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Preliminary communication

SYNTHESIS OF THIOCARBONYL-BRIDGED $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CS)$ AND CRYSTAL STRUCTURE OF AN *S*-ALKYLATED DERIVATIVE

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Summary

The reaction of $CpFe(CO)_2^-$ with $(PhO)_2C{=}S$, a new method of introducing a thiocarbonyl bridging ligand into a metal complex, yielded $Cp_2Fe_2(CO)_3(CS)$. The molecule exists as a *cis—trans* mixture in solution as evidenced by IR and NMR studies. On reaction with a variety of alkyl halides or other alkylating agents, stable *S*-alkyl derivatives are formed. The X-ray structure of $[Cp_2Fe_2(CO)_3(CS{-}Et)]BF_4$ is reported, and the nature of the bonding of the unusual $CS{-}Et^+$ bridging group is discussed.

We have recently described the bridging thiocarbonyl complexes $[CpFe(CS)(CO)]_2$ [1], $[CpRu(CS)(CO)]_2$ [2], and $Cp_2Ru_2(CO)_3(CS)$, where Cp = η-C_5H_5. The only other molecule reported to contain a bridging thiocarbonyl group is $[CpMn(CS)(NO)]_2$ [3]. All evidence to date suggests that the thiocarbonyl group prefers a bridging over a terminal position in all of these molecules [2]. In the present communication, we report a new method of introducing a bridging thiocarbonyl group into a transition metal complex and the first X-ray structure of a complex containing an alkylated bridging thiocarbonyl ligand.

The new bridging thiocarbonyl complex was prepared according to equation 1.

$$2\,CpFe(CO)_2^- + (PhO)_2CS \rightarrow Cp_2Fe_2(CO)_3CS + 2\,PhO^- + CO \qquad (1)$$

Addition of diphenyl thiocarbonate, $(PhO)_2CS$ (4.60 g, 20.0 mmol), in 20 ml of THF to a solution of $Na[CpFe(CO)_2]$, prepared by Na(Hg) reduction of $[CpFe(CO)_2]_2$ (7.43 g, 21.0 mmol) in 130 ml of THF, gave a rapid reaction with vigorous evolution of CO. Evaporation to dryness, extraction with 200 ml CS_2, and chromatography on a 25 mm × 1 m Florisil column in 5/1 CS_2/CH_2Cl_2 separated the $Cp_2Fe_2(CO)_3CS$ from the other major product, $[CpFe(CO)_2]_2$. Slow evaporation of a CS_2 solution of the compound gave black crystals in 40—43% yield. (Anal. Found: C, 45.32; H, 2.70; S, 8.66. $C_{14}H_{10}Fe_2O_3S$ calcd.: C, 45.45; H, 2.72; S, 8.13%. Its mass spectrum shows the parent ion and peaks corresponding to the successive loss of three CO ligands.)

Infrared spectra of $Cp_2Fe_2(CO)_3CS$ display a marked dependence on solvent polarity, as shown by the following ν(CO) absorptions (cm^{-1}): 2012vs, 1972vs, 1813s in hexane; 2006vs, 1969s, 1805m in CS_2; 2004vs, 1968m, 1805m in CH_2Cl_2; and 1999s, 1962w, 1803m in CH_3CN. This variation in the relative intensities of the two high frequency ν(CO) bands is also observed for $[CpFe(CO)_2]_2$ [4], $[CpRu(CO)_2]_2$ [5], $[CpRu(CO)(CS)]_2$ [2] and $Cp_2Ru_2(CO)_3CS$ [2], and it indicates the presence of *cis* and *trans* isomers of $Cp_2Fe_2(CO)_3CS$ in solution. Isomer interconversion is rapid, since the equilibrium isomer ratio in a particular solvent is established immediately on dissolving the compound. Only one ν(CS) band is observed for $Cp_2Fe_2(CO)_3CS$, at 1130m, 1124m and 1120m in CS_2, CH_2Cl_2 and CH_3CN, respectively. Its low frequency indicates that the CS ligand occupies a bridging position.

The ambient temperature ^1H NMR spectrum of $Cp_2Fe_2(CO)_3CS$ in C_6D_6 shows two Cp resonances at τ 5.74 and 5.68 ppm (2/1 ratio), indicating that the rate of *cis—trans* interconversion is much slower than that for $[CpFe(CO)_2]_2$ [6]. Therefore, in the iron series of carbonyl-thiocarbonyl analogs the rates of *cis—trans* isomerization decrease in the order $[CpFe(CO)_2]_2$ [6] > $Cp_2Fe_2(CO)_3CS$ > $[CpFe(CO)(CS)]_2$ [1]. The ^1H NMR spectrum of $Cp_2Fe_2(CO)_3CS$ in CD_3CN shows a single peak at τ 5.08 ppm; thus it appears that only one isomer, probably the *cis* [4], is present in very polar solvents.

Only one alkylated bridging thiocarbonyl complex, $Cp_2Fe_2(CO)_2(CS)(CS{-}Me)^+$, is cited in the literature [1]. We now find that the bridging thiocarbonyl group of $Cp_2Fe_2(CO)_3(CS)$ may be alkylated using a variety of reagents. For example, stirring $Cp_2Fe_2(CO)_3(CS)$ with $[Et_3O]BF_4$ in CH_2Cl_2 for 30 minutes at room temperature gave $[Cp_2Fe_2(CO)_3(CS{-}Et)]BF_4$ (80% yield) whose infrared spectrum in CH_2Cl_2 solvent shows ν(CO) absorptions at 2040s, 2007w, and 1854m. As expected, these values are all higher in frequency than for the starting complex. Although the reactions required approximately 24 h, $Cp_2Fe(CO)_3(CS)$ was also alkylated by MeI, EtI, n-PrI, n-BuI and $BrCH_2CO_2Et$ to yield the corresponding *S*-alkylated derivatives.

To establish the structure of one of these derivatives and to understand the nature of the $CS{-}R^+$ bridging ligand, an X-ray crystal structural determination of $[Cp_2Fe_2(CO)_3(CS{-}Et)]BF_4$ (Anal. Found: C, 39.39; H, 3.05. $C_{16}H_{15}BF_4Fe_2O_3S$ calcd.: C, 39.55; H, 3.11%) was undertaken. Suitable crystals were obtained by crystallization from 1/1 hexane/acetone at –20°C.

A rectangular shaped crystal of $[Cp_2Fe_2(CO)_3(CS{-}Et)]BF_4$ with dimensions of approximately 0.1 x 0.1 x 0.2 mm was selected for structure determination. The reduced cell and associated reduced cell scalars obtained from our automatic indexing program [7] indicated a monoclinic crystal system. This was confirmed by three axial ω-oscillation photographs.

Data were collected at 25°C using an automated four-circle diffractometer designed and built in the Ames Laboratory. Graphite monochromated Mo-K_α radiation (λ 0.70954 Å) was used for data collection. All data within a 2θ sphere of 40° were measured using an ω-scan technique, and of the reflections collected, 2132 were judged to have intensities above $3\sigma(I)$ and were used for the structure determination. No significant decomposition was noted throughout the period of data collection. Systematic absences indicated $P2_1/c$ symmetry. Diffractometer measured cell constants, found by carefully centering 12 reflections occurring between 20 and 30° in 2θ, are a 10.666(4), b 10.342(3), c 17.035(8) Å and β 100.4(3)°.

The structure was solved by use of the heavy atom technique. Some disorder was observed in the fluorine atom positions. To compensate for this, two partially occupied positions were used for each fluorine atom. The final conventional discrepancy factor, R, was 0.09 after inclusion of the hydrogen atoms and anisotropic refinement of all non-hydrogen atoms.

A computer-generated perspective drawing is shown in Fig. 1. Folding of the molecule along the Fe—Fe axis, which moves the bridging groups away from the Cp rings, is indicated by a Fe(1)C(3)O(3)—Fe(1)C(4)S dihedral angle of 160.8(6)°. With the exception of the distances and angles given below, these parameters are very similar to those in *cis*-$[\mathrm{CpFe(CO)_2}]_2$ [8] and *cis*-$[\mathrm{CpFe(CS)(CO)}]_2$ [1]. The Fe(1)—Fe(2) bond distance, 2.510(2) Å is between those found in *cis*-$[\mathrm{CpFe(CO)_2}]_2$ [7], 2.531(2), and *cis*-$[\mathrm{CpFe(CS)(CO)}]_2$ [1], 2.482(1) Å.

Figure 2 displays the bond distances and angles associated with the portion of the molecule which is significantly affected by the CS—Et$^+$ group. In square brackets are corresponding values for the closely related bridging thiocarbonyl complex *cis*-$[\mathrm{CpFe(CS)(CO)}]_2$ [1]. The addition of Et$^+$ to the bridging CS group has lengthened the C—S bond distance, 1.666(11) Å, from its value, 1.590(average) in *cis*-$[\mathrm{CpFe(CS)(CO)}]_2$ [1]. This presumably results from reduced S→C(4)

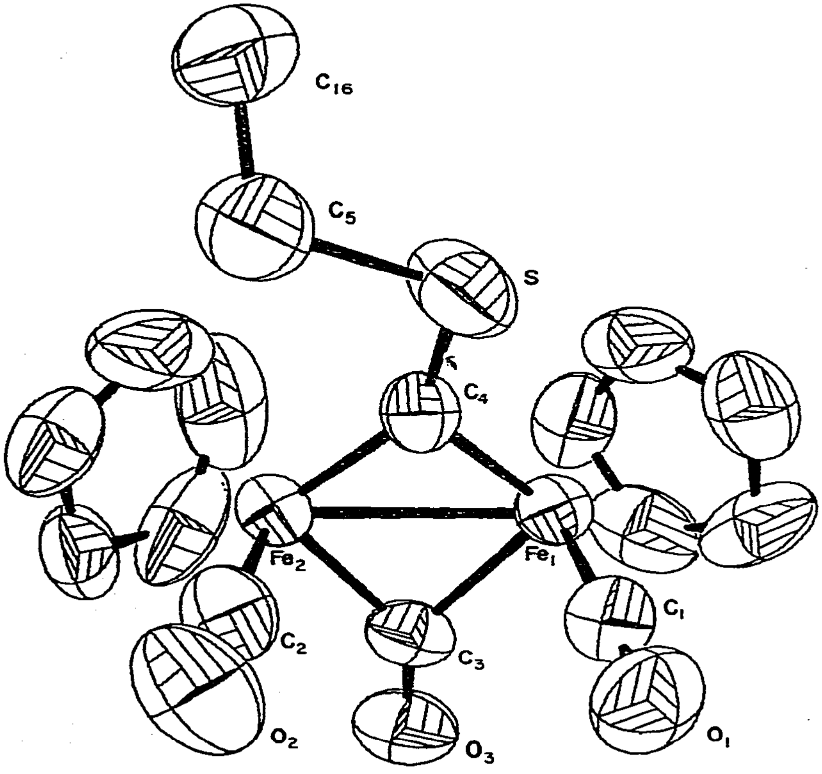

Fig. 1.

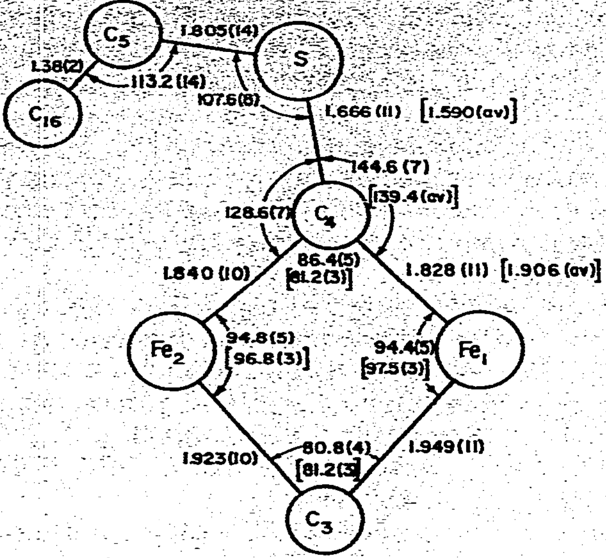

Fig. 2.

π-bonding, which promotes Fe→C(4) π-bonding giving the shortened Fe—C distances that are observed. This shortening produces an increase in the Fe(2)C(4)Fe(1) angle and decreases in the two CFeC angles.

Fischer et al. [9], have described bridging carbyne (C—R) ligands; if there were no π-bonding in the C(4)—S bond of the present molecule, the CS—Et$^+$ ligand could be considered a bridging carbyne. However, the C(4)—S bond is substantially shorter than a single C—S bond [10] (see the C(5)—S distance), and, in fact, compares quite favorably with a C=S double bond [10, 11]. Thus while the ligand cannot be accurately labelled a carbyne, there is significant Fe—C(4) π-bonding as indicated by the 1.840 and 1.828 Å bond lengths as compared to normal Fe—C single bond lengths of 2.0—2.1 Å [12].

Although there are no other structural reports of alkylated bridging thiocarbonyl groups, Shriver et al. [13] have described the structure of an alkylated bridging carbonyl complex, $HFe_3(CO)_{10}(COCH_3)$, resulting from the alkylation of $HFe_3(CO)_{11}^-$. Alkylation in this molecule like that in $Cp_2Fe_2(CO)_3(CS{-}Et)^+$, increased the bridging CO bond length and decreased the Fe—C bond distances as compared to the unalkylated precursor. Further synthetic and structural studies of bridging thiocarbonyl complexes and their derivatives are in progress.

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