

However, the extent to which this interaction is significant in these systems appears to be small and of secondary importance compared to metal-aryl σ bonding,⁷⁶ in contrast to previous suggestions.^{5,7,9,12,18-21} We therefore feel that arguments based on thermal stabilities of transition metal-aryl compounds (relative to the analogous alkyl derivatives) or on shortened metal-carbon bond distances⁷⁷ are without adequate support.

(76) Recent esr studies on *trans*-(*p*-XC₆H₄)₂CoL₂ complexes (L = P(C₂H₅)₂C₆H₅) support this contention; see K. Matsuzaki and T. Yasukawa, *Chem. Commun.*, 1460 (1968).

(77) Metal-aryl carbon bond lengths are known for a variety of transition metal-aryl complexes,¹⁸⁻²⁷ but to date none of the corresponding metal-alkyl carbon distances have been determined. Instead the latter distances must be estimated from the appropriate metal-carbon covalent radii sum. Although the covalent radii of sp³ and sp² hybridized carbon are well established and roughly constant, metallic radii are influenced by (a) the effective charge on the metal nucleus, (b) the metal coordination number, (c) the coordination geometry, and (d) the electronic and steric requirements imposed by other ligands bonded to the metal.⁷⁸⁻⁸⁰ Until the corresponding metal-alkyl and metal-aryl distances are obtained in completely analogous complexes, the present crystallographic evidence for a strong contribution to the metal-aryl bond must be considered inconclusive.

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It is possible, however, under certain circumstances involving metal-aryl complexes with ligands of generally low back-bonding abilities, that metal \rightarrow aryl π delocalization could have substantial importance. A similar conclusion can be drawn for other ligands. For example, 2,2'-bipyridyl can stabilize many low-valent complexes presumably by virtue of π back-bonding ability,⁸¹ yet this ligand seems to possess a vanishingly small back-bonding capacity in carbonyl complexes.⁵¹

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Nuclear Magnetic Resonance Investigation of Complexes Formed by Arsenic Pentafluoride and Some Very Weak Bases

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Abstract: The ¹⁹F nmr spectra of the following systems have been studied over a range of temperature: AsF₅-SO₂F₂, AsF₅-SOF₂-SO₂F₂, AsF₅-SO₂FCl, AsF₅-SO₂-SO₂F₂, AsF₅-CH₃SO₂F-SO₂F₂, and AsF₅-CH₃SO₂F-SO₂F₂-SO₂. It has been found that AsF₅ forms very labile complexes with SOF₂, SO₂, SO₂FCl, and CH₃SO₂F, but no complex formation was observed with SO₂F₂.

It has been shown recently that antimony pentafluoride forms complexes with the very weak bases SO₂FCl, SOF₂, SO₂, and CH₃SO₂F.¹ Although evidence has been obtained for stable complexes of arsenic pentafluoride with relatively strong bases such as CH₃CN,² (CH₃)₃N, and (CH₃)₂O,³ except for a study of the AsF₅-SO₂ system,⁴ in which it was concluded that no adduct formation occurred, there has been no investigation of the possibility of adduct formation with very weak bases. We have used ¹H and ¹⁹F nmr to investigate the interaction of AsF₅ with SO₂F₂, SOF₂, SO₂FCl, SO₂, and CH₃SO₂F.

Results and Discussion

The AsF₅-SO₂F₂ System. No complex formation occurs between AsF₅ and SO₂F₂ even at -140°. The

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¹⁹F spectra of a 1:4.25 AsF₅:SO₂F₂ sample showed only a single F-on-S peak with the same chemical shift as that found for pure SO₂F₂. The F-on-As peak was very broad (more than 1000 Hz at -35°) as for pure AsF₅, and in contrast to our findings for AsF₅ with stronger donors which form complexes. This result is not surprising as SO₂F₂ does not form any complex with SbF₅.¹ In fact in solution in SO₂F₂, SbF₅ forms fluorine-bridged chains as in liquid SbF₅, rather than complex with SO₂F₂. It is known from vibrational spectroscopy that AsF₅ is monomeric in the liquid as well as the gas phase⁵ so that in this case the formation of polymeric fluorine bridged chains does not compete with the formation of an AsF₅·SO₂F₂ complex. Since no interaction occurs, SO₂F₂ was used as a solvent for the other potential bases that were studied in order to obtain the nmr spectra at temperatures down to the freezing point of SO₂F₂ (-135.8°).⁶

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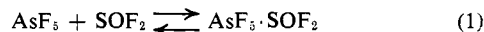
Table I. ^{19}F Shift (ppm from CFCl_3) in $\text{AsF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$

Temp, °C	Sample composition, $\text{AsF}_5\text{:SO}_2\text{:SO}_2\text{F}_2$								
	1:0.56:3.2			1:0.79:3.8			1:2.3:6.2		
	SO_2	AsF ₅		SO_2	AsF ₅		SO_2	AsF ₅	
		Shift	Width ^a		Shift	Width		Shift	Width
6	-70.6	+62.5	240	-71.5	+62.9	250	-71.4	+61.0	185
-6	-69.6	+61.7	230	-71.1	+62.0	160	-71.1	+59.5	110
-28	-66.6	+59.0	130	-66.8	+58.8	110	-69.6	+56.9	110
-51	-58.8	+57.7	130	-59.8	+55.2	75	-65.9	+51.8	110
-76	-52.0	+57.0	75	-54.0	+52.5	60	-63.3	+49.4	50
-100 ^b	-48.6	+58.1	75	-50.8	+57.8	50	-62.0	+48.7	25
-125	-46.2	+57.5	60	-45.7	+57.3	50			

^a Width of AsF_5 peak at half-height in Hz. ^b At -100° shift of pure SO_2 = -73.5 ppm and shift of F on S in $\text{SbF}_5\cdot\text{SO}_2$ is -46.7 ppm.

The $\text{AsF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$ System. In addition to the SO_2F_2 solvent peak, only two lines were visible in the ^{19}F nmr spectrum at all temperatures and for varying concentrations. The peak due to the fluorine in SO_2 was a sharp singlet. The chemical shift varied over a range of 22 ppm from near that of uncomplexed SO_2 when the sample was at $+20^\circ$ to near that of SO_2 complexed by SbF_5 for a sample at -100° containing excess AsF_5 (Table I). The F-on-As peak was much narrower than for the AsF_5 solution in SO_2F_2 . The chemical shift changed from near that of AsF_5 in SO_2F_2 ($+63$ ppm at -35°) for a sample at $+20^\circ$ to near the average value for F on As in the complex $\text{C}_5\text{H}_5\text{N}\cdot\text{AsF}_5$ ⁷ for a sample at -100° containing excess SO_2 .

These results can be explained by assuming that, by analogy with the $\text{SbF}_5\text{-SO}_2$ system, a 1:1 complex is formed, but that in this case it is rather labile and is in equilibrium with its components (1). At room tempera-



ture, the equilibrium lies far to the left, shifting to the right on cooling. The rate of formation and dissociation of the complex must be very rapid, as the F-on- SO_2 peak remained narrow even at -125° .

The sharpness of the F-on-As peak is indicative of a much greater rate of quadrupole relaxation of the coupling between ^{75}As ($I = 3/2$) and ^{19}F than in AsF_5 alone. This is expected as the electric field gradient about the arsenic will be greater in the complexed molecule than in uncomplexed AsF_5 , in which the very rapid intramolecular exchange of fluorine (pseudo-rotation) causes a rapid averaging of the electric field gradient to a very low value. In complexed AsF_5 , there is a more symmetric octahedral arrangement of bonds about arsenic, but five are strong As-F bonds, while the sixth is the As-O complex bond. The resultant electric field gradient is likely to be larger than for the AsF_5 molecule.

The $\text{AsF}_5\text{-SO}_2\text{CIF}$ System. In addition to the peak of SO_2F_2 present as an internal reference, only two single lines are visible in the ^{19}F nmr spectrum at all temperatures (Table II). As in the $\text{AsF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$ system, the F-on-As peak was shifted downfield from that of AsF_5 in SO_2F_2 , and its width was much less than for AsF_5 and decreased with decreasing temperature again indicating that there is an interaction with the SO_2CIF . However, even with a large excess of SO_2CIF , the AsF_5 peak did not shift as far as in the SO_2 samples. These observations would indicate an equilibrium (2)



lying farther to the left than in (1). This is in agreement with the finding that SO_2CIF is a weaker base than SO_2 toward SbF_5 .¹

Table II. ^{19}F Shift (ppm from CFCl_3) in $\text{AsF}_5\cdot\text{SO}_2\text{CIF}$ ^a

Temp, °C	SO_2CIF	AsF ₅	
		Shift	Width ^b
+30 ^c	-97.7	+61.0	100
-20	-97.2	+58.8	84
-35	-97.1	+57.5	88
-51	-96.8	+56.5	88
-68	-96.6	+55.2	80
-85	-96.3	+53.9	56
-100	-96.0	+52.8	44
-125		+52.0	46

^a Converted from SO_2F_2 internal reference ($\delta_{\text{SO}_2\text{F}_2} = \delta_{\text{CFCl}_3} + 31.0$ ppm). ^b Width of AsF_5 peak at half-height in Hz. ^c Shift of SO_2CIF at $30^\circ = -97.7$ ppm.

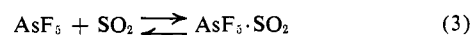
The $\text{AsF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$ System. In addition to the SO_2F_2 solvent peak only a single sharp F-on-As peak was seen in the spectrum of a 1:2.0:5.7 $\text{AsF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$ sample (Table III). The chemical shift as a func-

Table III. ^{19}F Shift (ppm from CFCl_3) of AsF_5 in $\text{AsF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$ ^a

Temp, °C	Shift	Width, Hz
6	+57.8	55
-6	+56.3	55
-28	+53.2	50
-50	+51.0	50
-76	+49.9	50
-100	+49.6	48

^a Measured from solvent SO_2F_2 and converted to CFCl_3 using $\delta_{\text{SO}_2\text{F}_2} = \delta_{\text{CFCl}_3} + 31.0$ ppm.

tion of temperature and width of the peak are quite similar to that found for AsF_5 complexed to SO_2 . In this case though, even at room temperature, the F-on-As resonance is not as close to uncomplexed AsF_5 as it is in an SO_2 sample of similar ratio, indicating an equilibrium (3) shifted farther to the right than (1). This is con-



sistent with the previous finding that SO_2 is a stronger

(7) $\text{C}_5\text{H}_5\text{N}\cdot\text{AsF}_5$: $F_{\text{equatorial}} = +41.0$ ppm, $F_{\text{apical}} = +82.7$ ppm, $F_{\text{average}} = +45.3$ ppm, from ref 2.

base than SO_2 .¹ It is not unexpected to find that SO_2 interacts with AsF_5 , since it has been shown that it forms a solid 1:1 complex with the even weaker Lewis acid BF_3 , although there is considerable dissociation above the melting point.⁸

The $\text{AsF}_5\text{-CH}_3\text{SO}_2\text{F-SO}_2\text{F}_2$ System. In addition to the SO_2F_2 solvent peak only two lines are visible in the ^{19}F nmr spectra at all temperatures and for varying concentrations. The chemical shift of the lines, the coupling constant J_{HF} in $\text{CH}_3\text{SO}_2\text{F}$, and the width of the F-on-As line indicates that complex formation is occurring. However, unlike the $\text{AsF}_5\text{-SO}_2\text{F}_2$ samples, the chemical shifts do not change appreciably with varying temperature (Tables IV and V).

Table IV. ^{19}F Shift (ppm) of $\text{CH}_3\text{SO}_2\text{F}^a$

Temp, °C	—Sample composition, $\text{AsF}_5:\text{CH}_3\text{SO}_2\text{F}:\text{SO}_2\text{F}_2:\text{SO}_2$ —					
	1:0.65:8.5:0		1:0.96:2.0:2.7		1:1.2:4.3:2.8	
	J_{HF} , Hz	Shift	J_{HF} , Hz	Shift	J_{HF} , Hz	Shift
-6			6.2	+3.49		
-12			6.5	+3.50	6.0	+3.42
-20			6.3	+3.52	6.2	+3.40
-28	6.3	+3.63	6.2	+3.61	6.0	+3.47
-35	6.7	+3.68	6.3	+3.65	6.2	+3.42
-43			6.5	+3.63	6.2	+3.43
-51			6.3	+3.61		
-59	6.7	+3.75	6.3	+3.58	6.3	+3.38
-68	6.3	+3.77	6.3	+3.56	6.3	+3.40
-76			6.5		6.2	
-85			6.5		6.3	

^a Shift from $\text{CH}_3\text{SO}_2\text{F}$ in SO_2F_2 (1:15) at the same temperature, both originally measured from solvent SO_2F_2 .

Table V. ^{19}F Shift (ppm from CFCl_3) of F in AsF_5 Complexed to $\text{CH}_3\text{SO}_2\text{F}^a$

Temp, °C	—Sample composition, $\text{AsF}_5:\text{CH}_3\text{SO}_2\text{F}:\text{SO}_2\text{F}_2:\text{SO}_2$ —					
	1:0.65:8.5:0		1:0.96:2.0:2.7		1:1.2:4.3:2.8	
	Shift	Width, Hz	Shift	Width, Hz	Shift	Width, Hz
-28					+49.3	45
-51	+50.9	45			+50.9	35
-59			+50.6	38		
-68	+53.9	45	+50.0	42		
-76					+50.5	70
-85			+49.8	30		
-100					+41.5	250

^a Measured from solvent SO_2F_2 and converted using $\delta_{\text{SO}_2\text{F}_2} = \delta_{\text{CFCl}_3} + 31.0$ ppm.

The position of F on $\text{CH}_3\text{SO}_2\text{F}$ shifts upfield in the complex even further than in the $\text{SbF}_5\cdot\text{CH}_3\text{SO}_2\text{F}$ complex (+2.1 ppm). The coupling constant J_{HF} in $\text{CH}_3\text{SO}_2\text{F}$ increases from 5.3 Hz for uncomplexed $\text{CH}_3\text{SO}_2\text{F}$ to 6.3 Hz for the complex $\text{AsF}_5\cdot\text{CH}_3\text{SO}_2\text{F}$. This again parallels the behavior of $\text{SbF}_5\cdot\text{CH}_3\text{SO}_2\text{F}$ for which J_{HF} increases to 6.8 Hz. With less than a stoichiometric amount of AsF_5 , the changes in the chemical shift and J_{HF} were correspondingly less. For samples containing large amounts of $\text{CH}_3\text{SO}_2\text{F}$, SO_2 was added in order to ensure that the system remained homogenous. This SO_2 did not have any effect on the

spectra showing that it is a weaker base than $\text{CH}_3\text{SO}_2\text{F}$ toward AsF_5 as it also is toward SbF_5 .¹ Similar changes in chemical shifts and coupling constants were observed in the proton spectra (Table VI). The proton resonance shifts farther to lower field for the complex with SbF_5 than with AsF_5 , presumably due to the greater electron withdrawing ability of SbF_5 . This is similar to earlier findings with complexes of stronger bases with PF_5 and AsF_5 .³

Table VI. ^1H Shift (ppm from TMS) of $\text{CH}_3\text{SO}_2\text{F}$

Temp, °C	—Sample composition—			
	$\text{CH}_3\text{SO}_2\text{F}:\text{SO}_2\text{F}_2$		$\text{AsF}_5:\text{CH}_3\text{SO}_2\text{F}:\text{SO}_2\text{F}_2:\text{SO}_2$	
	—1:15—		1:0.96:2.0:2.7	
	δ	J_{HF} , Hz	δ	J_{HF} , Hz
+30 ^a	-2.50	5.0	-3.13	6.4
-20	-2.61	5.5	-3.36	6.0
-37	-2.50	5.5	-3.30	6.5
-55	-2.70	5.5	-3.25	6.5
Av	-2.58	5.3	-3.26	6.3

^a $\text{CH}_3\text{SO}_2\text{F}$ in $\text{SbF}_5\cdot\text{CH}_3\text{SO}_2\text{F}$, $J_{\text{HF}} = 6.8$ Hz, $\delta = -3.71$ at +30°.

The absence of changes in the chemical shift and in the coupling constant with temperature indicate that the $\text{CH}_3\text{SO}_2\text{F}$ is essentially fully complexed even at +20°. However, there is still a very labile exchange occurring, as evidenced by the single $\text{CH}_3\text{SO}_2\text{F}$ peak, and the lack of any fine structure in the AsF_5 peak.

Conclusions

Arsenic pentafluoride forms very labile complexes with SOF_2 , SO_2ClF , SO_2 , and $\text{CH}_3\text{SO}_2\text{F}$. The lability of these complexes suggests that AsF_5 is a weaker acid toward these bases than is SbF_5 . Sulfuryl fluoride was found to act as an inert diluent for AsF_5 . The donors considered were found to have the following base strengths toward AsF_5 : $\text{CH}_3\text{SO}_2\text{F} > \text{SO}_2 > \text{SOF}_2 > \text{SO}_2\text{ClF} > \text{SO}_2\text{F}_2$. This is the same order of base strength that had been previously found toward SbF_5 .¹ In that work the hexafluoroantimonate ion was found to be a stronger base than $\text{CH}_3\text{SO}_2\text{F}$ toward SbF_5 . The hexafluoroantimonate ion has also been shown to complex with AsF_5 .⁹

Experimental Section

Fluorine nmr spectra were measured using a Varian DA-60IL spectrometer operating at 56.4 MHz. The 2500-Hz audio-modulation side bands forming part of the base line stabilization circuitry of the instrument usually overlapped part of the centerband spectrum, and the lock box was therefore modified to take an external manual oscillator frequency from a Muirhead D-890-A audio frequency oscillator. Spectra were then measured using the first upper side band in the field sweep unlock mode. Fluorine chemical shifts were measured from CFCl_3 , contained in a sealed capillary within the sample tube. In some cases, and particularly below the freezing point of CFCl_3 , shifts were measured from solvent SO_2F_2 , and converted to shifts from CFCl_3 by means of the relation $\delta_{\text{SO}_2\text{F}_2} = \delta_{\text{CFCl}_3} + 31.0$ ppm. Low-temperature spectra were obtained using a Varian V4540 temperature controller with the low temperature probe. Proton spectra were measured using a Varian A-60 spectrometer.

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Materials. The purity of the arsenic pentafluoride (Ozark Mahoning) was checked by determining its ir spectrum in a 10-cm Monel gas cell with silver chloride windows. No extraneous bands were found so it was used without further purification.

Sulfuryl fluoride (Matheson of Canada Ltd.) and thionyl fluoride (Peninsular ChemResearch Inc.) showed only one line in their ^{19}F nmr spectra and were used without further purification. Anhydrous grade sulfur dioxide (Matheson of Canada Ltd.) was used without further purification. Methyl sulfuryl fluoride (Eastman Organic Chemicals) was distilled, and the middle cut was stored over molecular sieves. Sulfuryl chlorofluoride was prepared from potassium fluorosulfinate and chlorine according to Seel and Riehl.¹⁰ In order to remove some sulfur dioxide impurity, it was condensed onto antimony pentafluoride and subsequently distilled off. Sulfur dioxide forms a much stronger complex with antimony pentafluoride than does sulfuryl chlorofluoride, and remains be-

hind.¹ The gas-phase ir spectrum of the final product showed no bands due to sulfur dioxide.

Sample Preparation. Known amounts of gases were condensed into an nmr tube from a calibrated vacuum line and the tube was sealed. If one of the components was $\text{CH}_3\text{SO}_2\text{F}$, a known weight was added from a hypodermic syringe, prior to placing the tube on the vacuum line.

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The Crystal, Molecular, and Electronic Structure of Bisacetatobis(ethylenethiourea)cobalt(II)

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Abstract: The crystal and molecular structure of bisacetatobis(ethylenethiourea)cobalt(II) [$\text{CoS}_2\text{O}_4\text{C}_{10}\text{N}_4\text{H}_{18}$] has been determined using three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares methods to a conventional R factor of 0.061 (based on anisotropic temperature factors). This complex crystallizes in the orthorhombic system in space group $D_{2h}^{14}\text{-Pbna}$ with 4 molecules in a unit cell of dimensions $a = 12.460 \pm 0.041$, $b = 13.550 \pm 0.036$, and $c = 9.393 \pm 0.032$ Å. The geometry about the cobalt is distorted tetrahedral with two normal cobalt-sulfur, two normal cobalt-oxygen, and two long cobalt-oxygen bonds. The 80°K polarized spectrum of this compound is also presented and rationalized in terms of pseudo-tetrahedral symmetry modified by next-nearest-neighbor interactions. The room-temperature polarized spectrum of bisacetatobis(thiourea)cobalt(II) is also presented.

Although much attention has been given in recent years to the correlation of crystal field calculations with experiment,² to the source of intensity of spectral lines in trigonally distorted complexes,³ and to the identification of structure types through absorption spectroscopy,⁴ little has been said about systems in which the transition metal ion finds itself in an environment which deviates greatly from idealized, tetrahedral, octahedral, etc., symmetries. That this is an important problem has recently been pointed out.⁵

In a study of complexes of cobalt(II) with ethylenethiourea (etu) it was found impossible to definitely assign a structure to the complex $\text{Co}(\text{etu})_2(\text{CH}_3\text{COO})_2$ on

the basis of its spectrum and magnetism. It was finally concluded that the acetate groups were coordinated in a bidentate fashion and that the overall geometry was octahedral.

In order to check the accuracy of this structural assignment we have completed a determination of the crystal and molecular structure of the compound in question. We have also furthered our investigations by examining the electronic structure of $\text{Co}(\text{etu})_2(\text{CH}_3\text{COO})_2$.

Experimental Section

Reagents. Fisher Reagent grade $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ were used without further purification. Ethylenethiourea was obtained from K & K and recrystallized twice from H_2O . Reagent grade thiourea was obtained from Fisher Scientific and used as received.

Crystal Growth and Preparation. Mixed crystals of the isomorphous Zn- and Co-etu compounds suitable for optical measurements were grown from hot aqueous solution which had been acidified with a small amount of acetic acid. Single crystals of $\text{Zn}(\text{tu})_2(\text{CH}_3\text{COO})_2$ containing small amounts of Co were prepared in a manner analogous to that used for the etu complex. Crystals of

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