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Reaction of $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-[Et_3NH]^+$ (E = S, Se, Te) Salts with Benzenesulfinyl Chloride and Carbon Disulfide

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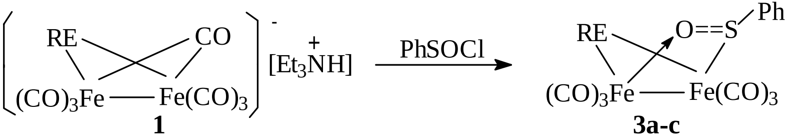
Abstract: The salts of $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-[Et_3NH]^+$(E = S, Se, Te) react with benzenesulfinyl chloride to give the μ-sulfinyl group bridged complexes $(\mu\text{-RE})(\mu\text{-PhS=O})Fe_2(CO)_6$ in good yields. Whereas the salts $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-[Et_3NH]^+$ (R = t-Bu, Ph) react with carbon disulfide to yield the dithioformato-bridged anionic salts $[(\mu\text{-RS})(\mu\text{-S=C-S})Fe_2(CO)_6]^-[Et_3NH]^+$, which react *in situ* at the exo-sulfur atom of the dithioformato-group with diverse α, β-unsaturated carbonyl compounds to give Michael addition products in moderate yields.

Keywords: Cluster, carbonyl iron, sulfur, selenium, synthesis.

Over the past decade, the chemical reactivities of reactive anion salts of the $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-[Et_3NH]^+$ (E = S, Se, Te) have been studied extensively and their reactions have been used to synthesize versatile S, Se, Te-containing cluster complexes [1-3]. From their reaction with carbon disulfide, the dithioformato-bridged anionic salts $[(\mu\text{-RS})(\mu\text{-S=C-S})Fe_2(CO)_6]^-[Et_3NH]^+$ (E = S, Se) were prepared and reacted with various organic and organometallic electrophiles, in which the electrophilic group was attached the exo sulfur atom of the dithioformato-bridged group [4-6]. As a continuation of this project, we further investigated the reactivity of this kind of salts toward organic α, β-unsaturated carbonyl compounds. Here we report our preliminary findings of Michael-type addition reactions.

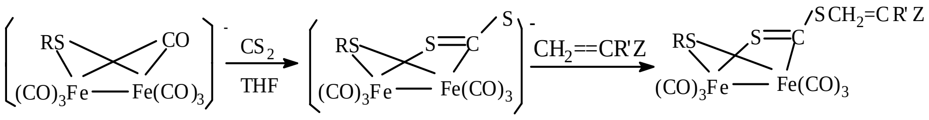
The anion salts $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-[Et_3NH]^+$ (E = S, Se, Te) **1a-c**, which were prepared by reaction of $Fe_3(CO)_{12}$ /PhSH, PhSeH/Et_3N for **1a**, **1**b, or $Fe_3(CO)_{12}$ /PhTeMgBr for **1c** in THF, react smoothly *in situ* with benzenesulfinyl chloride in about two hours to give the expected μ-sulfinyl group bridged complexes $(\mu\text{-RE})(\mu\text{-PhS=O})Fe_2(CO)_6$ **3a-c** as slightly air-sensitive red solids in good yields (40- 67%). This may be the first reported example of sulfinyl group bridge coordinated on the two iron atoms. Their structures were similar to our previously reported μ-sulfonyl group bridged complexes $(\mu\text{-RS})(\mu\text{-4-MePhSO_2})Fe_2(CO)_6$ [2].



1 **3a-c**

RE= PhS(67%), PhSe(40%), PhTe(46%)

The cherry red dithioformato-bridged anionic salts [(μ-RS)(μ-S=C-S)Fe2(CO)6]— [Et3NH]+ 4 (R = t- Bu, Ph) were easily prepared in reaction of carbon disulfide with the red-brown THF solution of (μ-RS)(μ-CO)Fe2(CO)6]—[Et3NH]+ 1(R = t-Bu, Ph) at room temperature in about half an hour. Then the α, β-unsaturated substances 5 was added in situ and the mixture was stirred at room temperature for additional 24 hours. After work up the Michael additional products **6a-h** were obtained as red oils or low melting point solids in 21- 45% yields. They were characterized with elemental analysis, ^{1}H NMR and IR spectroscopy. The formation of the clusters **6a-h** were apparently derived from the addition of the exo-sulfur atom of dithioformato-bridged anion **4** to the carbon-carbon double bond of the α, β-unsaturated substances. The terminally unsubstituted substances such as methyl vinyl ketone, acrylonitrile, methyl acrylate, ethyl acrylate and methyl methacrylate all gave moderate yields of adducts, accompanied with the butterfly clusters of (μ-RS)$_2$Fe$_2$(CO)$_6$ (R = t-Bu, Ph) as the byproducts. On the other hand, the terminal substituted α, β-unsaturated substance mesityl oxide did not yield the Michael adduct. From the reaction mixture only the butterfly clusters of (μ-RS)$_2$Fe$_2$(CO)$_6$ can be separated. Comparing with the previously reported fact that both monoanions (μ-RS)(μ-S$^-$)Fe$_2$(CO)$_6$$^{7-9}$ and dianions (μ-S$^-$)$_2$Fe$_2$(CO)$_6$^{10} underwent addition to α, β-unsaturated substances and gave Michael adducts in very high yields, the exo-sulfur anion of dithioformato-bridged anionic salts [(μ-RS)(μ-S=C-S)Fe$_2$(CO)$_6$]$^-$[Et$_3$NH]$^+$ **4** gave lower yields of adducts. This difference represents that the exo-sufur anions **4** are much more unreactive toward the unsaturated substance. The investigation of the reactivity of selenato- and Telluro-bridged anions [(μ-RE)(μ-S=C-S)Fe$_2$(CO)$_6$]$^-$ [Et$_3$NH]$^+$ (E = Se, Te) in these Michael addition type reactions is now under way.



1a-b **4a-b** **6a-b**

R= *t*-Bu, Ph; R'= H, Me; Z= COMe, CN, CO$_2$Me,CO$_2$Et

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