreproducible NMR line shapes are observed when the experiments are conducted in Pyrex tubes. Using the technique of matching the observed and computer simulated spectra, it was possible to calculate the rates of, and activation parameters for, the fluorine exchange processes in **1** and **4**. The fluorine exchange in **1** and **4** proceeds by either the ae or aae process, corresponding to either the M_2 or M_4 rearrangement mode, respectively (or combinations thereof). Finally, attention is drawn to the fact that, in phosphoranes of the type R_3PF_2 (e.g., **2**), it is impossible to decide on DNMR evidence whether the structures are stereochemically rigid or whether they are interconverting between degenerate conformations.

The literature is replete with examples of NMR detectable ligand exchange processes of pentacoordinate phosphorus compounds.[4] In the majority of these examples, ligand exchange has been demonstrated or assumed to be intramolecular in character, the so-called Berry[5] "pseudo rotation process" being the mechanism of popular choice. Other studies have, however, revealed the following additional possibilities: (1) intramolecular ligand exchange via "turnstile rotation",[6] square pyramidal intermediates,[7] and other[8] mechanisms; (2) intermolecular fluorine exchange;[9] (3) solvent assisted exchange;[10] (4) exchange via dimeric intermediates;[11] (5) impurity catalyzed exchange.[10b,12] The suggestion of intermolecular exchange in $(CH_3)_2PF_3$ (**1**) and $(CH_3)_3PF_2$ (**2**) was based on (a) the observation that *F*-P-C-*H* coupling is absent in the ambient temperature ^1H spectra, (b) the (bimolecular) substrate concentration dependence, (c) the independence of the results of the method of preparation of the fluorophosphorane, and (d) the insensitivity of the results to the presence of NaF in the NMR tube. However, since that time Moreland, Doak, and Littlefield[13] have demonstrated that the ligand exchange in the closely related phosphorane $(C_6H_5)_2PF_3$ is intramolecular, thereby raising a modicum of doubt concerning the validity of the results which were obtained with the methyl analog. Furthermore, these authors demonstrated that reproducible results cannot be obtained if the NMR experiments are conducted in Pyrex tubes. In view of the foregoing, it seemed necessary to repeat the dynamic NMR (DNMR) experiments on **1** and **2** in Teflon or Kel-F NMR cells.

The primary purpose of the present paper is to point out that the fluorine exchange in **1** and **2** is intramolecular and not intermolecular as claimed previously.[9a] The earlier results on these compounds are artifactual and presumably due to the reaction of **1** and **2** with the Pyrex glass, the fluorine exchange being catalyzed by the consequent adventitious impurities.

It has also been possible to calculate the activation parameters for the intramolecular fluorine exchange in **1** and $[(CH_3)_2N]_2PF_3$ (**4**) by standard line-shape analyses of the ^1H and ^{31}P DNMR spectra. Finally, the intramolecular fluorine exchange in **1**, **4**, and $(C_2H_5)_2PF_3$ (**3**) and the temperature insensitivity of the NMR spectra of **2** (and its analogs) are discussed on the basis of rearrangement modes[14] and observable processes.[15]

Experimental Section

The dialkyltrifluorophosphoranes **1** and **3** were prepared by the action of SbF_3 on R_2PCl[16] or $R_4P_2S_2$[17] (R = CH_3 or C_2H_5), and **2** was prepared by the reaction of $(CH_3)_3P$ with SF_4 at −78 °C.[18] Compound **4** was prepared by the action of $(CH_3)_2NSi(CH_3)_3$ on PF_5.[19] All compounds were purified by fractional condensation in a Kel-F/stainless steel vacuum line until they were tensimetrically homogeneous. The ir spectral frequencies were in good agreement with the literature values.[20] All samples were stored over anhydrous NaF in a Kel-F/stainless steel vessel prior to use. The NMR samples were prepared by condensing the appropriate fluorophosphorane into a piece of 3 mm o.d. flexible Kel-F or Teflon tubing at −196 °C which had been sealed at one end. The Kel-F or Teflon tubing was attached to the vacuum system via a stainless steel valve, and the vacuum seal was effected by bringing a hot coil of nichrome wire *near* the Kel-F or Teflon tubing. After this preliminary sealing procedure, a final seal was effected by squeezing the top of the sample tube with a pair of warm tongs. During the sealing operations, the sample was maintained at −196 °C. After allowing the sample tube containing the fluorophosphorane to warm up to ambient temperature, the sealed flexible tube was inserted into a standard 5-mm NMR tube containing a small amount of the external standard. The length of the Kel-F or Teflon insert was such that it was possible to place a cap on the external NMR tube. In order to obtain reproducible line shapes, it is important to avoid any contact of **1** or **2** with Pyrex glass during either the purification or sample preparation stages. Furthermore, it is essential that the Kel-F or Teflon cells containing **1** or **2** be removed from the Pyrex NMR tubes when NMR experiments are not being conducted. Presumably it is possible for **1** or **2** to diffuse outside of the Kel-F or Teflon cell and to come into contact with the Pyrex tube. Similar precautions were taken with **3** and **4**.

NMR Spectra. All spectra were determined on a Varian Associates HA-100 spectrometer equipped with variable-temperature and heteronuclear decoupling accessories. Probe temperatures were calibrated using a Wilmad NMR thermometer. The spectrometer frequencies for the ^1H, ^{19}F, and ^{31}P spectra were 100, 94.1, and 40.5 MHz, respectively.

Line-Shape Calculations. Theoretical spectra were calculated using the many-site program NMRLS which is based on the equations of Anderson and Kubo.[21] The program was devised by Professor M. Saunders[22] and modified for a CDC 6400/6600 computer. Input included the frequencies of the lines measured from an arbitrary zero, their natural line widths and relative intensities in the absence of exchange, and a transition probability matrix.

Results

A selection of ^1H, ^{19}F, and ^{31}P NMR spectra for **1**, **3**, and **4** may be found in Figures 1–5. A summary of the

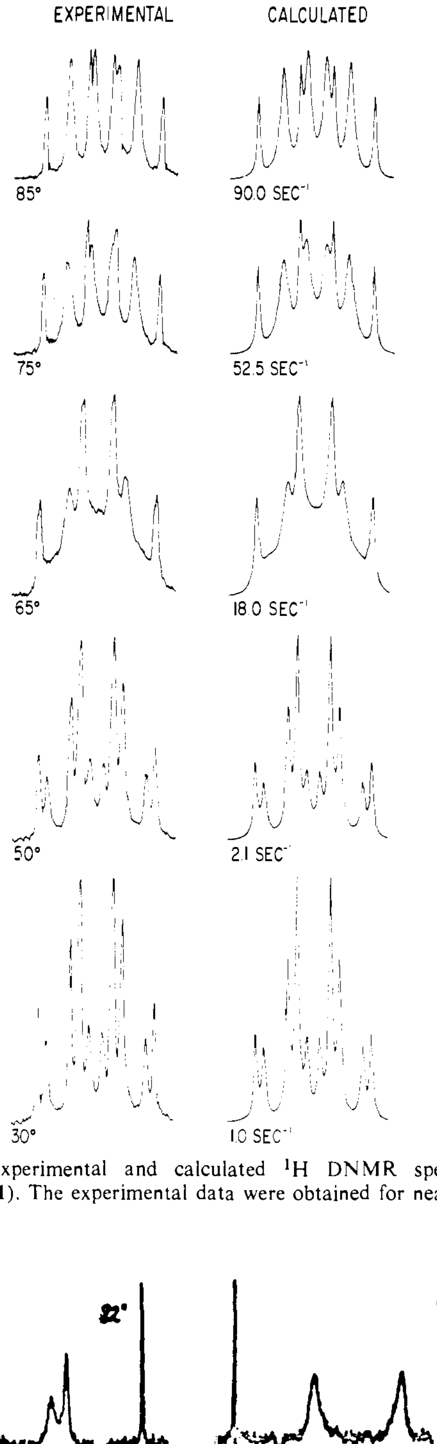


Figure 1. Experimental and calculated ^1H DNMR spectra of $(CH_3)_2PF_3$ (**1**). The experimental data were obtained for neat **1** in a Kel-F cell.

Figure 2. Experimental ^{31}P DNMR spectra of neat $(CH_3)_2PF_3$ (**1**) in a Teflon cell. The 82-, 91-, and 100 °C spectra were run with the ^1H decoupler on. The 32 °C spectrum was run with the ^1H decoupler off.

NMR data for **1-4** is presented in Table I.

The simulated spectra which are displayed beside the experimental ^1H spectra in Figures 1 and 5 were computed for the indicated rate constants by means of the NMRLS program (see Experimental Section). For the ^1H (and ^{31}P) spectra, the only probability matrix that would accommodate the experimental data was one in which the equatorial fluorine of **1** or **4** had an equal chance of intramolecular exchange with an axial fluorine.[23] For the ^1H spectra of **1**, the transition probability matrix took the form where the line

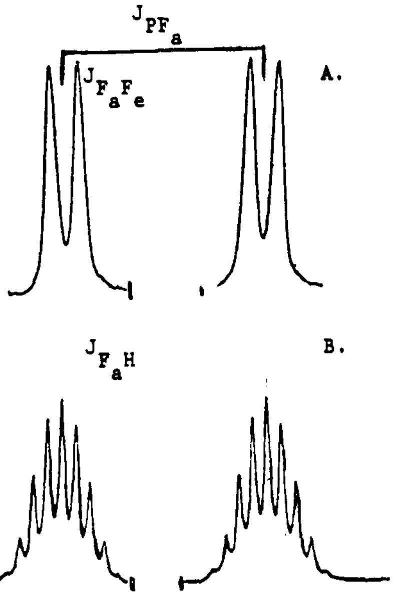


Figure 3. ^{19}F NMR spectra of neat $(CH_3)_2PF_3$ (**1**) in a Teflon cell with (a) ^1H decoupler on and (b) ^1H decoupler off.

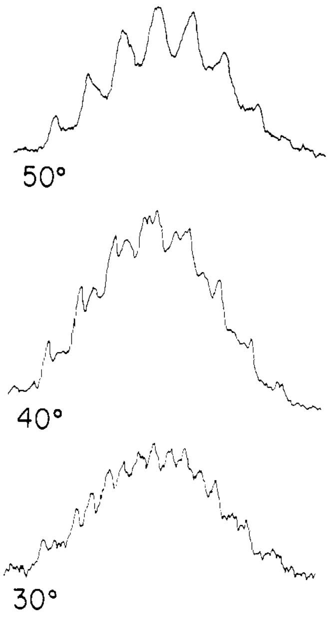


Figure 4. ^1H NMR spectra of neat $(C_2H_5)_2PF_3$ (**3**) in a Kel-F cell at various temperatures. Only the CH_2 resonance is shown.

Line Number	1	2	3	4	5	6	7	8	9	10	11	12
1	1	0	0	0	0	0	0	0	0	0	0	0
2	0	0	1	0	0	0	0	0	0	0	0	0
3	0	0.5	0.5	0	0	0	0	0	0	0	0	0
4	0	0	0	0.5	0	0	0.5	0	0	0	0	0
5	0	0	0	0	1	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	1	0	0	0
7	0	0	0	1	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0	1	0	0	0	0
9	0	0	0	0	0	0.5	0	0	0.5	0	0	0
10	0	0	0	0	0	0	0	0	0	0.5	0.5	0
11	0	0	0	0	0	0	0	0	0	1	0	0
12	0	0	0	0	0	0	0	0	0	0	0	1

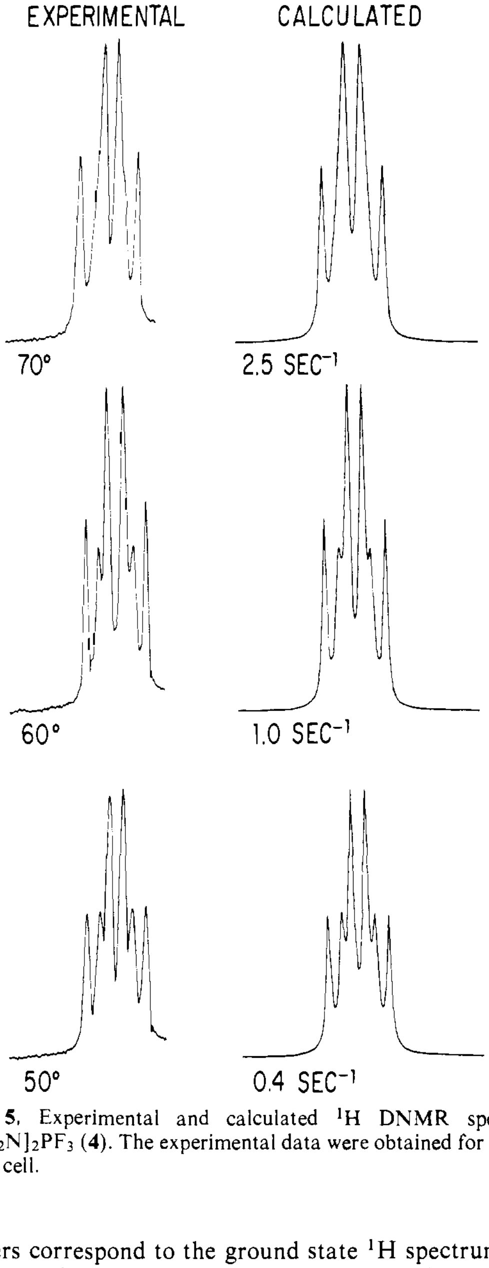


Figure 5. Experimental and calculated ${}^1H$ DNMR spectra of $[(CH_3)_2N]_2PF_3$ (**4**). The experimental data were obtained for neat **4** in a Kel-F cell.

numbers correspond to the ground state ${}^1H$ spectrum (Figure 1), reading from left to right. Note that lines 4 and 5, and 8 and 9 occur at the same frequency. The matrix that was employed for the ${}^{31}P$ DNMR data of **1** has been published elsewhere.[13,24] In the case of **1**, a key feature of this rearrangement process is the fact that, as predicted, lines 1 and 12 of the ${}^1H$ spectra remain sharp (as should lines 5 and 8; however, as pointed out above, these are overlapping with lines 4 and 9, respectively). Using the k values from Figure 1, the best straight-line Arrhenius plots afforded the following activation parameters for **1**: $E_a = 15.5$ kcal/mol, $\Delta G^{\dagger}_{333} = 17.8$ kcal/mol, $\Delta S^{\dagger} = -8.8$ eu from the ${}^1H$ spectra. The values $E_a = 15.1$ kcal/mol, $\Delta G^{\dagger}_{359} = 17.3$ kcal/mol, $\Delta S^{\dagger} = -8.1$ eu were obtained from the ${}^{31}P$ spectra. The use of a similar approach for **4** yielded the activation parameters, $E_a = 20.2$ kcal/mol, $\Delta G^{\dagger}_{343} = 19.6$ kcal/mol, $\Delta S^{\dagger} = -0.1$ eu from the ${}^1H$ DNMR spectra (Figure 5).

Discussion

The salient feature that emerges from the present study is the observation that, when the NMR experiments for **1** and **2** are done in Kel-F or Teflon cells, there is *no evidence for an intermolecular exchange process.*[25] The earlier experiments were conducted in Pyrex glass NMR tubes and the erroneous conclusion that **1** and **2** exhibit intermolecular exchange was based inter alia on the absence of ${}^1H$-C-P-${}^{19}F$ coupling in the ${}^1H$ NMR spectra. Furthermore, we find that it is absolutely essential to avoid Pyrex glass in both the purification and sample preparation stages. Regardless of the rigor with which the samples of **1** and **2** are purified, variable and nonreproducible results are obtained if the substrates are placed in Pyrex glass NMR tubes. In Kel-F or Teflon tubes, both **1** and **2** retain ${}^1H$-C-P-${}^{19}F$ coupling up to 85 °C (Figure 1).[26] The intramolecular nature of the exchange process in **1** receives additional confirmation from the following facts: (a) only an intramolecular exchange transition probability matrix will accommodate the observed ${}^1H$ and ${}^{31}P$ DNMR spectral changes, and (b) the average ${}^1H$-C-P-${}^{19}F$ and ${}^{31}P$-${}^{19}F$ high-temperature coupling constants correspond to the appropriately weighted averages of the low-temperature axial and equatorial values.

The retention of ${}^1H$-C-N-P-${}^{19}F$ coupling in **4** indicates that the fluorine positional interchange process is also intramolecular in this molecule, a deduction which is confirmed by the fact that the ${}^1H$ DNMR spectra (Figure 5) can be simulated only with an intramolecular exchange probability matrix. In the case of the ethyl derivative **3**, the ${}^1H$ DNMR spectra (Figure 4) were somewhat too complex for line-shape analysis. Furthermore, no attempt has been made to evaluate all the coupling constants. However, it is apparent from the ${}^1H$ DNMR spectra of the methylene protons that ${}^1H$-C-P-${}^{19}F$ coupling is preserved up to 70 °C, thereby indicating that the fluorine exchange in **3** is also intramolecular.

The activation parameters for the intramolecular fluorine exchange processes in **1** and **4** are comparable to those which have been observed for other trifluorophosphoranes

Table I. Summary of NMR Data for Trifluorophosphoranes

Compd		Temp, °C	Chemical shifts[a] ${}^1H$	${}^{31}P$	${}^{19}F$	Coupling constants, Hz[b] J_{PF}	J_{PCH}	J_{HCPF}	J_{PNCH}	J_{HNCPF}
$(CH_3)_2PF_3$	(1)	30	8.525	104	4.14 (a) 86.2 (e)	$J_{PF_a} = 777$ $J_{PF_e} = 966$	17.0	$J_{HCPF_a} = 13.0$ $J_{HCPF_e} = 3.3$		
$(CH_3)_2PF_3$	(1)	85	8.525				17.2	$J_{HCPF}{}^c = 9.5$		
$(CH_3)_3PF_2$	(2)	30	8.545				17.5	11.4		
$(C_2H_5)_2PF_3$	(3)	30	8.92 (CH_3) 8.05 (CH_2)							
$[(CH_3)_2N]_2PF_3$	(4)	30	7.405						10.8	$J_{HNCPF_a} = 2.6$ $J_{HNCPF_e} = 1.6$

[a] Proton chemical shifts in τ units relative to external Me_4Si; ${}^{31}P$ chemical shifts in parts per million upfield from external P_4O_6; ${}^{19}F$ chemical shifts in parts per million upfield from external $CFCl_3$. [b] a = axial; e = equatorial. [c] Denotes average value.

Table II. Intramolecular Fluorine Exchange Barriers in Trifluorophosphoranes

Compd		$\Delta G^{\dagger}$, kcal/mol	Temp, K	Ref
$(CH_3)_2PF_3$	(1)	17.8	333	*a*
$[(CH_3)_2N]_2PF_3$	(4)	19.6	343	*a*
$(C_6H_5)_2PF_3$		18.7	379	*b*
H_2PF_3		10.2	218	*c*
$CF_3(H)PF_3$		6.3	133	*c*
Cl_2PF_3		$E_a = 7.2 \pm 0.5$		*d*
Br_2PF_3		$E_a = 7.2 \pm 0.5$		*d*
$(CF_3)_2PF_3$		Fluxional at −120 °C		*e*

[a] Present work. [b] Reference 13 and unpublished observations. [c] Reference 32. [d] W. Mahler and E. L. Muetterties, *Inorg. Chem.*, 4, 1520 (1965). [e] Reference 4a.

(Table II). For X_2PF_3 molecules, the barriers depend on the substituent X in the order $(CH_3)_2N > C_6H_5 > CH_3 > H > Cl \sim Br > CF_3$. As with the XPF_4 molecules,[7a] the factors which are responsible for the magnitudes of the barriers are not immediately apparent. (Note, however, that the orders are different for the XPF_4 and X_2PF_3 molecules.) π-Bonding has been suggested[27] to be an important contributor to the barrier magnitude in XPF_4 compounds such as $(CH_3)_2NPF_4$ and CH_3SPF_4. It is interesting to note that $[(CH_3)_2N]_2PF_3$ also possesses a high barrier to fluorine exchange. However, the π-bonding postulate cannot be employed to explain the position of H_2PF_3 in the above order.

Attention is drawn next to a discussion of the fluorine positional exchange processes in **1** and **4**. At the outset it might be stressed that the rearrangements of pentacoordinated molecules can proceed via an almost infinite variety of mechanisms including intramolecular, intermolecular, collision activated exchange, solvent assisted exchange, and others. However, since DNMR data are interpreted within the framework of the "jump model" (i.e., transitions are effectively instantaneous),[28] they cannot provide mechanistic information; rather such data are best discussed in terms of rearrangement modes (M_i),[14] which are, of course, merely permutational in character. Furthermore, due to the DNMR spectroscopic indistinguishability of several of the rearrangement modes, it is convenient to effect a further classification into observable processes (OP_i).[15] The modes and observable processes for XPF_4, X_2PF_3, and X_3PF_2 molecules are summarized in Table III. As an example, consider first the rearrangements in the $PA_4B(EQ)$[29] molecule, $(CH_3)_2NPF_4$. The DNMR data[7a,30] can be accommodated by either the aeae[31] (mode M_1) or aexae (mode M_5) intramolecular process. The experimental data provide no means of distinguishing between these two rearrangements; hence modes M_1 and M_5 are included in the same observable process (OP_1).

In the case of the $PA_3B_2(EQ)$[29] molecules **1** and **4**, the only probability matrix (vide supra) which is capable of reproducing the experimental ^{1}H and ^{31}P DNMR spectra is one in which the equatorial fluorine ligand[23] has an equal probability of exchanging with either of the axial fluorine ligands, i.e., the ae[31] or aae rearrangement. In turn the ae and aae rearrangements correspond to modes M_2 and M_4, respectively. Furthermore, since these modes are DNMR indistinguishable, they are included in the same observable process (OP_2). Previously it has been shown the H_2PF_3 and $CF_3(H)PF_3$ also rearrange by the same observable process.[32]

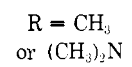
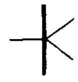


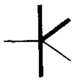
Table III. Rearrangement Modes, M_i[a], and Observable Processes, OP_i[b], for Various Phosphoranes

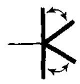
Compd	M_0[c]	M_1	M_2	M_3	M_4	M_5	Total modes	Total OP's
	OP_0	OP_2	OP_1	OP_0	OP_1	OP_2		
$PA_4B(EQ)$[d]	1	1	4	1	4	1	12	3
$PA_3B_2(EQ)$[d]	1	0	2	1	2	0	6	2
$PA_3B_2(EQ)$[d]	1	0	0	1	0	0	2	1
$PA_4B(AX)$[d]	1	0	3	1	3	0	8	2


M_1
aeae[e]


M_2
ae


M_3
aa


M_4
aae


M_5
aexae

[a] See ref 14 for a discussion of rearrangement modes. [b] See ref 15 for a discussion of observable processes. [c] Identity operation. [d] See ref 29 for definition of symbols. [e] See ref 31 for definition of symbols.

Finally, attention is drawn to the $PA_2B_3(EQ)$[29] molecule, **2**. Reference to Table III indicates that there is only one observable process (OP_0) if it is assumed that the placement of a B ligand in an axial position would require a prohibitively large amount of energy. Unless intermolecular or impurity catalyzed exchange is extant, this implies that the NMR spectra of molecules of the type R_3PF_2 cannot exhibit temperature sensitivity since the observable process OP_0 comprises only the identity operation and the aa[31] process (mode M_3), both of which yield a product which is identical with the initial structure.

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References and Notes

(1) North Carolina State University.
(2) The University of Texas at Austin.
(3) On sabbatical leave from the Chemistry Department, University of Hawaii, Honolulu, Hawaii, during the 1972–1973 academic year.
(4) See, e.g., (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) R. Schmutzler, *Adv. Fluorine Chem.*, **5**, 31 (1965); (c) R. Schmutzler, *Halogen Chem.*, *31ff* (1967); (d) K. Mislow, *Acc. Chem. Res.*, **3**, 321 (1970); (e) E. L. Muetterties, *ibid.*, **3**, 266 (1970); (f) A. T. Balaban, *Rev. Roum. Chim.*, **18**, 855 (1973); (g) M. Gielen, "Stéréochimie Dynamique", Scientific Publications Division, Freund Publishing House, Ltd., Tel Aviv, Israel, 1973; (h) W. G. Klemperer in "DNMR Spectroscopy", F. A. Cotton and L. M. Jackman, Ed., Academic Press, New York, N.Y., 1975; (i) R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Verlag, Stuttgart, 1973.
(5) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(6) (a) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel and P. Gillespie, *Angew. Chem., Int. Ed. Engl.*, 9, 703 (1970); (b) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, **4**, 288 (1971); (c) F. Ramirez and I. Ugi, *Adv. Phys. Org. Chem.*, **9**, 25 (1971).
(7) (a) M. Eisenhut, H. L. Mitchell, D. D. Traficante, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 5385 (1974); (b) G. M. Whitesides, M. Eisenhut, and W. M. Bunting, *ibid.*, **96**, 5398 (1974).
(8) R. R. Holmes, *Acc. Chem. Res.*, **5**, 296 (1972).
(9) (a) T. A. Furtsch, D. S. Dierdorf, and A. H. Cowley, *J. Am. Chem. Soc.*, **92**, 5759 (1970); (b) H. Dreeskamp and K. Hildenbrand, *Z. Naturforsch. B*, **26**, 269 (1971).
(10) (a) J. D. Macomber, *J. Magn. Reson.*, **1**, 677 (1969); (b) J. A. Gibson, D. G. Ibbott, and A. F. Janzen, *Can. J. Chem.*, **51**, 3203 (1973).
(11) J. I. Musher, *Tetrahedron Lett.*, 1093 (1973).

(12) For a discussion of impurity catalyzed exchange in analogous sulfur compounds, see W. G. Klemperer, J. K. Krieger, M. D. McCreary, E. L. Muetterties, D. D. Traficante, and G. M. Whitesides, *J. Am. Chem. Soc.*, **97**, 7023 (1975).
(13) C. G. Moreland, G. O. Doak, and L. B. Littlefield, *J. Am. Chem. Soc.*, **95**, 255 (1973).
(14) J. I. Musher, *J. Am. Chem. Soc.*, **94**, 5662 (1972).
(15) (a) J. I. Musher, *J. Chem. Educ.*, **51**, 94 (1974); (b) J. I. Musher and W. C. Agosta, *J. Am. Chem. Soc.*, **96**, 1320 (1974).
(16) R. Schmutzler, *Inorg. Chem.*, **3**, 421 (1964).
(17) R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).
(18) The procedure employed was similar to that described by W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).
(19) R. Schmutzler, *J. Chem. Soc., Dalton Trans.*, 2687 (1973).
(20) (a) A. J. Downs and R. Schmutzler, *Spectrochim. Acta, Part A*, **23**, 681 (1967); (b) J. Grosse and R. Schmutzler, *Phosphorus*, **4**, 49 (1974).
(21) (a) P. W. Anderson, *J. Phys. Soc. Jpn.*, **9**, 316 (1954); (b) R. Kubo, *ibid.*, **9**, 935 (1954); (c) *Nuovo Cimento, Suppl.*, **6**, 1063 (1957).
(22) (a) M. Saunders, *Tetrahedron Lett.*, 1699 (1963); (b) M. Saunders in "Magnetic Resonance in Biological Systems", A. Ehrenberg, B. G. Malmstrom, and T. Vanngard, Ed., Pergamon Press, Oxford, 1967, p 85.
(23) Electron diffraction studies indicate that the methyl groups in **1** adopt the equatorial sites of a trigonal bipyramid [see K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965)]. A similar structure may be assumed for **4** on the basis of NMR (ref 19) and photoelectron spectroscopic data [A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and J. R. Schweiger, *J. Am. Chem. Soc.*, **95**, 6506 (1973)].
(24) C. S. Johnson and C. G. Moreland, *J. Chem. Educ.*, **50**, 477 (1973).
(25) A similar conclusion has been arrived at independently by O. Schlak and R. Schmutzler. The authors are grateful to Professor Schmutzler for informing us of this work.
(26) The proton spectra of **2** in the range 30–85 °C are essentially the same as Figure 1a of ref 9a.
(27) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 5674 (1972).
(28) For a discussion of the effects of intermediates on DNMR spectra, see ref 7 and references therein.
(29) AX or EQ denotes respectively the axial or equatorial location(s) of the B ligand(s) within a trigonal bipyramidal phosphorane structure of general formula PA_nB_{5-n}, $n = 3, 4$.
(30) G. M. Whitesides and H. L. Mitchell, *J. Am. Chem. Soc.*, **91**, 5384 (1969).
(31) The letters a and e symbolize axial and equatorial ligands, respectively, within a trigonal bipyramidal framework. The various sequences of these letters correspond to the ligand permutations which are depicted in Table III.
(32) J. W. Gilje, R. W. Braun, and A. H. Cowley, *J. Chem. Soc., Chem. Commun.*, 15 (1974).

Stereochemistry of Eight-Coordinate Mixed-Ligand Complexes of Zirconium. II. Characterization and the Crystal and Molecular Structure of Nitratotris(acetylacetonato)zirconium(IV)[1,2]

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Abstract: The crystal and molecular structure of nitratotris(acetylacetonato)zirconium(IV), $Zr(acac)_3(NO_3)$, has been determined by single-crystal x-ray diffraction and has been refined (anisotropically for Zr, N, O, and C atoms; isotropically for H atoms) by full-matrix least-squares techniques to $R_1 = 0.030$ and $R_2 = 0.032$ using 5110 independent diffractometer-recorded reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 71°$ and $I > 3\sigma(I)$. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions: $a = 9.204$ (1), $b = 15.648$ (2), $c = 13.471$ (1) Å, $\beta = 91.364$ (8)° ($\rho_{\mathrm{calcd}} = 1.543$, $\rho_{\mathrm{obsd}} = 1.538$ (5) g/cm^3). The crystal contains discrete eight-coordinate molecules in which the bidentate nitrate ligand spans an *a* edge and the three bidentate acetylacetonate ligands span *b*, *m*, and *g* edges, respectively, of a (necessarily distorted) D_{2d}-$\bar{4}2m$ dodecahedron. Distortions are in the direction of a pseudo-seven-coordinate pentagonal bipyramid. Complexing bonds to the acetylacetonate ligands are systematically shorter than those to the nitrate ligand, averaging 2.141 (1) and 2.366 (2) Å, respectively. The averaged length for all eight Zr–O bonds is 2.197 Å. Differences in the two Zr–O bond lengths within a particular chelate ring are propagated in the C–O, C–C, and N–O bonds of the ligands. The acac ligand "bite" shows significant variation with the type of polyhedral edge it spans: *m* (2.618 (2) Å) < *g* (2.689 (2) Å) < *b* (2.786 (2) Å). The ligands are planar, and the acetylacetonate methyl groups adopt a conformation in which one methyl hydrogen atom and the —CH= hydrogen atom are eclipsed. The relative merits of the observed C_1-*abmg* stereoisomer and other possible stereoisomers are discussed in terms of ligand bite, polyhedral edge lengths, and nonbonded contacts. In inert solvents, $Zr(acac)_3(NO_3)$ is a monomeric nonelectrolyte which is stereochemically nonrigid on the NMR time scale. Retention of coordination number eight in solution is suggested by the similarity of solid-state and solution-state infrared spectra.

This is the second of two papers dealing with the structure and stereochemistry of eight-coordinate mixed-ligand nitrato(acetylacetonato)zirconium complexes of the type $Zr(acac)_2(NO_3)_2$ and $Zr(acac)_3(NO_3)$. The single-crystal x-ray study reported in Part I[1] revealed that $Zr(acac)_2(NO_3)_2$ is an eight-coordinate complex in which the acetylacetonate and nitrate ligands (both bidentate) span the four *m* edges of a (necessarily distorted) D_{2d}-$\bar{4}2m$ dodecahedron (*mmmm* stereoisomer[4]). Each BAAB trapezoid of the dodecahedron[5] contains one acetylacetonate and one nitrate ligand; thus the approximate molecular point group symmetry is C_2-2. The ligand wrapping pattern observed for $Zr(acac)_2(NO_3)_2$ and the dimensions of the coordination polyhedron suggest that the relatively large bite of the acetylacetonate ligand does not permit two acac ligands to be located on the same trapezoid of a ZrO_8 dodecahedron. In support of this view, we note that $Zr(acac)_4$ adopts the alternate eight-coordination polyhedron, a D_{4d}-$\bar{8}2m$ square antiprism, with the ligands located on the *s* edges (*ssss* stereoisomer).[6]

In view of the different stereochemistries exhibited by $Zr(acac)_2(NO_3)_2$ and $Zr(acac)_4$, it was of interest to determine the structure of the intermediate mixed-ligand complex $Zr(acac)_3(NO_3)$. Neither the dodecahedral *mmmm* stereoisomer nor the antiprismatic *ssss* stereoisomer is likely for $Zr(acac)_3(NO_3)$; the former requires that two acac li-