as a function of pH show that water ligand deprotonation is the only acid–base preequilibrium. In other words, if expression 20 is generally valid, then in the case of the alkyl cobaloximes it must be $k_bK_2 \ll k_a(K_1 + K_2)$.

Registry No. $\{C_6H_5Co[(DO)(DOH)pn]H_2O\}^+$, 26334-77-0; $\{CH_3Co[(DO)(DOH)pn]H_2O\}^+$, 26334-78-1; $\{C_2H_5Co[(DO)(DOH)pn]H_2O\}^+$, 26317-25-9; $\{C_6H_5Co[(DO)(DOH)pn]NH_3\}^+$, 74779-51-4; $\{CH_3Co[(DO)(DOH)pn]NH_3\}^+$, 47021-87-4; $\{C_2H_5Co[(DO)(DOH)pn]NH_3\}^+$, 74764-00-4; $\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+ClO_4^-$, 74764-02-6; $CH_3Co[(DO)(DOH)pn]OH$, 41975-58-0; NH_3, 7664-41-7.

Contribution from the McPherson Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Synthesis of (Alkyl sulfito)dicarbonyl(η^5-cyclopentadienyl)iron(II) Complexes and Reactions of Ligated Alkyl Sulfite[1]

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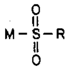
A series of alkyl sulfito complexes, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$, have been prepared by substitution reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$ with $Na[S(O)_2OR]$ in ROH (R = CH_3, C_2H_5), $Na[S(O)_2OR']$ (R′ = C_2H_5) in ROH (R = 1-C_3H_7, 2-C_3H_7), and Na_2SO_3 in ROH (R = C_2H_5), as well as by treatment of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]\cdot 0.5SO_2$ with $ROSO_2F$ or R_3OPF_6 (R = CH_3). However, attempts at similar substitution reactions of various other organometallic complexes were largely unsuccessful and furnished only $Mn(CO)_3(bpy)[S(O)_2OCH_3]$. The alkyl sulfito ligand in $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ undergoes transesterification with the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR']$ on heating in R′OH at reflux or on storage in R′OH in the presence of HBF_4 at room temperature. By use of $(+)_{589}$-2-octanol, it was shown that this exchange proceeds with cleavage of the S–OR bond. Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with R_2NH (R = CH_3, C_2H_5) leads to the formation of $R_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$, whereas hydrolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ affords the hydrogen sulfito complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$, which is a strong acid. The hydrolysis is reversible, and the regeneration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ occurs at ambient temperature via scission of the S–OH bond. Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with $(C_2H_5)_3OPF_6$ affords the dialkyl sulfite complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OR]]PF_6$, whereas reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with the acids HCl and CF_3CO_2H furnish $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2[OC(O)CF_3]$, respectively. Where possible, these reactions are compared with the corresponding reactions of the organic sulfonic esters, $RS(O)_2OR'$.

Introduction

Organometallic complexes containing diverse sulfur–oxygen ligands have been reported in recent years. Some of them, viz., metal sulfinates-*S* (I) and -*O* (II) and metal sulfonates (III), are accessible by insertion of SO_2[2,3] and SO_3,[4] respectively, into metal–carbon σ bonds. Other types of compounds have been obtained by a variety of methods to provide derivatives with terminal and bridging SO_2[5,6] (IV, V), dithionito[7] (VI), sulfoxide[8,9] (VII, VIII), sulfenato[10] (IX), alkoxysulfenato[10] (X), alkyl sulfito[11,12] (XI), and dialkyl sulfite[8] (XII) ligands (η^2-bonded ligands are not included).

In the course of an investigation of comparative chemistry of organometallic compounds containing sulfur–oxygen ligands, our attention was directed to alkyl sulfito complexes (XI). Such complexes are of considerable interest in that the $S(O)_2OR$ ligand may be viewed as the product of reaction of coordinated SO_2 with alkoxide. This presumed behavior finds a striking analogy in the observed formation of carboalkoxy ligands, C(O)OR, by nucleophilic attack of alkoxide on ligated CO.[13] Treatment of coordinated C(O)OR with acid regenerates the carbonyl ligand. From the foregoing comparison, neutral complexes XI represent possible precursors of cationic metal–SO_2 species, which may exhibit interesting and novel reactions with nucleophiles.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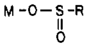
I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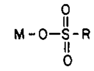
II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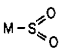
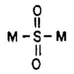
III


$\mathrm{M{-}SO_2}$

IV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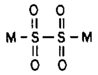
V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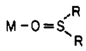
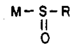
VI


$\mathrm{M{-}\overset{R}{\underset{O}{S}}{-}R}$

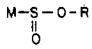
VII


$\mathrm{M{-}O{=}SR_2}$

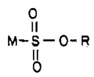
VIII


$\mathrm{M{-}\underset{O}{S}{-}R}$

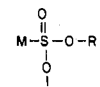
IX


$\mathrm{M{-}\underset{O}{S}{-}O{-}R}$

X


$\mathrm{M{-}\overset{O}{\underset{O}{S}}{-}O{-}R}$

XI


$\mathrm{M{-}\overset{O}{\underset{OR}{S}}{-}O{-}R}$

XII

Although examples of alkyl sulfito complexes are known for nickel,[14] palladium,[15–17] platinum,[16–18] cobalt,[14] and rutheni-

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(1) Presented in part at the IXth International Conference on Organometallic Chemistry, Dijon, France, Sept 1979; see Abstracts, P 19 T.

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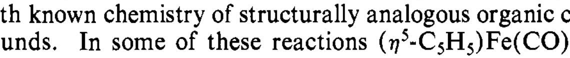
um,[11,12] no general synthetic routes to such compounds have been developed. Metal–sulfur bonding was established in $[Ni(S(O)_2OC_2H_5)(np_3)]BF_4{\cdot}0.5C_2H_5OH{\cdot}0.5H_2O$ (np_3 = tris(2-(diphenylphosphino)ethyl)amine) by X-ray crystallography.[14]

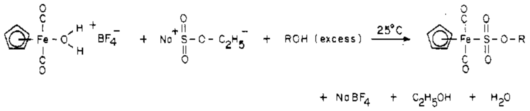
In this paper we report synthesis of a number of organometallic alkyl sulfito complexes, largely of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$. Reaction chemistry of the alkyl sulfito ligand was investigated and, where possible, compared with known chemistry of structurally analogous organic compounds. In some of these reactions $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ functions as a useful precursor of complexes with other sulfur–oxygen ligands, such as dialkyl sulfite, hydrogen sulfite, and sulfite. Certain aspects of this study were disclosed in a preliminary form.[19]

Results and Discussion

Synthesis and Characterization of Metal–Alkyl Sulfito Complexes. The alkyl sulfito complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ were prepared by several methods. The most direct and convenient procedure involved ligand substitution (eq 1) where R = CH_3 and C_2H_5. Since only the methyl and ethyl salts $Na[S(O)_2OR]$ are sufficiently stable to isolation,[20] the aforementioned procedure was slightly modified (eq 2) for the synthesis of 1- and 2-propyl sulfito complexes (R = 1-C_3H_7, 2-C_3H_7). The reactions in eq 2 undoubtedly proceed via an equilibrium (eq 3) as evidenced by the complete interconversion of $[S(O)_2OCH_3]^-$ and $[S(O)_2OC_2H_5]^-$ through dissolution and storage for ca. 24 h at room temperature in excess ethanol and methanol, respectively. However, when the synthesis according to eq 2 was attempted at 50–55 °C with ROH = phenol, the only isolated organometallic product was $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$. Thus, in this case, equilibrium 3 evidently lies far on the left. The ethyl sulfito complex was also prepared by another modification of the ligand substitution reaction, i.e., eq 4.

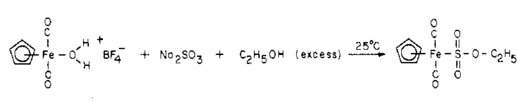


(1)



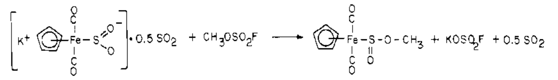
(2)

$$[S(O)_2OC_2H_5]^- + ROH \rightleftharpoons [S(O)_2OR]^- + C_2H_5OH \quad (3)$$



(4)

It was recently reported[21] that reaction of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]{\cdot}0.5SO_2$ with CH_3OSO_2F affords the methoxysulfenato complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)OCH_3]$, in addition to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]_2$. The apparent availability of a synthetic procedure for $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)OR]$ presented another potential entry into iron–alkyl sulfito complexes, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$, via expected oxidation with, e.g., *m*-$ClC_6H_4C(O)OOH$. Accordingly, the literature preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)OCH_3]$ was repeated and found to be entirely reproducible. However, the ^1H NMR and infrared spectra of the supposed $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)OCH_3]$, prepared here and earlier,[21] match exactly those of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ obtained according to eq 1. This leaves little doubt that the purported methoxysulfenato complex is actually the corresponding methyl sulfito complex. It would appear that the former is the initial product of the alkylation seen in eq 5 but is then readily oxidized to the isolable $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ (eq 6). The nature of this oxidation process remains obscure.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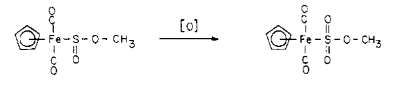

(6)

Both $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]_2$ also arise from reaction of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]{\cdot}0.5SO_2$ with $(CH_3)_3OPF_6$ in CH_2Cl_2 at reflux.

Attempts at extending the range of organometallic alkyl sulfito complexes beyond $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ have met with only very limited success. Thus, interaction between $Mn(CO)_3(bpy)Cl$ (bpy = 2,2′-bipyridine) and $Na[S(O)_2OCH_3]$ in methanol resulted in the isolation of $Mn(CO)_3(bpy)[S(O)_2OCH_3]$; however, other attempted ligand substitution reactions proved fruitless. $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, $(n\text{-}C_4H_9)_4N[W(CO)_5I]$, $[Mn(CO)_5NCCH_3]PF_6$, and $Mn(CO)_3[P(C_6H_5)_3]_2Cl$ failed to react with $Na[S(O)_2OCH_3]$ in methanol at reflux within 3–4 h. Furthermore, all efforts at obtaining the phosphine-substituted monocarbonyl $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3][S(O)_2OCH_3]$ proved unsuccessful. Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ with $P(C_6H_5)_3$ in benzene under irradiation and in $CHCl_3$ in the presence of $(CH_3)_3NO$, which oxidizes ligated CO,[22] as well as reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]I$ with $Na[S(O)_2OCH_3]$ in methanol at reflux, afforded extensive decomposition and no isolable organometallic products.

Of the aforementioned routes to $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$, the most convenient and the highest yield (32–51% after purification) methods are those represented by eq 1 and 2. The alkylation of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]{\cdot}0.5SO_2$ is more tedious, and the yields are low ($\lesssim$23%).

The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ and $Mn(CO)_3(bpy)[S(O)_2OCH_3]$ (facial isomer) were isolated as yellow or orange, air-stable solids, which are soluble in partly chlorinated hydrocarbons and common polar organic solvents. Their composition was generally ascertained by elemental analysis or mass spectrometry, or by both. Thus, for example, the mass spectra of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ (R = CH_3, C_2H_5) exhibit peaks corresponding to $(P - CO)^+$ and $(P - 2CO)^+$, although the parent ion, P^+, is either absent or barely discernible.

Metal–sulfur bonding in the new alkyl sulfito complexes was inferred with the aid of the infrared spectra, which are set out in Table I. The spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ in the 1300–800-cm^{-1} region is reproduced in Figure 1. For each complex, strong absorptions are observed at 1214–1198 and 1095–1077 cm^{-1}. These bands match well those observed for known metal–alkyl sulfito complexes[11,12,14-18] and are assigned to the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes, respectively. They occur at higher frequencies (20–50 cm^{-1}) than the corresponding absorptions of the analogous metal–sulfinato-*S* complexes,[23] indicating that replacement of an R group in $M{-}S(O)_2R$ with an OR group in $M{-}S(O)_2OR$ increases the extent of S=O π bonding in the $S(O)_2$ moiety. The carbonyl

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Table I. Infrared Spectra (cm^{-1}) of Metal-Alkyl Sulfito and Related Sulfur-Oxygen Compounds[a]

compd	ν(C≡O)	$\nu(SO_2)$ or ν(S=O)	ν(C-O)	ν(S-O)	other
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$	2064 (vs), 2007 (vs)	1214 (s), 1095 (s)	971 (s)	636 (s)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$	2062 (vs), 2000 (vs)	1214 (s), 1088 (s)	971 (s)		
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_3H_7\text{-}1]$	2068 (vs), 2014 (vs)	1211 (s), 1087 (s)	973 (m)		
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_3H_7\text{-}2]$	2070 (vs), 2010 (vs)	1211 (s), 1112 (s), 1084 (s)	918 (s)	640 (s)	
$(+)_{589}\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$	2065 (vs), 2010 (vs)	1212 (s), 1088 (s)	966 (m)	634 (s)	
$Mn(CO)_3(bpy)[S(O)_2OCH_3]$	2054 (s), 1940 (vs)	1198 (s), 1077 (s)		656 (s)	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2CH_3]$[b]	2059 (vs), 2002 (vs)	1193 (s), 1051 (s)			
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2C_2H_5]$[c]	2061 (vs), 2055 (vs), 2016 (vs), 2011 (vs)[f]	1185 (s), 1051 (s)[h]			
$Mn(CO)_3(bpy)[S(O)_2CH_3]$[d]	2033 (s), 1952 (s), 1931 (s)[g]	1148 (s), 1044 (s)[h]			
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$	2062 (vs), 2018 (vs)	1184 (s), 1038 (s)		811 (s)	2940 (w, br)[k]
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OD]$	2062 (vs), 2018 (vs)	1184 (s), 1038 (s)		807 (s)	2230 (w, br)[l]
$Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$	2050 (vs), 1994 (vs)	1129 (sh), 1107 (sh), 1084 (s), 1072 (s), 984 (s)			
$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2N(CH_3)_2]$	2045 (vs), 1985 (vs)[h]	1220 (s), 1064 (s)[h]			
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OCH_3]]PF_6$	2085 (vs), 2050 (vs)[i]	1228 (s)[h]	988 (m)[h]		
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)_2]]PF_6$	2085 (vs), 2050 (vs)[i]	1224 (s)[h]	990 (s)[h]		
$OS(OC_2H_5)_2$[e]		1205 (s)[j]	1010 (s)[j]		
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)CH_3]]PF_6$	2077 (vs), 2040 (vs)	1190 (s)	980 (s)		
$[(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3][S(O)(OC_2H_5)CH_3]]PF_6$	1990 (vs)	1188 (s)	968 (s)		

[a] KBr pellet except as noted. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder, br, broad. [b] Reference 21. [c] Reference 23a. [d] Reference 23b. [e] Reference 34. Simon, A.; Kriegsmann, H.; Dutz, H. *Chem. Ber.* 1956, *89*, 2390. [f] $CHCl_3$ solution. [g] CH_2Cl_2 solution. [h] Nujol mull. [i] Hexachlorobutadiene mull. [j] Neat liquid. [k] ν(OH). [l] ν(OD).

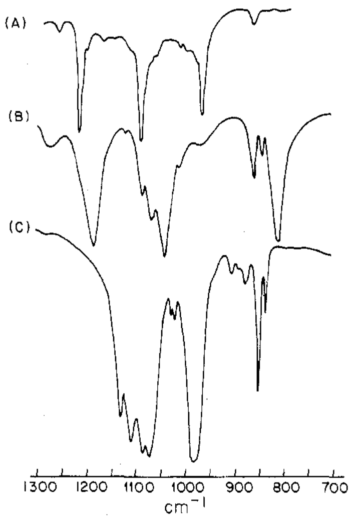


Figure 1. Infrared spectra (KBr pellet) in the 1300–700-cm^{-1} region of (A) $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$, (B) $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$, and (C) $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$.

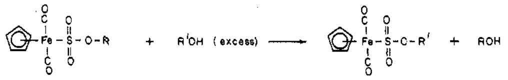
stretching frequencies, ν(C≡O), of the alkyl sulfito complexes are somewhat higher than those of the analogous sulfinato-*S* complexes,[23] reflecting slightly better metal π-electron acceptor properties of $S(O)_2OR$ compared to those of $S(O)_2R$. Both phenomena are explicable by an electronegative OR group lowering the energy of the 3d orbitals of sulfur. The ^1H NMR spectra of the alkyl sulfito complexes, listed in the Experimental Section, display no unusual features, being entirely consistent with the assigned structures.

Reactions of Ligated Alkyl Sulfite. Coordination to a metal can profoundly affect chemical reactivity of a ligand.[13,24] In this section we describe our studies on reactions of ligated alkyl sulfite and, to the extent possible, draw comparisons with the corresponding chemistry of structurally similar organic sulfonic esters, $RS(O)_2OR'$.

A. Transesterification Reactions. Heating sulfonic esters and alcohols results in the formation of sulfonic acids and ethers (eq 7).[25] By way of contrast, when alcohol ($R' = CH_3$,

$$RS(O)_2OR' + R''OH \xrightarrow{\Delta} RS(O)_2OH + R'OR'' \quad (7)$$

C_2H_5) solutions of the iron-alkyl sulfito complexes ($R = C_2H_5$, CH_3) are heated at reflux for ca. 24 h, transesterification occurs to afford the exchanged iron-alkyl sulfito products as seen in eq 8. Some decomposition was observed in these



(8)

reactions, which accounts for the less than quantitative yields of 52–65%. The exchange does not take place at 25 °C with or without added benzoyl peroxide, a radical initiator. However, in the presence of small amounts of HBF_4 ($(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]:HBF_4$ molar ratio $\geq$ 30:1), transesterification of the alkyl sulfito complexes was accomplished in shorter reaction times (10 h), under milder conditions (25 °C), and in higher yields (ca. 84%) than in the absence of the acid. This acid-promoted exchange is general for alcohols, but both phenol and *p*-toluenethiol failed to react under similar conditions. Furthermore, no transesterification was observed at ambient temperatures between $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ and $NaOCH_3$ or between the ethyl sulfito complex and CH_3OH in the presence of KOH.

In order to obtain some insight into the mechanism of the aforementioned transesterifications, a reaction was carried out between $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ and $(+)_{589}$-2-octanol ($[\alpha]^{22.5}{}_{589} = +8.75°$) in the presence of HBF_4. The isolated optically active ($[\alpha]^{22.5}{}_{589} = +23.8°$) $(+)_{589}\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$ was converted by the action of CH_3OH and HBF_4 back to $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ and 2-octanol, which exhibited essentially unchanged rotation ($[\alpha]^{21}{}_{589} = +8.60°$). Furthermore, maintaining at reflux a methanol solution of the above optically active $(+)_{589}\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$ led to the isolation of 2-oc-

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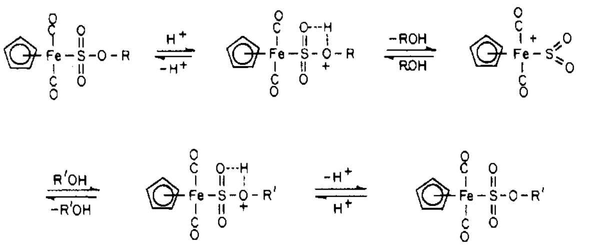
(24) Anderson, B.; Milburn, R. M.; Harrowfield, J. M.; Robertson, G. B.; Sargeson, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 2652 and references therein.

(25) Noller, C. R. "Chemistry of Organic Compounds", 3rd ed.; W. B. Saunders: Philadelphia, Pa., 1966; p 315.

Scheme I

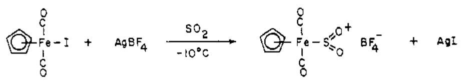


tanol with $[\alpha]^{26}_{589} = +8.40°$. These results indicate that the integrity of the O–C (asymmetric) linkage in the 2-octoxy group is substantially (≳96%) preserved in the reacting alcohol under acid conditions and in the iron–alkyl sulfito complex under both acid and thermal conditions.[26]

A particularly attractive mechanism for the acid-promoted exchange which leaves intact the O–C bond of the alkoxy group is depicted in Scheme I. In the absence of HBF_4, cleavage of the S–OR bond of the alkyl sulfite may be initiated by interaction of the OH proton of the reacting alcohol with the oxygen of the $S(O)_2OR$.

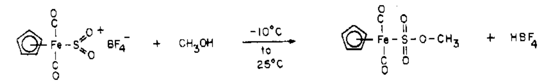
A feature of considerable interest in the mechanism in Scheme I is the involvement of the iron–sulfur dioxide cation $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^+$. The formation of such a species is not unreasonable since cationic manganese– and rhenium–sulfur dioxide complexes, $[M(CO)_5SO_2]AsF_6$ (M = Mn, Re), have recently been synthesized.[27]

As a test of the viability of Scheme I we undertook to synthesize $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^+$ and show that it reacts readily with alcohols to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$. In that vein, a reaction analogous to that for the preparation of $[M(CO)_5SO_2]AsF_6$ (M = Mn, Re) was carried out (eq 9).



(9)

After the original purple solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ had changed to bright red, a characteristic color of many cations $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$,[28,29] the reaction mixture was treated with methanol. Usual workup afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ (eq 10), thus indicating a facile nucleophilic attack of CH_3OH on the ligated SO_2 and lending strong support to the mechanism in Scheme I.



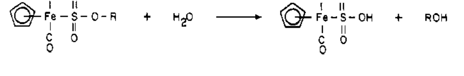
(10)

It is noteworthy that the in situ synthesis of the cation $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^+$ completes the series $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^n$ (n = 1–, 0, 1+). The previously prepared[21] anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^-$ represents an isolable entity, whereas the 17-electron radical $(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2\cdot$ appears to be a short-lived species which dimerizes readily to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]_2$.[7] As would be expected, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^+$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^-$ are susceptible to attack by nucleophilic and electrophilic reagents, respectively.

B. Hydrolysis. Synthesis, Characterization, and Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$. Hydrolysis of sulfonic esters proceeds according to eq 11.[30,31] Except when R' = aryl,[32,33] this reaction occurs with scission of the O–C(R') bond and inversion at the alkoxy carbon.[30,31]

$$RS(O)_2OR' + H_2O \rightarrow RS(O)_2OH + R'OH \qquad (11)$$

Stirring an aqueous solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ at room temperature for 16 h followed by evaporation to dryness affords $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ as an air-stable, yellow solid in high yield (eq 12). The deuterium analogue of the hydrogen sulfite was obtained similarly by hydrolysis in D_2O.



(12)

The hydrogen sulfito product was characterized by elemental analysis and infrared (Table I) and ^1H NMR spectroscopy. The positions of the two $\nu(C\equiv O)$ bands at 2062 and 2018 cm^{-1} match well those of the corresponding absorptions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$, and the $\nu(SO_2)$ bands at 1184 and 1038 cm^{-1}, shown in Figure 1, are in the range expected for the assigned structure. A broad peak at 2940 cm^{-1} is due to $\nu(OH)$; consistent with this assignment, the above absorption disappears and a new one ($\nu(OD)$) appears at 2230 cm^{-1} for $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OD]$. Organic sulfonic acids exhibit the corresponding band at ca. 2900 cm^{-1}, with shifts to ca. 2225 cm^{-1} upon deuteration.[34] The ^1H NMR spectrum of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ in $(CD_3)_2SO$ shows, in addition to a sharp signal of the C_5H_5 protons (τ 4.70), a broad resonance of the OH proton (τ −1.16) in the range reported[35] for the sulfonic acids.

The complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ represents the first well-characterized organometallic analogue of sulfonic acids,[36] and, consistent with this analogy, it furnishes a titration curve typical of strong acids on neutralization with NaOH in aqueous solution. When the titration was conducted to a pH of 7.00, an equivalent weight of 260 was obtained, which compares well with the calculated value of 258 for the assigned formula.

Removal of water from an aqueous solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ neutralized with NaOH affords a yellow, air-stable solid $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$. This iron–sulfito complex is a 1:1 electrolyte in methanol,[37] and its infrared spectrum in the 1300–700-cm^{-1} region (Table I and Figure 1) is consistent with the presence of a sulfur-bonded SO_3^{2-} (C_{3v} local symmetry).[38] The recent synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^-$ from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ and SO_2[21] permits a comparison of nucleophilicity to be made between this anion and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]^-$. The latter may be viewed as a 1:1 adduct of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ and SO_3, a much stronger acid than SO_2. Consistent with such an analogy, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]^-$ was found to be a weaker nucleophile than $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^-$. Whereas the latter

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(26) The only alternative to the proposed two retentions at the OC carbon of the 2-octoxy moiety on going from $(+)_{589}$-2-octanol to $(+)_{589}$-$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$ and back to $(+)_{589}$-2-octanol is two inversions. However, the latter scheme would necessitate backside nucleophilic displacement of the 2-octyl group from the alcohol and then from the alkyl sulfito complex—a sequence that must be regarded as *extremely unlikely*.

(27) Mews, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 640.

(28) Dombeck, B. D.; Angelici, R. J. *Inorg. Chim. Acta* **1973**, *7*, 345.

(29) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.

(30) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1977; p 450.

(31) Kenyon, J.; Phillips, H.; Turley, H. G. *J. Chem. Soc., Trans.* **1925**, *127*, 399.

(32) Bender, M. L.; Dewey, R. J. *J. Am. Chem. Soc.* **1956**, *78*, 317.

(33) Oae, S.; Fukumoto, T.; Kiritani, R. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 346.

(34) Detoni, S.; Hadzi, D. *Spectrochim. Acta* **1957**, *11*, 601.

(35) Dyer, J. R. "Applications of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall: Englewood Cliffs, N.J., 1965; p 85.

(36) The formulation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2FeSO_3H\cdot H_2O$, made solely on the basis of elemental analysis and an infrared spectrum, is to be regarded as tentative: Field, D. S.; Newlands, M. J. *J. Organomet. Chem.* **1971**, *27*, 221.

(37) Typical values of Λ_m for ca. 10^{-3} M solutions of 1:1 electrolytes in methanol and nitromethane are given by: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(38) Newman, G.; Powell, D. B. *Spectrochim. Acta* **1963**, *19*, 213.

readily undergoes reaction with CH_3I,[21] the former failed to react with CH_3I, even on heating at reflux in acetone–ethanol for 10 h.

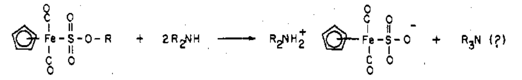
The hydrolysis reaction in eq 12 is reversible, and the alkyl sulfito complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ (R = CH_3, C_2H_5, 2-C_8H_{17}) can be obtained in high yield by treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ with the appropriate alcohol at 25 °C. This alkylation reaction, like the transesterification, proceeds with the preservation of the O–C bond of the alcohol. This conclusion derives from the observations that treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ with $(+)_{589}$-2-octanol ($[\alpha]^{22.5}{}_{589} = +8.75°$) affords $(+)_{589}$-$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$, which on reaction with methanol regenerates $(+)_{589}$-2-octanol with only slightly lower rotation ($[\alpha]^{28}{}_{589} = +8.20°$). Since the second transformation was shown earlier to proceed with retention at the OC carbon of the 2-octoxy group, the first reaction must also lead to substantial retention.

Attempts were made at conversion of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2Cl]$ by action of $SOCl_2$ in $CHCl_3$ and $ClC(O)C(O)Cl$ in benzene at 25 °C. However, in each case, the only organometallic product obtained was $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$.

C. Reactions with Amines. In general, organic sulfonic esters alkylate amines in a 1:1 reaction[25] as illustrated in eq 13 for secondary amines.

$$RS(O)_2OR' + R''_2NH \rightarrow R''_2R'NH[RSO_3] \qquad (13)$$

Dissolution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ in excess R_2NH (R = CH_3, C_2H_5) at 25 °C leads to the formation of a yellow, air-stable precipitate in high yield (eq 14). Added benzoyl peroxide does not affect the rate of this reaction when R = C_2H_5. The precipitate was characterized by infrared and ^1H NMR spectroscopy (Experimental Section) as $R_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$. The identity of the anion was further ascertained by conversion of the product to the previously prepared (vide supra) $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$ via metathesis with $NaB(C_6H_5)_4$. Furthermore, when R = C_2H_5, the same organoiron salt was obtained by neutralization of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ with $(C_2H_5)_2NH$ in acetonitrile.



(14)

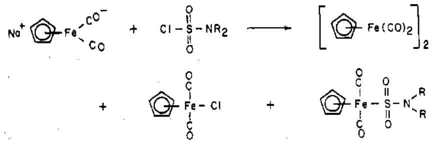
The anomalous 1:2 alkylation in eq 14 finds some precedent in the organic chemistry of $C_6H_5S(O)_2OR$ (R = $CH{=}CH_2$, $CH_2C(CH_3){=}CH_2$, $CH_2CH{=}CHC_6H_5$).[39,40] These compounds react with 2 mol of various $R'NH_2$ compounds according to eq 15. In both reactions, transamination is involved.

$$C_6H_5S(O)_2OR + 2R'NH_2 \rightarrow R'RNH + R'NH_3[C_6H_5SO_3] \qquad (15)$$

Such transamination appears to be essential to the transformation in eq 14 since $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ failed to react with neat $(C_2H_5)_3N$ even at reflux.

It is noteworthy that the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with R_2NH, unlike that with $R'OH$, proceeds with cleavage of the O–C bond of the alkyl sulfito ligand. In this respect, the behavior toward the amines of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ differs from that of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[C(O)OR]$. The carboalkoxy complexes and R_2NH react to afford $(\eta^5\text{-}C_5H_5)Fe(CO)_2[C(O)NR_2]$,[13] i.e., with nucleophilic displacement of OR^- from C(O)OR.

An analogous displacement of OR^- from $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ by R_2NH would have afforded the sulfonamido complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2NR_2]$. Although no evidence was obtained for the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2NR_2]$ in the aforementioned reactions, this type of complex can be prepared, albeit in very low yield, by treatment of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with $ClS(O)_2NR_2$ (R = CH_3) according to eq 16. The characterization of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2N(CH_3)_2]$ by infrared and ^1H NMR spectroscopy is detailed in the Experimental Section.



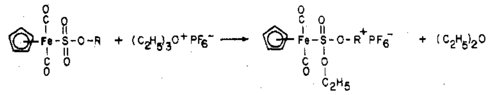
(16)

D. Reactions with Protic Acids. Since the rate of the reaction between $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ and $R'OH$ is enhanced by the presence of HBF_4, it was of interest to examine interaction of the alkyl sulfito complexes with various protic acids.

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with HCl (R = C_2H_5) and CF_3CO_2H (R = CH_3) at ambient temperature resulted in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2[OC(O)CF_3]$, respectively, in high yield. These substitution reactions probably proceed by protonation of the alkyl sulfito ligand and loss of ROH (Scheme I), followed by replacement of SO_2 in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^+$ with Cl^- or $CF_3CO_2^-$. Somewhat surprisingly, no reaction was observed between $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ and HF in $CHCl_3$ at 25 °C, possibly owing to an insufficient acid strength of HF to effect loss of alcohol from the alkyl sulfito complex.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ with equimolar $HBF_4{\cdot}(C_2H_5)_2O$ in $CDCl_3$ at 25 °C was monitored by ^1H NMR spectroscopy and reached completion in ca. 75 min. Although no organoiron product was isolated and fully characterized, the NMR data (Experimental Section) appear to be compatible with the presence of $(\eta^5\text{-}C_5H_5)Fe(CO)_2FBF_3$ in solution. Similar organometallic complexes containing coordinated PF_6^- ion have recently been reported.[41,42] The formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[OC(O)CF_3]$, and possibly $(\eta^5\text{-}C_5H_5)Fe(CO)_2FBF_3$ from $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ and the appropriate acid would seem to indicate considerable lability of ligated SO_2 in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]^+$.

E. Alkylation Reactions. The alkyl sulfito ligand in $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ (R = CH_3, C_2H_5) can be alkylated with $(C_2H_5)_3OPF_6$ in CH_2Cl_2 at 25 °C according to eq 17.



(17)

The resultant yellow, air-stable solids $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OR]]PF_6$ represent the first examples of organoiron complexes containing a dialkyl sulfite ligand. The new complexes were characterized by elemental analysis, conductivity measurements in nitromethane which show them to be 1:1 electrolytes,[37] and infrared (Table I) and ^1H NMR spectroscopy. The infrared spectra prominently exhibit two $\nu(C{\equiv}O)$ bands at 2085 and 2050 cm^{-1}, characteristic of cationic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$,[28,29] and a single $\nu(S{=}O)$ band at 1228–1224 cm^{-1}. In the ^1H NMR spectra, the C_5H_5 resonance is, as expected, shifted ca. 0.5 ppm downfield from the corresponding resonance of the parent $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$. Another noteworthy feature in the ^1H NMR spectra of the dialkyl sulfite complexes is the appearance of the CH_2 signal as a multiplet at τ 5.45–5.67. The CH_2

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[39] Vizgert, R. V.; Sendega, R. V.; Zhovnirchuk, V. M. *J. Org. Chem. USSR (Engl. Transl.)* **1969**, *5*, 914.

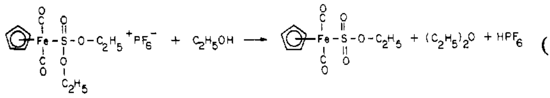
[40] Freundenberg, K.; Hess, H. *Liebigs Ann. Chem.* **1926**, *448*, 121.

[41] Beck, W.; Schloter, K. *Z. Naturforsch. B, Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214.

[42] Regina, F. J.; Wojcicki, A. *Inorg. Chem.*, following paper in this issue.

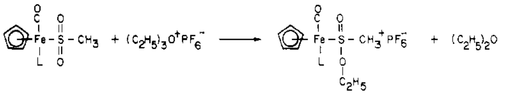
protons of the C_2H_5 group in the two complexes (R = CH_3, C_2H_5) are diastereotopic, in each case giving rise to the (incompletely resolved) AB part of an ABX_3 type of spectrum. A similar spectrum has been reported[43] for the CH_2 protons of diethyl sulfite.

Storage of a solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)_2]]PF_6$ in ethanol for 16 h at 25 °C results in the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ and $(C_2H_5)_2O$ according to eq 18. In contrast, no alkylation of acetone by $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OR]]PF_6$ (R = CH_3, C_2H_5) was observed under comparable conditions.


(18)

The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PR_3)[S(O)_2CH_3]$ (R = C_4H_9, C_6H_5) behave as Lewis bases in undergoing protonation and/or interaction with BF_3 at the sulfinate oxygen.[44,45] Therefore, it was of interest to extend the alkylation reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ to the analogous sulfinato-*S* complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(L)[S(O)_2R]$.

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)(L)[S(O)_2R]$ (L = CO, $P(C_6H_5)_3$) with $(C_2H_5)_3OPF_6$ in CH_2Cl_2 at 25 °C was found to proceed according to eq 19 to afford yellow, air-stable complexes containing the novel ethyl methanesulfinate ligand. The characterization of these complexes by elemental analysis, conductivity measurements, and infrared and ^1H NMR spectroscopy is detailed in the Experimental Section. Prominent features of the infrared spectra parallel those of the previously considered spectra of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OR]]PF_6$ and need not be discussed further; they are provided for comparison in Table I.


(19)

Summary of Reactions. Reactions of the alkyl sulfito ligand in $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ proceed with heterolytic cleavage of either the S–OR bond or the O–R bond. The former mode of scission occurs on treatment of the complex with alcohols and results in transesterification, whereas the latter mode of scission takes place on reaction with secondary amines, R_2NH, and yields $R_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$. The alkyl sulfite undergoes alkylation by R'_3OPF_6 to afford the corresponding dialkyl sulfite complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OR)OR']]PF_6$ and substitution by the anion of strong acids, HX, to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$. Hydrolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ yields the hydrogen sulfito complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$, a strong acid, which affords the anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]^-$ on neutralization.

Experimental Section

General Procedures. All reactions that did not involve use of oxygen were conducted under an atmosphere of dry nitrogen. Standard techniques were employed for the manipulation of air-sensitive compounds.[46] Irradiation experiments were carried out in Pyrex tubes with use of a Rayonet Model RPR-100 photochemical reactor with 350-nm lamps. Chromatography was performed on columns packed with 60–100 mesh Florisil. Melting points were measured in vacuo on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Titrations were performed by using a Radiometer Copenhagen Model ABU12 autoburette, Model No. 11 titrator, and Model No. 26 pH meter. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. ^1H NMR spectra were recorded on Varian Associates A-60A and EM360L spectrometers with use of Me_4Si as an internal reference. ^{19}F NMR spectra were measured on a Bruker HX-90 spectrometer at 84.6 MHz with the assistance of Dr. C. E. Cottrell.

Infrared (IR) spectra were recorded on Beckman IR-9 and Perkin-Elmer Model 337 spectrophotometers. Mass spectra were obtained at 70 eV on an AEI Model MS-9 spectrometer by Mr. C. R. Weisenberger. Specific rotations were measured on a Perkin-Elmer Model 241 polarimeter in a 10-cm cell. Conductivity data were obtained on ca. 10^{-3} M solutions by using a Lab-Line No. 11200 beaker-type conductivity cell in conjunction with an Industrial Instruments, Inc., Model RC 16B2 conductivity bridge.

Materials. Chloroform was distilled first from P_4O_{10} and then from K_2CO_3. Dichloromethane was purified by distillation from P_4O_{10}. Acetonitrile was distilled three times from P_4O_{10} and once from K_2CO_3. Nitromethane was dried over $CaCl_2$ and then distilled from $CaSO_4$. Methanol was distilled from magnesium turnings and I_2.[47] 1-Propanol and 2-propanol were distilled from $CaSO_4$. All of these solvents were stored over 4-A molecular sieves. THF was distilled from Na/K and benzophenone immediately before use. Cyclohexane was purified by distillation from $LiAlH_4$. Benzene was dried by passage through a column of alumina.[48] Other solvents were of reagent grade quality and were used as received.

Sulfur dioxide, from Matheson, was purified before use by passage through concentrated H_2SO_4 and a column packed with P_4O_{10}. Dimethylamine, diethylamine, and triethylamine, from Fisher, were stored over 4-A molecular sieves. $(+)_{589}$-2-Octanol, from Aldrich, was distilled at 86 °C (20 torr) before use. Dimethylsulfamoyl chloride was distilled at 114 °C (75 torr) prior to use. Silver tetrafluoroborate, from Alfa, was dehydrated by heating at 120 °C (1 torr) for 24 h and then at 145 °C (1 torr) for 1.5 h. $(C_2H_5)_3OPF_6$, $P(C_6H_5)_3$, and $NaB(C_6H_5)_4$ were recrystallized from CH_2Cl_2, benzene, and $CHCl_3$, respectively. Other commercially procured chemicals were of reagent grade or equivalent quality and were used without further purification.

The compounds $Na[S(O)_2OR]$ (R = CH_3, C_2H_5) were prepared by slow passage of gaseous SO_2 into a cooled (0 °C) alcoholic solution of NaOR, obtained by reaction of Na with ROH.[20,49] $(CH_3)_3NO$ was synthesized as reported.[50]

Literature procedures were used to prepare the following metal complexes: $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$,[28] $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]\cdot 0.5SO_2$,[21] $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2CH_3]$,[23a] $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3][S(O)_2CH_3]$,[44] $Mn(CO)_3(bpy)Cl$,[51] $[Mn(CO)_5NCCH_3]PF_6$,[52] $Mn(CO)_3[P(C_6H_5)_3]_2Cl$,[51] and $(n\text{-}C_4H_9)_4N[W(CO)_5I]$.[53] Ms. G. Arzaga provided $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $(\eta^5\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]Cl$, and Mr. F. J. Regina furnished $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$. A. By Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$ with $Na[S(O)_2OR]$ (R = CH_3, C_2H_5). Passage of oxygen through a solution of 1.00 g (2.83 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and 1.05 g (6.00 mmol) of 48% aqueous HBF_4 in 50 mL of acetone resulted in a gradual change of color from purple to bright red. Acetone and H_2O were removed by rotary evaporation, and the residual red-purple oil was dissolved in 70 mL of CH_3OH and treated with 0.8 g (7 mmol) of $Na[S(O)_2OCH_3]$. The resulting solution was stirred for 12 h at 25 °C, during which time it changed color from red to yellow. Methanol was removed under reduced pressure, and the residue was extracted with 30 mL of $CHCl_3$. The extract was chromatographed on Florisil eluting with 5:1 (v/v) $CHCl_3$–acetone to remove a long yellow band. Concentration of the effluent to 15 mL and addition of 30 mL of cyclohexane with stirring afforded 0.78 g (51% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ as yellow crystals: mp 156 °C dec; ^1H NMR ($CDCl_3$) τ 4.79 (s, C_5H_5), 6.41 (s, CH_3); IR (KBr) 3106 (m), 2942 (m), 2064 (vs), 2007 (vs), 1988 (sh), 1426 (m), 1214 (s), 1173 (sh), 1095 (s), 1061 (s), 995 (sh),

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971 (s), 913 (m), 868 (m), 686 (s), 636 (s), 604 (s), 579 (s), 566 (m), 558 (s) cm^{-1}; mass spectrum (70 °C, relative intensities in parentheses), prominent peaks at m/e 242 $(P - CO)^+$ (4), 216 $(P - 2CO)^+$ (16), 186 $(C_5H_5)_2Fe^+$ (62), 177 $(P - SO_3CH_3)^+$ (32), 149 $(P - CO - SO_3CH_3)^+$ (42), 121 $(P - 2CO - SO_3CH_3)^+$ (100), 64 SO_2^+ (>100).

Similarly, reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$, prepared from 2.00 g (5.65 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and 2.10 g (12.0 mmol) of 48% aqueous HBF_4 in 100 mL of acetone and freed of the solvent, with 1.77 g (14.4 mmol) of $Na[S(O)_2OC_2H_5]$ in 120 mL of C_2H_5OH afforded 1.67 g (51% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ as yellow crystals: mp 96 °C; ^1H NMR ($CDCl_3$) τ 4.60 (s, C_5H_5), 5.99 (q, J = 7 Hz, CH_2), 8.77 (t, J = 7 Hz, CH_3); IR (KBr) 3120 (m), 3110 (sh), 2984 (w), 2938 (w), 2906 (w), 2062 (vs), 2000 (vs), 1434 (m), 1424 (sh), 1388 (w), 1214 (s), 1105 (sh), 1088 (s), 1020 (s), 971 (s), 904 (s), 891 (m), 869 (s), 839 (m), 731 (s), 615 (s), 592 (s), 578 (s), 568 (s), 505 (m), 494 (sh) cm^{-1}; mass spectrum (80 °C, relative intensities in parentheses), prominent peaks at m/e 287 P^+ (2), 258 $(P - CO)^+$ (10), 230 $(P - 2CO)^+$ (40), 186 $(C_5H_5)_2Fe^+$ (80), 177 $(P - SO_3C_2H_5)^+$ (41), 149 $(P - CO - SO_3C_2H_5)^+$ (40), 121 $(P - 2CO - SO_3C_2H_5)^+$ (100), 64 SO_2^+ (>100). Anal. Calcd for $C_9H_{10}FeO_5S$: C, 37.87; H, 3.52. Found: C, 37.17; H, 3.46.

B. By Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$ with $Na[S(O)_2OC_2H_5]$ and ROH (R = 1-C_3H_7OH, 2-C_3H_7OH). $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$, prepared from 1.00 g (2.83 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and 1.05 g (6.00 mmol) of 48% aqueous HBF_4 in acetone and freed of the solvent, was treated with 0.86 g (6.5 mmol) of $Na[S(O)_2OC_2H_2]$ in 100 mL of 1-C_3H_7OH. The resulting solution was stirred for 16 h at 25 °C and then evaporated to dryness. After extraction with $CHCl_3$ and chromatography on Florisil, 0.82 g (48% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_3H_7\text{-}1]$, mp 94–96 °C, was obtained as a yellow powder upon evaporation of the solvent: ^1H NMR ($CDCl_3$) τ 4.68 (s, C_5H_5), 6.14 (t, J = 6 Hz, OCH_2C), 8.14 (m, $J = J'$ = 6 Hz, CCH_2C), 9.08 (t, J' = 6 Hz, CH_3); IR (KBr) 3112 (m), 2966 (m), 2938 (m), 2890 (w), 2828 (sh), 2068 (vs), 2052 (sh), 2014 (vs), 1427 (m), 1418 (m), 1388 (w), 1249 (m), 1211 (s), 1087 (s), 1050 (sh), 1013 (w), 993 (w), 973 (m), 940 (m), 906 (w), 873 (w), 793 (m), 733 (m), 709 (m), 672 (w), 639 (m), 608 (m), 574 (m), 558 (m), 520 (w), 515 (sh) cm^{-1}; mass spectrum (120 °C), no peaks corresponding to $SO_3C_3H_7$-containing species.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_3H_7\text{-}2]$ was obtained similarly as a yellow-orange powder by using 2-C_3H_7OH in place of 1-C_3H_7OH: 32% yield; mp 164–165 °C dec; ^1H NMR ($CDCl_3$) τ 4.83 (s, C_5H_5), 5.10 (apparent septet with only five component peaks discernible, J = 6.1 Hz, CH), 8.25 (d, J = 6.1 Hz, $2CH_3$); IR (KBr) 3120 (m), 2990 (sh), 2978 (s), 2930 (w), 2070 (vs), 2052 (sh), 2010 (vs), 1420 (m), 1401 (m), 1370 (w), 1352 (w), 1342 (w), 1211 (s), 1208 (sh), 1178 (w), 1112 (s), 1084 (s), 1065 (m), 918 (s), 865 (sh), 845 (s), 718 (m), 640 (s), 606 (m), 581 (s), 560 (m), 524 (m) cm^{-1}; mass spectrum (120 °C), no peaks corresponding to $SO_3C_3H_7$-containing species.

C. By Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$ with Na_2SO_3 and ROH (R = C_2H_5). $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$, prepared from 2.00 g (5.65 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and 2.10 g (12.0 mmol) of 48% aqueous HBF_4 in acetone and freed of the solvent, was treated with 2.5 g (20 mmol) of Na_2SO_3 in 150 mL of C_2H_5OH. The mixture was stirred for 3 days at 25 °C, during which time the color changed from red to yellow. The solvent was removed, the residue was extracted with 100 mL of $CHCl_3$, and the extract was filtered. The filtrate was chromatographed on Florisil by using 5:1 (v/v) $CHCl_3$–acetone to elute off first a band containing 0.02 g of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and then a band that yielded 1.29 g (40%) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ on concentration and addition of cyclohexane.

D. By Reaction of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]\cdot 0.5SO_2$ with $ROSO_2F$ (R = CH_3).[54] To 4.1 g (14 mmol) of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]\cdot 0.5SO_2$ in a 250-mL round-bottom flask were added 1.8 g (16 mmol) of CH_3OSO_2F and 100 mL of CH_2Cl_2. The resulting solution was maintained at reflux for 2 h and then was cooled to 25 °C and evaporated to dryness. The orange residue was extracted with 70 mL of ethyl acetate, and the extract was chromatographed on Florisil. Elution with ethyl acetate afforded a narrow purple band containing $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and a long yellow-orange band which was collected and evaporated to dryness. The residue was dissolved in 60 mL of $CHCl_3$, and the resulting solution was treated with hexane until it turned cloudy. Concentration on a rotary evaporator yielded 0.33 g (5.0%) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]_2$[7] as orange crystals which were collected by filtration. Evaporation to dryness of the filtrate afforded 0.86 g (23% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$.

E. By Reaction of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]\cdot 0.5SO_2$ with R_3OPF_6 (R = CH_3). To 3.88 g (12.4 mmol) of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]\cdot 0.5SO_2$ were added 2.00 g (14.1 mmol) of $(CH_3)_3OPF_6$, 125 mL of CH_2Cl_2, and 5 mL of nitromethane, and the resulting solution was kept at reflux for 3 h. The rest of the procedure was identical with that for the preceding synthesis and led to the isolation of a trace amount of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 0.14 g (4.5% yield) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]_2$,[7] and 0.105 g (2.0% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$. A large amount of brown decomposition material remained at the top of the chromatography column.

F. By Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]BF_4$ with ROH (R = CH_3). A 100-mL round-bottom flask equipped with a dry-ice condenser was charged with 1.40 g (7.20 mmol) of $AgBF_4$ and 2.17 g (7.20 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. Sulfur dioxide (30 mL of liquid) was then condensed onto the solids, and the resulting solution was maintained at reflux for 8 h, during which time it changed color from dark purple to bright red. The mixture was filtered at −78 °C to remove AgI, and 15 mL of CH_3OH was syringed into the filtrate. The resulting solution was warmed to 25 °C over 12 h as the SO_2 boiled off. Evaporation of the solvent yielded a red-brown oil which was extracted with CH_2Cl_2, and the extract was chromatographed on Florisil to give two bands. The leading orange band was eluted off and solvent was removed to afford 0.24 g of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$. The second band, dark red, was collected and rechromatographed by using 5:1 (v/v) CH_2Cl_2–acetone for elution to give a long yellow band and an immobile orange band. The yellow band was collected and evaporated to dryness to give an additional 0.33 g of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$. Total yield was 0.57 g (29%).

Preparation of $Mn(CO)_3(bpy)[S(O)_2OCH_3]$. A solution of 1.00 g (3.02 mmol) of $Mn(CO)_3(bpy)Cl$ and 0.420 g (3.56 mmol) of $Na[S(O)_2OCH_3]$ in 175 mL of CH_3OH was maintained at reflux for 4 h and then was filtered. The filtrate was evaporated to dryness, the orange residue was extracted with 500 mL of $CHCl_3$, and the extract was filtered. Concentration of the filtrate to 25 mL resulted in the precipitation of 1.05 g (90% yield) of air-stable $Mn(CO)_3(bpy)[S(O)_2OCH_3]$ as an orange powder: mp 166–168 °C; ^1H NMR ($(CD_3)_2SO$) τ 0.19–2.28 (m, $C_{10}H_8N_2$), 7.33 (s, CH_3); IR (KBr) 3070 (w), 2054 (s), 1940 (vs), 1465 (m), 1435 (m), 1310 (m), 1224 (w), 1198 (s), 1174 (w), 1156 (m), 1121 (w), 1106 (w), 1077 (s), 759 (w), 736 (m), 686 (m), 656 (s), 642 (s), 620 (s), 526 (m) cm^{-1}.

Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with R′OH (R, R′ = CH_3, C_2H_5, $(+)_{589}$-2-C_8H_{17}) in the Presence of HBF_4. A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ (0.580 g, 2.02 mmol) and HBF_4 (1 mL of 1.92×10^{-2} M solution in CH_3OH) in 50 mL of CH_3OH was stirred for 10 h at 25 °C. Solvent was then removed, the residue was dissolved in 15 mL of $CHCl_3$, and the resulting solution was chromatographed on Florisil. Elution with 5:1 (v/v) $CHCl_3$–acetone removed a yellow band which on evaporation to dryness afforded 0.463 g (84% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$.

In a similar manner, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ was converted to $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ in 83% yield by the action of C_2H_5OH and HBF_4.

A solution containing 0.252 g (1.00 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$, 4.11 g (31.5 mmol) of $(+)_{589}$-2-$C_8H_{17}OH$ ($[\alpha]^{22.5}_{589} = +8.75°$, $CHCl_3$ solution), and 0.011 g (ca. 8×10^{-6} mmol) of 48% aqueous HBF_4 in 2 mL of $CHCl_3$ was stirred for 24 h at 25 °C. The volatiles were removed on a vacuum line at 25 °C (0.1 torr), the residue was dissolved in 10 mL of $CHCl_3$, and 20 mL of cyclohexane was added to produce a small amount of oil. The solution was decanted from the oil, and the decantate was evaporated to dryness to afford $(+)_{589}$-$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$ as a yellow powder: 0.321 g (83% yield); mp 118 °C dec; $[\alpha]^{22.5}_{589} = +23.8°$ ($CHCl_3$); ^1H NMR ($CDCl_3$) τ 4.79 (s, C_5H_5), 5.27 (br, CH), 8.70–9.14 (m, $(CH_2)_5$, $2CH_3$); IR (KBr) 3105 (m), 2950 (m), 2925 (m), 2870 (m), 2855 (m), 2070 (sh), 2065 (vs), 2010 (vs), 1470 (m), 1430 (m), 1415 (m), 1375 (m), 1212 (s), 1120 (m), 1088 (s), 1016 (m), 966 (m), 914 (s), 882 (sh), 868 (sh), 850 (m), 838 (sh), 726 (m), 696 (m), 634 (s), 600 (s), 560 (s), 555 (s), 516 (s), 475 (w) cm^{-1}.

After a solution of $(+)_{589}$-$(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$ (1.98 g, 5.12 mmol) and HBF_4 (1 mL of 5.32×10^{-2} M solution in CH_3OH) in 50 mL of CH_3OH had been stirred for 48 h at 25 °C, the solvent

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(54) Adapted from a procedure communicated to C.A.P. by Professor C. R. Jablonski.

was removed by rotary evaporation. 2-Octanol was evaporated at 25 °C (0.1 torr) and collected in a trap at 0 °C: 0.193 g; $[\alpha]^{21}_{589} = +8.60°$ ($CHCl_3$). The resulting yellow residue was extracted with 10 mL of $CHCl_3$, the extract was filtered, and the filtrate was evaporated to dryness to yield 1.16 g (83%) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$.

Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with $R'OH$ ($R, R' = CH_3, C_2H_5, (+)_{589}\text{-}2\text{-}C_8H_{17}$) at Reflux. A solution of 0.465 g (1.63 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ in 40 mL of CH_3OH was kept at reflux for 24 h and then was cooled to 25 °C and evaporated to dryness. The residue was extracted with $CHCl_3$, the extract was chromatographed, and a single yellow band was collected and evaporated to dryness to yield 0.233 g (52%) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$. A large amount of brown decomposition material remained at the top of the column.

Under similar conditions, reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ with C_2H_5OH afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ in 65% yield, and reaction of $(+)_{589}\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$ with CH_3OH gave $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ in 96% yield as well as 2-octanol (51% yield), $[\alpha]^{26}_{589} = +8.40°$ ($CHCl_3$).

Hydrolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ ($R = CH_3, C_2H_5, 1\text{-}C_3H_7, 2\text{-}C_3H_7$). An aqueous solution (30 mL) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ (0.646 g, 2.26 mmol) was stirred for 16 h at 25 °C, and then volatile matter was removed at 25 °C (0.1 torr). The solid residue was dissolved in 200 mL of CH_3CN, the resulting solution was filtered, and the filtrate was concentrated to afford a yellow, air-stable precipitate identified as $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$: 0.546 g (94% yield); mp 104 °C; ^1H NMR ($(CD_3)_2SO$) τ −1.16 (s, br, OH), 4.70 (s, C_5H_5); IR (KBr) 3022 (m), 2940 (w, br), 2510 (w, br), 2062 (vs), 2018 (vs), 1434 (m), 1423 (m), 1275 (m, br), 1184 (s), 1084 (m), 1066 (sh), 1038 (s), 1005 (sh), 859 (s), 839 (w), 811 (s), 610 (sh), 601 (sh), 588 (s), 567 (s), 548 (s), 487 (m), 466 (m) cm^{-1}. Anal. Calcd for $C_7H_6FeO_5S$: C, 32.58; H, 2.34. Found: C, 32.79; H, 2.51.

This product was also obtained, in comparable yields, by hydrolysis of other alkyl sulfito complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ ($R = CH_3, 1\text{-}C_3H_7, 2\text{-}C_3H_7$) under similar conditions.

The deuterium analogue of the above, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OD]$, was prepared similarly by reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ with D_2O: IR (KBr, >2000 cm^{-1} only) 3022 (m), 2510 (w, br), 2230 (w, br), 2062 (vs), 2018 (vs) cm^{-1}.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ with NaOH. To a solution of 0.396 g (1.43 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ in 10 mL of H_2O was added dropwise with stirring at 25 °C 14 mL of 0.101 M NaOH. Volatile matter was removed at 25 °C (0.1 torr), the residue was extracted with 10 mL of CH_3CN, and the resulting suspension was filtered to collect 0.390 g (97%) of yellow, air-stable $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$: ^1H NMR ($D_2O/(CD_3)_2CO$) τ 4.95 (s, C_5H_5); IR (KBr) (prominent absorptions) 2065 (sh), 2050 (vs), 1994 (vs), 1129 (sh), 1107 (sh), 1084 (s), 1072 (s), 1035 (sh), 984 (s), 974 (sh) cm^{-1}; Λ_m (CH_3OH) 69.7 Ω^{-1} cm^2 mol^{-1}.

Titration of 10 mL of a solution containing 0.0331 g of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ in 25 mL of H_2O to a pH of 7.00 required 1.030 mL of 0.4492 M NaOH (5.14×10^{-2} mmol). Molecular weight for $C_7H_6FeO_5S$: calcd, 258; found, 260.

Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ with ROH ($R = CH_3, C_2H_5, (+)_{589}\text{-}2\text{-}C_8H_{17}$). A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ (0.213 g, 0.827 mmol) in 30 mL of CH_3OH was stirred for 24 h at 25 °C. Volatile matter was then removed, the solid residue was dissolved in $CHCl_3$, and the resulting solution was filtered. The filtrate was evaporated to dryness to yield 0.134 g (60%) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$.

By an analogous procedure, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ was isolated in 95% yield from the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ with C_2H_5OH.

An acetonitrile solution (25 mL) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$ (0.651 g, 2.52 mmol), 48% aqueous HBF_4 (0.040 g, ca. 4×10^{-2} mmol), and $(+)_{589}\text{-}2\text{-}C_8H_{17}OH$ (4.11 g, 31.6 mmol) was stirred for 48 h at 25 °C. Removal of the volatiles, dissolution of the residue in $CHCl_3$, and chromatography on Florisil led to the isolation of 0.787 g (81% yield) of $(+)_{589}\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_8H_{17}\text{-}2]$. Treatment of this complex in 50 mL of CH_3OH with 1 mL of 1.92×10^{-2} M HBF_4 in CH_3OH followed by rotary evaporation resulted in the isolation of 0.123 g of $(+)_{589}\text{-}2\text{-}C_8H_{17}OH$, $[\alpha]^{28}_{589} = +8.20$ ($CHCl_3$).

Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with R_2NH ($R = CH_3, C_2H_5$). When 20 mL of $(CH_3)_2NH$ was added to 0.300 g (1.10 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ at 0 °C, the resulting solution darkened within 2 min and a yellow solid precipitated. The mixture was stirred for 1.5 h, excess amine was removed in a stream of N_2, and the yellow-brown solid was extracted with 10 mL of $CHCl_3$. The extract was filtered, and the filtrate was treated with 30 mL of cyclohexane. Concentration of the resulting solution to ca. 30 mL afforded $(CH_3)_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$ as a yellow, air-stable solid: 0.284 g (85% yield); ^1H NMR ($CDCl_3$) τ 0.92 (br, NH_2), 5.00 (s, C_5H_5), 7.43 (br, $2CH_3$); IR (KBr) (prominent absorptions) 2040 (vs), 1980 (vs), 1434 (m), 1430 (m), 1110 (s), 1060 (s), 960 (s), 848 (m), 628 (s), 609 (s), 572 (s), 554 (s), 506 (s) cm^{-1}.

$(CH_3)_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$ was converted to $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$ on treatment with an equimolar amount of $NaB(C_6H_5)_4$ in $CHCl_3$ for 24 h at 25 °C. The insoluble product was filtered off and washed thoroughly with $CHCl_3$ and acetone (yield 74%).

In a similar fashion, $(C_2H_5)_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$ was synthesized in 67% yield as a yellow, air-stable solid from $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ and $(C_2H_5)_2NH$: ^1H NMR ($CDCl_3$) τ 1.88 (br, NH_2), 4.96 (s, C_5H_5), 7.04 (br, CH_2), 8.62 (br, CH_3); IR (KBr) (prominent absorptions) 2030 (vs), 1990 (vs), 1960 (sh), 1432 (m), 1428 (m), 1170 (sh), 1110 (s), 1080 (s), 1055 (sh), 1045 (s), 962 (s), 640 (s), 612 (s), 598 (m), 578 (s), 568 (s), 502 (s), 485 (s) cm^{-1}.

Metathetical reaction between equimolar amounts of $(C_2H_5)_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$ and $NaB(C_6H_5)_4$ in 120:1 (v/v) $CHCl_3$–acetone for 16 h at 25 °C afforded the precipitate $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$, which was washed thoroughly with CH_3CN (yield 82%).

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2N(CH_3)_2]$. A solution of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, prepared from 2.66 g (7.51 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and excess 1% sodium amalgam in 200 mL of THF, was treated dropwise with 1.6 mL (15 mmol) of $ClS(O)_2N(CH_3)_2$ in 20 mL of THF. The resulting red solution was stirred for 14 h at 25 °C, the volatiles were removed at 25 °C (0.1 torr), the purple residue was extracted with 250 mL of $CHCl_3$, and the extract was filtered. The filtrate was concentrated to 40 mL and chromatographed on Florisil by eluting with $CHCl_3$. The first band, purple, afforded 1.65 g (62% yield) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, whereas the second band, bright red, gave 0.152 g (5.0% yield) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$. Then removal of a narrow yellow band with 3:1 (v/v) $CHCl_3$–acetone and evaporation of the solvent yielded 0.075 g (1.8%) of the title compound as a yellow, air-stable solid: ^1H NMR ($CDCl_3$) τ 4.82 (s, C_5H_5), 7.28 (s, $2CH_3$); IR (Nujol) 3095 (m), 2045 (vs), 2002 (sh), 1985 (vs), 1220 (s), 1095 (w), 1075 (sh), 1064 (s), 1025 (w), 1008 (sh), 933 (m), 900 (w), 870 (m), 855 (sh), 655 (s), 612 (s), 555 (s), 498 (m), 460 (m) cm^{-1}.

Reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ ($R = CH_3, C_2H_5$) with Acids. A. HCl. Gaseous HCl was slowly passed through a solution of 0.301 g (1.05 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OC_2H_5]$ in 30 mL of THF for 10 min. This solution was then stirred for 2 h at 25 °C and concentrated to a red oil. The oil was dissolved in 10 mL of $CHCl_3$, the resulting solution was filtered, and to the filtrate was added 10 mL of cyclohexane. Slow rotary evaporation of this solution afforded red crystals, identified by infrared and ^1H NMR spectroscopy as $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, 0.183 g (86% yield).

B. CF_3CO_2H. $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ was treated with a fivefold excess of CF_3CO_2H in an NMR tube, and the spectrum of the resulting solution was monitored. The color of the solution gradually changed from yellow to red, and after 7.5 h proton resonances were observed at τ 4.90 (C_5H_5, mainly of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[OC(O)CF_3]$[55]) and 6.46 (very weak, CH_3 of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$), as well as 5.13 (relative intensity 1) and 6.18 (relative intensity 3).

C. HBF_4. A solution of 0.200 g (0.742 mmol) of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$ in 2.5 mL of $CDCl_3$ was treated with 0.1 mL (ca. 0.7 mmol) of $HBF_4\cdot(C_2H_5)_2O$ in an NMR tube. As the reaction progressed, the proton resonance at τ 4.55 (C_5H_5 of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OCH_3]$) slowly decreased in intensity and two new signals of equal height appeared at τ 4.67 and 4.73 and increased in intensity. After 75 min, the peak at τ 4.55 was barely detectable but the C_5H_5

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resonances at τ 4.67 and 4.73 were strong and of equal intensity and new peaks of relative intensity 1:3 were observed at τ 6.35 and 6.90. The ^{19}F NMR spectrum of the solution showed a broad signal throughout the course of the reaction 6.74 ppm from C_6F_6 (BF_4).

Reactions of (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OR] (R = CH_3, C_2H_5) with (C_2H_5)$_3$OPF$_6$. A solution of 0.723 g (2.53 mmol) of (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OC$_2$H$_5$] and 0.613 g (2.47 mmol) of (C_2H_5)$_3$OPF$_6$ in 35 mL of $CHCl_3$ was stirred for 6 h at 25 °C, during which time it changed color from yellow to brown. The volatiles were removed, the solid residue was extracted with 25 mL of CH_2Cl_2, and the extract was filtered. Addition of 25 mL of cyclohexane to the filtrate immediately induced the formation of yellow-brown, air-stable crystals. The volume of the solution was reduced to 30 mL, and the crystals were collected by filtration, 0.641 g (60% yield) of [(η^5-C_5H_5)Fe(CO)$_2$[S(O)(OC$_2$H$_5$)$_2$]]PF$_6$: ^1H NMR ((CD$_3$)$_2$CO) τ 4.08 (s, C_5H_5), 5.25–5.75 (m, 2CH$_2$), 8.56 (t, J = 7 Hz, 2CH$_3$); IR (hexachlorobutadiene) 3130 (m), 2960 (sh), 2925 (m), 2860 (m), 2085 (vs), 2050 (vs), 1420 (m) cm^{-1}; IR (Nujol) 1264 (m), 1224 (s), 1095 (w), 990 (s), 920 (s), 880 (s), 842–822 (s), 755 (m), 738 (m), 582 (m), 551 (s), 540 (sh) cm^{-1}; Λ_m (CH_3NO_2) 86.5 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{11}H_{15}F_6FeO_5PS$: C, 28.69; H, 3.29. Found: C, 29.09; H, 3.31.

In a strictly analogous manner, reaction of (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OCH$_3$] with (C_2H_5)$_3$OPF$_6$ gave [(η^5-C_5H_5)Fe(CO)$_2$[S(O)(OC$_2$H$_5$)OCH$_3$]]PF$_6$ as yellow, air-stable crystals in 59% yield: ^1H NMR ((CD$_3$)$_2$CO) τ 4.15 (s, C_5H_5), 5.2–5.7 (m, CH$_2$), 5.97 (s, OCH$_3$), 8.57 (t, J = 7 Hz, CCH$_3$); IR (hexachlorobutadiene) 3095 (m), 2085 (vs), 2050 (vs) cm^{-1}; IR (Nujol) 1260 (w), 1228 (s), 1152 (w), 1102 (w), 988 (m), 920 (s), 880 (s), 840–820 (s), 770 (m), 602 (sh), 588 (s) cm^{-1}; Λ_m (CH_3NO_2) 89.6 Ω^{-1} cm^2 mol^{-1}.

Reactions of (η^5-C_5H_5)Fe(CO)(L)[S(O)$_2$CH$_3$] (L = CO, P(C_6H_5)$_3$) with (C_2H_5)$_3$OPF$_6$. Reaction between equimolar amounts of (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$CH$_3$] and (C_2H_5)$_3$OPF$_6$ was conducted analogously to the foregoing syntheses to afford [(η^5-C_5H_5)Fe(CO)$_2$[S(O)(OC$_2$H$_5$)CH$_3$]]PF$_6$ as a yellow solid in 75% yield: ^1H NMR ((CD$_3$)$_2$CO) τ 4.33 (br, C_5H_5), 5.66 (br, CH$_2$), 6.36 (br, SCH$_3$), 8.56 (br, CCH$_3$); IR (KBr) (prominent absorptions) 2077 (vs), 2040 (vs), 1190 (s), 980 (s), 880 (s) cm^{-1}; Λ_m (CH_3NO_2) 85 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{10}H_{13}F_6FeO_4PS$: C, 27.93; H, 3.05. Found: C, 27.86; H, 3.00.

In a similar manner, [(η^5-C_5H_5)Fe(CO)[P(C_6H_5)$_3$][S(O)(OC$_2$H$_5$)CH$_3$]]PF$_6$ was prepared in 70% yield from (η^5-C_5H_5)Fe(CO)[P(C_6H_5)$_3$][S(O)$_2$CH$_3$] and (C_2H_5)$_3$OPF$_6$: ^1H NMR ((CD$_3$)$_2$CO) τ 2.38 (m, 3C$_6$H$_5$), 4.76 (s, C_5H_5), 6.00 (br, CH$_2$), 6.55 (br, SCH$_3$), 8.92 (br, CCH$_3$); IR (KBr) (prominent absorptions) 1990 (vs), 1435 (s), 1188 (s), 1100 (s), 1008 (m), 968 (s), 888 (s), 850 (s), 842 (s) cm^{-1}; Λ_m (CH_3NO_2) 80 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{27}H_{28}F_6FeO_3P_2S$: C, 48.81; H, 4.25. Found: C, 48.98; H, 4.45.

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Registry No. (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OCH$_3$], 75111-95-4; (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OC$_2$H$_5$], 75111-96-5; (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OC$_3$H$_7$-1], 75111-97-6; (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OC$_3$H$_7$-2], 75111-98-7; (+)$_{589}$-(η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OC$_8$H$_{17}$-2], 75172-30-4; Mn(CO)$_3$(bpy)[S(O)$_2$OCH$_3$], 75111-99-8; (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OH], 69526-44-9; (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$OD], 75112-00-4; Na[(η^5-C_5H_5)Fe(CO)$_2$SO$_3$], 69363-96-8; (η^5-C_5H_5)Fe(CO)$_2$[S(O)$_2$N(CH$_3$)$_2$], 75112-01-5; [(η^5-C_5H_5)Fe(CO)$_2$[S(O)(OC$_2$H$_5$)OCH$_3$]]PF$_6$, 75112-03-7; [(η^5-C_5H_5)Fe(CO)$_2$[S(O)(OC$_2$H$_5$)$_2$]]PF$_6$, 75112-30-0; [(η^5-C_5H_5)Fe(CO)$_2$[S(O)(OC$_2$H$_5$)CH$_3$]]PF$_6$, 75112-32-2; [(η^5-C_5H_5)Fe(CO)[P(C_6H_5)$_3$][S(O)(OC$_2$H$_5$)CH$_3$]]PF$_6$, 75112-34-4; [(η^5-C_5H_5)Fe(CO)$_2$SO$_2$]$_2$, 58657-88-8; (CH$_3$)$_2$NH$_2$[(η^5-C_5H_5)Fe(CO)$_2$SO$_3$], 75112-35-5; (C_2H_5)$_2$NH$_2$[(η^5-C_5H_5)Fe(CO)$_2$SO$_3$], 75112-36-6; (η^5-C_5H_5)Fe(CO)[P(C_6H_5)$_3$][S(O)$_2$CH$_3$], 31811-87-7; [(η^5-C_5H_5)Fe(CO)$_2$]$_2$, 12154-95-9; K[(η^5-C_5H_5)Fe(CO)$_2$SO$_2$], 65669-26-3; (η^5-C_5H_5)Fe(CO)$_2$I, 12078-28-3; Mn(CO)$_3$(bpy)Cl, 14881-43-7; (η^5-C_5H_5)Fe(CO)$_2$Cl, 12107-04-9; 1-C_3H_7OH, 71-23-8; 2-C_3H_7OH, 67-63-0; C_2H_5OH, 64-17-5; (CH$_3$)$_3$OPF$_6$, 12116-05-1; CH_3OH, 67-56-1; (+)$_{589}$-2-$C_8H_{17}OH$, 6169-06-8; (C_2H_5)$_3$OPF$_6$, 17950-40-2; [(η^5-C_5H_5)Fe(CO)$_2$H$_2$O]BF$_4$, 62077-08-1; ClS(O)$_2$N(CH$_3$)$_2$, 13360-57-1; CH_3OSO_2F, 421-20-5.

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Cationic Cyclopentadienylchromium–Nitrosyl Complexes: Synthesis and Reactions[1]

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Reaction of η^5-C_5H_5Cr(NO)$_2$Cl with AgPF$_6$ in CH$_3$CN or of η^5-C_5H_5Cr(NO)$_2$CH$_3$ with HPF$_6$·(C_2H_5)$_2$O, also in CH$_3$CN, affords [η^5-C_5H_5Cr(NO)$_2$(CH$_3$CN)]PF$_6$ in high yield. However, when the latter reaction takes place in ether, the organochromium product is η^5-C_5H_5Cr(NO)$_2$FPF$_5$. The complexes [η^5-C_5H_5Cr(NO)$_2$(CH$_3$CN)]PF$_6$ and η^5-C_5H_5Cr(NO)$_2$FPF$_5$ yield a series of cationic cyclopentadienylchromium dinitrosyls, [η^5-C_5H_5Cr(NO)$_2$L]PF$_6$, when treated with L (L = an aromatic amine, pyridine, and organic cyanide or isocyanide) in CH$_3$NO$_2$ at 25 °C. Treatment of [η^5-C_5H_5Cr(NO)$_2$(CH$_3$CN)]PF$_6$ with 2,2′-bipyridine and with 1,10-phenanthroline (L–L) in CH$_3$NO$_2$ at reflux affords 17-electron complexes, [η^5-C_5H_5Cr(NO)(L–L)]PF$_6$. The isocyanide complex [η^5-C_5H_5Cr(NO)$_2$(CH$_3$NC)]PF$_6$ reacts with NaOR (R = CH$_3$, C_2H_5) to give the relatively unstable η^5-C_5H_5Cr(NO)$_2$[C(OR)NCH$_3$] complexes, which on protonation with HPF$_6$·(C_2H_5)$_2$O yield the corresponding carbene complexes {η^5-C_5H_5Cr(NO)$_2$[C(OR)NHCH$_3$]}PF$_6$. In a similar reaction, [η^5-C_5H_5Cr(NO)$_2$(CH$_3$NC)]PF$_6$ was converted by action of KOH to the carbamoyl complex η^5-C_5H_5Cr(NO)$_2$[C(O)NHCH$_3$], which on treatment with HPF$_6$·(C_3H_5)$_2$O furnished known [η^5-C_5H_5Cr(NO)$_2$(CO)]PF$_6$. The characterization of all new complexes is described.

Introduction

The paucity of well-characterized cationic complexes [η^5-C_5H_5Cr(NO)$_2$L]X (L = neutral monodentate ligand, X = uninegative ion)[2,3] presents a striking contrast with the abundance of their isoelectronic analogues, [η^5-C_5H_5Fe(CO)$_2$L]X.[4,5] This is further surprising in view of the existence of corresponding molybdenum and tungsten complexes, [η^5-C_5H_5M(NO)$_2$L]X (M = Mo, W), for a variety of ligands L.[6] To fill this void we set out to develop general synthetic routes to [η^5-C_5H_5Cr(NO)$_2$L]X. Reported here are our results

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