Scheme I) as donor atoms although the hydride ligands could not be located in the X-ray analysis. The geometry around tungsten, as in compound **4**, may be regarded as pseudotetrahedral with the two cyclopentadienyl rings in an almost eclipsed conformation. The plane defined by the centers of gravity of the two rings and the tungsten atom and the plane defined by the platinum and the two phosphorus atoms make a dihedral angle of 93.1°, implying that the two hydride ligands are approximately coplanar with P(1), C(1), and P(2). Compound **3b** contains a single W–H–Pt bridge with its hydrogen atom completing the square-planar coordination around the platinum atom. The second hydride ligand is present as a terminal ligand. This structural assignment can be inferred from the significantly different P–Pt–W bond angles (see Table I) and the corresponding ligand arrangements about the tungsten and platinum centers. Unlike in **4**, the two Cp rings in **3b** are not symmetrically placed relative to the $Pt(Ph)(PEt_3)_2$ fragment, indicating that the two Pt–H separations are markedly different.

A similar, albeit less marked, increase in M–M bond distance, associated with a decrease in number of M–H–M bridging units, has been observed in the case of the two isomeric compounds $[(Et_3P)_2Pt(\mu\text{-}H)_2Pt(Ph)(PEt_3)_2][BPh_4]$ (Pt–Pt = 2.819 (1) Å) and $[(Et_3P)_2(H)Pt(\mu\text{-}H)Pt(Ph)(PEt_3)_2][BPh_4]$ (Pt–Pt = 3.093 (1) Å).[12]

Finally, mention should be made of the Pt–P bond lengths which are longer in **3b** (average value 2.334 (5) Å) than in **4** (2.216 (5) Å) presumably as a result of the addition of another electron-rich phosphine to the platinum center.

The $^{31}P\{^1H\}$ NMR spectrum of **3a** shows a multiplet centered at +8.4 ppm. While the phosphorus atoms are strongly coupled to platinum ($^1J(^{195}Pt-^{31}P)$ = 2736 Hz), no coupling to tungsten is observed. The ^{31}P NMR spectrum of **3a**, recorded under "off-resonance" condition, shows the presence of two hydrogen atoms coupled to phosphorus. The ^1H NMR spectrum of **3a** in CD_2Cl_2 shows that the two hydride ligands are equivalent on the NMR time scale. At ca. −20 °C they appear as a triplet centered at −18.7 ppm arising from couplings to the two phosphosrus atoms ($^2J(^{31}P-^1H)$ = 3.7 Hz). In addition one observes signals associated with the isotopomers ^{183}W and ^{195}Pt ($^1J(^{183}W-^1H)$ = 59.7 Hz and $^1J(^{195}Pt-^1H)$ = 192.3 Hz). The spectrum is temperature dependent: (1) the multiplet broadens at ca. −40 °C, (2) it coalesces to a single very broad resonance at ca. −80 °C, and (3) no further change is observed on lowering the temperature to ca. −100 °C in THF-d_8. These observations are consistent with the postulate that there are one terminal and one bridging hydride ligand in this compound exchanging rapidly even at the lowest temperature that could be reached.

Another significant difference in NMR parameters between **3** and **4** is the larger value of $^1J(^{195}Pt-^1H)$ in **4** (620–720 Hz) than in **3** (192.3 Hz). The latter value could arise as the average of a large value of $^1J(^{195}Pt-^1H^2)$ and a small value of $^3J(^{195}Pt-^1H^1)$ if one assumes that the bridging hydride exchange is fast on the NMR time scale.

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Registry No. 1, 1271-33-6; 2, 85799-24-2; 3a, 85762-70-5; 3b, 85799-25-3; 4, 85762-72-7.

Supplementary Material Available: Tables containing positional and thermal parameters for non-hydrogen atoms (Table S1), bond lengths and angles (Table S2), and observed and calculated structure factors (Table S3) for both structures (51 pages). Ordering information is given on any current masthead page.

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[12] Bachechi, F.; Zambonelli, L.; Venanzi, L. M., unpublished observations. See also: Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251.

[13] Petersen, J. L.; Masino, A.; Stewart, R. P. *J. Organomet. Chem.* **1981**, *203*, 55.

Unexpected Intramolecular Nucleophilic Substitution in an Anionic $Fe_2(CO)_6$ Complex with an Organosulfur Ligand. A Novel Preparation of $Fe_2(CO)_6$ Complexes of Dithioformic Acid Esters

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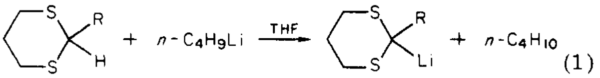
Received March 10, 1983

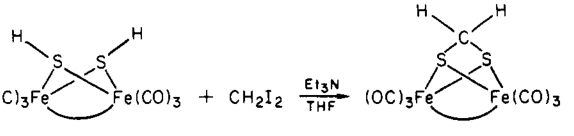
Summary: The carbanion formed by lithium diisopropylamide deprotonation of $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$ undergoes intramolecular nucleophilic attack at iron to give a C–Fe bond and a sulfur-centered anion. Alkylation then forms a bridging alkylthio ligand. The structure of the alkylation product obtained by reaction with $CH_3C(O)CH_2Br$ was determined by X-ray crystallography, as was the structure of an isomer obtained by the piperidine-induced reaction of $(\mu\text{-}HS)_2Fe_2(CO)_6$ with $HC{\equiv}CC(O)CH_3$.

The facile metalation of 1,3-dithianes (eq 1) provides the basis for the very useful nucleophilic acylation method developed by Corey and Seebach.[2] During our initial



(1)

studies of the chemistry of (μ-dithio)bis(tricarbonyliron)[3] we prepared $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$, **1**,[4] by reaction of the $[(\mu\text{-}S)_2Fe(CO)_6]^{2-}$ anion with diiodomethane. In subsequent work, we developed another procedure which produced this compound in higher yield (eq 2).[5] Since it may



1 (2)

be expected that the sulfur atoms in **1** bear a partial positive charge as a consequence of lone-pair donation to iron, an organolithium reagent derived from **1**, i.e., **2**,

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[1] (a) Massachusetts Institute of Technology. (b) University of Alberta. (c) On leave from Nankai University, Tian-Jin, PRC, 1979–1981. (d) Natural Sciences and Engineering Research Council Postdoctoral Fellow.

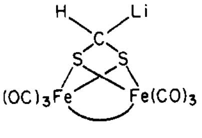
[2] Corey, E. J.; Seebach, D. *Angew. Chem.* **1965**, *77*, 1135. See also: Seebach, D. *Synthesis* **1969**, 21.

[3] Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

[4] Prepared previously by another method: Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

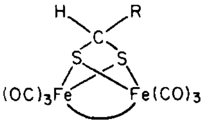
[5] Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *218*, C34.

should be accessible and relatively stable. We report here concerning the generation of **2** and its very unexpected chemistry.



2

Complex **2** reacted readily with an equimolar quantity of lithium diisopropylamide (LDA) in THF at −78 °C (under nitrogen). A red-to-green color change was observed, which was surprising, since this is the characteristic color change when sulfur-centered anions are formed from $(\mu\text{-}S_2)Fe_2(CO)_6$.[3,6,7] The addition of iodomethane to this solution and slow warming to −20 °C resulted in a second color change to red-brown. Removal of solvent at reduced pressure followed by filtration chromatography (silicic acid; elution first with pentane, then with 1:9 CH_2Cl_2–pentane) gave 0.35 g (67% yield) of a deep red oil.[8] Initially, the reasonable assumption was made that this product was complex **3a**, formed by methylation of lithium reagent **2**.



3a, R = CH_3
b, R = C_2H_5
c, R = $CH_2C(=O)CH_3$

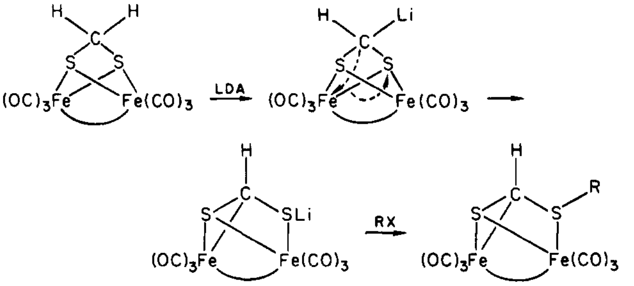
However, the disturbing observation was made that there was no coupling between the methine and the methyl protons in the proton NMR spectrum of the red oil product; in $CDCl_3$ solution, the methine proton signal occurred at δ 3.89 and the methyl group signal at δ 2.33. Both signals were sharp singlets in the expected 1:3 integrated ratio.

An ethyl derivative, assumed to be **3b**, also a red oil, was prepared as well (56% yield).[9] Here also there was no coupling in the proton NMR spectrum between the methine proton (δ 3.98 (s) and the ethyl protons.

In related research we later prepared complex **3c**, an air-stable red solid, mp 90–91 °C, by the piperidine-induced addition of $(\mu\text{-}HS)_2Fe_2(CO)_6$ to $HC{\equiv}CC(O)CH_3$.[10] This species had, to the best of our knowledge, a one-carbon bridge between the sulfur atoms, and in this case, spin–spin coupling was observed between the methine and methylene protons: ^1H NMR ($CDCl_3$) δ 2.10 (s, 3 H, CH_3), 3.08 (d, J = 6.5 Hz, 2 H, CH_2), 5.02 (t, J = 6.5 Hz, 1 H, CH).[11]

In order to have a direct comparison, lithium reagent **2** was allowed to react with bromoacetone by using the procedure indicated above. The product, after column chromatography on Florisil (20% by volume CH_2Cl_2 in pentane eluent), was obtained as a red solid, mp 80–82 °C, in 55% yield.[12] Its ^1H NMR spectrum ($CDCl_3$), in contrast, showed the methine proton signal as a *singlet* at δ 3.94. The CH_3 resonance was observed at δ 2.23 as a singlet and the CH_2 resonance as an AX quartet at δ 3.50 and 3.69 (J = 15.9 Hz).

Scheme I

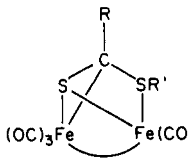


4a, R = CH_3
b, R = C_2H_5
c, R = $CH_2C(=O)CH_3$

It is obvious that these two products of the same stoichiometry obtained in two very different reactions are of different structure. The **2**-derived product is *not* **3c**. However, the $(\mu\text{-}HS)_2Fe_2(CO)_6$-derived product has the structure **3c**, as shown by its proton NMR spectrum.

The proton and the alkyl substituent in the alkyl-substitution products of anion **2** obviously are not *both* attached to the carbon atom of the original methylene group of **1**. As the red-to-green color change was indicative of the formation of a sulfur-centered anion, alternatives with that structural feature were considered. One possibility was intramolecular nucleophilic attack by the organolithium center at iron with displacement of mercaptide from iron. Alkylation would then result at the coordinated sulfide ion (Scheme I). Structure **4** is fully compatible with the spectroscopic properties of the three anion **2**-derived products. In particular, no spin–spin coupling would be expected between the methine proton on the carbon atom and the protons of the alkyl substituent on sulfur. This structure also is in agreement with the observation that the CH_2 protons in the proton NMR spectrum of **4c** are diastereotopic, since the bridging carbon atom is a chiral center.

Compounds of type **4** may be regarded as $Fe_2(CO)_6$ complexes of dithioformic acid esters, HC(S)SR. It is noteworthy that Patin and his co-workers[13] have reported that dithiocarboxylic acid esters, RC(S)SR′, react with $Fe_2(CO)_9$ to give structurally very similar complexes, **5**.



5

In order to confirm these structural ideas, an X-ray crystal structure study of complexes **3c** and **4c** was undertaken.

Compound **3c** crystallizes in the space group $C2/c$[14] with

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(6) Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508.

(7) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.

(8) IR (pentane): ν(CO) 2076 (s), 2031 (vs), 2006 (vs), 1994 (vs), 1982 (vs), 1975 (vs) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ_C 35.4 (q, J = 141 Hz, CH_3), 55.4 (d, J = 188 Hz, CH), 208.0 (br, CO), 211.2 (s, CO). Anal. Calcd for $C_8H_4O_6S_2Fe_2$: C, 25.83; H, 1.08. Found: C, 26.09; H, 1.16.

(9) IR ($CHCl_3$): ν(CO) 2075 (s), 2025 (vs), 2005 (vs), 1990 (vs), 1979 (vs), 1973 (vs) cm^{-1}. Anal. Calcd for $C_9H_6O_6S_2Fe_2$: C, 28.00; H, 1.57. Found: C, 28.31; H, 1.67.

(10) Seyferth, D.; Womack, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6839.

(11) IR ($CHCl_3$): ν(CO) 2079 (s), 2039 (vs), 1996 (vs), 1716 (s, ketone CO) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ_C 30.0 (q, J = 128 Hz, CH_3), 56.3 (t, J = 128 Hz, CH_2), 72.3 (dt, J(C–H) = 160 Hz, ^2J(C–H) = 7.0 Hz, CH), 201.9 (s, ketone CO), 208.0, 208.4 (s, FeCO). Anal. Calcd for $C_{10}H_6O_7S_2Fe_2$: C, 29.01; H, 1.46. Found: C, 29.12; H, 1.57.

(12) IR ($CHCl_3$): ν(CO) 2070 (s), 2015 (vs), 2003 (vs), 1994 (s), 1715 (s, ketone CO) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ_C 29.4 (q, J = 128 Hz, CH_3), 53.4 (d, J = 190 Hz, CH), 62.0 (t, J = 140 Hz, CH_2), 199.4 (s, ketone CO), 208.3 (br), 210.9 (s, FeCO). Anal. Calcd for $C_{10}H_6O_7S_2Fe_2$: C, 29.01; H, 1.46. Found: C, 28.96; H, 1.61.

(13) Benoit, A.; LeMarouille, J.-Y.; Mahe, C.; Patin, H. *J. Organomet. Chem.* **1981**, *218*, C67.

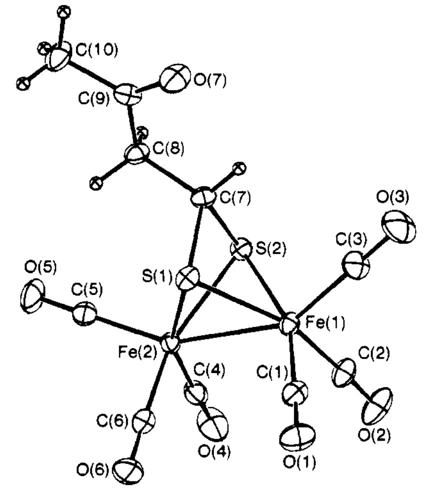

Figure 1. Perspective drawing of (μ-$CH_3C(O)CH_2CHS_2$)$Fe_2(CO)_6$ (**3c**). Thermal ellipsoids on both figures are drawn at the 20% probability level except for hydrogens which are drawn artificially small.

eight molecules in the unit cell, which has dimensions a = 15.378 (2) Å, b = 9.6620 (9) Å, c = 21.768 (3) Å, β = 108.23 (1)°, and V = 3072.0 Å^3. Compound **4c** crystallizes in $P\bar{1}$ with Z = 2 and cell dimensions a = 10.296 (2) Å, b = 11.306 (1) Å, c = 6.617 (1) Å, α = 100.45 (1)°, β = 93.36 (2)°, γ = 103.38 (1)°, and V = 732.9 Å^3. Data were collected for both structures on an Enraf-Nonius CAD-4 diffractometer up to 2θ = 50.0° using graphite-monochromated Mo Kα radiation. In compound **3c**, the Fe and S atoms were located by using MULTAN-80, whereas Patterson techniques were used to locate these heavy atoms in **4c**. Subsequent difference Fourier syntheses were used to locate all other atoms except the methyl hydrogens of **4c** which were not unambiguously located. On both structures the hydrogens which were located were input to the least-squares program as fixed contributions in their idealized positions (C–H distances = 0.95 Å) except for the methine hydrogen on C(7) of compound **4c** which was refined isotropically. All non-hydrogen atoms were refined anisotropically. Absorption corrections have been applied to **3c** but not to **4c**. Both structures were refined by full-matrix least-squares techniques; for **3c**, R = 0.040 and R_w = 0.047[15] for 1593 unique observed reflections ($F_o^2 \geq 3\sigma(F_o^2)$) and 190 parameters varied; for **4c**, R = 0.042 and R_w = 0.055 for 1944 unique observed reflections with 194 parameters varied.

In both complexes, **3c** and **4c**, the overall structural features are those suggested by the spectroscopic evidence. Thus, in **3c** (Figure 1) the $S_2C(H)CH_2C(O)CH_3$ ligand functions as a six-electron donor with both sulfur atoms bound to both metals in a "butterfly" arrangement in which the sulfur atoms are also bridged by the $C(H)CH_2C(O)CH_3$ group. Although the substituted dithiomethane group is rather symmetrically bonded to both metals, this group is skewed slightly such that S(1) is closer to Fe(1) and S(2) is closer to Fe(2) (Fe(1)–S(1) = 2.258 (2)Å, Fe(1)–S(2) = 2.270 (2) Å, Fe(2)–S(1) = 2.276 (2) Å, Fe(2)–S(2) = 2.257 (2) Å). Both C–S distances of the bridging substituted methylene group agree well (1.835 (6), 1.836 (6) Å) and are normal for C–S single bonds. However, the S(1)–C(7)–S(2) angle, at 92.9 (3)°, is rather acute, indicating significant strain in this part of the molecule. The Fe–Fe bond (2.485 (1) Å) is a normal single bond[16] and is identical with that found in the analogous methylene-bridged species (μ-CH_2S_2)$Fe_2(CO)_6$;[4] indeed the presence of the $CH_2C(O)CH_3$ substituent in the present compound leads to only minor deviations from the geometry observed in this CH_2-bridged analogue.

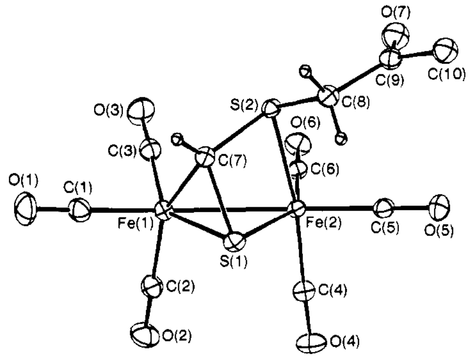

Figure 2. Perspective drawing of (μ-$CH_3C(O)CH_2SCHS$)$Fe_2(CO)_6$ (**4c**).

In compound **4c** (Figure 2) the bridging group is again a six-electron donor but the ligand geometry and the way in which it binds to the metals are significantly different from that in **3c**. The $CH_2C(O)CH_3$ group is now bonded to S(2) instead of to C(7), and the ligand is bound to Fe(2) through S(1) and S(2) but to Fe(1) through S(1) and C(7). This S(1)–C(7) moiety can formally be viewed as a C–S fragment which is π bonded in a side-on manner to Fe(1); indeed the Fe(1)–C(7) distance of 1.998 (4) Å is quite typical of side-on bound C–S groups[17,18] and the C(7)–S(1) and C(7)–S(2) bonds (1.771 (5) and 1.775 (5) Å, respectively) are shorter than normal C–S single bonds, suggesting some multiple-bond character. These C–S distances can be contrasted to that of C(8)–S(2) (1.831 (4) Å), which represents a normal C–S single bond, and to the C–S distances in **3c**. The wide range in Fe–S bonds (Fe(1)–S(1) = 2.193 (1) Å, Fe(2)–S(1) = 2.284 (1) Å, and Fe(2)–S(2) = 2.304 (1) Å) reflects the unsymmetrical ligand bonding mode. In **4c** the Fe–Fe distance (2.627 (1) Å) is significantly longer than that in **3c** but compares favorably to that observed (2.618 (1) Å) in the closely related dithioester complex (μ-$CH_3SC(C_4SH_3)S$)$Fe_2(CO)_6$.[13] Other metrical parameters within **4c** are normal and agree well with those in this dithioester species.

This novel and unexpected anionic rearrangement is receiving further study, as is the chemistry of the interesting type **4** complexes.

Acknowledgment. We are grateful to the National Science Foundation, the Natural Sciences and Engineering Research Council of Canada, and the University of Alberta for support of this work and to Dr. R. G. Ball for X-ray data collection.

Registry No. 1, 69878-86-0; 2, 85534-07-2; **3c**, 83650-00-4; **4a**, 85534-04-9; **4b**, 85534-05-0; **4c**, 85534-06-1; (μ-CHS_2Li)$Fe_2(CO)_6$, 85534-03-8; bromoacetone, 598-31-2; iodomethane, 74-88-4; Fe, 7439-89-6.

Supplementary Material Available: Tables of positional and thermal parameters, of bond lengths and angles, and of the observed and calculated structure amplitudes (16 pages). Ordering information is given on any current masthead page.

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(14) The other possible space group *Cc* has been ruled out owing to successful refinement of the structure in *C2/c*.

(15) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(16) "Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Toronto, 1982; Vol. 9, pp 1312–24 and references therein.

(17) Southern, T. G.; Oehmichen, U.; LeMarouille, J. Y.; LeBozec, H.; Grandjean, D.; Dixneuf, P. H. *Inorg. Chem.* **1980**, *19*, 2976.

(18) LeBozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2569.