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**Preliminary communication**

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# SYNTHESIS AND STRUCTURE OF DICARBONYLDI-$\eta$-CYCLOPENTADIENYLBIS($\mu$-THIOCARBONYL)DIIRON, A THIOCARBONYL ANALOG OF THE DICARBONYL-$\eta$-CYCLOPENTADIENYLIRON DIMER

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## Summary

Sodium hydride reduction of ($\eta$-$C_5H_5$)Fe$(CO)_2$(CS)$^+$ gives *cis*- and *trans*-[($\eta$-$C_5H_5$)Fe(CS)(CO)]$_2$. The *trans* isomer slowly converts to a *cis—trans* mixture in xylene solution. An X-ray structural study of the *cis* isomer shows the CS groups to be in the bridging positions, but otherwise, its structure is nearly identical to that of *cia*-[($\eta$-$C_5H_5$)Fe$(CO)_2$]$_2$. The *cis* isomer reacts with $CH_3OSO_2F$ to give the compound, ($\eta$-$C_5H_5$)$_2$Fe$_2$(CSCH$_3$)(CS)(CO)$_2^+$, with a methylated bridging thiocarbonyl group.

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The first reported complex containing a bridging thiocarbonyl ligand was that with an end-to-end bridging CS group, (DPE)$_2$(CO)W—C≡S—W(CO)$_5$, where DPE = $Ph_2PCH_2CH_2PPh_2$ [1]. Very recently Efraty, Arneri, and Huang [2] reported the preparation of [($\eta$-$C_5H_5$)Mn(CS)(NO)]$_2$, which was the first example of a compound with carbon-bridging thiocarbonyl ligands. While spectral results suggested the presence of *cis* and *trans* isomers, they could not be separated. Trace amounts of the *trans*-[($\eta$-$CH_3C_5H_4$)Mn(CS)(NO)]$_2$ analog, however, were isolated.

In this communication, we report the preparation and structure of [($\eta$-$C_5H_5$)Fe(CS)(CO)]$_2$, a thiocarbonyl analog of the well-known [($\eta$-$C_5H_5$)Fe$(CO)_2$]$_2$. A mixture of 27.1 mmol of [($\eta$-$C_5H_5$)Fe$(CO)_2$(CS)]$CF_3SO_3$ [3] and 31.3 mmol of NaH (mineral oil dispersion) in 200 ml of tetrahydrofuran was stirred under $N_2$ for 2 h. Chromatography of the product mixture in benzene on Florisil gave 2.1 g (40% yield) of a mixture of *cis*- and *trans*-[($\eta$-$C_5H_5$)Fe(CS)(CO)]$_2$. Chromatography of this mixture in 1:1 benzene/hexane on Florisil yielded *trans*-[($\eta$-$C_5H_5$)Fe(CS)(CO)]$_2$ (Infrared in $CS_2$: $\nu$(CO) at 1979vs and $\nu$(CS) at 1131s cm$^{-1}$. $^1$H NMR in $CS_2$: $\tau$ 5.32 ppm ($C_5H_5$)) in the initial fractions. Later fractions contained the predominant isomer, *cis*-[($\eta$-$C_5H_5$)Fe(CS)(CO)]$_2$ (Anal. Found: C, 43.47; H, 2.69; S, 15.87. $C_{14}H_{10}Fe_2O_2S_2$ calcd.: C, 43.55;

H, 2.61; S, 16.61%. Infrared in $CS_2$: $\nu$(CO) at 2011vs and 1982m and $\nu$(CS) at 1124s $cm^{-1}$. $^1H$ NMR in $CS_2$: $\tau$ 5.22 ppm ($C_5H_5$). $^{13}C$ NMR in $CDCl_3$ with ~0.1 *M* Cr(acac)$_3$: −287.6(CS), −208.9(CO), −93.8($C_5H_5$) ppm downfield relative to tetramethylsilane. Parent ion peaks are observed for both isomers in their mass spectra.) These spectral results are consistent with structures for both isomers in which the two CS groups are in bridging positions, and the CO groups are terminal. Thus, it appears that CS prefers a bridging over a terminal position as compared to CO.

Unlike $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ which undergoes facile bridge-terminal CO interchange and facile *cis—trans* isomerization [4], $[(\eta\text{-}C_5H_5)Fe(CS)(CO)]_2$ does not show bridging CS—terminal CO exchange. It does undergo relatively slow *cis—trans* isomerization. At 50°C in xylene, *trans*-$[(\eta\text{-}C_5H_5)Fe(CS)(CO)]_2$ isomerizes to an equilibrium mixture of the *cis* and *trans* isomers with a half-life of approximately 20 minutes; this isomerization cannot occur by the Adams—Cotton mechanism [4] proposed for the isomerization of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$.

Black crystals of *cis*-$[(\eta\text{-}C_5H_5)Fe(CS)(CO)]_2$ were obtained by fractional crystallization at −20°C of a $CS_2$ solution containing a mixture of *cis*- and *trans*-$[(\eta\text{-}C_5H_5)Fe(CS)(CO)]_2$. Diffractometer-measured cell constants, found by carefully centering on 12 strong reflections between 35 and 45°C in $\theta$ with monochromated Cu-$K_\alpha$ radiation (1.54178 Å), for the monoclinic unit cell are: *a* 14.409(5), *b* 12.560(4), *c* 8.177(3) Å and $\beta$ 90.3(2)°. A calculated density indicated four molecules of the complex in the unit cell. Systematic extinctions indicated the common space group $P2_1/c$. Data were collected on a fully-automated Hilger—Watts four-circle diffractometer using Zr-filtered Mo radiation (0.7107 Å). A total of 3080 reflections with $\theta < 25°$ were measured. After correction for background, Lorentz and polarization effects, 2187 reflections were judged observed. The structure was solved routinely using direct methods [5]. At this stage 187 reflections which were judged to be subject to systematic errors were eliminated from the data set. Full-matrix, least-squares refinement on 2000 reflections varying positional and anisotropic thermal parameters for all non-hydrogen atoms reduced the discrepency index, $R_1$, to 0.077 for the observed reflections.

A computer-generated drawing of the molecule is shown in Fig. 1. The Fe—C distances (in Å) to the bridging CS ligands are longer than those to the terminal CO groups: Fe(1)—C(1), 1.912(8); Fe(1)—C(2), 1.910(7); Fe(2)—C(1), 1.901(8); Fe(2)—C(2), 1.902(7); Fe(1)—C(3), 1.723(7); Fe(2)—C(4), 1.756(8). The distances from the Fe atoms to the centers of gravity of the $C_5H_5$ rings are Fe(1)—CG(1), 1.765(1) and Fe(2)—CG(2), 1.752(1). The Fe—C(ring) distances range from 2.100 to 2.148(9) Å, and the C—C distances in the rings range from 1.354 to 1.422(15). The C(3)—O(3) and C(4)—O(4) distances are 1.166(8) and 1.139(9), respectively. All of the above distances are the same, within experimental error, as those of *cis*-$[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ [6]. Only the Fe(1)—Fe(2) distance, 2.482(1), is significantly shorter than that (2.531(2)) in *cis*-$[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, perhaps suggesting stronger bonding of the two halves of the molecule in the thiocarbonyl derivative. The C(1)—S(1) and C(2)—S(2) distances are 1.592(8) and 1.587(7), significantly longer than the 1.51—1.54 Å distances [7] observed for terminal C≡S groups.

The Fe(1)—C—Fe(2) angles are 81.2(3)°. The following angles are given with

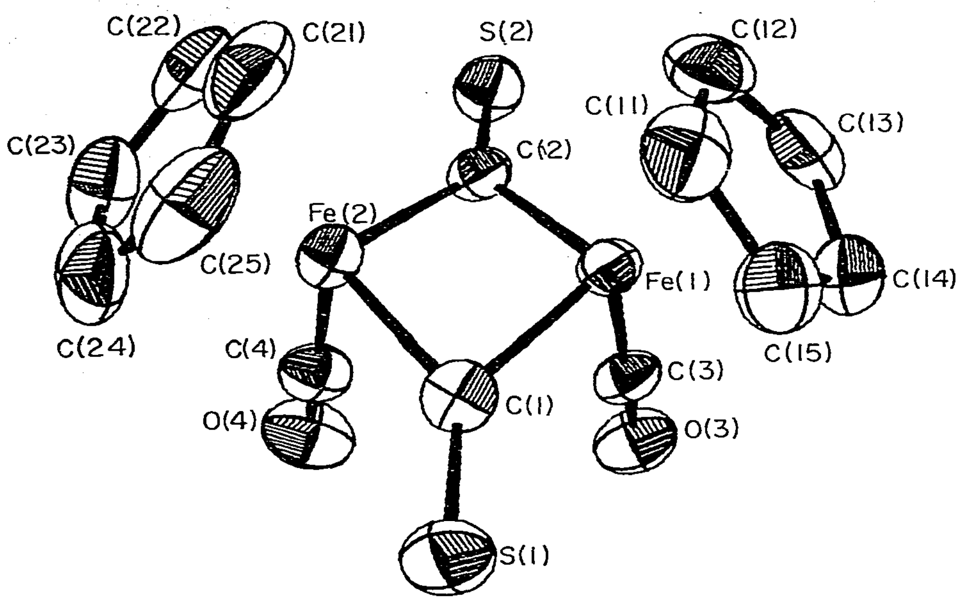

Fig. 1. Computer-generated drawing of the $[(\eta\text{-}C_5H_5)Fe(CS)(CO)]_2$ molecule.

the listed angle given first followed by the corresponding angle at the other Fe atom: C(1)—Fe(1)—C(2), 96.8, 97.5(3)°; Fe(1)—C(1)—S(1), 138.5, 140.3(5)°; Fe(1)—C(2)—S(2), 139.2, 139.5(5)°; C(1)—Fe(1)—C(3), 89.5, 88.2(3)°; C(2)—Fe(1)—C(3), 87.9, 89.8(3)°; C(3)—Fe(1)—CG(1), 124.9, 124.2(3)°; Fe(1)—C(3)—O(3), 178.5, 177.8(8)°; Fe(1)—Fe(2)—C(4), 98.8, 98.3(3)°. The C(3)—Fe(1)—Fe(2)—C(4) torsional angle is 2.1(3)°. The Fe(2)C(1)S(1)—Fe(2)C(2)S(2) dihedral angle is 163.4° with the folding along the Fe—Fe axis bending the CS groups away from the $C_5H_5$ rings. All of the features and angles are the same in *cis*-$[(C_5H_5)Fe(CO)_2]_2$. Thus, *cis*-$[(C_5H_5)Fe(CS)(CO)]_2$ is nearly an exact copy of its CO analog.

Like electron-rich terminal thiocarbonyl groups [8], *cis*-$[(\eta\text{-}C_5H_5)Fe(CS)(CO)]_2$ reacts with excess $CH_3OSO_2F$ at room temperature within 15 minutes to give the black, air-stable, methylated bridging CS compound, $(\eta\text{-}C_5H_5)_2Fe_2(CSCH_3)(CS)(CO)_2{}^+$, which was isolated as its $PF_6{}^-$ salt (74% yield. Anal. Found: C, 32.85; H, 2.43. $C_{15}H_{13}F_6Fe_2O_2PS_2$ calcd.: C, 33.00; H, 2.40%. Infrared in $CH_2Cl_2$: $\nu$(CO) at 2043s, 2016m and $\nu$(CS) at 1173s $cm^{-1}$. $^1H$ NMR in acetone-$d_6$: $\tau$ 6.20 ($CH_3$), 4.17 ($C_5H_5$), and 4.27 ppm ($C_5H_5$)). The $\nu$(CO) and $\nu$(CS) values of the terminal CO groups and the unmethylated bridging CS are, as expected, at higher frequencies than in the original *cis* dimer. The presence of two $C_5H_5$ proton resonances indicates that the C—S—$CH_3$ bond is bent. Other studies are underway which also indicate that bridging CS groups are substantially more reactive than bridging carbonyls [9].

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