SOME VIEWS ON THE STRUCTURE AND CHEMISTRY OF IRON π-ALLYL COMPLEXES

A. N. NESMEYANOV AND I. I. KRITSKAYA

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

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SUMMARY

The structure and some reactions of allylcarbonyliron complexes, $C_3H_5Fe(CO)_3X$, have been studied. Their decay was shown to proceed through, or without, addition of evolving CO, to the allyl radical. Dimethyl sulfoxide caused no π–σ-rearrangement but it completely replaced the allyl ligand.

$[(CH_3)_2SO]_5FeX_2$-like sulfoxide complexes of iron have been prepared. They were shown to convert readily into $[(CH_3)_2SO]_6FeX_3$. The diallyliron complex, $(π\text{-}C_3H_5)_2Fe(CO)_2$, has also been prepared and identified.

This and subsequent[1] communications report on the π-allylirontricarbonyl complexes of structure, $C_3H_5Fe(CO)_3X$, (X = I, Br, Cl, NO_3) and $(C_3H_5)_2Fe(CO)_2$; some parts of this study have already been published[2-6].

Until very recently, the only intensive studies on the structures and chemical properties of this class of compounds were those for the allyl derivatives of palladium. These complexes usually had square planar structures. On the other hand, in the allyl iron complexes coordination of a central atom is completely satisfied.

Since halogen and carbonyl ligands are readily exchangeable, the complexes may be used for preparative purposes.

We have followed the method of Plowman and Stone[7] for the preparation of allylirontricarbonyl iodide from allyl iodide and $Fe(CO)_5$. Since this complex is fairly stable and available, further reactions led to other halides and related derivatives. Thus, it was possible to use an exchange reaction between the iodide and quaternary ammonium salts to prepare allylirontricarbonyl bromide and chloride. Other authors have prepared the same complexes from allyl halides and either $Fe_2(CO)_9$ available[8] or using the latter in *statu nascendi*[9]. In the paper of one of us in collaboration with Gubin and Rubezhov[10], allylirontricarbonyl chloride was prepared by the transfer of the allyl ligand from palladium to the iron atom:

$$\tfrac{1}{2}C_3H_5PdCl + Fe_2(CO)_9 \rightarrow C_3H_5Fe(CO)_3Cl + Fe(CO)_5 + Pd + CO$$
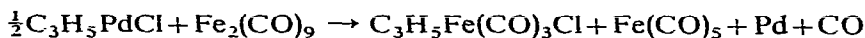
No reverse transfer from iron to palladium was observed. The complexes with a substituent in the allyl group have been prepared by an analogous procedure.

The characteristics of all compounds prepared, presented in the *Experimental* section, agree with the corresponding data of other authors.

In the study of these compounds molecular (and, in particular, allyl ligand) structures and chemical properties of the complex were first considered. A complete

X-ray analysis was performed for $C_3H_5Fe(CO)_3I$[3], and those for $C_3H_5Fe(CO)_3NO_3$ and $C_3H_5Fe(CO)_2P(C_6H_5)_3I$ are also almost completed. Structural and NMR data are discussed in ref. 1. The Fe–I bond may be regarded as covalent strongly polarized. Some alternations in C–C bond lengths in the allyl group and the Fe–C_1 and Fe–C_3 distances were discovered, where a longer C–C corresponds to a smaller Fe–C distance. Thus, in the crystal of allylirontricarbonyl iodide, some asymmetry of the allyl group seems possible. However, since two CO groups in the *trans*-position to allyl are practically equivalent and should not distort the symmetry, it is suggested that the above alternations may be caused by intermolecular interactions in a crystal lattice. NMR data[1] indicate that the allyl group may be considered to be symmetrical in solutions. The symmetry of the $Fe(CO)_3$ fragment was also stated to be somewhat distorted which again is consistent with a number of the carbonyl bands in the IR spectra of these compounds.

In solution, allylirontricarbonyl iodide was suggested[7] as existing as an equilibrium mixture of the mono- and dimeric forms, the latter formed as a result of a linkage through the allyl group:
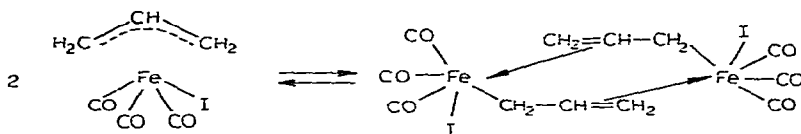
This compound has been cited[11] as the only example of an allyl group performing such a function. This suggestion was supported by the greater complexity of pattern of the NMR spectrum of this compound than would be expected for a symmetrical π-allyl group. On the other hand the molecular weight (cryoscopic method in cyclohexane) was notably increased.

We have established[1] that the NMR spectrum pattern was consistent with an equilibrium of an other type, i.e. ,with the existence of rotation isomers having different orientations of the allyl group with respect to the halogen.
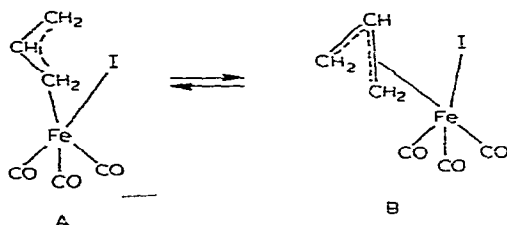

For all three halides, the predominant isomer in the mixture was shown to be of structure (A) found as crystal.

We have determined the molecular weights of a variety of specimens in cyclohexane and benzene. In cyclohexane the molecular weight greatly exceeded that of the monomer but in benzene, when the concentration of $C_3H_5Fe(CO)_3I$ was about 5%, only the monomeric form was found (found 312.7, 313.4, 311.9, calculated 307). However, the nuclear γ-resonance spectra of the benzene and cyclohexane solutions were almost identical and indicate two forms of similar symmetry which cannot be provided by a monomer–dimer mixture (the spectra were scanned for frozen solutions).
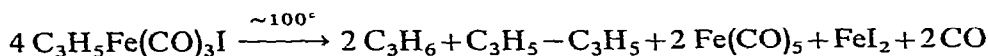
The NMR spectrum of this compound in benzene solution is also inconsistent with the dimeric form but is satisfactorily explained by the A–B equilibrium.

The increased molecular weight in C_6H_{12} may probably be explained by an experimental error associated with the high cryoscopic constant of the solvent.

The investigation of allylirontricarbonyl iodide decay under a variety of conditions[4] has shown that thermal decomposition in an inert medium (toluene) proceeds with formation of diallyl, $Fe(CO)_5$ and FeI_2. No carbonylation products were found.
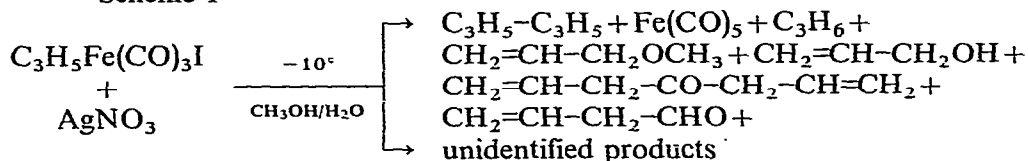
$$2\,C_3H_5Fe(CO)_3I \xrightarrow{110°} C_3H_5-C_3H_5 + Fe(CO)_5 + FeI_2 + CO$$
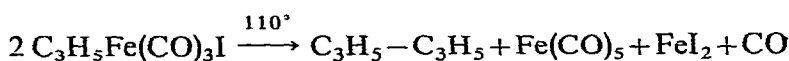
Pyrolysis in anhydrous alcohol also gave a great deal of propylene

$$4\,C_3H_5Fe(CO)_3I \xrightarrow{\sim100°} 2\,C_3H_6 + C_3H_5 - C_3H_5 + 2\,Fe(CO)_5 + FeI_2 + 2\,CO$$
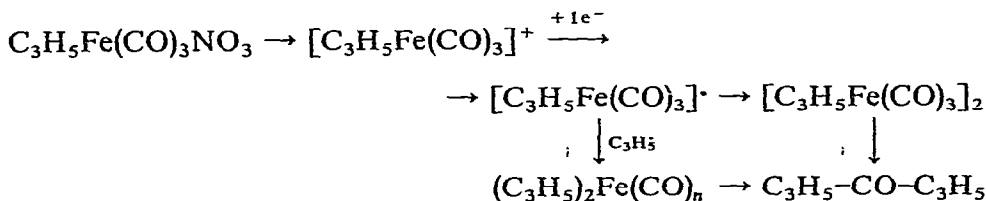
We have also investigated the decay of $C_3H_5Fe(CO)_3NO_3$ in *statu nascendi* in 70% methanol which led to the products shown in Scheme 1.

Scheme 1

$$
\begin{array}{l}
C_3H_5Fe(CO)_3I \\
\quad + \\
AgNO_3
\end{array}
\xrightarrow[\substack{CH_3OH/H_2O}]{-10°}
\left[
\begin{array}{l}
C_3H_5-C_3H_5 + Fe(CO)_5 + C_3H_6 + \\
CH_2=CH-CH_2OCH_3 + CH_2=CH-CH_2OH + \\
CH_2=CH-CH_2-CO-CH_2-CH=CH_2 + \\
CH_2=CH-CH_2-CHO + \\
\text{unidentified products}
\end{array}
\right.
$$

The total yield of aldehydes and ketones was small (25%), although their formation is an indication of the probable addition of CO to a splitting allyl radical under very mild conditions, even when there is only a limited quantity of CO and a competitive reaction leading to $Fe(CO)_5$. We suggest that diallylketone is a reaction product of allylirontricarbonyl dimer or diallylironcarbonyl complex which are possibly formed in the reaction.

$$C_3H_5Fe(CO)_3NO_3 \rightarrow [C_3H_5Fe(CO)_3]^+ \xrightarrow{+1e^-}$$

$$\rightarrow [C_3H_5Fe(CO)_3]^{\boldsymbol{\cdot}} \rightarrow [C_3H_5Fe(CO)_3]_2$$
$$\downarrow_{C_3H_5} \qquad\qquad \downarrow$$
$$(C_3H_5)_2Fe(CO)_n \rightarrow C_3H_5-CO-C_3H_5$$

It seemed worthwhile to investigate the effect of such solvents as dimethyl-sulfoxide (DMSO) on $C_3H_5Fe(CO)_3X$. Unlike known examples of the rearrangement of π into σ (or into intermediate σ, π) forms for C_3H_5[12,13], our compounds completely decomposed in DMSO[6]:

$$4\,C_3H_5Fe(CO)_3X + 10(CH_3)_2SO \rightarrow [(CH_3)_2SO]_5FeX_2 + C_3H_5-C_3H_5 +$$
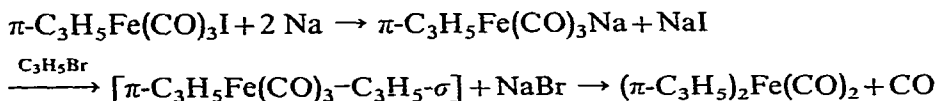$$+ [C_3H_5Fe(CO)_3]_2 + 6\,CO$$
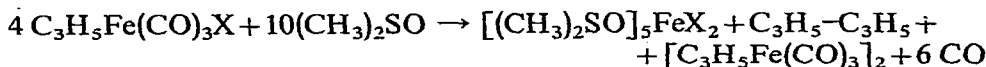
The reaction is unaffected by the amount of DMSO. The formation of allyl-irontricarbonyl dimer in DMSO medium suppressing radical reaction seems inconsistent at first sight. This is probably due to transition of the second halogen atom to a molecule of the sulfoxide complex formed. Indeed, the substitution of π-C_3H_5 and

three CO groups by five DMSO molecules is likely to provide a particle with one electron unpaired, splitting X from the starting complex and simultaneously giving the radical, $[C_3H_5Fe(CO)_3]^{\cdot}$, and its dimer.

As far as we know, the FeX_2–DMSO complexes of the above structure have not been described. They are very hygroscopic, easily oxidizable compounds readily giving $[(CH_3)_2SO]_6FeX_3$-like complexes. The compounds produce S–O stretching vibration frequencies lower by ~ 100 cm^{-1} with respect to the same bands in the spectrum of free DMSO. This suggests that the iron atom is coordinated with the sulfoxy group through its oxygen.

A number of further attempts to substitute the halogen atom in $C_3H_5Fe(CO)_3X$ by a hydrocarbon radical using a Grignard reagent or RLi failed because dimerization of the $C_3H_5Fe(CO)_3^{\cdot}$ radical was the predominating reaction. However, we have successfully introduced the second allyl group by reaction of C_3H_5X with allyliron-tricarbonyl sodium salt[5]. This procedure gave bis-π-allylirondicarbonyl. An attempt to isolate π-allyl-σ-allylirontricarbonyl also failed, since the latter easily rearranged into the π-form.

$$\pi\text{-}C_3H_5Fe(CO)_3I + 2\ Na \rightarrow \pi\text{-}C_3H_5Fe(CO)_3Na + NaI$$

$$\xrightarrow{\ C_3H_5Br\ } [\pi\text{-}C_3H_5Fe(CO)_3\text{-}C_3H_5\text{-}\sigma] + NaBr \rightarrow (\pi\text{-}C_3H_5)_2Fe(CO)_2 + CO$$

Bis-π-allylirondicarbonyl is a volatile solid, unstable in air even in the solid state. We failed to substitute the CO groups in this complex by phosphines, phosphites and amines. The temperature-dependency of the NMR spectrum of the complex[1,5] can be explained by the unrestricted rotation at 20° of the π-allyl group about an axis metal–allyl plane center with rotational barrier about 5 kcal/mole. Decrease in temperature to $-70°$ completely suppresses the rotation, and both groups exhibit their own bands in the spectrum.

Thus NMR demonstrated the rotation of the π-allyl groups in mono- and diallyliron complexes. Possible reasons for the suppression of this rotation are discussed in ref. 1.

Finally, one of us, in collaboration with Gubin and Denisovich[14], studied the polarographic reduction of allylirontricarbonyl halides and nitrates. The reduction was shown to involve a two-step mechanism: homolytic cleavage of the Fe–X σ-bond, giving the stable $C_3H_5Fe(CO)_3^{\cdot}$ radical, and its subsequent reduction into the $C_3H_5Fe(CO)_3^{-}$ anion. A comparison of the polarographic data for $C_3H_5Fe(CO)_3X$ and $C_5H_5Fe(CO)_2X$ showed that $C_3H_5Fe(CO)_3^{\cdot}$ is more stable than the $C_5H_5Fe(CO)_2^{\cdot}$ radical.

EXPERIMENTAL

$C_3H_5Fe(CO)_3I$

A mixture of 60 g (0.3 mole) of $Fe(CO)_5$ and 66.5 g (0.39 mole) of C_3H_5I was stirred with heating (40–45°) for 40 h without an inert atmosphere. Excess reagents were evaporated and the residue extracted with hexane. 81 g (86 %) of $C_3H_5Fe(CO)_3I$ precipitated from this solution on cooling to $-76°$. This was the maximum yield achieved; the yield sometimes varied notably even under a nitrogen atmosphere. Dark brown crystals, m.p. 96–98° (decomp.) (lit. m.p. 85–86° [8], 97–98° [9]). (Found:

C, 23.26; H, 1.59; Fe, 18.11; I, 41.36; mol.wt. 312 (cryoscopic method, 5% solution in benzene). $C_6H_5FeIO_3$ calcd.: C, 23.41; H, 1.64; Fe, 18.11; I, 41.21%, mol.wt. 307.9). IR spectrum*: 2012, 2033, 2083 cm^{-1}. Nuclear γ-resonance spectrum: (benzene solution) δ_1 0.42, Δ_1 1.35, δ_2 0.38, Δ_2 1.05; (C_6H_{12} solution) δ_1 0.42, Δ_1 1.35, δ_2 ~0.38, Δ_2 ~1.05.

$C_3H_5Fe(CO)_3Br$

A solution of 0.8 g (0.0025 mole) of $C_3H_5Fe(CO)_3I$ and 0.8 g (0.004 mole) of $(C_2H_5)_4NBr$ in 30 ml of $CHCl_3$ were stirred for 1 h under a nitrogen atmosphere at room temperature. The solvent was evaporated and the residue extracted with hexane and triply-recrystallized from the same solvent; 0.22 g (35%) of the product was obtained. Yellow-brown crystals, m.p. 91° (decomp.) (lit. m.p. 86–87° [8], 92–93° [9]). (Found: C, 27.6; H, 1.98; Br, 30.87; Fe, 21.43; mol.wt. 258 (cryoscopic method in benzene). $C_6H_5BrFeO_3$ calcd.: C, 27.62; H, 1.93; Br, 30.63; Fe, 21.40%, mol.wt. 260.8). IR spectrum: 2016, 2047, 2090 cm^{-1}.

$C_3H_5Fe(CO)_3Cl$

An analogous procedure was used for the preparation of $C_3H_5Fe(CO)_3Cl$ from $C_3H_5Fe(CO)_3I$ and $(CH_3)_4NCl$ in anhydrous CH_3OH, yield 20%, yellow crystals, m.p. 82–85° (decomp.) (lit. m.p. 88–89° [8], 81–83° [9]). (Found: C, 33.05; H, 2.42; Cl, 16.42; Fe, 25.30; mol.wt. 190 (cryoscopic method in benzene). $C_6H_5FeClO_3$ calcd.: C, 33.25; H, 2.31; Cl, 16.36; Fe, 25.77%; mol.wt. 216). IR spectrum 2012, 2048, 2095 cm^{-1}.

$2\text{-}BrC_3H_4Fe(CO)_3Br$

Prepared as described in ref. 8, yield 30%, yellow-brown crystals, m.p. 84° (decomp.) (lit. m.p. 84–85° [8]). (Found: C, 21.15; H, 1.23; Br, 46.80; Fe, 16,37; mol.wt. 338 (cryoscopic method in benzene) $C_6H_4Br_2FeO_3$ calcd.: C, 21.19; H, 1.18; Br, 47.07; Fe, 16.44%, mol.wt. 340). IR spectrum 2020, 2049, 2092 cm^{-1}.

$2\text{-}CH_3C_3H_4Fe(CO)_3Cl$

Prepared by an analogous procedure, yield 12%; yellow crystals, m.p. 83–86° (decomp.) (lit. m.p. 98–99° [9]). (Found: C, 36.66; H, 3.18; Cl, 15.28; Fe, 24.30. $C_7H_7ClFeO_3$ calcd.: C, 36.51; H, 3.06; Cl, 15.39; Fe, 24.24%.).

$C_3H_5Fe(CO)_2P(C_6H_5)_3I$

To a solution of 3.07 g (0.01 mole) of $C_3H_5Fe(CO)_3I$ in 30 ml of THF was added 2.62 g (0.01 mole) of $P(C_6H_5)_3$ in 10 ml of THF. There was an immediate vigorous evolution of gas and the solution became dark-red. The mixture was stirred for 1 h at room temperature and a solid precipitate filtered off. The filtrate was evaporated exhaustively *in vacuo* and extracted with THF. The insoluble residue was combined with the original precipitate and purified by repeated precipitation from a CH_2Cl_2–THF mixture. The product allyltriphenylphosphonium iodide gave a 31% yield (based on starting complex), m.p. 225–229°. (Found: C, 58.76; H, 4.67; I, 29.23; P, 7.11. $C_{21}H_{20}IP$ calcd.: C, 58.60; H, 4.65; I, 29.46; P, 7.20%). The THF solution

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* Scanned with IKS-14 model spectrophotometer. In all cases, a suspension in vaseline oil was prepared.

contained $C_3H_5Fe(CO)_2P(C_6H_5)_3I$, red-brown crystals, m.p. 121–122° (from CH_3-OH). (lit. m.p. 121–122° [9]). (Found: C, 50.80; H, 3.79; I, 23.44; Fe, 10.43; P, 5.81. $C_{23}H_{20}IFeO_2P$ calcd.: C, 50.94; H, 3.72; I, 23.42; Fe, 10.30; P, 5.71%).

$C_3H_5Fe(CO)_3NO_3$

A solution of 3.07 g (0.01 mole) of $C_3H_5Fe(CO)_3I$ in 50 ml of nitromethane was mixed with 1.7 g (0.01 mole) of $AgNO_3$ in 30 ml of dry CH_3OH. After 30 min, solid AgI was separated; the filtrate was evaporated *in vacuo* and the residue recrystallized from acetone, yield 1 g (50%), yellow crystals, m.p. 83–85° (decomp.), burns with explosion, stable in air. (Found: C, 30.01; H, 2.06; Fe, 22.49; N, 5.51; mol.wt. 241 (cryoscopic method in benzene). $C_6H_5FeNO_6$ calcd.: C, 29.66; H, 2.07; Fe, 22.98; N, 5.76%; mol.wt. 243).

$(C_3H_5)_2Fe(CO)_2$

The reduction of $C_3H_5Fe(CO)_3I$ with 1% sodium amalgam using 2.1 g-atom of sodium per 1 mole of the complex was carried out in THF under an argon atmosphere. The addition of the complex solution to the amalgam should be done gradually since the reduction is exothermic. The solution first turns green, then red and finally becomes yellow-brown in color. Excess amalgam and mercury were separated by means of a tap fitted in the flask bottom; C_3H_5Br in THF was then added dropwise to a solution of $C_3H_5Fe(CO)_3Na$. After 15 min, an inorganic precipitate was filtered off and the filtrate evaporated *in vacuo* at 20°. The residue was extracted with pentane and the solvent again evaporated. The semi-liquid residue (55% based on starting complex) was sublimed at 20–25° (5–10 mm). The yellow-orange $(C_3H_5)_2Fe(CO)_2$ complex easily sublimes and has m.p. 57–58° (decomp.). However, most of the intermediate product decomposed giving a pyrophoric residue. (Found: C, 49.31; H, 5.12; Fe, 28.98; mol.wt. 204 (cryoscopic method in benzene). $C_8H_{10}FeO_2$ calcd.: C, 49.53; H, 5.19; Fe, 28.79%, mol.wt. 194). IR spectrum: 1965, 2020 cm^{-1}. The product is unstable, can be stored at $-76°$ under an inert gas atmosphere, is readily soluble in most solvents and smells like ferrocene, (the smell is masked, however, by evolving diallyl). Reaction with $P(C_6H_5)_3$, $P(OC_6H_5)_3$ and C_5H_5N failed to provide any definable products.

REACTION WITH DIMETHYLSULFOXIDE

(A) An emulsion of 2 g (0.0064 mole) of $C_3H_5Fe(CO)_3I$ and 2 g (0.024 mole) of DMSO in pentane was stirred for 3 h at room temperature under an argon atmosphere. $[(CH_3)_2SO]_5FeI_2$ gradually precipitated with evolution of carbon monoxide and with development of a red color. The residue was separated, washed with dry ether and analyzed without further purification, yield 3.7 g (80%), white prisms, decomposed at 93–157°, (melt red in color). (Found: C, 17.06; H, 4.39; Fe, 7.92. $C_{10}H_{30}FeI_2O_5S_5$ calcd.: C, 17.15; H, 4.32; Fe, 7.97%). The product is readily soluble in water (colorless solution) insoluble in ether and hydrocarbons, highly hygroscopic and easily oxidizable. IR spectrum: 480, 950, 1010, 1045, 1060 cm^{-1}.

A pyrophoric dark-red product precipitated from the red pentane solution at $-76°$. Treatment with an ethereal I_2 solution gave $C_3H_5Fe(CO)_3I$. Thermal decomposition of the former in the absence of air (under G.L.C. conditions) gives

equivalent amounts of diallyl and $Fe(CO)_5$. These results indicate that the product was the dimeric allylirontricarbonyl, described by Murdoch[15]. An additional quantity of diallyl was found by GLC in the reaction mixture, which is in agreement with the reaction mechanism proposed. An experiment with $C_3H_5Fe(CO)_3I$ and DMSO in 1:1 mole ratio resulted in a 28% yield of $[(CH_3)_2SO]_5FeI_2$; about 50% of the starting material was recovered.

(B) An alcoholic solution of $[(CH_3)_2SO]_5FeI_2$ wa refluxed for 1.5 h. The resulting mixture was filtered and diluted with ether. A violet solid, $[(CH_3)_2SO]_5FeI_3$, precipitated, m.p. 118–119°. (Found: C, 14.42; H, 3.60; Fe, 5.66. $C_{10}H_{30}FeI_3O_5S_5$ calcd.: C, 14.51; H, 3.65; Fe, 6.75%). The compound is fairly soluble in water (decomposition). IR spectrum: 430, 875, 910, 960, 1010, 1040 cm^{-1}.

(C) Orange $[(CH_3)_2SO]_6 FeI_3$, m.p. 160–163°, gradually precipitated from a DMSO solution of $[(CH_3)_2SO]_5 FeI_3$. (Found: C, 15.83; H, 4.12; Fe, 6.27; $C_{12}H_{36}$-$FeI_3O_6S_6$ calcd.: C, 15.92; H, 4.01; Fe, 6.17%). The product is readily soluble in alcohol and ether, and decomposes in water. IR spectrum: 475, 950, 1010, 1060 cm^{-1}.

An analogous procedure was used for:

$[(CH_3)_2SO]_5FeBr_2$. White crystalline solid, 93% yield, m.p. 67–145°, soluble in water and alcohol, insoluble in ether and hydrocarbons. (Found: C, 20.04; H, 5.3; Fe, 8.24. $C_{10}H_{30}Br_2FeO_5S_5$ calcd.: C, 19.80; H, 4.99; Fe, 9.21%). IR spectrum: 945, 1005, 1022 cm^{-1}.

$[(CH_3)_2SO]_nFeBr_m$. Yellow-brown solid, m.p. 99–100°, soluble in water and alcohol. (Found: C, 12.60; H, 3.20; Fe, 13.36; S, 17.22. $C_{10}H_{30}Br_3FeO_5S_5$ calcd.: C, 17.50; H, 4.41; Fe, 8.14; S, 23.35%. $C_4H_{12}Br_2FeO_2S_2$ calcd.: C, 12.89; H, 3.25; Fe, 15.02; S, 17.25%). IR spectrum: 465, 870, 145, 990, 1035 cm^{-1}.

$[(CH_3)_2SO]_6FeBr_3$. Yellowish substance, m.p. 158–159°, soluble in water, insoluble in alcohol and ether. (Found: C, 18.71, H, 4.79; Fe, 7.44. $C_{12}H_{36}Br_3FeO_6S_6$ calcd.: C, 18.36; H, 4.74; Fe, 7.31%). IR spectrum: 475, 940, 1005, 1060 cm^{-1}.

The valence state of iron in all sulfoxide complexes prepared was confirmed by polarographic data and nuclear γ-resonance spectra.

DECOMPOSITION OF $C_3H_5Fe(CO)_3X$

The thermal decomposition of $C_3H_5Fe(CO)_3I$ in solution was carried out in a hermetically-sealed glass apparatus for 2 h at 100–110° and 215–230 p.s.i. The gaseous products were collected and analyzed by GLC. The reaction mixture was distilled *in vacuo* in the presence of a polymerization inhibitor and the distillate collected in a receiver cooled to −76°. The distillate was further analyzed by GLC, and spectroscopic methods, and the carbonyl derivatives precipitated with 2,4-nitrophenylhydrazine.

The decomposition in toluene led to diallyl, $Fe(CO)_5$ and FeI_2 (74%). Diallyl was identified by the 1,2,5,6-tetrabromohexane derivative, m.p. 53–54°. (Found: C, 17.99; H, 2.57; Br, 80.0. $C_6H_{10}Br_4$ calcd.: C, 17.94; H, 2.51; Br, 79.58%.)

The reaction in anhydrous ethanol gave the above products and propylene (26% from the complex involved). Dibromopropane, b.p. 138–139.5°/744, n_D^{20} 1.520. (Found: C, 17.74; H, 2.97; Br, 79.25. $C_3H_6Br_2$ calcd.: C, 17.84; H, 2.99; Br, 79.16%).

The decomposition of $C_3H_5Fe(CO)_3NO_3$ in 70% aqueous CH_3OH was carried out in an open system. To a solution of $C_3H_5Fe(CO)_3I$ in pure methanol, aqueous

AgNO$_3$ solution was added dropwise at $-10°$ under an atmosphere of nitrogen. Precipitation of AgI was followed by vigorous evolution of CO. The mixture was first stirred for 1.5 h at room temperature and the reaction completed at 45–60° in 3 h. AgI was separated and the filtrate distilled *in vacuo* according to the above procedure. Diallylketone was found in the distillate; 2,4-dinitrophenylhydrazone, m.p. 146–148°. (Found: C, 53.71; H, 4.86; N, 18.95. C$_{13}$H$_{14}$N$_4$O$_4$ calcd.: C, 53.79; H, 4.86; N, 19.36%) λ_{max} 338 mμ, ε 212·10^4; 256 mμ, ε 1.4·10^4 (CHCl$_3$). The butenal-2,4-dinitrophenylhydrazone derivative was probably also present (m.p. 210–212°). (Found: C, 48.51; H, 4.37; N, 22.23; mol.wt. 486 (ebullioscopic method in benzene). C$_{10}$H$_{10}$N$_4$O$_4$ calcd.: C, 48.0; H, 4.03; N, 22.40%, mol.wt. 250.2) λ_{max} 360 mμ, ε 2.34·10^4; 260 mμ, ε 194·10^4 (CHCl)$_3$. Other aldehydes and ketones, as yet unidentified, were found. The total yield of carbonyl derivatives was 15–25% (based on starting C$_3$H$_5$Fe(CO)$_3$I). GLC has also indicated diallyl, FeCO$_5$, methylallyl ether, propylene (molar ratio 14.3:1:34.3:5.7) and some traces of allyl alcohol.

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