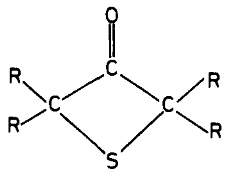
Communications to the Editor

A Stable Enolate Complex from Tetramethyl-3-thietanone and Diiron Nonacarbonyl: μ-*O*,μ-*S*-(2,4-Dimethyl-4-thiolato-2-penten-3-olato)-diiron Hexacarbonyl

Sir:

We wish to report the synthesis, characterization, and crystal structure analysis of the title compound, a stable iron-enolate complex prepared in the course of an investigation of the desulfurization of 3-thietanone (**1a**, R = H) and its tetramethyl derivative (**1b**, R = CH_3).



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A 1:1 mixture of **1b** with diiron nonacarbonyl, $Fe_2(CO)_9$, in *n*-hexane maintained at 60 °C under an argon stream liberated 3 molar equiv of carbon monoxide in approximately 120 h. The reaction mixture was then filtered to remove a black precipitate;[1] the dark filtrate was subsequently brought to dryness in vacuo. Fractional sublimation of the resultant black-brown crystalline residue at 30-35 °C (0.01 Torr) (cold finger maintained at −35 °C) resulted in the separation of two fractions: unreacted starting material, **1b**, and a dark red crystalline product (mp. 78-80 °C), **2**, which was subsequently recrystallized twice by cooling a *n*-hexane solution to −78 °C. Compound **2** was also obtained upon photolysis of iron pentacarbonyl with **1b** in *n*-hexane at 35 °C (quartz apparatus, Rayonet photochemical reactor, 2537 Å lamps, argon atmosphere).

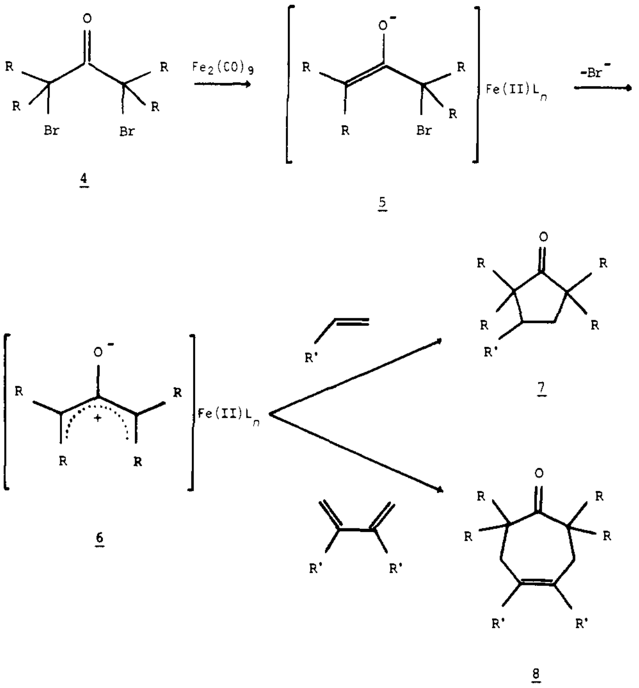
When **2** is heated with 2,3-dimethyl-1,3-butadiene a mixture of products results, the major component of which has been shown by GLC to be 2,2,4,5,7,7-hexamethyl-4-cyclohepten-one[2] (**3**), which indicates that **2** may undergo reductive rearrangement similar to that reported for the α,α′-dibromoketones.[2-7]

The molecular formula of **2**, $C_{13}H_{12}Fe_2O_7S$ (mol wt 423.99) was determined from elemental analyses (Calcd: C, 36.83; H, 2.85; Fe, 26.34; S, 7.56. Found: C, 36.49; H, 2.84; Fe, 26.26; S, 8.10) and from the mass spectrum (70 eV) (*m/e* 424 (27.7%, M^+), 396 (13.9%, $M^+ - CO$), 368 (9.7%, $M^+ - 2CO$), 340 (15.5%, $M^+ - 3CO$), 312 (9.7%, $M^+ - 4CO$), 284 (21.2%, $M^+ - 5CO$), 256 (49.8%, $M^+ - 6CO$), base peak 28 (CO)), which suggested that at least six CO molecules served as ligands in the iron complex.

The ^1H NMR spectrum (CCl_4, tetramethylsilane as an external standard) showed two singlets at δ 1.40 and 1.67 in the ratio 1:1. Alteration of the thietanone moiety was suggested by the infrared spectrum which did not show the characteristic high frequency band of the 3-thietanone carbonyl (**1a** 1790 cm^{-1}; **1b** 1770 cm^{-1} in *n*-hexane). A single-crystal x-ray diffraction structure analysis was undertaken to determine the chemical structure.

The title compound, **2**, crystallizes with space-group symmetry $P2_1/c$ and one formula unit per asymmetric unit. All crystallographic data were measured with monochromated Mo Kα radiation on a Syntex $P\bar{1}$ autodiffractometer equipped with a low temperature device (Syntex LT-1) operating at ca. −150 °C. A 0.5 × 0.5 × 0.3 mm crystal encased in a thin-walled glass capillary was used for the diffraction intensity and lattice parameter measurements. Lattice parameters (ca. −150 °C), a = 8.492 (1), b = 15.737 (1), c = 15.499 (1) Å, and β = 125.129 (5)°, were obtained from a least-squares refinement[8] with the automatically centered 2θ values for 81 reflections ($41 < 2\theta < 66°$). Diffraction intensities were measured in an ω-scan mode (scan rate 2.0-24.0° min^{-1}, scan range 0.75°, background counting time = scan time). The three reference reflections, which were periodically measured, displayed neither systematic nor significant deviations from their initial intensities. A total of 7265 unique reflections were measured within the range $0.0 < \sin\theta/\lambda < 0.807$ Å^{-1} of which 6568 were classified as objectively observed, $I > 2\sigma(I)$.

Scheme I[4]



The initial model for the crystal structure was determined by application of the heavy atom technique through which all atomic coordinates were determined. Variable block-block diagonal least-squares refinement of 256 parameters (all fractional atomic coordinates, anisotropic temperature factor coefficients for Fe, S, O, and C atoms and isotropic temperature factors for the H atoms) utilizing all observed data resulted in conventional residuals R = 0.039, R_w = 0.057, and an estimated standard deviation in an observation of unit weight, σ = 1.19.

Analysis of the molecular geometry, presented in stereoscopic projection[9] in Figure 1, has established the chemical structure of **2**, Figure 2, to be that of a doubly μ-bridged diiron hexacarbonyl complex of the $Fe_2(XY)(CO)_6$ class.[10-12]

The XY ligand of the complex, which has resulted from an opening of the 3-thietanone ring, displays an enolate structure which is particularly interesting with respect to the mechanism for the reductive rearrangement of α,α′-dibromoketones. A

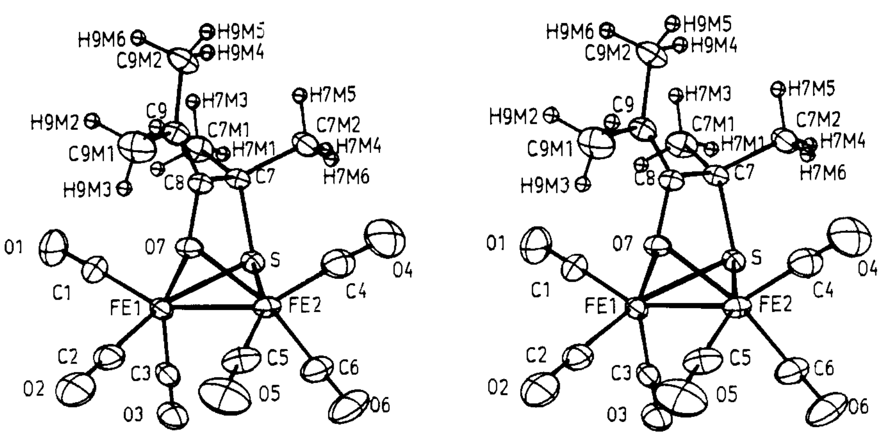


Figure 1. Stereoscopic projection of μ-O,μ-S-(2,4-dimethyl-4-thiolato-2-pentene-3-olato)diiron hexacarbonyl. Thermal ellipsoids are represented at the 75% probability level.

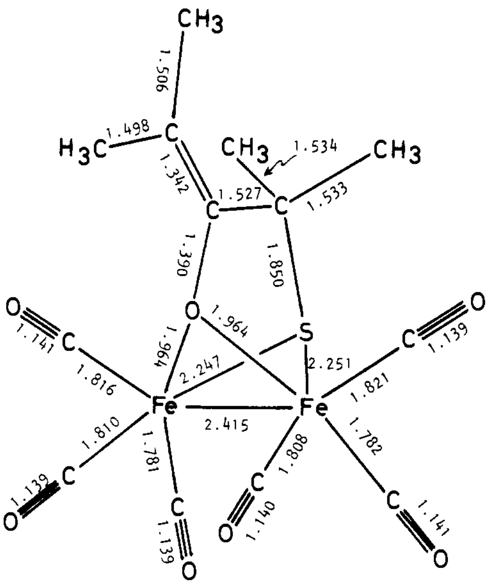
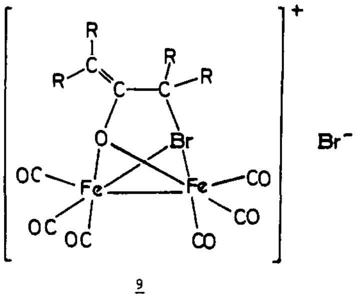


Figure 2. The chemical structure of **2**. The maximum standard deviation on the bond distances presented is 0.004 Å.

possible mechanism involving an uncharacterized enolate complex with Fe^{II} L_n has been proposed,[4] Scheme I.

As indicated above, **2** has been shown to give rise to **8** ($R = R' = CH_3$, **3**) upon heating with 2,3-dimethyl-1,3-butadiene. With these observations in mind it is interesting to speculate as to the appropriateness of **2** as a model structure for an intermediate in the reduction of α,α'-dibromoketones. For example, an analogue of **2** may be a precursor to intermediates **5** or **6**. One such analogue may be achieved by removal of a bromide ion from the dibromoketone to give a short-lived cationic intermediate **9** for which the valence electron system is isoelectronic with **2**. The cationic intermediate provides a ready electron transfer path through either the oxygen of the enolate or through the bromine leaving group, thus giving rise to the oxidation-reduction reaction. This reaction is probably accompanied by elimination of $Fe(CO)_5$, transfer of a bromide ion to the Fe(II) coordination sphere, and formation of a species describable as **6**. The formation of an intermediate such as **9** may explain why $Fe_2(CO)_9$ is a superior reagent for the reductive debromination of α,α'-dibromoketones.[4]



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Acknowledgment. This study was supported in part by grants from Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

References and Notes

(1) The black precipitate was insoluble in organic solvents but dissolved in 20% aqueous HCl with evolution of H_2S and thus may be an iron sulfide.
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Regiospecific Homolytic Displacement, with Rearrangement, of Cobaloxime(II) from Allylcobaloxime(III) Complexes by Trichloromethyl Radicals

Sir:

In an earlier communication[1] we described the bimolecular homolytic displacement of cobaloxime(II) from alkylcobaloxime(III) complexes by other cobaloxime(II) species (eq 1).