Table V. Negative Ion-Molecule Reactions Observed in Arsine Mixtures

Mixture	Reaction	dk/dE^a	Thermochemical inferences^b
AsH_3-PH_3	$PH_2^- + AsH_3 \underset{\not\leftarrow}{\rightarrow} AsH_2^- + PH_3$	∓	PA(AsH_2^-) ⩽ 369^c
	$C_2H_5O^- + AsH_3 \rightarrow AsH_2^- + C_2H_5OH$	–	PA(AsH_2^-) ⩽ 376^d
	$C_2H_5O^- + H_2S \rightarrow HS^- + C_2H_5OH$	–	PA(HS^-) ⩽ 376^d
AsH_3-H_2S-C_2H_5ONO (+C_2H_5OH)	$C_2H_3O^- + H_2S \rightarrow HS^- + C_2H_4O$	–	PA($C_2H_3O^-$) ⩾ 350^e
	$C_2H_5O^- + C_2H_5ONO \rightarrow NO_2^- + (C_2H_5)_2O$	–	
	$C_2H_5O^- + C_2H_5OH \rightarrow C_2H_3O^- + H_2 + C_2H_5OH$	–	
	$AsH_2^- + H_2S \underset{\not\leftarrow}{\rightarrow} HS^- + AsH_3$	∓	PA(AsH_2^-) ⩾ 350^e

[a] Unless otherwise indicated, the reverse reaction was investigated by double-resonance experiments and found not to occur. [b] All values given in kcal/mol. [c] Reference 50. [d] Reference 51. [e] Reference 49.

value and eq 33, $D(H_2As\text{-}H)$ is calculated to be 79 kcal/mol.

$$PA(M^-) = D(M\text{-}H) + IP(H\cdot) - EA(M\cdot) \qquad (33)$$

This value, not unexpectedly, is somewhat higher than the average As-H bond energy in AsH_3 (71.2 kcal/mol).[53]

Table VI summarizes D(M-H), EA(M·), and PA(M^-) for the first three group V hydrides. In proceeding from NH_3 to PH_3 to AsH_3, the gas-phase acidities are seen to increase monotonically while the bond dissociation energies decrease. However, the electron affinities of the radical species are not constant and do not follow any recognizable trend. Hence, both D(M-H) and EA(M·) appear to be important in establishing the trend in acidities observed for the group V hydrides.[6,11]

Table VI. Some Thermochemical Quantities Related to the Acidities of the Group V Hydrides^a

MH	D(M-H)	EA(M·)	PA(M^-)
NH_3	107^b	17^{b,e}	405^b
PH_3	84^c	29^f	369^f
AsH_3	79^d	29^e	360^g

[a] All values are given in kcal/mol. [b] D. K. Bohme, R. S. Hemsworth, and H. W. Rundle, *J. Chem. Phys.*, **59**, 77 (1973). [c] T. McAllister and F. P. Lossing, *J. Phys. Chem.*, **73**, 2996 (1969). [d] See text for discussion. The average bond energy is 71 kcal/mol.[53] [e] Reference 52. [f] Reference 50. [g] This work.

Registry No. AsH_3, 7784-42-1; PH_3, 7803-51-2; H_2S, 7783-06-4; CH_3CHCH_2, 115-07-1; CH_3OH, 67-56-1; CH_3Cl, 74-87-3; C_2H_5ONO, 109-95-5.

(53) The average As-H bond energy in AsH_3 (71.2 kcal/mol) was calculated employing $\Delta H_f(AsH_3)$ = 14.6 kcal/mol, ΔH_f(As) = 72.3 kcal/mol, and $\Delta H_f(H\cdot)$ = 52.1 kcal/mol (S. R. Gunn, *Inorg. Chem.*, **11**, 796 (1972)).

Notes

Contribution from the Department of Chemistry,
Emory University, Atlanta, Georgia 30322

Preparation and Characterization of Vinyldifluorophosphine

E. L. Lines and L. F. Centofanti*

Received August 6, 1973 AIC30589*

Recently there has been considerable interest in the basicity toward borane of certain phosphines.[1-3] Of particular interest is the report by Foester and Cohn[4] that PF_2CH_3 is a relatively strong base. Thus as one moves across the periodic chart ($PF_2CH_3 \rightarrow PF_2N(CH_3)_2 \rightarrow PF_2OCH_3 \rightarrow PF_3$), basicity decreases following electronegativity. Past arguments for the high basicity of $PF_2N(CH_3)_2$ were based on basicity enhancement of the phosphorus by the formation of a dative π bond between the nitrogen electron pair and the vacant orbitals of the phosphorus.[16] This effect would be absent in PF_2CH_3; therefore basicity parameters may require revision.

A comparison of the basicity of alkene- and alkynylphosphines to alkylphosphines could help clarify the role of π bonding and electronegativity in phosphorus basicity. Toward this goal we wish to report the preparation and characterization of vinyldifluorophosphine and its borane adduct.

Experimental Section

General Techniques. All volatile materials were handled in high-vacuum manifolds with interconnecting U traps.[5] Infrared spectra were measured on a Perkin-Elmer 137 NaCl spectrophotometer and on a Perkin-Elmer 421 grating spectrophotometer using a 10-cm gas cell with KBr windows. Mass spectra were obtained on a Varian M66 (70 eV), while ^{19}F nmr spectra were traced on a Varian T-60 operating at 56.4 MHz and on a Varian Associates HR-100 nmr spectrometer operating at 94.1 MHz. ^{11}B nmr spectra were recorded on a Varian XL-100 operating at 32.1 MHz. Proton nmr spectra were determined with a Jeol MN-100 operating at 100 MHz. Internal TMS and external $CFCl_3$ and $B(C_2H_5)_3$ served as references for ^1H, ^{19}F, and ^{11}B spectra, respectively, unless noted otherwise.

Material. Commercial B_2H_6 (Callery), HBr (Matheson), ZnF_2 (Ozark-Mahoning), $P(OCH_2CH{=}CH_2)_3$ (City Chemical Corp.), and $(CH_2{=}CH)_2Hg$ (Orgmet, Inc.) were used without further purification. PF_2Br[6] was prepared by literature methods.

Synthesis of $PF_2CH{=}CH_2$. A 15.5-mmol sample of PF_2Br was condensed at −196° on 20.0 mmol (~2.55 g) of $(CH_2{=}CH)_2Hg$ in a 500-cm^3 reaction vessel with a removable tube. The mixture was warmed to room temperature where the formation of yellow-white solids indicated immediate reaction. The reaction vessel was shaken for 8 hr and then allowed to sit at ambient temperature for 12 hr. The volatile contents of the bulb were led through traps at −105, −135, and 196°. The −105° trap held an unidentified liquid (possibly excess $(CH_2{=}CH)_2Hg$), while the −196° trap contained 6.52 mmol of PF_3, identified by ir. The −135° trap contained 4.7 mmol of $PF_2CH{=}CH_2$ for a yield based on consumed PF_2Br of 27%.

Care must be taken to avoid using excess PF_2Br as the separation of $PF_2CH{=}CH_2$ and PF_2Br is extremely difficult. Under the reac-

---

* To whom correspondence should be addressed at Monsanto Industrial Chemicals Co., St. Louis, Mo. 63166.

(1) E. L. Lines and L. F. Centofanti, *Inorg. Chem.*, **12**, 2111 (1973).

(2) A. H. Cowley and M. C. Damasco, *J. Amer. Chem. Soc.*, **93**, 6815 (1971).

(3) R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, **93**, 6821 (1971).

(4) R. Foester and K. Cohn, *Inorg. Chem.*, **11**, 2590 (1972).

(5) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(6) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, **10**, 147 (1967).

tion conditions employed PF_2Br and $(H_2C{=}CH)_2Hg$ must be combined in at least a 1:1 ratio to effect this. If PF_2Br and $(H_2C{=}CH)_2$-Hg are mixed in a 2:1 fashion, the reaction is incomplete, and excess PF_2Br cannot be separated from $PF_2C_2H_3$ by distillation. Also the PF_2Br cannot be fluorinated by ZnF_2 to PF_3 since $PF_2C_2H_3$ is partially oxidized to $PF_4C_2H_3$ over ZnF_2 and these two compounds are inseparable by distillation.

Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of $PF_2C_2H_3$: 97 ($PF_2C_2H_4^+$), 6.9; 96 ($PF_2C_2H_3^+$), 100.0; 95 ($PF_2C_2H_2^+$), 1.7; 94 ($PF_2C_2H^+$), 4.3; 77 $(PFC_2H_3)^+$, 3.0; 75 (PFC_2H^+), 6.0; 70 (PF_2H^+), 10.5; 69 (PF_2^+), 55.5; 57 ($PC_2H_2^+$), 4.3; 56 (PC_2H^+), 3.9; 55 (PC_2^+), 3.0; 51 (PFH^+), 11.2; 50 (PF^+), 15.5; 32 (PH^+, O_2^+), 18.1; 31 (P^+), 2.6; 28 ($C_2H_4^+$, N_2^+), 38.3; 27 ($C_2H_3^+$), 43.2; 26 ($C_2H_2^+$), 11.2; 18 (H_2O^+), 8.1; 17 (OH^+), 2.6; 14 (CH_2^+, N^+), 1.7. The vapor pressure values (−97.8°, 0.7 mm; −89.5°, 1.2 mm; −63.5°, 11.9 mm; −22.9°, 133.9 mm) can be expressed by the equation

$$\log P\,(\mathrm{mm}) = -1364/T + 7.560$$

where T is in degrees Kelvin. The entropy of vaporization at the normal boiling point is 21.4 cal/mol deg. Little association is apparent. The extrapolated boiling point is 18.4°.

Decomposition of $PF_2C_2H_3$ over ZnF_2. A 1.29-mmol sample of $PF_2C_2H_3$ was condensed at −196° on an excess of ZnF_2 in a 50-cm^3 reaction bulb and allowed to warm to ambient temperature. After 144 hr $PF_4C_2H_3$[7] was evident in the ir spectrum of the reaction mixture.

Synthesis of $PF_2CH{=}CH_2{\cdot}BH_3$. A 0.90-mmol sample of B_2H_6 was condensed at −196° in a 50 cm^3 reaction bulb open to a manometer. A 1.57-mmol sample of $PF_2C_2H_3$ was frozen on top of the B_2H_6 and the mixture was allowed to warm to room temperature. The reaction was alternately warmed and frozen for 2 hr. The mixture was then frozen and allowed to warm slowly through traps held at −135 and −196°. A 0.20-mmol sample of B_2H_6 was found in the −196° trap, while the −135° trap contained 1.41 mmol of $PF_2C_2H_3{\cdot}BH_3$ for a yield based on consumed ligand of 90%. An unidentified oil remained behind in the flask.

Following are the mass numbers (species) and relative abundances of the ions in the mass spectrum of $PF_2C_2H_3{\cdot}BH_3$: 110 ($PF_2C_2{}^{11}BH_6^+$), 2.2; 109 ($PF_2C^{11}BH_5^+$), 64.3; 108 ($PF_2C_2{}^{11}BH_4^+$), 21.1; 107 ($PF_2C_2BH_3^+$), 5.6; 106 ($PF_2C_2BH_2^+$), 6.7; 105 ($PF_2C_2{}^{11}BH^+$), 11.1; 104 ($PF_2C_2{}^{11}B^+$), 2.2; 97 ($PF_2C_2H_4^+$), 12.2; 96 ($PF_2C_2H_3^+$), 100.0; 94 ($PF_2C_2H^+$), 1.7; 93 ($PF_2C_2^+$), 8.9; 92 ($PFC_2{}^{11}BH_7^+$), 2.2; 86 ($PFC_2{}^{11}BH^+$), 1.7; 82 ($PF_2{}^{11}BH_2^+$), 3.1; 81 ($PF_2{}^{11}BH^+$), 1.7; 80 ($PF_2{}^{11}B^+$), 1.7; 78 ($PFC_2H_4^+$), 11.1; 77 ($PFC_2H_3^+$), 70.0; 75 (PFC_2H^+), 6.7; 70 (PF_2H^+), 3.3; 69 (PF_2^+), 65.5; 63 ($PFCH^+$), 3.3; 62 (PFC^+), 2.2; 60 ($PC_2H_5^+$), 1.7; 59 ($PC_2H_4^+$), 23.2; 58 ($PC_2H_3^+$), 72.2; 57 ($PC_2H_2^+$), 41.1; 56 (PC_2H^+), 6.7; 55 (PC_2^+), 3.9; 51 (PFH^+), 26.7; 50 (PF^+), 25.5; 49 (BF_2^+), 6.1; 45 (PCH_2^+, $P^{11}BH_3^+$), 13.3; 44 (PCH^+), 3.3; 41 ($C_2H_6{}^{11}B^+$), 44.5; 40 ($C_2H_5{}^{11}B^+$), 22.2; 39 ($C_2H_4{}^{11}B^+$), 36.7; 38 ($C_2H_3{}^{11}B^+$), 12.2; 37 ($C_2H_2{}^{11}B^+$), 31.1; 36 ($C_2H{}^{11}B^+$), 8.9; 32 (PH^+, O_2^+), 25.5; 31 (P^+), 14.4; 30 (BF^+), 3.3; 28 (C_2H_4, N_2^+), 46.1; 27 ($C_2H_3^+$), 41.4; 26 ($C_2H_2^+$), 6.7; 14 ($^{11}BH_3^+$, CH_2^+), 2.0; 13 (CH^+, $^{11}BH_2^+$), 6.7; 12 (C^+, $^{11}BH^+$), 3.3; 11 ($^{11}B^+$), 2.2. Nmr spectra: ^1H (ambient temperature, $CHCl_3$): δ_{BH_3} 0.75 ppm[8,9] (q, J_{BH} = 101 Hz); each member of a quartet is a triplet (t, $J_{FBH} \approx 20$ Hz); each member of a triplet is a doublet (d, $J_{PBH} \approx$ 18.0 Hz); δ_{vinyl} ~6.6 ppm (spectrum is complex). ^{19}F (ambient temperature, $CHCl_3$): δ_F 82.9 ppm, (d, J_{PF} = 1131 Hz); each member of a doublet is a quartet (q, J_{FBH} = 20.5 Hz); fine structure is evident on the quartet peaks. ^{11}B (ambient temperature, $CHCl_3$): δ_B 130 ppm, (q, J_{BH} = 100.0 Hz); each member of a quartet is a doublet (d, J_{PB} = 60.0 Hz).

Results and Discussion

Vinyldifluorophosphine was prepared *via* the reaction

$$PF_2Br + Hg(CH{=}CH_2)_2 \rightarrow PF_2CH{=}CH_2 + PF_3 + \text{solids}$$

in yields of 27-30%. $PF_2C_2H_3$ is a clear volatile liquid which does not decompose *in vacuo* in the gas phase (98 hr); however, after 144 hr at ambient temperature in the gas phase over an excess of ZnF_2, $PF_4C_2H_3$[7] is evident in the ir spectrum of the mixture. Vapor density measurements at 19.4° and 63.7 mm pressure gave a molecular weight of 96.8, which compared very well to the calculated value of 98.0. $PF_2CH{=}CH_2$ was characterized by ir, mass, and ^{19}F and ^1H nmr spectra.

The ^{19}F nmr (ambient temperature, $CHCl_3$) shows a basic doublet (J_{PF} = 1150 Hz) from coupling with the directly bonded phosphorus atom which is centered 92.4 ppm upfield from $CFCl_3$. Higher resolution reveals a distinctly complex situation. The proton spectrum (ambient temperature, $CHCl_3$; δ_{vinyl} ~6.1 ppm) is also complicated by fine structure. Evaluation of coupling constants is not possible without a detailed analysis. The J_{PF} coupling constant is similar to those reported for other alkyldifluorophosphines.[10]

The infrared spectrum provides further confirmation of the vinylic structure.[11] Stretching frequencies at 3089 and 3029 cm^{-1} are indicative of the HC= and $=CH_2$ moieties of a $RCH{=}CH_2$ structure. No C=C stretch is visible in the low pressure ir spectrum, but two weak stretches appear at 1649 and 1619 cm^{-1} when the spectrum is recorded at higher pressure. $H_2C{=}$ deformations, 1414, 1406, 1398 cm^{-1}, and HC= deformations, 1013, 994, 977 cm^{-1}, are also evident in the spectrum. The ir spectrum of $PF_2C_2H_3$ with tentative assignments is listed in Table I.

The mass spectrum is relatively simple and can be fitted nicely to the compound. A complete mass spectrum and vapor pressure data appear in the Experimental Section.

Borane Adduct of $PF_2C_2H_3$. Since hydroboration of vinyl compounds occur readily,[12] it was not clear whether borane would add across the double bond or form a phosphine-borane adduct; however, infrared, nmr, and mass spectral evidence indicates that the initial reaction product is a borane adduct.

$PF_2CH{=}CH_2{\cdot}BH_3$ was prepared in 90% yields by the direct reaction of $^1/_2$ B_2H_6 and the ligand. The adduct was characterized by vapor-phase molecular weight (23.2°, P = 41.0 mm) [found, 111.4; calcd, 109.8] and its ir, mass, and ^{19}F, ^{11}B, and ^1H nmr spectra.

The presence of a J_{PB} coupling constant in the ^{11}B nmr of $PF_2CH{=}CH_2BH_3$ confirms the PB bond in the adduct. The proton spectrum also provides indirect evidence for the formation of a PB bond. The spectrum consists of two sets of absorptions. The high-field peaks are attributed to the BH protons while the low-field peaks can be identified as being distinctly vinyl by their complexity.[13] As in the case of the ligand a detailed analysis is required for identification of the vinyl coupling constants. The appearance in the mass spectrum of fragments with the following mass numbers (species) and relative abundance also supports the presence of a PB bond: 82 ($PF_2{}^{11}BH_2^+$), 2.8; 81 ($PF_2{}^{11}BH^+$), 1.5; 80 ($PF_2{}^{11}B^+$), 1.5; 45 ($P^{11}BH_3^+$), 12.0. Complete mass and nmr spectra appear in the Experimental Section.

The infrared spectrum of $PF_2CH{=}CH_2{\cdot}BH_3$ is very similar to that of the ligand. The double-bond stretch and the vinyl proton stretches remain intact in the spectrum of the adduct while a stretch at 577 cm^{-1} can be assigned tentatively as a

---

[7] P. M. Treichel and R. A. Goodrich, *Inorg. Chem.*, 4, 1424 (1965).

[8] Conventions from IUPAC International Bulletin No. 4, "Appendices on Tentative Nomenclature, Symbols, Units, and Standards," 1970. Signals downfield from TMS are reported as positive.

[9] Key: s, singlet; d, doublet; t, triplet; q, quartet.

[10] J. F. Nixon, *Advan. Inorg. Chem. Radiochem.*, 13, 363 (1970).

[11] L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, Chapter 2.

[12] H. C. Brown "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, p 287.

[13] J. A. Pople, W. A. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 192.

Table I[a]

$PF_2C_2H_3$ 7 mm	$PF_2C_2H_3$ 45 mm	$PF_2C_2H_3{\cdot}BH_3$ 7 mm	$PF_2C_2H_3{\cdot}BH_3$ 45 mm	Tentative assignment
3089 vw	3089 m		3109 w	
3029 vw, br	3029 mw		3049 w, br	CH str
2978 vw	2978 m		2997 w	
			2615 mw	
		2441 m	2441 vvs	
		2417 m, sh	2417 vvs, sh	BH str
			2230 mw	
1949 vvw, br	1949 w, br		1987 w	
			1789 w	
	1649 w, br		1627 mw	
	1614 w, br	1619 vw, br	1619 m	C=C str
			1612 mw	
			1562 vw	
			1472 vw	
1414 m, br	1414 s	1418 m	1418 vs	
1406 m	1406 vs	1411 m	1411 vvs	$=CH_2$ def (PQR)
1398 m, br	1398 s	1404 m	1274 vw	
	1133 w, br			
		1119 mw, br	1124 s	
			1117 s, sh	BH_3 def
			1073 m, sh	
			1067 m	
1013 w, sh	1013 s	1028 mw, sh	1028 vs	
994 mw, sh	994 vs	998 mw, sh	1017 vs, sh	=CH def
977 m, br	977 vs, br	981 mw, sh	998 vs, sh	
		973 w, sh	981 vs, sh	
		902 vvs	902 vvs	BH_3 rock
829 vs	829 vvs, br	799 vs	799 vvs	PF str
751 s, sh				
744 s	742 vvs, br			PC str (PQR)
	706 mw			
	697 m			
	688 mw			
			687 vvw, br	
			659 vvw, br	
	597 m		624 vvw, br	
	583 m, sh			
		577 w, br	584 m	PB str
			574 m	

[a] Vibrational frequencies are given in cm^{-1}. Notation for intensities: v, very; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

PB stretch.[14] A complete ir spectrum is included in Table I where it can be compared with that of the free ligand.

A PB bond can also be inferred from the ir data in a manner similar to that for $PF_2N_3{\cdot}BH_3$[15] and $PF_2NMe_2{\cdot}BH_3$.[16] Upon coordination the PC ligand vibration at 751, 744 cm^{-1} is altered in area significantly, so much that it does not appear in the high pressure (45 mm) spectrum of $PF_2C_2H_3{\cdot}BH_3$. For a group to exhibit absorption, the vibration must give rise to a change in the dipole moment.[17] The absorption area is dependent upon the magnitude of the change in dipole moment associated with the PC stretching mode. Considering the resonance structures for $PF_2CH{=}CH_2$

$$F_2PCH{=}CH_2 \longleftrightarrow F_2\overset{-}{P}{=}CH{-}\overset{+}{C}H_2$$

$$F_2PCH{=}CH_2 \longleftrightarrow F_2\overset{+}{P}{=}CH{-}\overset{-}{C}H_2$$

coordination of the borane through the phosphorus would be expected to lessen the change in dipole moment associated with the PC stretch and subsequently decrease the area of this absorption. The observed decrease in area of the PC absorption in the adduct and the tentative assignment of a PB stretch indicate that the boron is bonded to the phosphorus. A similar effect is seen for $PF_2NMe_2{\cdot}BH_3$[16] and $PF_2C{\equiv}CMe{\cdot}BH_3$,[18] where PB bonds have been confirmed by the presence of J_{PB} coupling constants in the ^{11}B spectra.

Base Strength of $PF_2C_2H_3$. The infrared spectrum and molecular weight of $PF_2C_2H_3{\cdot}BH_3$ indicate that this adduct is undissociated at room temperature in the gaseous state. A more thorough examination of the basicity of $PF_2C_2H_3$ was hampered by the small amounts of ligand available and its instability with other phosphines.

From the stability of the adduct in the gaseous state it can be concluded that $PF_2C_2H_3$ is a relatively strong base toward borane. A comparison of the base strength with electronegativity and π-bonding ability of $-HC{=}CH_2$ provide insight into contributing factors of base strength. The group electronegativity of $-CH{=}CH_2$ (2.8) and $-C{\equiv}C-$ (3.3)[19] would indicate that when compared to Cl (3.2) and Br (3.0) the adducts $PF_2C_2H_3{\cdot}BH_3$ and $PF_2C_3H_3BH_3$ would be dissociated as are PF_2ClBH_3 and PF_2BrBH_3,[20] but both are undissociated at room temperatures;[18] thus electronegativity alone cannot fully explain the trends observed in the basicity of the PF_2X series.

A satisfactory explanation for the basicity of the PF_2X series might include both of the above effects plus other

---

(14) R. C. Taylor and T. C. Bissot, *J. Chem. Phys.*, 25, 780 (1956).

(15) E. L. Lines and L. F. Centofanti, *Inorg. Chem.*, 11, 2269 (1972).

(16) S. Fleming and R. W. Parry, *Inorg. Chem.*, 11, 1 (1972).

(17) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1945, Chapter III.

(18) E. L. Lines and L. F. Centofanti, *Inorg. Chem.*, 12, 598 (1973).

(19) J. E. HuHeey, "Inorganic Chemistry," Harper and Row, New York, N. Y., 1972, Chapters 4 and 6.

(20) R. T. Paine and R. W. Parry, *Inorg. Chem.*, 11, 1237 (1972).

parameters that have not been extensively examined (electron repulsions, steric interference, etc., might be advanced).

Acknowledgment. The authors are grateful for the assistance of Dr. David Goldsmith with the mass spectra and Dr. Gogi Kodama with the ^{11}B nmr spectra. Appreciation is also expressed to the Air Force for the use of a Jeol 60-MHz nmr at Robins Air Force Base. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $PF_2CH{=}CH_2$, 51130-03-1; PF_2Br, 15597-40-7; $(CH_2{=}CH)_2Hg$, 1119-20-6; $PF_2CH{=}CH_2{\cdot}BH_3$, 51130-04-2; B_2H_6, 19287-45-7.

Contribution from the Department of Chemistry,
Wollongong University College, Wollongong, NSW 2500, Australia

Magnetic Behavior of Some Polynuclear Methoxide Complexes of Iron(III) with Meta-Substituted Benzoates

E. Kokot,* G. M. Mockler, and G. L. Sefton

Received September 7, 1973 AIC30657S

The interest in recent years in alkoxide as a ligand has resulted in the synthesis of a number of polynuclear complexes of tervalent iron. The presence of bridging alkoxide usually leads to antiferromagnetic coupling between the metal atoms. Antiferromagnetic trimeric *n*-alkoxides $(Fe_3(OR)_9)^{1-3}$ have been characterized. Kakos and Winter[4] prepared the antiferromagnetic trimer $FeCl(OMe)_2$ and the tetramers $Fe_4X_6(OMe)_6{\cdot}4MeOH$ and $Fe_4X_3(OMe)_9$, where X is Cl or Br. In previous papers we have described compounds of the type $FeL(OMe)_2$. All the compounds are antiferromagnets. The complex with L = acetylacetonate is probably a dimer.[5] The others for which L is alkanoate[6] and aromatic acid[7] are probably tetramers. All compounds show a single C-O stretching band. A structure involving trigonal prismatic iron atoms was found to agree best with the experimental evidence. We now report the results on complexes of the same type where L is meta-substituted benzoate.

Experimental Section

All complexes were prepared according to Kokot, *et al.*[5] They are all yellow, unstable to heat above 250°, insoluble in organic solvents and moisture sensitive. Iron was determined volumetrically with potassium dichromate and sodium diphenylaminesulfonate indicator. Carbon and hydrogen were determined in The University of New South Wales Microanalytical Laboratory and by the Australian Microanalytical Service (Melbourne).

Physical Measurements. Magnetic measurements were carried out as described previously.[8] The infrared spectra in KBr were recorded with a Jasco DS 4039 infrared spectrophotometer between 4000 and 300 cm^{-1}. The electronic reflectance spectra were obtained with a Zeiss PMQ II spectrophotometer fitted with an RA-3 reflectance

Table I. Magnetic Data at Various Temperatures of Complexes

Temp, °K	$10^6\chi_A$, cgsu	μ, BM	Temp, °K	$10^6\chi_A$, cgsu	μ, BM
		m-Methylbenzoate ($-10^6\Delta = 117$)			
78.5	17,036	3.28	220.0	11,716	4.56
95.5	16,387	3.55	250.0	10,828	4.67
110.0	15,759	3.74	280.0	10,088	4.77
130.0	14,936	3.96	295.8	9,715	4.79
150.0	14,165	4.14	310.0	9,421	4.85
170.0	13,427	4.29	340.0	8,817	4.92
195.0	12,517	4.44			
		m-Methoxybenzoate ($-10^6\Delta = 121$)			
78.5	18,614	3.43	220.5	12,266	4.67
95.0	17,765	3.69	250.0	11,263	4.76
109.5	17,124	3.89	280.5	10,466	4.86
132.5	16,060	4.14	295.5	10,106	4.89
150.0	15,155	4.28	310.0	9,764	4.94
170.0	14,277	4.42	340.5	9,096	5.00
195.5	13,195	4.56			
		m-Chlorobenzoate ($-10^6\Delta = 119$)			
78.0	18,274	3.39	220.5	12,364	4.69
95.5	17,599	3.68	250.0	11,386	4.79
110.0	16,985	3.88	280.0	10,605	4.89
130.5	16,076	4.11	296.9	10,185	4.92
150.0	15,191	4.29	310.0	9,845	4.96
170.0	14,321	4.43	340.0	9,242	5.03
195.5	13,264	4.57			
		m-Nitrobenzoate ($-10^6\Delta = 112$)			
81.5	14,440	3.08	220.5	10,962	4.41
97.0	14,246	3.34	250.0	10,247	4.54
110.5	13,924	3.52	280.0	9,556	4.64
131.0	13,571	3.79	295.5	9,237	4.67
150.5	13,016	3.97	310.0	8,979	4.74
170.5	12,436	4.13	340.0	8,443	4.81
195.5	11,705	4.29			

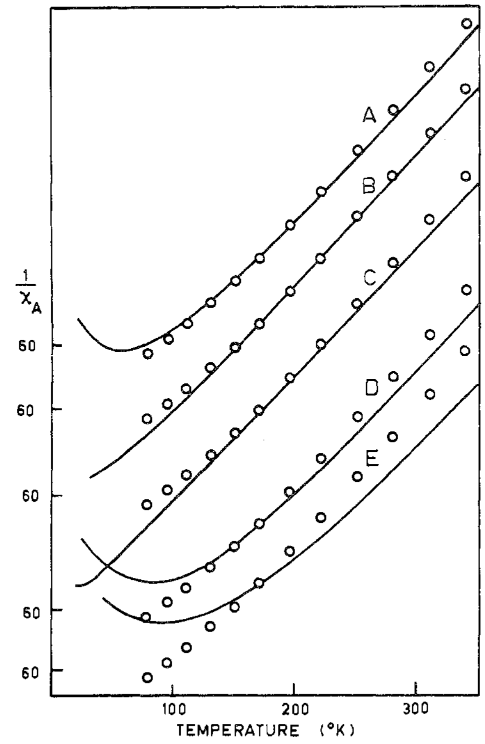

Figure 1. Comparison of best-fit $\chi_A^{-1}(T)$ curves for the *m*-methylbenzoate complex for the following cluster models: Fe_4 planar (A), Fe_4 tetrahedral (B), Fe_3 equilateral triangle (C), infinite chain (D), and Fe_2 (E).

---

(1) D. C. Bradley, R. K. Multani, and W. Wardlaw, *J. Chem. Soc.*, 126 (1958).

(2) R. W. Adams, R. L. Martin, and G. Winter, *Aust. J. Chem.*, 19, 363 (1966).

(3) R. W. Adams, C. G. Barraclough, R. L. Martin, and G. Winter, *Inorg. Chem.*, 5, 346 (1966).

(4) G. A. Kakos and G. Winter, *Aust. J. Chem.*, 22, 97 (1969).

(5) E. Kokot, G. M. Mockler, and G. L. Sefton, *Aust. J. Chem.*, 26, 875 (1973).

(6) E. Kokot, G. M. Mockler, and G. L. Sefton, *Aust. J. Chem.*, 26, 2105 (1973).

(7) E. Kokot, G. M. Mockler, and G. L. Sefton, *Aust. J. Chem.*, in press.

(8) E. Kokot and G. A. Ryder, *Aust. J. Chem.*, 24, 649 (1971).