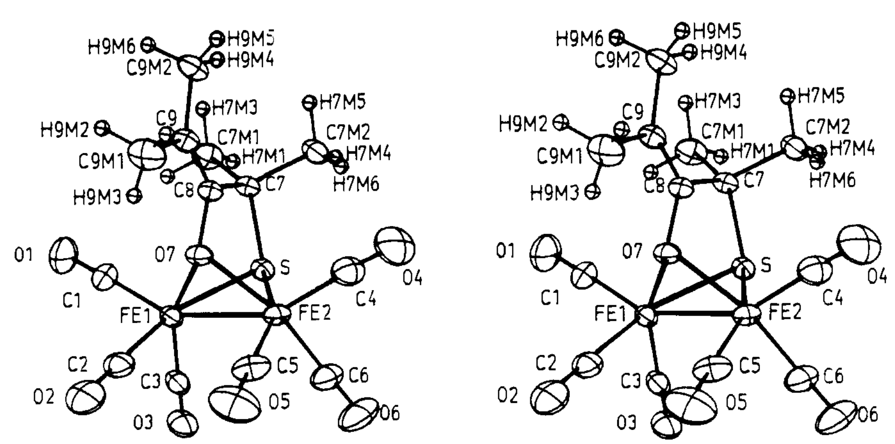


Figure 1. Stereoscopic projection of μ-*O*,μ-*S*-(2,4-dimethyl-4-thiolato-2-pentene-3-olato)diiron hexacarbonyl. Thermal ellipsoids are represented at the 75% probability level.

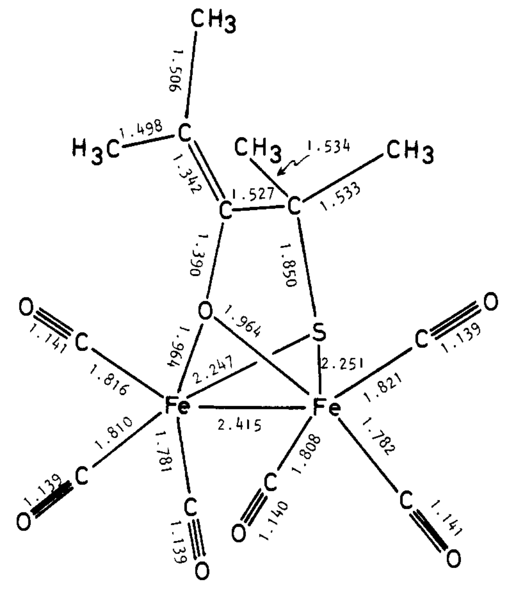
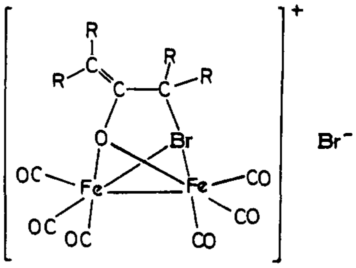


Figure 2. The chemical structure of **2**. The maximum standard deviation on the bond distances presented is 0.004 Å.

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.

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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).

$$\mathrm{RCo^{III}(chgH)_2py + Co^{II}(dmgH)_2py \rightleftharpoons RCo^{III}(dmgH)_2py + Co^{II}(chgH)_2py} \quad (1)$$

where chgH and dmgH are the conjugate bases of cyclohexanedionedioxime and dimethylglyoxime, respectively. Though it was reasonably suggested[2] that the cobaloxime(II) reagent was not directly comparable with conventional organic free radical reagents, such as the methyl radical, the reaction did demonstrate the capability of cobaloxime(II) as a leaving group in homolytic substitution and indicated that other homolytic displacement reactions might be both useful in organic synthesis and important in a number of biosynthetic reactions of organocobalamins.[3]

We here describe the first examples of homolytic displacement of cobalt(II) from organocobalt(III) complexes by conventional organic radicals.[4] Thus, allylbis(dimethylglyoximato)pyridinecobalt(III) (**1**) reacts with bromotrichloromethane at ambient temperature in chloroform to give near quantitative yields of 4,4,4-trichlorobut-1-ene (**2**).[5] The time necessary for the reaction varies from a few minutes to an hour; the reaction is noticeably faster in the case of impure samples of the allylcobaloxime containing traces of cobaloxime(II) species. The corresponding reaction takes several hours at 40 °C when carbon tetrachloride is used both as solvent[6] and as reagent; it is inhibited by added galvinoxyl but is markedly faster in the presence of added benzoyl peroxide (5% w/w) and in the presence of light.

Corresponding reactions of the substituted allylcobaloximes **3–6** with bromotrichloromethane and with carbon tetrachloride each gave only a single low molecular weight olefinic product and, in all cases for which a distinction can be made, the reactions were 100% regiospecific, giving the rearranged allyl product **7–10**, respectively. Small deviations from quantitative recovery of the monomeric olefin could be ascribed to partial oligomerization of the initial product. The inorganic product in each case was the bromo- or chlorobis(dimethylglyoximato)pyridinecobalt(III) complex.

$$\begin{array}{ll}
\mathrm{R(R')C{:}CR''{\cdot}CH_2Co(dmgH)_2py} & \mathrm{+\ XCCl_3} \\
\mathbf{1}, \mathrm{R = R' = R'' = H} & \mathrm{X = Br\ or\ Cl} \\
\mathbf{3}, \mathrm{R = Me;\ R' = R'' = H} & \\
\mathbf{4}, \mathrm{R = Ph;\ R' = R'' = H} & \\
\mathbf{5}, \mathrm{R = R' = H;\ R'' = Me} & \\
\mathbf{6}, \mathrm{R = R' = Me;\ R'' = H} & \\
\multicolumn{2}{l}{\quad \rightarrow \mathrm{XCo(dmgH)_2py + CH_2{:}CR''{\cdot}CR(R')CCl_3} \quad (2)} \\
\multicolumn{2}{c}{\mathbf{2}, \mathrm{R = R' = R'' = H}} \\
\multicolumn{2}{c}{\mathbf{7}, \mathrm{R = Me;\ R' = R'' = H}} \\
\multicolumn{2}{c}{\mathbf{8}, \mathrm{R = Ph;\ R' = R'' = H}} \\
\multicolumn{2}{c}{\mathbf{9}, \mathrm{R = R' = H;\ R'' = Me}} \\
\multicolumn{2}{c}{\mathbf{10}, \mathrm{R = R' = Me;\ R'' = H}}
\end{array}$$

From the influence of initiators, inhibitors, and the nature of the reagent on the rates of the above reactions, we believe that they involve chain reactions in which trichloromethyl radicals and cobaloxime(II) complexes are the chain carriers[7] (eq 3–5). The main initiating species are probably allyl radicals and cobaloxime(II) species formed by either thermolysis or photolysis of small quantities of the reagent allylcobaloxime.[8,9] At this stage we cannot distinguish whether the reaction (4) is completely concerted with species **11** as a transition state, or a two-step reaction in which species **11** is a short-lived intermediate.

$$\mathrm{initiator + XCCl_3 \rightarrow Cl_3C{\cdot}} \quad (3)$$

$$\begin{array}{l}
\mathrm{Cl_3C{\cdot} + RCH{:}CH{\cdot}CH_2Co(dmgH)_2py \rightarrow} \\
\qquad \mathrm{Cl_3C{\cdot}CHR{\cdot}\dot{C}H{\cdot}CH_2Co(dmgH)_2py} \\
\qquad\qquad\qquad \mathbf{11} \\
\qquad \mathrm{\rightarrow Cl_3{\cdot}CHR{\cdot}CH{:}CH_2 + Co(dmgH)_2py} \quad (4)
\end{array}$$

$$\mathrm{Co(dmgH)_2py + XCCl_3 \rightarrow Cl_3C{\cdot} + XCo(dmgH)_2py} \quad (5)$$

Similar reactions proceed with allylcobaloximes and other polyhalogenomethanes known to give polyhalogenomethyl radicals, though the yields of organic product decrease with increasing requirement for long reaction times.

Acknowledgment. We thank the Science Research Council and NATO for financial support.

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(4) This is also probably the first clear example of homolytic displacement of any transition metal from carbon.

(5) All reagents and products described have been characterized by ^{1}H NMR and elemental analysis.

(6) Under the reaction conditions the allylcobaloxime was only partially soluble in carbon tetrachloride, but this alone did not account for the slowness of the reaction.

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Manganese(II) and Manganese(III) 8-Quinolinol Complexes. Redox Model for Mitochondrial Superoxide Dismutase

Sir:

The discovery in 1969[1] that superoxide ion (O_2^-) is a common respiratory intermediate of aerobic organisms with its concentration controlled by the superoxide dismutase (SOD) enzyme has revolutionized the interpretation of biological oxidation–reduction processes. A subsequent discovery is that there is a manganese-containing version of superoxide dismutase as well as the originally discovered copper–zinc form from erythrocytes; the manganese SOD has been isolated from bacterial sources[2,3] and from mitochondria.[4] At present there is still controversy as to whether the manganese SOD contains one or two manganese atoms per enzyme molecule.[2,4] Unfortunately, because the enzyme is not well characterized and a crystal structure has not been reported as yet, the chemical properties are not known; i.e., the exact role of the manganese atom(s) in the enzyme, the oxidation state(s) of the manganese atom(s), the degree of association of the two manganese atoms if two are indeed present, the type of ligands coordinated to the manganese atom(s), and the stereochemistry around the metal(s).

The most recent report on the chemistry of this system indicates that the catalytic cycle can be represented by[5]

$$\mathrm{E + O_2^- \rightarrow E^- + O_2} \quad (1)$$

$$\mathrm{E^- + O_2^- \xrightarrow{H^+} E + H_2O_2} \quad (2)$$