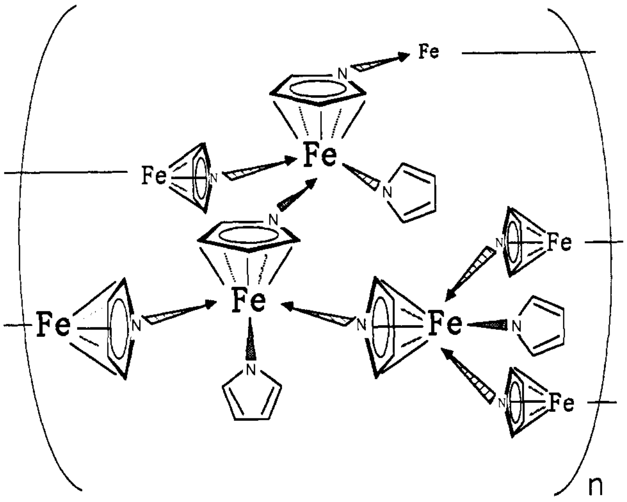

IV

analagous with the observed chemistry of azaferrocene[2,4,6] and supports the presence of a similar moiety in the polymer. Each pyrrolyl π-to-σ rearrangement opens two coordination sites, hence the addition of two bidentate π-acidic ligands to each iron site in IV might account for the breakdown of the polymeric structure and the formation of the octahedral complexes II and III reported in Scheme I.

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Complexes of Ir(III) Containing the Novel SF_3 Ligand

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This paper describes the synthesis and characterization of the complexes $Ir(CO)FX(PEt_3)_2SF_3$, where X is Cl, Br, or I; we believe that these are the first complexes described that contain the SF_3 ligand, and they are formed by an unusual[1] oxidative addition of an SF bond to 4-coordinated Ir(I).

Reaction between *trans*-$Ir(CO)Cl(PEt_3)_2$ (A) and a small excess of SF_4 occurs rapidly in CD_2Cl_2 at 200 K. The single product has been identified from its ^{19}F- and $^{31}P\{H\}$ NMR spectra as $Ir(CO)ClF(PEt_3)_2SF_3$ (B). In the ^{19}F spectrum at 200 K we observed four resonances of equal intensity. One, at very low frequency (δ −337), was in the region associated[2] with Ir−*F* nuclei in phosphine fluorocomplexes of Ir(III). It appeared as a near triplet [$^2J(PF_{av})$ = 33 Hz] of narrower doublets of doublets of doublets. The other three resonances were in the region associated with F bound to a main-group element such as S (73.5, 45.2, −66.8 ppm). All appeared as complicated multiplets that could be analyzed as first-order patterns of overlapping doublets derived from coupling to five different spin-one-half nuclei. We assign these three resonances to the three S*F* nuclei in complex B, which must then be in different environments at this temperature in solution. The $^{31}P\{H\}$ spectrum at 190 K showed what was basically an AB pattern, with further splittings in both A and B sections of the spectrum; the further splittings could also be analyzed in simple first-order terms as derived from coupling to four different spin-one-half nuclei, which are clearly the three S*F* and one Ir*F* nuclei whose resonances were observed in the ^{19}F spectrum. The nonequivalance of the two phosphorus nuclei arises from the asymmetry at S, whose coordination positions are occupied by the metal, by three fluorine atoms (each chemically distinct), and by a lone pair (Table I).

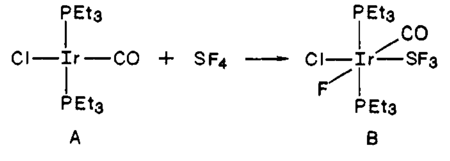

Table I. NMR Parameters for Ir−SF Complex $Ir(CO)XF(PEt_3)_2(SF_3)$

	chem shifts/ppm					
	SF			IrF	P	
X	F_1	F_2	F_3	F_4	P_A	P_B
Cl	75.53	45.22	−66.81	−336.9	7.56	0.28
Br	74.4	44.8	−66.11	−344.1	3.62	−3.58
I	72.8	41.7	−67.6	−356.2	−1.68	−8.72

	coupling constants/Hz		
	X = Cl	X = Br	X = I
$^2J(PP)$	340	336	331
$^2J(F_1F_2)$	179.7	182.2	183.2
$^2J(F_1F_3)$	58.8	58.0	60.0
$^3J(F_1F_4)$	3.6	3.5	3.5
$^2J(F_2F_3)$	80.6	78.9	80.3
$^3J(F_2F_4)$	9.6	10.0	10.0
$^3J(F_3F_4)$	nr	nr	nr
$^3J(F_1P_A)$	nr	nr	nr
$^3J(F_1P_B)$	11.2	10.4	9.1
$^3J(F_2P_A)$	22.9	20.7	18.4
$^3J(F_2P_B)$	13.0	14.3	13.4
$^3J(F_3P_A)$	nr	nr	nr
$^3J(F_3P_B)$	5.1	5.8	5.9
$^2J(F_4P_A)$	31.0	31.9	32.5
$^2J(F_4P_B)$	35.7	36.6	37.6

When the solution was allowed to warm, the spectra showed marked changes. The resonances assigned to the three S*F* nuclei broadened and collapsed, and at 298 K they gave a single very broad peak that could scarcely be distinguished from the base line. The Ir*F* resonance became a sharp triplet and lost the narrower doublet splittings. The $^{31}P\{H\}$ spectrum showed associated changes. At 220 K the detail in the A and B sections of the spectrum could no longer be resolved; at 298 K the P resonance appeared as a single very broad line ($w \sim 100$ Hz) which sharpened into a doublet at 325 K (see Figure 1). All these changes were reversible. Similar spectra were obtained from solutions in toluene; heating a solution of B in toluene to 345 K, however, resulted in irreversible decomposition. It is clear that the SF_3 group undergoes some fluxional or exchange process which is slow on the NMR time scale at 190 K but becomes fast on this time scale at temperatures above 300 K. We have no direct evidence to show whether the process is inter- or intramolecular. The apparent loss of $^3J(FF)$ from the Ir*F* resonance at 300 K is consistent with an intermolecular mechanism, though intramolecular interchange cannot be excluded. In SF_4 it appears that both inter- and intramolecular processes can be significant;[3] in $Ir(CO)Cl_2(PEt_3)_2(P'F_4)$, the fluxional interchange round P′ is intramolecular[4] at least up to 300 K and fast on the NMR time scale at 200 K,

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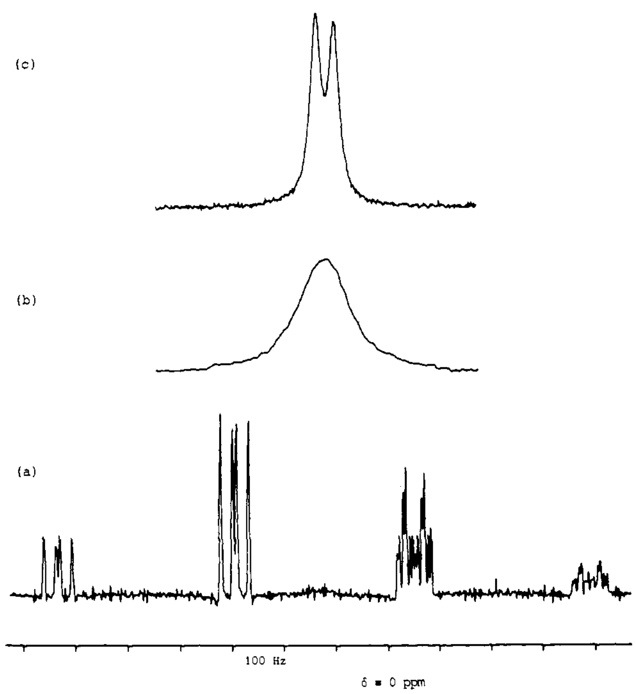

Figure 1. $^{31}P\{H\}$ NMR spectrum of $Ir(CO)ClF(PEt_3)_2SF_3$ recorded in CD_2Cl_2 at (a) 200, (b) 280, and (c) 325 K, with an operating frequency of 81 MHz. The centers of the resonances have been arranged to coincide, thus offsetting a small change in chemical shift with temperature.

only becoming slow enough to resolve distinct F environments at 130 K.

We have isolated B as a colorless solid, which is thermally stable, but it rapidly turns green if exposed to the atmosphere and is sensitive to moisture. The compound has been characterized by partial elemental analysis, by its infrared spectrum, and by single-crystal X-ray diffraction.[5] The determination of the crystal structure is not yet complete. Results so far confirm the geometry around iridium and show that fluoride is trans to carbonyl. We have been able to locate the fluorine atoms bound to sulfur, but we have not been able to refine them positionally; we are exploring various disorder models to try to overcome this difficulty. We have also prepared analogues of B from SF_4 and the corresponding iridium bromide or iodide.

Preliminary experiments show that B reacts with a small excess of BF_3 in CD_2Cl_2. The reaction is slow at 200 K but rapid at 270 K. The ^{19}F and ^{31}P NMR spectra of the product show it to be the novel complex $[Ir(CO)ClF(PEt_3)_2SF_2]^+[BF_4]^-$, formally analogous to $SF_3^+BF_4^-$ that is produced[6] from SF_4 and BF_3. The ^{19}F spectrum showed the resonance due to $[BF_4]^-$, together with two new resonances. One of these (δ -360.9) was in the region associated with Ir*F* and appeared as a triplet [$^2J(PF) = 33$ Hz] of triplets [$^3J(FF) = 17$ Hz]. The other (δ -51.8) was in the region associated with main-group fluorides; it appeared as a doublet [$^3J(FF) = 17$ Hz] of triplets [$^3J(FP) = 15$ Hz]. The P{H} resonance (δ 8.05) appeared as a doublet of triplets, with coupling constants corresponding to those observed in the ^{19}F spectrum. This complex decomposed slowly in solution at room temperature. We believe it to be the first reported example of a complex containing the SF_2^+ ligand, which is isoelectronic with PF_2.

We are studying the chemistry and structures of these and related complexes.

Acknowledgment. We thank Messrs Johnson Matthey for lending us chemicals.

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[5] Crystallographic parameters: space group $P2_1$; $Z = 2$; monoclinic; $a = 7.571$ (4), $b = 8.719$ (4), $c = 15.493$ (9) Å; $\beta = 100.92$ (4)°; $V = 1004$ Å; $T = 170$ K.

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Transition Structures for Intramolecular Hydrogen Atom Transfers: The Energetic Advantage of Seven-Membered over Six-Membered Transition Structures

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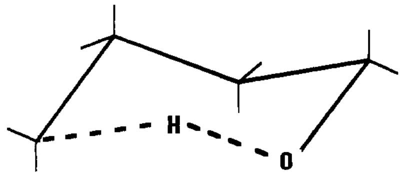
Intramolecular hydrogen abstractions by alkoxy radicals have been the subject of many mechanistic[1] and synthetic[2,3] investigations. In these systems, hydrogen transfer invariably takes place via a six-membered transition state. Reactions of substituted pentanols, hexanols, and octanols all give substituted tetrahydrofurans as the major products.[4-6] The preference for δ-hydrogen abstraction is usually rationalized by analogy: the carbocyclic six-membered cyclohexane ring is strain-free, while all other carbocyclic rings have some strain. However, as shown in **1**, a perfect analogy to cyclohexane requires a severely nonlinear geometry for hydrogen transfer.[7] By contrast, linearity is usually considered to be favored in hydrogen transfer.[8] Isotope effects and the stereoselectivity of hydrogen abstraction by the 2-hexyloxy radical have been interpreted as requiring a linear or nearly linear transition state.[9,10]



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We have carried out both ab initio molecular orbital calculations[11] and force-field modeling[12] which predict that abstraction of a δ-hydrogen atom is actually *disfavored* enthalpically with

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