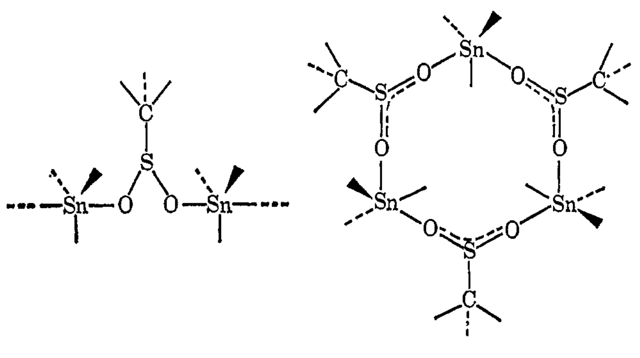
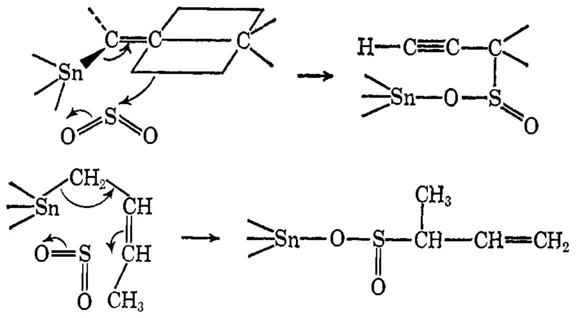


engage in intermolecular coordination.[17]

As regards mechanism, the following appear to account well for the high rate of reaction,[18] the complete rearrangements, and O-sulfinate structures. They may be considered variants of the S_E' processes now commonly encountered in electrophilic cleavages of allylic and related organometallics.[18]



We regard SO_2 insertion into carbon–tin, -lead,[19] and -mercury[6,20] bonds as examples of electrophilic cleavage, and details of these processes are being studied[21] by rate and stereochemical measurements.

Acknowledgments. The authors are grateful to Professors D. Seyferth and H. Kuivila for details concerning the preparation and spectra of some allylic tin compounds. Dr. G. Deacon of Monash University, Melbourne, kindly contributed information on the ir spectra of sulfinates.

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[17] The intermolecular coordination depicted may be considered a sulfoxide type of coordination to tin, and this may lower ν_{S-O} by 50–100 cm^{-1}. Sulfoxide complexes of organotin species are well known.[14]

[18] W. Kitching, *Rev. Pure Appl. Chem.*, in press.

[19] C. W. Fong, unpublished results.

[20] Allylmercuric acetate (which has the σ-allyl structure) also rapidly reacts with SO_2 to yield an insertion product considered[6] to have the structure $CH_2{=}CHCH_2SOOHgOAc$. This product, which is unstable in other than SO_2 solution, may be formed by an S_Ei process. Crotylmercuric acetate reacts very rapidly also, but yields an unstable, difficult to characterize product.

[21] Professor Kuivila kindly informed us that he had observed a reaction between crotyltrimethyltin and SO_2, but the product or the reaction was not characterized.

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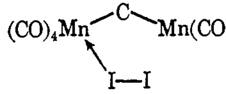
Cleavage of Tetracarbonyldi-π-cyclopentadienyldiiron and Its Monosubstituted Derivatives with Halogens

Sir:

A standard method of synthesis of neutral halogenometal carbonyl derivatives involves the fission of the metal–metal bond in dinuclear metal carbonyls or π-cyclopentadienylmetal carbonyls by halogens.[1] Thus treatment of $Mn_2(CO)_{10}$, $\{\pi\text{-}C_5H_5Mo(CO)_3\}_2$, and $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with iodine affords $Mn(CO)_5I$, $\pi\text{-}C_5H_5Mo(CO)_3I$, and $\pi\text{-}C_5H_5Fe(CO)_2I$, respectively.[2] The iodination of $Mn_2(CO)_{10}$ in solution has been studied kinetically, and a mechanism based upon the fission of $Mn_2(CO)_{10}$ to $Mn(CO)_5$ radical pairs has been postulated.[3] These radical pairs react further with the iodine to yield $Mn(CO)_5I$. Although the above mechanism was favored, an alternative involving the bridged intermediate



was also suggested.[3]

Infrared spectroscopic studies have shown the presence of two isomers of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in solution. One isomer contains both terminal and bridging carbonyl groups, while the other contains terminal carbonyls only.[4] The existence of the latter isomer, albeit a small percentage, suggests the possibility of iodination of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ occurring by a mechanism similar to that for $Mn_2(CO)_{10}$.

We have studied the halogenation of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ and have found that under certain experimental conditions products other than $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = Cl, Br, or I) are formed. Treatment of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with bromine or iodine in CH_2Cl_2 afforded the expected neutral compound $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = Br or I) only. However, the analogous reaction involving chlorine gave a second product in low yield which was shown by infrared spectroscopy to be $[\pi\text{-}C_5H_5Fe(CO)_3]Cl$.

By utilizing nonpolar solvents in the above halogenation reactions, it is expected that the yield of the ionic derivative relative to the neutral compound would be increased. The reaction of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with iodine in benzene has indeed been found to yield, as well as $\pi\text{-}C_5H_5Fe(CO)_2I$, an ionic compound which separates from solution as the triiodide. However, this has been characterized as $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2I]I_3$ containing a bridging iodine group (*cf.* $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2I]BF_4$ previously synthesized from $\pi\text{-}C_5H_5Fe(CO)_2I$[5]).

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[1] R. B. King, "Organometallic Syntheses," Vol. 1, "Transition Metal Compounds," Academic Press, New York, N. Y., 1965.

[2] E. O. Brimm, M. A. Lynch, and W. J. Sesny, *J. Amer. Chem. Soc.*, **76**, 3831 (1954); E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960); T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

[3] L. I. B. Haines and A. J. Poe, *Nature*, **215**, 699 (1967); L. I. B. Haines, D. Hopgood, and A. J. Poe, *J. Chem. Soc., A*, 421 (1968).

[4] F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967); R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).

[5] E. O. Fischer and E. Moser, *Z. Anorg. Allgem. Chem.*, **342**, 156 (1966).

When the iodination of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in benzene is performed in the presence of sodium tetraphenylboron, an almost quantitative yield of $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2I]BPh_4$ is obtained. That the bridging iodine derivative is an intermediate in the formation of $\pi\text{-}C_5H_5Fe(CO)_2I$ has been proved by monitoring a reaction of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with iodine in CH_2Cl_2 by infrared spectroscopy; the intensity of peaks corresponding to C–O stretching modes of $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2I]^+$ were found to decrease with increase of intensity of peaks corresponding to modes of $\pi\text{-}C_5H_5Fe(CO)_2I$. The reaction is fast, the formation of $\pi\text{-}C_5H_5Fe(CO)_2I$ being complete in 1–2 min.

The analogous reactions of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with bromine in benzene gave similar products and also a small amount of $[\pi\text{-}C_5H_5Fe(CO)_3]X$ (X = Br or BPh_4). The chlorination of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in benzene produced only $[\pi\text{-}C_5H_5Fe(CO)_3]Cl$ and $\pi\text{-}C_5H_5Fe(CO)_2Cl$ in approximately equal amounts, however. When this reaction was performed in the presence of $NaBPh_4$ the ionic complex $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2Cl]BPh_4$ was also obtained, but it could not be separated from $[\pi\text{-}C_5H_5Fe(CO)_3]BPh_4$.

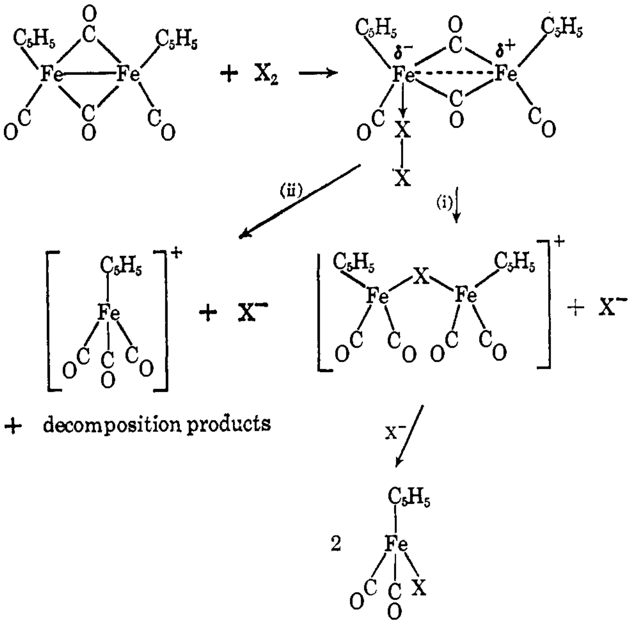
The reaction of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with the mixed halogens IBr and ICl in benzene has also been studied and shown to afford for each reagent the bridged iodo compound. There was no evidence for the formation of the bridged bromo or chloro species or for $[\pi\text{-}C_5H_5Fe(CO)_3]^+$.

The ionic derivatives $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2X]X^1$ (X = Br and I; X^1 = ClO_4 and BPh_4) react very fast with halide ions in CH_2Cl_2 at room temperature. For example, while the reaction of $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2I]ClO_4$ with iodide ions affords $\pi\text{-}C_5H_5Fe(CO)_2I$ only, the corresponding reaction with bromide ions affords $\pi\text{-}C_5H_5Fe(CO)_2Br$ and $\pi\text{-}C_5H_5Fe(CO)_2I$ in equal amounts. These ionic complexes have also been found to react with the halogens bromine and iodine in CH_2Cl_2, but the rates of reaction are only slightly faster than the rates of decomposition of the corresponding ionic compounds in CH_2Cl_2 and are much slower than the rates of reaction with halide ions.

Monosubstituted derivatives of formula $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3PR_3$ (R = Et, *n*-Pr, *n*-Bu, OMe, OEt, OPr-*i*, OBu-*n*, and OPh) have been synthesized, and these like the parent carbonyl have been shown to contain bridging and terminal carbonyl groups.[6] The reaction of these compounds with iodine in CH_2Cl_2 occurs with the formation of $[\pi\text{-}C_5H_5Fe(CO)_2PR_3]I$ as well as $\pi\text{-}C_5H_5Fe(CO)_2I$ and $\pi\text{-}C_5H_5Fe(CO)PR_3I$. With benzene as solvent, the ionic compound becomes the major product, only trace quantities of the two neutral compounds being formed. In neither solvent could complexes containing a bridging iodine group be detected.

No radical mechanism can adequately explain the formation of the various type products in the above reactions, and thus halogenation of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ does not occur by the type of mechanism postulated for the iodination of $Mn_2(CO)_{10}$. The experimental data do show that the reactions proceed by at least two mechanistic pathways which involve (i) ultimate symmetric cleavage and (ii) ultimate asymmetric cleavage of the parent compound. While the iodination of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in benzene and CH_2Cl_2 is shown to proceed solely *via* pathway i, the corresponding bromination and chlorination reactions also occur *via* pathway ii. Based on the experimental results presented above, the mechanism in Scheme I for the halogenation of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in solution is suggested. Interestingly pathway i is analogous to the mechanism postulated for the bromination of olefins.

Scheme I



An alternative mechanism for the formation of the ionic intermediate $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2X]^+$, *viz.*

$$\{\pi\text{-}C_5H_5Fe(CO)_2\}_2 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2^+ + \pi\text{-}C_5H_5Fe(CO)_2^-$$

$$\pi\text{-}C_5H_5Fe(CO)_2^- + X_2 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2X + X^-$$

$$\pi\text{-}C_5H_5Fe(CO)_2^+ + \pi\text{-}C_5H_5Fe(CO)_2X \longrightarrow [\{\pi\text{-}C_5H_5Fe(CO)_2\}_2X]^+$$

was eliminated by studying the halogenation reactions of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in the presence of excess $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = I and Br). For instance bromination of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in benzene in the presence of excess $\pi\text{-}C_5H_5Fe(CO)_2I$ as well as $NaBPh_4$ gave $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2Br]BPh_4$ only. There was no evidence for the formation of a bridged iodo compound.

The iodination of the monosubstituted derivatives is also shown to occur *via* two pathways. Although no compound containing a bridging halogen group could be detected, it is suggested that the mechanism of the halogenation of these complexes is analogous to that postulated for the parent compound.

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(6) R. J. Haines and A. L. du Preez, *Chem. Commun.*, 1513 (1968).

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