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Communications

Preparation of Dinuclear Iron Carbonyl Compounds Containing a Three-Electron CH_2–S Bridging Fragment

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Summary: Dithioacetals, $CH_2(SR^1)(SR^2)$, reacted with $Fe(CO)_5$ under UV irradiation to give, after scission of an S–C bond, the butterfly complexes $[Fe_2(CO)_6(\mu\text{-}SR^1)(\mu\text{-}CH_2SR^2)\text{-}C,S]$ [$R^1R^2 = CH_2SCH_2$ or $(CH_2)_3$ and $R^1 = R^2 = Me$]. A crystal structure determination and NMR study confirmed the similar structures and novel CH_2–S bridging units in all these complexes. The two protons of the thiomethoxymethyl groups are not equivalent, and the carbon atoms have a ^{13}C resonance at δ 12–19 ppm.

Metalated dithioacetals are important carbonyl synthons in organic chemistry, and their final conversion in this application involves cleavage of two C–S bonds.[1] The transition-metal complex chemistry of dithioacetals is still developing and already includes the formation of adduct carbonyl complexes,[2] the two-step synthesis of dithiocarbene complexes,[3] the cleavage of two C–S bonds to form bridged diiron compounds,[4] the transformation into heterometallacyclic carbene–thioether chelates by carbonyl insertion,[5] and the formation of thiocarbene complexes via ylide formation and C–S bond breaking.[6] Numerous reactions of organosulfur compounds with iron carbonyl complexes are known, and, although different types of C–S bridges have been reported,[7] they mostly derive from C–S double bonds and usually do not contain an alkyl–sulfur linkage.[8] A monomeric complex containing CH_2–SMe as a π-bonded ligand was prepared by King and Bisnette.[9]

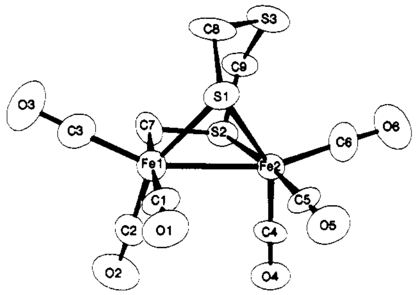

Figure 1. Molecular structure of 1. Selected bond lengths (Å) and angles (deg): Fe1–Fe2, 2.609 (3); Fe1–S1, 2.219 (5); Fe2–S1, 2.269 (5); Fe1–C7, 2.04 (2); Fe2–S2, 2.278 (4); C7–S2, 1.80 (2); S2–C9, 1.80 (2); Fe–CO(av), 1.74 (4); C–O(av), 1.17 (2); S1–Fe1–Fe2, 55.4 (1); S1–Fe2–Fe1, 53.6 (1); Fe1–S1–Fe2, 71.1 (1); Fe2–Fe1–C7, 82.0 (4); Fe1–Fe2–S2, 76.1 (1); Fe1–C7–S2, 103.9 (7); C7–S2–Fe2, 97.4 (5); Fe–C–O(av), 177.9 (9).

The recent report of Doherty et al.[10] concerning the synthesis of diiron carbonyls containing a CH_2–P bridge, as well as our concern with transition-metal complex–organosulfur interactions,[11] prompted the preparation of compounds with sulfur as one donor atom of the bridging ligand. We made use of the labile C–S bond in dithioacetals to prepare new complexes containing a novel CH_2–S bridge. Structures were assigned by means of ^1H and proton-coupled ^{13}C NMR, HETCOR, and DEPT studies and, in one instance, X-ray crystallography.

In the reaction between $Fe(CO)_5$ and 1,3,5-trithiane (eq 1)[12] scission of a CH_2–S bond gave the dinuclear compound 1. An Fe–C σ bond formed between the CH_2 group and a metal atom, while the adjacent sulfur acted as a neutral Lewis donor to the other metal atom. The diatomic bridging unit formally contributes three electrons to the complex as does the sulfur atom, from the broken C–S bond, which bridges the iron atoms and forms the other wingtip of an asymmetric, highly distorted butterfly compound. The structure was determined by X-ray crystallography (Figure 1).[13] The dominant feature of this

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[8] In the work of Alper[7d] a compound, derived from a thioketone ligand and characterized by mass, infrared, and ^1H NMR spectroscopy, is described which contains a ligand with a substituted aliphatic carbon bonded to a bridging sulfur atom.

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[12] In a typical experiment equimolar amounts of $Fe(CO)_5$ and the ligand (1,3,5-trithiane, Fluka; 1,3-dithiane, $MeSCH_2SMe$, Aldrich) in a THF solution were irradiated with a mercury vapour lamp for about 5 h, after which the solvent was removed and the residue chromatographed on silica gel with a hexane/CH_2Cl_2 mixture (~2:1) as eluant. The main orange zones were collected; **2** eluted before **1**; **3** and **4** were the only orange products. Significant decomposition occurred, resulting in yields between 10 and 15% and products that did not elute from the column. **1**: orange crystals; mp ≥140 °C dec; IR (hexane) ν(CO) 2072 (m), 2057 (w), 2032 (vs), 2005 (s), 1993 (s), 1981 (w), 1970 (w) cm^{-1}; MS *m/e* calcd 418.023, found 418. Anal. Calcd for $C_9H_6O_6S_3Fe_2$: C, 28.86; H, 1.45. Found: C, 28.89; H, 1.47. **3**: orange crystals, mp ≥127 °C dec; IR (hexane) ν(CO) 2069 (s), 2026 (vs), 2002 (vs), 1981 (s), 1966 (w) cm^{-1}; MS *m/e*; calcd 399.992, found: 400. Anal. Calcd for $C_{10}H_8O_6S_2Fe_2$: C, 30.03; H, 2.02. Found: C, 30.08; H, 2.06. **4**: orange crystals; mp 73–75 °C; IR (hexane) ν(CO) 2066 (s), 2025 (vs), 1994 (s), 1985 (s), 1969 (m) cm^{-1}; MS *m/e* calcd 387.981, found 388. Anal. Calcd for $C_9H_8O_6S_2Fe_2$: C, 27.86; H, 2.09. Found: C, 27.92; H, 2.13. ^1H and ^{13}C NMR data: see text. Spectra were measured in $CDCl_3$ (δ values in ppm relative to internal TMS).

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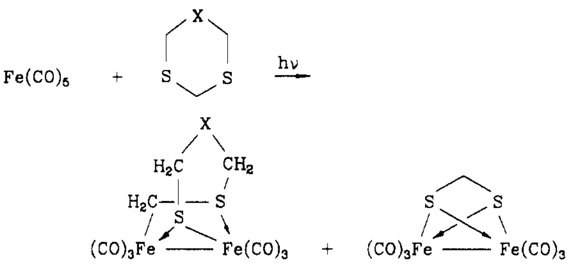


(1)

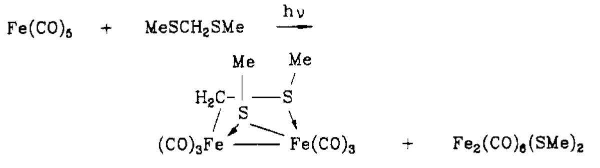
1 : X = S

2

3 : X = CH_2

compound compared to the Hieber-type structures $Fe_2(CO)_6(\mu\text{-}SR)_2$[14] is the lengthening of the Fe–Fe bond by ca. 0.35 to 2.609 (3) Å.[4]

Compounds structurally similar to 1, viz., 3 and 4, formed when $Fe(CO)_5$ reacted with 1,3-dithiane (eq 1) and the linear dithioacetal $MeSCH_2SMe$ (eq 2), respectively. The phenyl analogue $PhSCH_2SPh$, however, reacted by eliminating CH_2 (or CH_2SPh from two ligand molecules) and gave only the known compound $Fe_2(CO)_6(\mu\text{-}SPh)_2$.[15]



(2)

4

In addition, 1,3,5-trithiane, but not 1,3-dithiane, also underwent scission of two CH_2–S bonds, to split out SCH_2S, which coordinated and formed the known compound 2 (eq 1). The structure of 2 was assigned by comparison of its IR and mass spectra with published data.[4]

The ^1H NMR spectrum of complex 1 reflects its asymmetry in that the signals for two of the CH_2 groups are split into two pairs of doublets (at 1.42, 2.23, 3.36, and 4.25 ppm), indicating that each proton is in a different chemical environment. The pair of doublets at 1.42 and 2.23 ppm is attributed to the methylene group attached to a metal. One CH_2 group appears as a broad singlet at 3.22 ppm and, from a HETCOR diagram, was assigned to the hydrogen atoms on C9 (Figure 1). The $^{13}C\{^1H\}$ NMR spectrum shows resonances at 18.8, 31.3, and 44.2 ppm, and from the ^1H-coupled spectrum these are assigned to C7, C8, and C9, respectively. The carbon bonded to the metal was assumed to have the highest upfield shift. The CO resonances are at 207.1, 210.4, and 214.9 ppm.

It is difficult to account for the large differences in the chemical shifts of the protons. From a three-dimensional model of 1 it was seen that one of the protons on C7 might be subject to an anomeric effect because of its proximity to a C=O group, but the H atoms on C8, which also appear as a doublet of doublets, are too far from the C=O ligands for such an effect to be operative.

The ^1H NMR spectrum of complex 3 consists of a series of multiplets in the range 1.1–2.5 ppm, which includes doublets for the Fe–CH_2 protons at 1.15 and 2.00 ppm and a pair of multiplets at ca. 3.5 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows signals at 16.0, 26.6, 29.3, and 37.4 ppm for the four carbon atoms of the ligand. Resonances for the carbonyl carbons were not observed.

A proton-coupled ^{13}C NMR spectrum of the open chain compound 4 shows a triplet at 10.8 ppm for the Fe–CH_2 carbon, which confirmed our assignment of the highest field signal in the ^{13}C NMR spectrum of 1. The bridging SMe group gives rise to a simple quartet at 21.6 ppm, whereas for the methyl carbon, δ 32.4 ppm (as well as for the CH_2) in the CH_2SCH_3 group, the signals are split due to coupling through the S atom. Signals for the carbonyl carbons are at 208.6 and 209.5 ppm.

The proton NMR spectrum of 4 contains doublets at 1.07 and 1.59 ppm, assigned to the protons of Fe–CH_2, and singlets at 2.00 and 2.45 ppm for the SMe groups. A HETCOR diagram indicated that the signal at 2.00 ppm belongs to the bridging SMe and the one at 2.45 ppm to the CH_2SMe group.

There is only one isomer of complex 4 in solution, and the chemical shift of the bridging SMe is downfield compared to that of the equatorial Me in $Fe_2(CO)_6(SMe)_2$ (2.13 ppm).[16] From our data it is not possible to tell whether the configuration of the SCH_3 groups is equatorial or axial.

The scission reactions of dithioacetals by which compounds 1–4 formed have not been noted before, and in compounds 1, 3, and 4 a unique CH_2–SR bridging ligand appears for the first time. Studies on the ring opening of other heterocycles, products obtained from other metal carbonyls, and the reactivity of the products are in progress.

Acknowledgment. We thank Dr. P. H. van Rooyen for his assistance with the refinement of the crystal structure.

Registry No. 1, 121097-06-1; 2, 69878-86-0; 3, 121097-07-2; 4, 121097-08-3; $Fe(CO)_5$, 13463-40-6; $MeSCH_2SMe$, 1618-26-4; 1,3,5-trithiane, 291-21-4; 1,3-dithiane, 505-23-7.

Supplementary Material Available: Atomic coordinates (Table I), anisotropic temperature factors (Table II), calculated hydrogen atom coordinates (Table III), bond lengths and valence angles (Table IV), and crystal data (Table V) (9 pages); a listing of structure factors (12 pages). Ordering information is given on any current masthead page.

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[13] Crystal data for $C_9H_6O_6S_3Fe_2$: monoclinic, space group $P2_1$, a = 14.174 (1) Å, b = 12.293 (1) Å, c = 8.240 (1) Å, β = 90.71 (1)°, V = 1435.6 (4) Å^3, ρ(calcd) = 1.93 g·cm^{-3} for M_r 418.0, Z = 4, μ = 23.55 cm^{-1} for Mo Kα. R = 0.078; R_w = 0.060. An Enraf-Nonius CAD4F diffractometer with graphite-monochromated radiation was used for the experimental work. Three standard reflections were measured every hour (no appreciable decay of intensities was observed). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by blocked-matrix least-squares methods using the SHELX76 (Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, 1976) range of crystallographic programs. Weights equal to $1/\sigma^2(F)$ were used in the refinement. No significant difference in geometry was observed between the two molecules in the asymmetric unit. Bond lengths quoted refer to one molecule.

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Unusual Rate Acceleration in the Presence of Aldehydes of Distannoxane-Catalyzed Acetalization of Ketones and Deactivated Aldehydes: A New Mode of Carbonyl Activation

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Summary: A distannoxane, 1-hydroxy-3-isothiocyanatotetrabutyldistannoxane, catalyzes the acetalization of ketones and less reactive aldehydes in an unprecedented manner. This catalysis is discussed in terms of novel transcarbonylation.

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