Sulfur Dioxide Insertion. XII. Studies on Cyclopentadienyliron Sulfinato Monocarbonyl Complexes[1]

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The reactions of $C_5H_5Fe(CO)(L)R$ ($L = P(C_6H_5)_3$, $As(C_6H_5)_3$ or $P(n-C_4H_9)_3$; $R = CH_3$ or $CH_2C_6H_5$) with refluxing sulfur dioxide or with SO_2 in chloroform proceed very rapidly to yield the corresponding S-sulfinates, $C_5H_5Fe(CO)(L)(SO_2R)$. The monocarbonyls $C_5H_5Fe(CO)[P(C_6H_5)_3]R$ ($R = CH_3$ or $CH_2C_6H_5$) react with gaseous SO_2 also in the solid. This remarkable reactivity of $C_5H_5Fe(CO)(L)R$ toward SO_2 is discussed and compared with that found for carbon monoxide insertions. Ultraviolet irradiation of $C_5H_5Fe(CO)_2$-$(SO_2CH_2CH=CH_2)$ and $P(C_6H_5)_3$ affords $C_5H_5Fe(CO)$-$[P(C_5H_5)_3](SO_2CH_2CH=CH_2)$ and provides the alternative synthetic method for $C_5H_5Fe(CO)(L)(SO_2R)$. Attempts at desulfurylation of $C_5H_5Fe(CO)(L)(SO_2R)$ proved unsuccessful; however, protonation of C_5H_5Fe-$(CO)[P(n-C_4H_9)_3](SO_2CH_3)$ with HCl in benzene yielded $C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2HCH_3)^+$, isolated as the tetraphenylborate(III) salt. The infrared spectrum of the cation indicates structure with an $=S(O)$-OH moiety.

Introduction

Investigations on the reactions of sulfur dioxide with $Mn(CO)_4[P'C_6H_5)_3]CH_3$[2] or $Mn(CO)_5CH_3$[3] disclosed that the former carbonyl undergoes much more rapid insertion in solution. Similarly, qualitative observations indicate that the reactivity of C_5H_5Mo-$(CO)_2[P(C_6H_5)_3]CH_3$ toward SO_2 to form the corresponding sulfinate exceeds that of the parent tricarbonyl, $C_5H_5Mo(CO)_3CH_3$.[4]

In order to explore more completely the effect of replacement of CO in metal carbonyl alkyl complexes with a neutral ligand such as a phosphine or an arsine (L) on (1) the rate of sulfur dioxide insertion and (2) the properties of the resultant products we conducted a study on cyclopentadienyliron sulfinato monocarbonyls, $C_5H_5Fe(CO)(L)(SO_2R)$. Reported in this paper are the results of our investigation.

Experimental Section

Materials. The carbonyls $C_5H_5Fe(CO)_2CH_3$,[5] $C_5H_5Fe(CO)_2CH_2C_6H_5$,[6] $C_5H_5Fe(CO)_2(SO_2CH_2CH=CH_2)$,[7]

and $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$[8] were prepared according to the literature methods. The following were purchased from Metal and Thermit Co. and used as received: $P(C_6H_5)_3$, $As(C_6H_5)_3$, and $P(n-C_4H_9)_3$. Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a P_4O_{10}-$CaCl_2$ column before condensation. Tetrahydrofuran was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Technical grade pentane and hexane and petroleum ether (b.p., 30-60°) were used without further purification. All other chemicals and solvents were of reagent grade or equivalent. Ventron alumina (neutral, grade III) was employed in all chromatographic separations and purifications.

Three new complexes of the type $C_5H_5Fe(CO)(L)R$ were prepared by a general procedure of Treichel, *et al.*[8] Equimolar amounts of the corresponding $C_5H_5Fe(CO)_2R$ and L in petroleum ether and under nitrogen were irradiated at room temperature with a Hanovia 450-w high-pressure quartz mercury vapor lamp, Model 679- A-36.[6] Given below are reaction times and other pertinent data on the three monocarbonyls.

(a) $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$:[9] Reaction time, 3 hr; purified by chromatography; red solid; yield, 65%; m.p., 130°; ν_{CO}(CHCl$_3$ soln), 1905 cm^{-1}. *Anal.* Calcd. for $C_{31}H_{27}OPFe$: C, 74.1; H, 5.4. Found: C, 73.8; H, 5.2.

(b) $C_5H_5Fe(CO)[P(n-C_4H_9)_3]CH_3$: Reaction time, 6 hr; purified by chromatography; red oil; ν_{CO}(CS$_2$ soln), 1901 cm^{-1}; characterized by conversion to the corresponding sulfinate (*vide infra*).

(c) $C_5H_5Fe(CO)[As(C_6H_5)_3]CH_2C_6H_5$: Reaction time, 6 hr; purified by chromatography; red oil; ν_{CO}(CHCl$_3$ soln), 1910 cm^{-1}; attempts at isolation and purification failed; converted to the corresponding sulfinate (*vide infra*).

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(8) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 5, 1177 (1966).
(9) This compound was recently reported, but without preparative details: J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, 91, 1550 (1969).

Reactions of $C_5H_5Fe(CO)(L)R$ with SO_2. (*a*) *In Refluxing SO_2.* Sulfur dioxide was condensed onto *ca.* 1g of $C_5H_5Fe(CO)(L)R$ (L = $P(C_6H_5)_3$, R = CH_3; L = $P(C_6H_5)_3$, R = $CH_2C_6H_5$; L = $P(n-C_4H_9)_3$, R = CH_3) and the mixture was allowed to reflux for about 1 hr. Excess SO_2 was then removed, the residue was dissolved in $CHCl_3$ (10 ml), and the solution was chromatographed eluting with chloroform. The eluate was concentrated; addition of pentane with stirring afforded orange crystals, which were washed with pentane. The yields were around 90%. The analytical data and the melting points for these and other new complexes prepared herein are presented in Table I.

(*b*) *In Chloroform Solution.* $C_5H_5Fe(CO)(L)R$ (0.5 g) was dissolved in 50 ml of $CHCl_3$ and SO_2 was bubbled slowly through the solution at 27°, the reaction being monitored by infrared spectroscopy. After *ca.* 10 min, solvent was evaporated off and the residue chromatographed as described earlier. Yields, 80-90%.

To synthesize $C_5H_5Fe(CO)[As(C_6H_5)_3](SO_2CH_2-C_6H_5)$, petroleum ether was removed from a solution of freshly prepared $C_5H_5Fe(CO)[As(C_6H_5)_3]CH_2C_6H_5$, the residue was dissolved in $CHCl_3$, and the resulting solution was then treated with gaseous SO_2 as for the other complexes.

(*c*) *Solid-Gas Reaction.* Gaseuos SO_2 was introduced to an evacuated round-bottom flask containing a thin layer of finely ground $C_5H_5Fe(CO)[P(C_6H_5)_3]$-$CH_3$. After *ca.* 5 min, the infrared spectrum of the solid showed both $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ and $C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3)$; after 2 days, only the sulfinate was detected. The reaction of C_5H_5Fe-$(CO)[P(C_6H_5)_3]CH_2C_6H_5$ with SO_2 is slower and always yielded a mixture of the unreacted alkyl and the sulfinate.

A similar experiment using $C_5H_5Fe(CO)[P(C_6H_5)_3]$-$CH_3$ and CO revealed no reaction

Reaction of $C_5H_5Fe(CO)_2(SO_2CH_2CH=CH_2)$ with $P(C_6H_5)_3$. A solution of both $C_5H_5Fe(CO)_2(SO_2CH_2$-$CH=CH_2)$ (1.4 g, 5 mmoles) and $P(C_6H_5)_3$ (1.3 g, 5 mmoles) in benzene was irradiated for 2 hr with the Hanovia lamp described earlier. Extensive decomposition was noted. The solvent was removed, the residue extracted with $CHCl_3$, and the extract chromatographed using $CHCl_3$ eluent. Concentration of the eluate and addition of pentane yielded 0.25 g (10%) of orange $C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_2$-$CH=CH_2)$.

Protonation of $C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2CH_3)$. The sulfinate (1.08 g, 2.5 mmoles) was dissolved in a minimum amount of benzene; hydrogen chloride was then bubbled slowly through the solution, resulting in the formation of a red-brown oil. The oil was dissolved in acetone and treated with a solution of $NaB(C_6H_5)_4$ in the same solvent. The mixture was filtered; addition of pentane to the filtrate gave a pale yellow precipitate. Recrystallization from acetone-pentane yielded 0.7 g (35%) of {$C_5H_5Fe(CO)$-$[P(n-C_4H_9)_3](SO_2HCH_3)$}$B(C_6H_5)_4$.

A similar reaction between $C_5H_5Fe(CO)[P(C_6H_5)_3]$-$(SO_2CH_3)$ and HCl, followed by addition of NaB-$(C_6H_5)_4$, afforded a product which, however, could not be isolated in a sufficiently pure state for characterization. It appears to have a lower stability in solution than {$C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2HCH_3)$}$B$-$(C_6H_5)_4$.

Attempted Desulfurylation Reactions. Attempts at thermal or photolytic desulfurylation of $C_5H_5Fe(CO)$-$(L)(SO_2R)$ were made using conditions similar to those employed previously for $C_5H_5Fe(CO)_2(SO_2R)$.[6] In all cases, only the starting materials and/or intractable decomposition products were obtained after work-up of the reaction mixtures.

Infrared Spectra. Spectra were recorded using a Perkin-Elmer Model 337 spectrophotometer. A pair of matched 0.05-mm KBr cells was employed for solution measurements.

Proton Magnetic Resonance Spectra. Nmr spectra were recorded on a Varian Associates A-60 spectrometer. Tetramethylsilane (TMS) was used as a reference.

Analyses. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Mr. P. J. Kovi of these laboratories using a Coleman Model 29 analyzer.

Results and Discussion

Complexes of a general formula $C_5H_5Fe(CO)(L)R$ react rapidly either with refluxing sulfur dioxide or with SO_2 in chloroform to yield orange solids which are stable to air and which analyze as $C_5H_5Fe(CO)(L)$-(SO_2R) (equation (1)).

$$C_5H_5Fe(CO)(L)R + SO_2 \longrightarrow C_5H_5Fe(CO)(L)(SO_2R) \qquad (1)$$
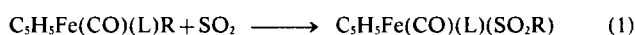
These products have been assigned S-sulfinato structures from their infrared and proton magnetic resonance spectra, given in Table II. The former show SO stretching frequencies at 1166-1152 cm^{-1} and 1036-1022 cm^{-1}, a single CO stretching absorption at 1968-1956 cm^{-1}, and no carbonyl bands attributable to metal acyl groups. The SO stretching frequencies are considerably (40-15 cm^{-1}) lower than those found for the corresponding dicarbonyls, $C_5H_5Fe(CO)_2(SO_2$-$R)$,[6] but comparable to those for substituted manganese(I) sulfinatocarbonyls, $Mn(CO)_4(L)(SO_2R)$ or Mn-$(CO)_3(L)_2(SO_2R)$ (L = a phosphine or an N-donor neutral ligand).[2] Since preliminary crystallographic data have shown $Mn(CO)_3(C_{10}H_8N_2)(SO_2CH_3)$ to contain an $Mn-S(O)_2CH_3$ moiety,[10] there is little doubt that $C_5H_5Fe(CO)(L)(SO_2R)$ possess similar S-sulfinato linkages. Infrared SO stretching frequency shifts to lower energy may be attributed to an increased amount of $M=SO_2R$ π bonding caused by a greater negative charge at the metal resulting from replacement of CO with a more basic L. Although strong π bonding between the RSO_2 group and the metal in the iridium(III)

(10) D. R. Swift, personal communication to A. W.

Table I. Melting Points and Analytical Data for $C_5H_5Fe(CO)(L)(SO_2R)$ Complexes.

Compound	M.p., °C [a]	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3)$	158	61.2	4.7	61.0	4.5
$C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_2C_6H_5)$	147	65.8	4.8	65.7	4.9
$C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH=CH_2)$	85	62.8	4.9	63.2	4.9
$C_5H_5Fe(CO)[As(C_6H_5)_3](SO_2CH_2C_6H_5)$	115	61.0	4.5	61.0	4.3
$C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2CH_3)$	108	53.2	8.2	53.4	8.4
$\{C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2HCH_3)\}B(C_6H_5)_4$	118 (dec.)	68.8	7.5	67.0	7.7

[a] Uncorrected.

Table II. Infrared (IR) and Proton Magnetic Resonance (PM R) Spectra of $C_5H_5Fe(CO)(L)(SO_2R)$ Complexes.

Compound	IR spectrum (cm^{-1}) CO stretch [a]	SO stretches [b]	Other prominent bands [c]	PMR spectrum [d] Chem. shift (τ)	Rel. intens.	Assignment
$C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3)$	1956	1152 s, 1025 s		7.45 s	3	CH_3
				5.35 d [e]	5	C_5H_5
				2.6 [f]	15	C_6H_5
$C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_2C_6H_5)$	1957	1166 s, 1035 s		6.06 \ [g] 5.74 /	2	CH_2
				5.58 d [e]	5	C_5H_5
				2.5 [f]	20	C_6H_5
$C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_2CH=CH_2)$	1968	1157 s, 1022 s				
$C_5H_5Fe(CO)[As(C_6H_5)_3](SO_2CH_2C_6H_5)$	1962	1166 s, 1035 s		5.85 \ [g] 5.56 /	2	CH_2
				5.52 s	5	C_5H_5
				2.3 [f]	20	C_6H_5
$C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2CH_3)$	1962(1946) [b]	1156 s, 1036 s				
$\{C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2HCH_3)\}B(C_6H_5)_4$	(1962) [b]	1115 s, 985 m	3600 w 3100.2850 br			

[a] $CHCl_3$ solution, all bands very strong. [b] Nujol mull. [c] Hexachlorobutadiene mull. [d] $CDCl_3$ solution. [e] $J \sim 1$ Hz. [f] Complex pattern. [g] An AB spectrum ($J = 13.5$ Hz), analyzed as in L.M. Jackman, «Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry», Pergamon Press, New York, 1959, pp. 89-90. IR abbreviations: s, strong; m, medium; w, weak; br, broad. PMR abbreviations: s, singlet; d, doublet.

and palladium(II) complexes has been recently questioned,[11] evidence presented elsewhere[2,3] suggests that such bonding is of importance in metal sulfinatocarbonyls. The CO stretching frequency in C_5H_5Fe-$(CO)(L)(SO_2R)$ is *ca.* 50-60 cm^{-1} higher than that of the corresponding alkyl, in agreement with a similar shift observed for $C_5H_5Fe(CO)_2R$ and their SO_2-insertion products.[6]

The salient feature in the proton magnetic resonance spectra of $C_5H_5Fe(CO)[E(C_6H_5)_3](SO_2CH_2C_6H_5)$ (E = P or As) is magnetic nonequivalence of the CH_2 protons; this gives rise to an AB type pattern in each case. A similar phenomenon has been recently reported for the methylene hydrogens of $C_5H_5Fe[P-(C_6H_5)_2R][COCH_2Si(CH_3)_3]$ (R = C_6H_5, C_2H_5, or CH_3)[12] and $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_2C_6H_5)$,[13] the geminal coupling constant J_{AB} being 12-13.5 Hz compared to $J_{AB} = 13.5$ Hz for the sulfinates. The nonequivalence observed undoubtedly stems from the presence of an asymmetric iron atom in these complexes. Also worth noting is a deshielding of the CH_3 and CH_2 protons in $C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3)$ and C_5H_5-$Fe(CO)[P(C_6H_5)_3](SO_2CH_2C_6H_5)$, respectively, when compared to the coresponding resonances for the parent monocarbonyl alkyls.[8,9] Such deshielding has been reported for other transition metal S-sulfina-

tes[3,4,6] and appears to be a general phenomenon.

The relative rates of insertion of various C_5H_5Fe-$(CO)(L)R$ with SO_2 in $CHCl_3$ solution at 27° increase in the following order (an approximate time required for completion of the reaction is given in parentheses): $C_5H_5Fe(CO)_2CH_3$ ($\geqslant 10$ hr)[14] < C_5H_5Fe-$(CO)[P(C_6H_5)_3]CH_2C_6H_5$ ($\geqslant 3$ min) < $C_5H_5Fe(CO)$-$[P(C_6H_5)_3]CH_3$ ($\leqslant 3$ min) < $C_5H_5Fe(CO)[P(n-C_4H_9)_3]$-$CH_3$ (virtually instantaneous). This sequence indicates that (1) as the basicity of L increases the rate of the reaction of its $C_5H_5Fe(CO)(L)R$ complex with SO_2 also increases and (2) other factors being equal, methyl compounds are more reactive than their benzyl analogs. The great affinity of $C_5H_5Fe(CO)(L)R$ for SO_2 is further manifested by the reaction between solid $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ and gaseous sulfur dioxide which proceeds to completion at 27°. In agreement with the lower reactivity of analogous benzyl complexes, solid $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ does not completely insert sulfur dioxide.

It is of interest to compare and contrast the effect of replacement of CO with L on the rates of CO and SO_2 insertion into transition metal-alkyl bonds. Treichel has reported[8] that $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ undergoes carbon monoxide insertion when CO is bubbled through its solution in petroleum ether for 18 hr at 90-100°; under similar conditions there is no

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(13) H. Brunner and E. Schmidt, *Angew. Chem.*, 81, 570 (1969).

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reaction between $C_5H_5Fe(CO)_2CH_3$ and CO. Thus both the CO and SO_2 insertions are promoted by replacement of carbon monoxide with a stronger base; however, the relative rates of reaction with $C_5H_5Fe(CO)(L)R$ are much greater for SO_2 than for CO. On the other hand, when the external reagent effecting carbon monoxide insertion is a phosphine (L), the reactions of the dicarbonyls (equation (2)) but not of the monocarbonyls (equation (3)) are known to occur.[15]

$$C_5H_5(CO)_2R + L \longrightarrow C_5H_5Fe(CO)(L)(COR) \quad (2)$$

$$C_5H_5Fe(CO)(L)R + L \longrightarrow\!\!\!|\!\!\!\longrightarrow C_5H_5Fe(L)_2(COR) \quad (3)$$

We believe that an increase in reactivity toward SO_2 of $C_5H_5Fe(CO)(L)R$ as L becomes a stronger base (and a weaker π-acceptor) may be ascribed to stabilization of the activated complex by the presence of sulfur dioxide. Accordingly, the ability of SO_2 to receive π electrons from the metal into its vacant d orbitals will lower the activation energy for the reaction; such an interaction will be particularly significant when electron density at the metal is high as, for example, in $C_5H_5Fe(CO)(L)R$ containing very basic and poorly π bonding ligands L. The analogous reactions of carbon monoxide may be expected also to be influenced by π bonding in the transition state; however, the situation is somewhat complicated by variations in the mechanism.[16] When CO interacts directly with the alkyl complex as, for example, it almost certainly does when reacting with $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ in petroleum ether, then stabilization by π bonding in the transition state should be important, although the available data (vide supra) suggest that SO_2 is more effective in this respect. By way of contrast, when the more basic ligands such as the phosphines or phosphites or when coordinating solvents such as tetrahydrofuran assume the role of a nucleophile in carbon monoxide insertion, then retardation in the rate may be expected as CO is replaced with L in the alkyl complex.

Although $C_5H_5Fe(CO)_2(SO_2R)$ fail to react with the phosphines or phosphites (L) on heating,[17] they do so upon ultraviolet irradiation. These reactions then provide the alternative method of synthesis for the substituted sulfinatocarbonyls $C_5H_5Fe(CO)(L)(SO_2R)$.

The above behavior of $C_5H_5Fe(CO)_2(SO_2R)$ places it closer to $C_5H_5Mn(CO)_3$ than to other $C_5H_5Fe(CO)_2X$ complexes (X=Cl, Br, I, CO_2R, etc.) as far as substitution reactions are concerned. The ability of both $C_5H_5Mn(CO)_3$[18] and $C_5H_5Fe(CO)_2(SO_2R)$ to undergo photolytic but not thermal reactions with Lewis bases may reflect on similarities in bonding properties of the « soft » ligands[19] CO and RSO_2. In this context it is of interest to note that another sulfinate system, $Mn(CO)_5(SO_2R)$, resembles $Cr(CO)_6$ in its relative reactivity toward various ligands.[2,20]

Attempts at desulfurylation of $C_5H_5Fe(CO)(L)(SO_2R)$ invariably afforded the starting materials and/ or noncarbonyl decomposition products. Our lack of success in effecting extrusion of SO_2 from these sulfinatocarbonyls may perhaps be related to preferential occurrence of decarbonylation followed by a rapid decomposition of the resulting species. It is pertinent that in the reaction of $C_5H_5Fe(CO)_2(SO_2R)$ with $Rh[P(C_6H_5)_3]_3Cl$ abstraction of CO from the iron carbonyl by the rhodium(I) complex leads to formation of ill-defined decomposition products.[21]

The lowering of the SO stretching frequencies in going from $C_5H_5Fe(CO)_2(SO_2R)$ to $C_5H_5Fe(CO)(L)(SO_2R)$ is indicative of a reduction in S–O bond order and may reflect greater basicity of the sulfinate oxygens in the latter complexes. To elucidate possible basic properties of the sulfinate moiety in $C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2CH_3)$, the compound was allowed to interact with HCl; subsequent addition of $NaB(C_6H_5)_4$ resulted in isolation of the tetraphenylborate(III) salt of the protonated sulfinatocarbonyl ion. From the infrared spectral data we favor for the cation a structure in which the proton is attached to one of the sulfinate oxygens, viz,
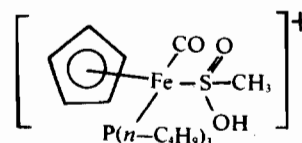
This preference is based on (1) the lowering of the SO stretching frequencies and a slight increase in the CO stretching frequency (as one would expect from acquisition of a positive charge but not from protonation of the carbonyl oxygen) upon protonation and (2) appearance of absorption bands at 3600 cm^{-1} and 3100-2850 cm^{-1} in the salt; these bands are probably due to the OH stretches of free and hydrogen-bonded hydroxy groups.[22] A similar reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3)$ and HCl afforded a product which manifested much lower stability, especially in solution, than the protonated $C_5H_5Fe(CO)[P(n-C_4H_9)_3](SO_2CH_3)$. This difference may be a result of the lower basicity (or greater π bonding ability) of $P(C_6H_5)_3$ compared to that of $P(n-C_4H_9)_3$ which would reduce electron density at the sulfinate oxygens making them less basic. It is of interest to note that the acyl counterpart of $C_5H_5Fe(CO)[P(C_6H_5)_3](SO_2CH_3)$, $C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$, can however be protonated under similar conditions.[23]

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