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Preliminary communication

ALKYLSULFITO, BISULFITO AND SULFITO COMPLEXES OF η^5-CYCLOPENTADIENYLDICARBONYLIRON(II)

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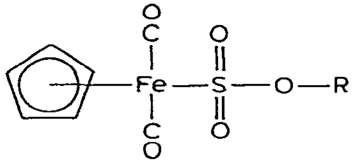
Summary

Alkylsulfito complexes η^5-$C_5H_5Fe(CO)_2S(O)_2OR$ (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7) have been prepared by reaction of $[\eta^5$-$C_5H_5Fe(CO)_2H_2O]BF_4$ with $Na[S(O)_2OR]$ (R = CH_3, C_2H_5) and the respective alcohol as solvent. These products may be interconverted by the use of the appropriate alcohol at reflux; such exchange occurs also at 25°C in the presence of HBF_4. Reaction of η^5-$C_5H_5Fe(CO)_2S(O)_2OCH_3$ with $(+)_{589}$-2-$C_8H_{17}OH$ and HBF_4 followed by treatment of the optically active product $(+)_{589}$-η^5-$C_5H_5Fe(CO)_2S(O)_2OC_8H_{17}$ with CH_3OH and HBF_4 regenerates $(+)_{589}$-2-$C_8H_{17}OH$ with unchanged specific rotation. Hydrolysis of η^5-$C_5H_5Fe(CO)_2S(O)_2OR$ affords η^5-$C_5H_5Fe(CO)_2S(O)_2OH$, which is a strong acid.

As part of an investigation of the comparative chemistry of organometallic complexes containing sulfur-oxygen ligands we have synthesized and examined some reactions of alkylsulfito compounds of the type η^5-$C_5H_5Fe(CO)_2S(O)_2OR$ (I). Previously reported complexes of η^5-$C_5H_5Fe(CO)_2$ with sulfur-oxygen ligands include η^5-$C_5H_5Fe(CO)_2S(O)_2R$ [1], η^5-$C_5H_5Fe(CO)_2OS(O)R$ [2], η^5-$C_5H_5Fe(CO)_2$-$S(O)OR$ [3], η^5-$C_5H_5Fe(CO)_2OS(O)_2R$ [4], $[\eta^5$-$C_5H_5Fe(CO)_2]_2S(O)_2$ [5], and $[\eta^5$-$C_5H_5Fe(CO)_2S(O)_2]_2$ [6]. Interest attaches to alkylsulfito complexes in that the $S(O)_2OR$ ligand may be viewed as the product of reaction of coordinated SO_2 with OR^-; this presumed behavior finds a strong analogy in the formation of carboalkoxy ligands, C(O)OR, by nucleophilic attack of OR^- on ligated CO, the reaction being reversed upon treatment of the MC(O)OR with acid [7]. Thus, neutral $MS(O)_2OR$ complexes represent possible precursors of cationic metal-SO_2 species, which may exhibit interesting reactions with nucleophiles.

Although examples of alkylsulfito complexes are known for nickel [8], palladium [9—11], platinum [10—12], cobalt [8], and ruthenium [13,14], 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-diphenylphosphinoethyl)amine) by X-ray crystallography [8].

We now find that reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2H_2O]BF_4$ [15] with a slight excess of $Na[S(O)_2OR]$ [16] in ROH ($R = CH_3$, C_2H_5) for 12 h at 25°C affords $\eta^5\text{-}C_5H_5Fe(CO)_2S(O)_2OR$ (Ia, Ib). Yields of ca. 50% have been realized after removal of the solvent, extraction of the residue with $CHCl_3$, and chromatography of the extract on Florisil with 5/1 $CHCl_3$/acetone.



(Ia-If)

(Ia, R = CH_3;
Ib, R = C_2H_5;
Ic, R = 1-C_3H_7;
Id, R = 2-C_3H_7;
Ie, R = $(+)_{589}$-2-C_8H_{17}
If, R = H)

Since only the methyl and the ethyl salts $Na[S(O)_2OR]$ are sufficiently stable to isolation [16], the aforementioned procedure was slightly modified for the synthesis of other alkylsulfito complexes I.

$$[\eta^5\text{-}C_5H_5Fe(CO)_2H_2O]BF_4 + Na[S(O)_2OR] + R'OH\ (\text{excess}) \xrightarrow{25^\circ C} \eta^5\text{-}C_5H_5Fe(CO)_2S(O)_2OR' + NaBF_4 + ROH \quad (1)$$

In this manner the n-propyl and the isopropyl complexes, Ic and Id, were prepared using the respective alcohols and $Na[S(O)_2OC_2H_5]$. These reactions undoubtedly proceed via a facile equilibrium (eq. 2) as evidenced by the interconversion of $Na[S(O)_2OCH_3]$ and $Na[S(O)_2OC_2H_5]$ through dissolution and storage in excess ethyl and methyl alcohol, respectively, at 25°C.

$$Na[S(O)_2OR] + R'OH \rightleftharpoons Na[S(O)_2OR'] + ROH \quad (2)$$

Complexes Ia—Id* are isolated as air-stable, yellow crystalline solids. In the mass spectra (70 eV, 75—80°C) of Ia and Ib the parent ion, P^+, is either absent or weak; however, peaks corresponding to $(P - CO)^+$ and $(P - 2CO)^+$ are readily discernible. The ^1H NMR spectra of Ia—Id, presented in Table 1, display no unusual features and are entirely consistent with the assigned structures. The alkylsulfite ligands exhibit characteristic IR absorptions for $\nu(SO_2)$ and $\nu(SO)$ (also in Table 1), which compare favorably with those reported for other $MS(O)_2OR$ complexes [8—14].

Keeping a solution of Ia in ethyl alcohol at reflux for 24 h leads to the isolation of Ib in 65% yield; similarly, Ia results (53% yield) from Ib and excess boiling methyl alcohol. These and related conversions occur also, in higher yields (55—85%), at ambient temperatures in the presence of small amounts of HBF_4 (metal complex/HBF_4 molar ratio ca. 30/1).

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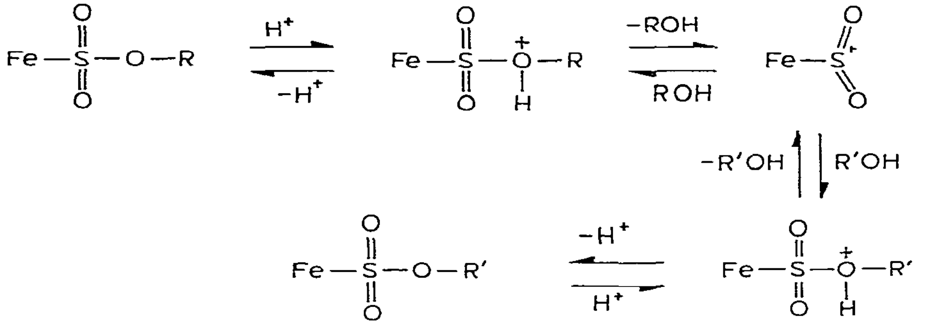
*The composition of Ib is supported by elemental analysis: C, 37.17; H, 3.46. $C_9H_{10}FeO_5S$ calcd.: C, 37.87; H, 3.52%.

$$\eta^5\text{-}C_5H_5Fe(CO)_2S(O)_2OR + R'OH\ (\text{excess}) \xrightarrow[25^\circ C]{HBF_4} \eta^5\text{-}C_5H_5Fe(CO)_2S(O)_2OR' + ROH \qquad (3)$$

To shed light on the mechanism of this acid-promoted exchange, a reaction was carried out between Ia and a five-fold excess of optically active 2-octanol ($[\alpha]^{22.5}_{589}$ +8.75°) in the presence of HBF_4. The isolated optically active iron complex Ie ($[\alpha]^{22.5}_{589}$ +23.8°; other properties in Table 1) was then converted by the action of methyl alcohol and HBF_4 back to Ia and 2-octanol, which exhibited essentially unchanged rotation ($[\alpha]^{21}_{589}$ +8.60°). This result indicates that the integrity of the O—C* linkage in the 2-octoxy group is preserved in both the reacting alcohol and the iron alkylsulfito complex Ie. A reasonable mechanism which accords with these results is depicted in Scheme 1.

Scheme 1



$Fe \equiv \eta^5\text{-}C_5H_5Fe(CO)_2$, $R = CH_3$, $R' = (+)_{589}\text{-}2\text{-}C_8H_{17}$

A feature of considerable interest in this mechanism is the involvement of a cationic iron—SO_2 complex; if such a spcies is indeed generated, it must exhibit high reactivity toward alcohol nucleophiles.

Hydrolysis of Ia or Ib for 16 h at 25°C, followed by removal of the water, extraction of the residue into CH_3CN, and evaporation of the extract to dryness, affords (95% yield) a yellow powder (If, spectroscopic data in Table 1; the deuterium analogue was obtained similarly in D_2O). This reaction is reversible, and Ia or Ib may be regenerated by treatment of If with the appropriate alcohol for 24 h at room temperature. Complex If represents the first well characterized organometallic analogue of organic sulfonic acids*, $RS(O)_2OH$, and, consistent with this analogy, it behaves as a strong acid when titrated with NaOH in aqueous solution, yielding an equivalent weight of 260 ($C_7H_6FeO_5S$ calcd.: 258).

Removal of H_2O from an aqueous solution of If neutralized with NaOH affords a yellow, air-stable solid, $Na[\eta^5\text{-}C_5H_5Fe(CO)_2SO_3]$ (II). Compound II, a 1/1 electrolyte in methyl alcohol (Λ_M 70 ohm^{-1} cm^2 mol^{-1} for 10^{-3} *M* solution) [17], shows IR SO stretching absorptions (Table 1) consistent with the presence of a sulfur-bonded $SO_3{}^{2-}$ ligand (C_{3v} local symmetry) [18]. Recently

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*The formulation of $\eta^5\text{-}C_5H_5Fe(CO)_2FeSO_3H\cdot H_2O$ solely on the basis of elemental analysis and an IR spectrum is to be regarded as tentative [22].

TABLE 1

MELTING POINTS AND SPECTROSCOPIC DATA FOR NEW COMPLEXES

Complex	M.p. (°C)	IR (cm^{-1})[a]				^{1}H NMR (τ,ppm)[b]
		ν(CO)	$\nu(SO_2)$	ν(SO)	Other	
Ia	156	2064, 2007	1214, 1095, 1061	971	ν(SOC) 636	4.79s(C_5H_5), 6.41s(CH_3)
Ib	96	2062, 2000	1214, 1088, 1020	971		4.60s(C_5H_5), 5.99q(J 7 Hz, CH_2), 8.77t(J 7 Hz, CH_3)
Ic	94–96	2068, 2014	1211, 1087	973		4.68s(C_5H_5), 6.14t(J 6 Hz, SO_3CH_2), 8.14m(J 6 Hz, J' 6 Hz, CH_2CH_3), 9.08t(J' 6 Hz, CH_3)
Id	164–165	2070, 2010	1211, 1112, 1084, 1065	918	ν(SOC) 640	4.83s(C_5H_5), 5.10sp[c](J 6.1 Hz, CH), 8.25d(J 6.1 Hz, $2CH_3$)
Ie	118	2065, 2010	1212, 1088	996	ν(SOC) 634	4.79s(C_5H_5), 5.27br(CH), 8.70–9.14m ($5CH_2$, $2CH_3$)
If	104	2062, 2018	1184, 1038	811	ν(OH) 2940, ν(OD) 2230	–1.16s(OH), 4.70s(C_5H_5)[d]
II		2050, 1994	$\nu(SO_3)$ 1129, 1107, 1084, 1072, 984			4.95s(C_5H_5)[e]

[a] KBr pellet. All absorptions are strong. [b] $CDCl_3$ solution except as noted. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; sp, septuplet; m, multiplet or complex pattern; br, broad. [c] Two component peaks of the presumed septuplet appear to overlap the C_5H_5 resonance. [d] $(CD_3)_2SO$ solution. [e] $D_2O/(CD_3)_2CO$ solution.

Jablonski prepared the complex $K[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]$ from $K[\eta^5\text{-}C_5H_5Fe(CO)_2]$ and SO_2 [3]. Complex II may be considered as the adduct of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ and SO_3, a much stronger acid than SO_2. Consistent with this analogy, II, unlike $K[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]$, was found not to react with CH_3I, even on heating at reflux in acetone/ethyl alcohol for 10 h.

Because of the structural analogy between Ia—Ie and esters of organic sulfonic acids, it was of interest to explore some comparative chemistry of the two classes of compounds. We find that dissolution of Ia or Ib in excess R_2NH ($R = CH_3$ or C_2H_5) at 25°C produces a yellow precipitate within 20 min. This solid was characterized by IR and ^1H NMR spectroscopy as $R_2NH_2[\eta^5\text{-}C_5H_5Fe(CO)_2SO_3]$, the reaction being as in eq. 4. It is noteworthy that a reaction analogous to that

$$\eta^5\text{-}C_5H_5Fe(CO)_2S(O)_2OR + 2\ R_2NH\ (\text{excess}) \xrightarrow{25^\circ C} R_2NH_2[\eta^5\text{-}C_5H_5Fe(CO)_2SO_3] + R_3N\ (?) \qquad (4)$$

between MC(O)OR and R_2NH to afford $MC(O)NR_2$ [7], i.e. nucleophilic displacement of OR from $FeS(O)_2OR$ by R_2NH, did not take place. Esters of the sulfonic acids are known to alkylate the amines [19]; in fact, a few examples are known [20,21] in which 2 moles of the amine are involved in an anomalous alkylation similar to that observed in this study.

Studies continue on reactions of coordinated alkylsulfite ligand and on a possible role of the metal in such processes.

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