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The Lewis Basicity of a Coordinated S-Sulfinate Ligand[1]

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The interaction of $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)$ *(R =* n—C_4H_9 *or* C_6H_5*) with* BF_3 *in toluene at 0° leads to the formation of the corresponding 1:1 addition compound. The* $P(n\text{—}C_4H_9)_3$ *adduct is stable with respect to decomposition into its components at 25°; however, the* $P(C_6H_5)_3$ *adduct undergoes appreciable dissociation after 8 hr at 25°. Several structures for these acid-base complexes are considered. From the infrared spectra it is inferred that boron-sulfinate oxygen linkages are present.*

Introduction

Replacement of a carbonyl group in $C_5H_5Fe(CO)_2$-(SO_2R) or $C_5H_5Fe(CO)_2(COR)$ with a stronger base such as a tertiary phosphine places an added burden for π-bonding with the metal on the remaining CO and SO_2R or COR.[2,3] This, in turn, should lead to an enhanced basicity of the sulfinate and the acyl oxygens.

The foregoing prediction has been borne out by the ability of $C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3](SO_2CH_3)$[2] and $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$[4] to undergo facile protonation with HCl. To extend the scope of acid-base reactions of metal sulfinato complexes we have now examined the interaction of $C_5H_5Fe(CO)(PR_3)$-(SO_2CH_3) (R = n—C_4H_9 or C_6H_5) with another Lewis acid, BF_3. Boron trifluoride was selected because of its recently demonstrated[5,6] high affinity toward complexes of low-valent transition metals. Reported here are the results of our study on the synthesis and characterization of two $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)$. BF_3 adducts.

Experimental Section

Toluene was refluxed over and freshly distilled from CaH_2 under nitrogen. All other chemicals were of reagent grade or equivalent. They were used without further purification.

$C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3)$ was prepared as described earlier,[2] whereas $C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3]$-$(SO_2CH_3)$ was obtained in 50% yield by a photochemical reaction between $C_5H_5Fe(CO)_2(SO_2CH_3)$[7] and $P(n\text{—}C_4H_9)_3$, using the general procedure of Graziani.[2] The n-butylphosphine complex was characterized by its infrared spectrum and melting point (108°; lit:[2] 108°).

The reaction of $C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3](SO_2CH_3)$ with BF_3 (Matheson, C. P. grade) was carried out using standard vacuum line techniques. A solution of 0.43 g (1 mmole) of $C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3]$-$(SO_2CH_3)$ in 25 ml of toluene at 0° was degassed and then treated with 2.0 mmoles of BF_3. An immediate reaction occurred, as evidenced by a drop in pressure. The mixture was allowed to react for 1 hr, after which time the gas and solvent were removed at 0° leaving an orange residue. The volatile mater was passed through a series of three traps, the first two cooled with Dry Ice-acetone and the third with liquid nitrogen. Toluene was recovered quantitatively; a pressure-temperature-volume measurement of the excess boron trifluoride showed that 0.9 mole of BF_3 was absorbed per mole of $C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3]$-$(SO_2CH_3)$. No other volatile substance could be detected. The flask containing the reaction product was transferred to an inert atmosphere dry-box, the residue was treated with 10 ml of CH_2Cl_2, and the resulting solution was filtered. Approximately 50 ml of pentane was added to the filtrate to give 0.45 g (90%) of orange, crystalline $C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3]$-$(SO_2CH_3)$. BF_3. *Anal.* Calcd. for $C_{19}H_{35}FeO_3PSBF_3$: C, 45.8; H, 7.08. Found (Galbraith Laboratories, Inc., Knoxville, Tenn.): C, 46.12; H, 7.35. The compound decomposes at 88-90°.

A similar reaction between $C_5H_5Fe(CO)[P(C_6H_5)_3]$-$(SO_2CH_3)$ and BF_3 afforded, in 85% yield, C_5H_5Fe-$(CO)[P(C_6H_5)_3](SO_2CH_3$. BF_3 as an orange solid. This compound is less stable with respect to dissociation than its n-butylphosphine counterpart; after storage for 8 hrs at 25° under nitrogen, appreciable decomposition to BF_3 and the parent $C_5H_5Fe(CO)[P)C_6H_5)_3](SO_2CH_3)$ was indicated by the appearance of ν_{CO} of the latter carbonyl in the infrared spectrum. Because of its relatively low stability, the adduct was not characterized through elemental analyses.

Results and Discussion

The interaction of $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)$ (R = n—C_4H_9 or C_6H_5) with BF_3 in toluene at 0° results in

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(1) Sulfur Dioxide Insertion. XIII. For part XII see ref. 2.
(2) M. Graziani and A. Wojcicki, *Inorg. Chim. Acta*, *4*, 347 (1970).
(3) J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, *5*, 889 (1966).
(4) M. L. H. Green and C. R. Hurley, *J. Organometal. Chem.*, *10*, 188 (1967).
(5) M. P. Johnson and D. F. Shriver, *J. Amer. Chem. Soc.*, *88*, 301 (1966).
(6) R. N. Scott, D. F. Shriver, and D. D. Lehman, *Inorg. Chim. Acta*, *4*, 73 (1970)
(7) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, *88*, 4862 (1966).

Table I. Infrared Spectra of $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)$ and $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)\,.\,BF_3$ in the 2500-500 cm^{-1} Region [a]

$C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3]\text{-}(SO_2CH_3)$		$C_5H_5Fe(CO)[P(n\text{—}C_4H_9)_3]\text{-}SO_2CH_3)\,.\,BF_3$		$C_5H_5Fe(CO)[P(C_6H_5)_3]\text{-}(SO_2CH_3)$		$C_5H_5Fe(CO)[P(C_6H_5)_3]\text{-}(SO_2CH_3)\,.\,BF_3$	
1946 s	νCO	1964 s	νCO	1950 s	νCO	1966 s	νCO
1295 w		1305 w		1300 w		1165 sh	$\nu_{as}SO_2$ $\nu_{as}BF$
1215 vw		1210 w		1287 w		1155 sh	
1156 s	$\nu_{as}SO_2$	1165 sh	$\nu_{as}SO_2$ $\nu_{as}BF$	1180 w		1125 s, br	
1085 w		1130 s, br		1155 s	$\nu_{as}SO_2$	1090 sh	
1070 sh	ν_sSO_2	1090 sh		1088 m		1065 w	
1036 s		1065 w		1030 s	ν_sSO_2	1010 s, br	ν_sSO_2
1020 sh		1005 s, br	ν_sSO_2	1000 w		995 s, br	
965 w		995 s, br		970 w		895 s, br	ν_sBF
935 m		945 sh		940 m		857 m	
910 w		920 sh		887 m		760 sh	
885 w		890 s, br	ν_sBF	845 m		745 m	
850 m		850 m		835 m		720 m	
830 m		770 vw		762 m		695 s	
770 w		715 s		750 m		615 vw	
700 s		605 vw		740 m		600 w	
605 w		575 m	δSO_2	710 s		570 m	δSO_2
580 m	δSO_2	555 sh		695 s		555 s	
555 s		550 s		600 w		530 s	
525 s		520 s		577 m	δSO_2	520 s	
				555 m			
				530 m			
				510 m			

[a] Nujol mull; recorded on a Perkin-Elmer Model 337 spectrophotometer. The absorptions masked by those of Nujol are not included. Abbreviations: vw, very weak; w, weak; m, medium; s, strong; sh, shoulder; br, broad.

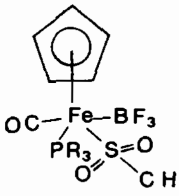
the formation of 1:1 addition compounds of the two reactants. This stoichiometry has been demonstrated by measuring the amount of BF_3 consumed by each sulfinate and has been confirmed by chemical analyses for the *n*-butylphosphine adduct.

The infrared spectra of the two $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)\,.\,BF_3$ complexes and of their parent sulfinates in the 2500-500 cm^{-1} region are given in Table I. Comparison of the spectrum of each sulfinate with that of its BF_3 adduct reveals similar changes after the reaction. Thus, for example, the carbonyl stretching band shifts to higher frequency by 18 cm^{-1} for the $P(n\text{—}C_4H_9)_3$ adduct and by 16 cm^{-1} for the $P(C_6H_5)_3$ adduct.

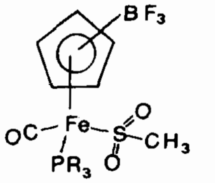
The spectra in the 1200-850 cm^{-1} region of the two addition compounds are also very similar. Since both the SO and the BF stretching frequencies occur in this range,[6,8] the assignment of bands given in Table I should be regarded as tentative. It is significant, however, that no strong absorptions, possibly attributable to the asymmetric SO stretching modes, are found above 1130 cm^{-1}. Hence the SO stretching frequencies of the BF_3 adducts must be lower than those of the parent sulfinates.

Several structures may be written for the $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)\,.\,BF_3$ complexes; those that are most plausible involve $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)$ to BF_3 donor-acceptor bonds, with the likely sites for boron trifluoride being (a) the metal (**I**), (b) the C_5H_5 ring (**II**), (c) the CO oxygen (**III**), and (d) one of the SO_2 oxygens (**IV**). One may resolve among these structures by comparing the infrared CO and SO stretching frequencies of the adducts with those predicted for each type of BF_3—parent compound attachment.

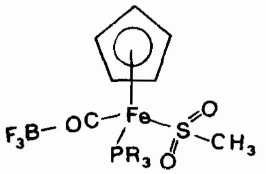
Structure **I** should give rise to higher CO and SO stretching frequencies compared with the corresponding absorptions for the parent sulfinates. For example, $Ir(CO)[P(C_6H_5)_3]_2Cl$ exhibits ν_{CO} at 1968 cm^{-1} whereas its BF_3 adduct absorbs at 2067 cm^{-1}.[6]



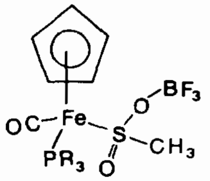
I



II



III



IV

Structure **II**, which has no precedent, is expected also to lead to an increase in both the CO and the SO stretching frequencies, although these differences should be smaller than those for **I**. If BF_3 is bonded to the carbonyl oxygen, then an appreciable decrease in ν_{CO} and a smaller decrease in ν_{SO} are predicted. In support of the former change is the report[9] that coordination of $Al(C_2H_5)_3$ to the oxygens of the bridging carbonyls in $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Fe(CO)]_4$ results in a lowering of the stretching frequencies of these CO's by 112-125 cm^{-1}. If structure **IV** is the correct one, then a small increase in ν_{CO} and a decrease in ν_{SO} are to be expected.

The observed small increase in ν_{CO} and a decrease

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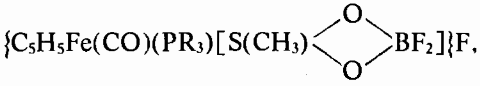
[8] T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 2339 (1960).

[9] N. J. Nelson, N. E. Kime, and D. F. Shriver, *J. Amer. Chem. Soc.*, *91*, 5173 (1969).

in ν_{SO} upon formation of the adducts by $C_5H_5Fe(CO)(PR_3)(SO_2CH_3)$ is consistent only with the last-mentioned coordination position for BF_3 in both complexes (structure **IV**). Although other formulations, including an ionic  $\{C_5H_5Fe(CO)(PR_3)[S(CH_3)(O)_2BF_2]\}F$, in which the BF_3 molecule has undergone dissociation into BF_2^+ and F^-, may be also proposed for consideration, they appear unlikely on the grounds of infrared spectral and physical properties of the compounds.

The lower stability of $C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3) \cdot BF_3$ compared with that of $C_5H_5Fe(CO)[P(n{-}C_4H_9)_3](SO_2CH_3) \cdot BF_3$ toward dissociation into their two respective components parallels the stabilities of the corresponding protonated species, $[C_5H_5Fe(CO)(PR_3)(SO_2HCH_3)]^+$.[2] In both cases, this order is probably due to a greater basicity of the sulfinate oxygens in the $P(n{-}C_4H_9)_3$ complex owing to a more extensive $Fe \rightleftharpoons S$ π-bonding and hence weaker $S \leftrightharpoons O$ π-bonding therein.

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