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Preliminary communication

THE USE OF PHOSPHORUS AND BORON SULFIDES AS SULFURIZING AGENTS: A GENERAL ROUTE TO DITHIOCARBOXYLATE COMPLEXES

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Summary

The sulfides P_4S_{10} and B_2S_3 react with the acyl complexes $(C_5H_5)Fe(CO)_2$-COR and $(CO)_5MCOR$ (M = Mn, Re; R = CH_3, C_6H_5) to yield dithiocarboxylate complexes $(C_5H_5)Fe(CO)SSCR$ and $(CO)_4MSSCR$ in which the dithio ligand is bidentate. With the iron complexes reactions lead also to $(C_5H_5)Fe(CO)_2SC(S)R$, and an X-ray structural study of the latter (X = CH_3) has confirmed that the dithioacetate ligand is S-monodentate.

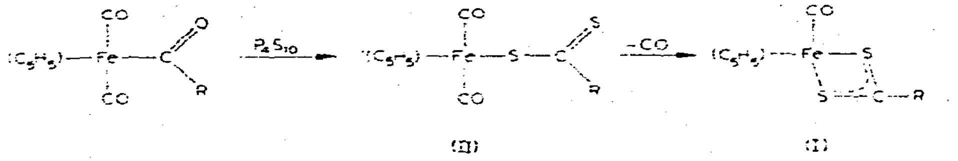
As part of our studies of thiocarbonyl complexes of transition metals [1] we have investigated sulfur—oxygen exchange in carbonyl complexes using inorganic sulfides such as P_4S_{10}, B_2S_3 and SiS_2. These sulfurizing agents have been used for converting a carbonyl group into a thiocarbonyl group and are important for the synthesis of organic thiono compounds [2, 3] and it seemed likely that P_4S_{10} might act similarly on transition metal acyl derivatives. The reactions, which unexpectedly provide dithiocarboxylate complexes, are described below.

A mixture of $(C_5H_5)Fe(CO)_2COR$ (R = CH_3, C_6H_5) and P_4S_{10} in a 1/2 molar ratio in dry ethyl ether was stirred under nitrogen for four days. Chromatography in hexane on alumina gave $(C_5H_5)Fe(CO)SSCR$ (I) (10%) as the first fraction. (R = C_6H_5, green crystals, m.p. 79°C. Anal.: Found: C, 51.66; H, 3.45; O, 6.31; S, 19.15; Fe, 18.04. $C_{13}H_{10}FeOS_2$ calcd.: C, 51.67; H, 3.33; O, 5.29; S, 21.22; Fe, 18.48%. Infrared: $\nu(CO)$ (hexane) 1972s cm^{-1}; $\nu_{as}(CS_2)$ (nujol mull) 1270m cm^{-1}. ^1H NMR ($CDCl_3$): τ (ppm) 5.08 (C_5H_5), 1.90—2.80 (C_6H_5). R = CH_3, red oil; infrared: $\nu(CO)$ (hexane) 1970s cm^{-1}, $\nu_{as}(CS_2)$ (film) 1265m cm^{-1}; ^1H NMR ($CDCl_3$): τ (ppm) 5.28 (C_5H_5), 7.58 (CH_3)).

The second fraction, eluted with a mixture of CH_2Cl_2 (40%)/hexane (60%), gave the main product, $(C_5H_5)Fe(CO)_2SC(S)R$ (II) (50%). (R = C_6H_5, red crystals, m.p. 110—112°C. Anal.: Found: C, 50.93; H, 3.05; O, 10.12; S, 19.15; Fe, 17.25.

$C_{14}H_{10}FeO_2S_2$ calcd.: C, 50.92; H, 3.03; O, 9.69; S, 19.42; Fe, 16.91%. Mol. wt. found 339 (osmometrically in benzene); calcd. 330. Infrared: ν(CO) (hexane) 2039s, 2000s cm^{-1}; ^{1}H NMR ($CDCl_3$): τ (ppm) 4.83 (C_5H_5), 1.75—2.75 (C_6H_5). R = CH_3, red crystals, m.p. 98—100°C; infrared: ν(CO) (hexane) 2040s, 1998s cm^{-1}; ν(CS) (nujol mull) 1160m cm^{-1}; ^{1}H NMR ($CDCl_3$): τ (ppm) 4.89 (C_5H_5), 6.90 (CH_3)).

A third fraction gave the unchanged starting material $(C_5H_5)Fe(CO)_2COR$ (10%). When the reaction was carried out at higher temperature (boiling hexane) the yield of I was increased (30%). This observation, together with the fact that II slowly decomposes in solution at room temperature to I, suggests the following reaction sequence:



The analytical data and the spectral results are consistent with the structures proposed for both I and II and the spectra are identical with those of the same derivatives obtained from $(C_5H_5)Fe(CO)_2Cl$ and HSSCR in refluxing acetone, a known method of preparing dithiocarboxylate [4] and dithiocarbamate derivatives of transition metals [5, 6].

A single crystal X-ray diffraction study on $(C_5H_5)Fe(CO)_2SC(S)CH_3$, obtained by crystallization from CH_2Cl_2/n-heptane at –25°C, has confirmed the *S*-bonded nature of the dithioligand. (Crystal data: monoclinic, space group $P2_1/c$, *a* 7.395, *b* 9.578, *c* 15.799 Å, β 101°.38, $Z = 4$. Intensities were collected with a Philips PW 1100 diffractometer using Mo-K_α (λ = 0.7107 Å) radiation; by comparison of *E* maps from direct methods and the Patterson map it was possible to identify positions of Fe and S atoms, while the rest of the molecule appeared in a subsequent Fourier map. Least squares refinement isotropically and then anisotropically has brought the agreement factor to 0.056). The molecular geometry is as shown in Fig. 1.

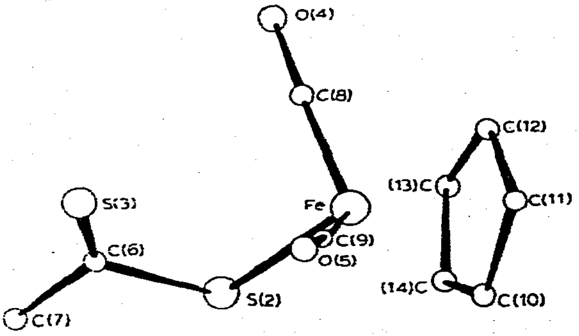
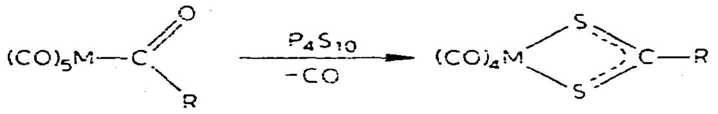


Fig. 1. Proposed molecular geometry of II.

The coordination around the iron atom can be described as pseudooctahedral with coordination to three monodentate ligands and a $C_5H_5^-$ tridentate ligand. Angles between the three monodentate ligands, C(8)—Fe—S(2) 95°.0(1), S(2)—Fe—C(9) 96°.8(1), C(9)—Fe—C(8) 93°.7(1), are consistent with this view. The mean Fe—CO and C—O bond lengths, 1.777(7) and 1.1348(8) Å, are in agreement with those in molecules containing a $(C_5H_5)Fe(CO)_2$ group [7]. The Fe—S bond distance (2.256(2) Å) is similar to an average value of 2.274(8) Å reported for Fe—SR bond distances in the thiol derivative $[CH_3SFe_2(CO)_6]_2S$ [8]. The S(2)—C(6) (1.702(6) Å) and the C(6)—S(3) (1.643(7) Å) bond lengths, which are between those of C—S single (1.819 Å in CH_3SH [9]) and double (1.61 Å in H_2CS [10]) bonds, indicate charge delocalization in the $S\overset{\cdots}{-}C\overset{\cdots}{-}S$ system, probably due to charge transfer from the lone pair on the S(2) atom to the lowest unfilled antibonding C=S orbital.

Acyl derivatives of Mn and Re have a similar tendency towards dithiocarboxylate formation.



(2)

$(M = Mn, Re; R = CH_3, C_6H_5)$

In a typical preparation 0.180 g (0.66 mmol) of $(CO)_5MnCOC_6H_5$ in 50 ml of dry ethyl ether were treated with 0.152 g (1.3 mmol) of P_4S_{10} at room temperature for 24 h with stirring; during this time the solution changed from orange-yellow to red-orange. Chromatography on Al_2O_3 in hexane gave a yellow band and removal of the solvent gave red crystals of $(CO)_4MnSSCC_6H_5$ (60%) (m.p. 144—145°C; infrared: ν(CO) (CCl_4) 2088m, 2012vs, 2002s, 1963s cm^{-1}, $\nu_{as}(CS_2)$ (nujol mull) 1256m cm^{-1}; mass spectrum: $(M - nCO)^+$ ($n = 0, 2, 3, 4$)). These spectra and those of the analogous rhenium complexes, are identical with those of authentic samples prepared by CS_2 insertion into M—R bonds (M = Mn, Re) [11, 12], and support a structure in which the dithiocarboxylate ligand is bidentate.

Preliminary results indicate that B_2S_3 reacts similarly, with $(C_5H_5)Fe(CO)_2$-COR and $(CO)_5MCOR$ under these conditions to form the corresponding dithiocarboxylate complexes[*]. Since both sulfides bring about the sulfur—oxygen conversion, though by different mechanisms [2, 3], it is reasonable to suppose that these sulfuration reactions proceed through a thioacyl intermediate L_nMCSR, which in turn undergoes ligand oxidation to give a dithiocarboxylate complex. Similar oxidative additions of sulfur have been observed in the P_4S_{10}, sulfur, or iodine oxidations of 1,1-dithiolate complexes, which yield trithioperoxy derivatives [13].

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[*] The reactions of the acyl derivatives with B_2S_3 are generally faster than that with P_4S_{10} and the yields of dithiocarboxylates are always higher (70%). The $(C_5H_5)Fe(CO)_2COR$ react with B_2S_3 to give both I and II derivatives as described for P_4S_{10}.

While we have not established the mechanism of the sulfurations here described, it is clear that both P_4S_{10} and B_2S_3 are useful for preparing dithiocarboxylate derivatives of transition metals.

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