the hydrolysis reaction of metal ions, but the phenomenon is different from that in the dissociation reactions of acetic acid and other carboxylic acids and phenols[18] and ammonium ion and anilinium and their homologs.[18-20] The dissociation constants of carboxylic acids and phenols decrease almost invariably on addition of a miscible organic solvent, and the solvent effect is qualitatively interpreted in terms of the decrease of the dielectric constant of the solvent and the decrease of the concentration of water which solvates the proton released in the dissociation.[21] The dissociation constants of ammonium ion and its related compounds,[18-20] on the other hand, increase on addition of methanol or other organic solvents and then sharply decrease. The hydrolytic reaction of metal ions differs from these two dissociation reactions and the dissociation constant, that is, the formation constant of a complex, is relatively unaffected by the addition of dioxane. A study of the medium effect on activity coefficients of ions and on variation of water activity might give some interpretation of the solvent effect on the equilibrium constants of metal hydrolysis, on which a study is in progress in our laboratory.

Acknowledgment.—The author wishes to thank Professor Motoharu Tanaka for his continued interest in this work. The work has been supported in part by the Tokai Educational and Scientific Study Promotion Association (Tokai Gakujutsu Shōrei-Kai).

[18] R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964, p 154.

[19] M. Paabo, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, **70**, 247 (1966).

[20] G. Douhéret, *Bull. Soc. Chim. France*, 1412 (1967).

[21] M. Yasuda, *Bull. Chem. Soc. Japan*, **32**, 429 (1959).

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Organometallic Compounds with Metal–Metal Bonds. XIII. Reactions of Iron Pentacarbonyl with Halides and Organometallic Halides of Germanium(IV) and Tin(IV)[1]

BY R. KUMMER AND W. A. G. GRAHAM

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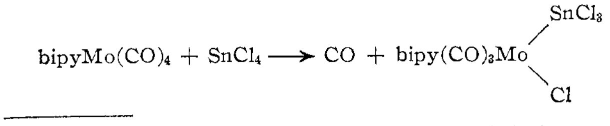
Iron pentacarbonyl has been found to undergo an oxidative elimination reaction with tetrahalides of germanium and tin (MX_4). Under mild conditions, the initial product is *cis*-octahedral $(OC)_4XFeMX_3$ (I). Heating of I or reaction of $Fe(CO)_5$ with MX_4 under more vigorous conditions affords octahedral $(OC)_4Fe(MX_3)_2$ (II). In reactions with GeX_4, only *trans*-II is formed for X = Br or I, while for X = Cl, a mixture of *cis*- and *trans*-II results. Reaction with SnX_4 (X = Cl, Br) affords only *cis*-II, although *trans*-$(OC)_4Fe(SnCl_3)_2$ was formed in an unusual reaction with $C_6H_5SnCl_3$. The *trans* forms of both $(OC)_4Fe(GeCl_3)_2$ and $(OC)_4Fe(SnCl_3)_2$ isomerized to *cis* in solution. Reaction of GeX_4 with $Fe(CO)_5$ under still more vigorous conditions or of II (M = Ge) with $Fe(CO)_5$ affords the cyclic derivatives $[(OC)_4FeGeX_2]_2$ (III). Reaction of $LFe(CO)_4$ or $L_2Fe(CO)_3$ (L = triphenylphosphine) with SnX_4 (X = Cl, I) yields $L(OC)_3XFeSnX_3$. Carbonyl stretching frequencies of all compounds are reported and qualitatively discussed.

Introduction

A number of metal carbonyls and their derivatives undergo a reaction with halogens in which one of the carbonyl groups is expelled and replaced by two univalent ligands, as illustrated by the example[2]

$$\text{bipyMo(CO)}_4 + I_2 \longrightarrow CO + \text{bipy(CO)}_3\text{MoI}_2$$

The useful term "oxidative elimination" has been applied to processes of this kind.[3] We have recently reported the results of a study of formally similar reactions involving tetrahalides and organometallic halides of germanium and tin,[1,4] of which the following is typical



$$\text{bipyMo(CO)}_4 + SnCl_4 \longrightarrow CO + \text{bipy(CO)}_3\text{Mo}\begin{smallmatrix} \diagup SnCl_3 \\ \diagdown Cl \end{smallmatrix}$$

It has long been known that iron pentacarbonyl reacts with halogens to form the tetracarbonyl dihalides $(OC)_4FeX_2$.[5] In view of the foregoing, it might be expected that an analogous reaction with tetrahalides of the fourth main group would be possible. Indeed, Hieber and Wirsching[6] in 1940 investigated the reaction of iron pentacarbonyl with tin tetrachloride, obtaining a compound of composition $Fe(CO)_4 \cdot SnCl_4$. A correct structural formulation was difficult at that early date, as 17 years were to pass before the concept of strong covalent bonding between transition metals was established.[7] The established position of $SnCl_3^-$ as a ligand[8] would now suggest that the Hieber–Wirsching compound be formulated as

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[1] Presented in part at the 50th Canadian Chemical Conference and Exhibition, Toronto, June 4–7, 1967. Part XII: R. Kummer and W. A. G. Graham, submitted for publication in *Inorg. Chem.*

[2] M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962); bipy = 2,2′-bipyridyl.

[3] J. Lewis and S. B. Wild, *ibid.*, *A*, 69 (1966).

[4] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 310 (1968).

[5] W. Hieber and G. Bader, *Ber.*, **61**, 1717 (1928).

[6] W. Hieber and A. Wirsching, *Z. Anorg. Allgem. Chem.*, **245**, 35 (1940).

[7] Concerning 1957 as a turning point in this field, *cf.* H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

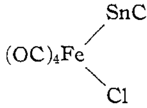
[8] R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962); R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963); J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

TABLE I

ANALYTICAL RESULTS

Compound	Color	% calcd C	H	O	X	% found C	H	O	X
$(OC)_4IFeGeI_3$	Red-brown	6.4	0.0	8.5	67.8	5.2	0.0	8.1	65.7[a]
$(OC)_4ClFeSnCl_3$[b]	Yellow	11.2	0.0	14.9	33.1	10.9	0.2	14.7	32.3
$(OC)_4BrFeSnBr_3$	Orange	7.9	0.0	10.6	52.7	8.1	0.2	10.8	52.7
$(OC)_4IFeSnI_3$	Red-brown	6.1	0.0	8.0	63.9	6.4	0.1	7.2	55.5[a]
$(OC)_4IFeSnC_6H_5I_2$	Red-brown	16.1	0.7	8.6	51.1	16.4	0.7	8.6	51.9
cis-$(OC)_4Fe(GeCl_3)_2$	Yellow	9.1	0.0	12.2	40.5	9.4	0.2	12.3	40.6
trans-$(OC)_4Fe(GeCl_3)_2$[c]	White	9.1	0.0	12.2	40.5	9.3	0.0	12.2	40.4
trans-$(OC)_4Fe(GeBr_3)_2$	Pale yellow	6.1	0.0	8.1	60.5	6.2	0.0	8.2	...
trans-$(OC)_4Fe(GeI_3)_2$[d]	Red-brown	4.5	0.0	6.0	70.9	4.9	0.0	6.0	70.3
cis-$(OC)_4Fe(SnCl_3)_2$	Yellow-orange	7.8	0.0	10.4	34.4	7.8	0.0	...	33.8
trans-$(OC)_4Fe(SnCl_3)_2$	Yellow	7.8	0.0	10.4	34.4	8.2	0.0	10.4	34.3
cis-$(OC)_4Fe(SnBr_3)_2$	Orange-brown	5.4	0.0	7.2	54.2	7.3	0.5	7.5	53.8
$[(OC)_4FeGeCl_2]_2$[e]	Yellow	15.4	0.0	20.5	22.7	15.2	0.0	20.7	22.7
$[(OC)_4FeGeBr_2]_2$[f]	Orange	12.0	0.0	39.9	16.0	11.9	0.0	39.8	15.9
$[(OC)_4FeGeI_2]_2$[g]	Dark red	9.7	0.0	12.9	51.3	10.2	0.0	13.3	51.5
$(C_6H_5)_3P(OC)_3ClFeSnCl_3$	Yellow	38.1	2.3	7.2	21.4	38.6	3.1	...	22.5
$(C_6H_5)_3P(OC)_3IFeSnI_3$	Brown	24.5	1.5	4.7	49.4	25.7	1.6	...	49.3

[a] Loses iodine at room temperature. [b] Weak molecular ion observed at *m/e* 428; exact mass of $[(OC)_4FeSnCl_3]^+$ fragment: calcd for $^{12}C_4{}^{16}O_4{}^{35}Cl_3{}^{56}Fe^{120}Sn$, 392.7232; found, 392.7233. [c] Weak molecular ion observed at *m/e* 526; exact mass of $[(OC)_4Fe(GeCl_3)GeCl_2]^+$ fragment: calcd for $^{12}C_4{}^{16}O_4{}^{35}Cl_4{}^{37}Cl^{56}Fe^{72}Ge^{74}Ge$, 490.5968; found, 490.5966. [d] Molecular ion observed at *m/e* 1076. [e] Dec pt 210°. Exact mass of molecular ion: calcd for $^{12}C_8{}^{16}O_8{}^{35}Cl_4{}^{72}Ge^{74}Ge^{56}Fe_2$, 621.5475; found, 621.5466. [f] Dec pt 190°. [g] Dec pt 150°.



The work reported here was carried out in order to confirm this interpretation and with the hope of extending the reaction to the formation of new compounds containing iron–tin and iron–germanium bonds.

Experimental Section

All reactions were carried out under a nitrogen atmosphere with careful exclusion of air and moisture, mainly by the use of Schlenk-tube techniques. Benzene and petroleum ether (bp 37–56°) were dried over a lead–sodium alloy; chloroform and dichloromethane were distilled from phosphorus pentoxide. Solvents were saturated with nitrogen. Published procedures were followed for the preparation of $SnBr_4$,[9] SnI_4,[9] GeI_4,[9] and $C_6H_5SnI_3$.[10] The complex $(C_6H_5)_3PFe(CO)_4$[11] was prepared by heating $(C_6H_5)_3P$ and $Fe(CO)_5$ in xylene at 120° for 4 days. Other starting materials were obtained from commercial sources and were used without additional purification.

Infrared spectra were measured using a Perkin-Elmer Model 337 grating spectrometer fitted with a slow-speed motor such that the scanning rate was 39 $cm^{-1}\,min^{-1}$. Spectra were recorded in expanded form on an external recorder, with bands located by interpolation between gaseous CO and DBr, as previously described.[12] The solvent was cyclohexane unless otherwise indicated; to achieve sufficient solubility, chloroform or dichloromethane was sometimes used.

Mass spectra were taken with an Associated Electrical Industries MS-9 instrument, using direct introduction of solid samples. Tin- and germanium-containing fragments were readily identified by the characteristic pattern of stable isotopes. Mass numbers quoted refer to the most abundant isotopic species containing ^{120}Sn and ^{74}Ge.

Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium (Mülheim), by Pascher Mikroanalytisches Laboratorium (Bonn), and by the microanalytical laboratory of this department. In view of the rather low thermal stability of some of the compounds and their sensitivity to air and moisture, good analyses could not be obtained in all cases. This was especially so for the iodo derivatives, which lost iodine fairly quickly even at room temperature. The results are summarized in Table I. Melting points are not given because these compounds have only a very unsharp decomposition range. Representative synthetic procedures are given below.

Preparation of $(OC)_4BrFeSnBr_3$.—Iron pentacarbonyl (0.4 ml, 0.56 g, 2.9 mmol) and tin(IV) bromide (1.2 g, 2.7 mmol) were stirred in 15 ml of benzene for 7 days. The solution became orange-red and a yellow precipitate of $FeBr_2$ formed (apparently a decomposition product). Solvent and unreacted $Fe(CO_5)$ were removed at reducea pressure and the residue was extracted with pentane. Concentration of the extracts and cooling afforded orange crystals (0.3 g, 17%) which were recrystallized from pentane and dried under vacuum. The compound may be sublimed at 60–70° (0.1 mm). It is soluble in all organic solvents, but at temperatures of 50° and above, conversion to $(OC)_4Fe(SnBr_3)_2$ becomes appreciable. In donor solvents such as acetone and ether it is rapidly decomposed forming a red solution. The compound seems stable to light but is rapidly decomposed by moist air. Samples for storage must be sealed off in glass ampoules; the usual plastic-capped vial is insufficient, even when kept in the refrigerator.

In similar fashion, $(OC)_4ClFeSnCl_3$[6] was prepared in petroleum ether solution at a temperature of 0° with a reaction time of several months; the compound was recrystallized from benzene–petroleum ether. The iodo derivative $(OC)_4IFeSnI_3$ was prepared in benzene at 25° with a reaction time of 20 hr, while $(OC)_4IFeSnC_6H_5I_2$ was prepared by reaction of $C_6H_5SnI_3$ and $Fe(CO)_5$ at 50° in benzene solution for 15 days. The latter reaction was carried out in a heavy-walled Pyrex bottle capped with a rubber-lined metal cap. A substantial pressure of carbon monoxide built up as the reaction proceeded, undoubtedly an important factor in stabilizing the product.

Preparation of $(OC)_4IFeGeI_3$.—Germanium(IV) iodide (4 g, 6.9 mmol) and iron pentacarbonyl (1.5 g, 8 mmol) were heated at 50° in 15 ml of benzene for 6–7 hr. There was no appreciable decomposition and pure product was recovered by addition of petroleum ether to the reaction solution. Attempts at recrystallization led to much decomposition into $(OC)_4Fe(GeI_3)_2$.

Preparation of *cis*- and *trans*-Bis(trichlorogermanium)tetracarbonyliron, $(OC)_4Fe(GeCl_3)_2$.—Iron pentacarbonyl (2 ml, 2.9 g, 15 mmol) and germanium(IV) chloride (3.76 g, 17.5

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[9] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. I, 2nd ed, Academic Press Inc., New York, N. Y., 1963.

[10] K. A. Kocheshkov, *Ber.*, **62**, 996 (1929).

[11] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

[12] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

mmol) were combined in 10 ml of benzene at room temperature. After 3 weeks, all volatile material was removed under vacuum and the dry residue was extracted as follows. (a) Extraction with two 20-ml portions of cold hexane, followed by concentration of the extracts at reduced pressure, afforded an orange-red oil. This oil was extracted again with petroleum ether; the extract was concentrated to 10 ml and cooled to −80°. This afforded yellow crystals (approximately 100 mg) of *cis*-$(OC)_4Fe(GeCl_3)_2$, which may be sublimed with considerable decomposition at 40–50° (0.02 mm). (b) After the cold hexane extraction, the residue was extracted with several portions of warm pentane. Concentration of the extracts and cooling afforded almost pure white crystals of *trans*-$(OC)_4Fe(GeCl_3)_2$; yield, about 0.40 g. An analytical sample was prepared by slow sublimation at 45° (0.01 mm). In one experiment with a reaction time of 7 weeks, several large (7 mm on a side), very pale yellow octahedral crystals of the pure *trans* isomer had formed in the reaction vessel.

Preparation of *trans*-$(OC)_4Fe(GeBr_3)_2$.—Iron pentacarbonyl (0.7 ml, 1.0 g, 5.1 mmol) and $GeBr_4$ (2.0 g, 5.1 mmol) were kept in 15 ml of benzene for 4 weeks at room temperature. After removal of solvent and excess $Fe(CO)_5$ under vacuum, the residue was extracted with four 15-ml portions of pentane. An infrared spectrum of the extract showed traces of an impurity presumed to be $(OC)_4BrFeGeBr_3$ in addition to the main product. Concentration and cooling of the extracts afforded pale yellow crystals of *trans*-$(OC)_4Fe(GeBr_3)_2$. The analytical sample was obtained by sublimation at 50–55° (0.1 mm).

Preparation of *trans*-$(OC)_4Fe(GeI_3)_2$.—This compound was best obtained by heating $(OC)_4IFeGeI_3$ in benzene at 70–80° for 4 hr. The solution was filtered to remove FeI_2 (finely divided, pyrophoric when dry) and concentrated. Addition of petroleum ether followed by several days at −20° afforded red-brown crystals which were washed with ice-cold petroleum ether and dried under vacuum.

Preparation of *cis*-$(OC)_4Fe(SnCl_3)_2$.—Tin(IV) chloride (1.5 ml, 3.3 g, 12.6 mmol) and $(OC)_4ClFeSnCl_3$ (0.8 g, 1.8 mmol) were dissolved in 25 ml of chloroform and heated in a pressure bottle at 50° for 24 hr. The precipitate of $FeCl_2$ was filtered off and the solution was concentrated to 5 ml under reduced pressure. Petroleum ether (40 ml) was added and the solution was placed in the refrigerator for 3 hr. A precipitate of unreacted starting material formed and was filtered off; the filtrate was evaporated under reduced pressure and the residue was extracted with two 20-ml portions of pentane. Concentration of the pentane extracts to 15 ml and cooling to −80° afforded yellow-orange crystals (0.15 g, 27%) which were dried under vacuum.

Formation of *trans*-$(OC)_4Fe(SnCl_3)_2$.—This compound arose in an unusual reaction. Iron pentacarbonyl (3 ml, 4.3 g) and $C_6H_5SnCl_3$ (3 ml, approximately 6 g) were allowed to react in 20 ml of petroleum ether at 0–5° for 7 days. In addition to much white decomposition product (mainly $FeCl_2$), large yellow crystals were precipitated which could easily be separated by hand. They were washed with cold pentane and dried under vacuum. By analysis, and by their infrared and mass spectra, the large crystals were identified as pure *trans*-$(OC)_4Fe(SnCl_3)_2$. It is *less soluble* than the *cis* isomer, dissolving only in *warm* cyclohexane with partial isomerization. The *trans* isomer is very soluble in dichloromethane but isomerizes completely to the *cis* isomer within 1 hr in that solvent. The reaction solution contained several other compounds (*cis*-$(OC)_4Fe(SnCl_3)_2$ and presumably $(OC)_4Fe(SnCl_3)SnC_6H_5Cl_2$), which could not be separated.

Preparation of *cis*-$(OC)_4Fe(SnBr_3)_2$.—Iron pentacarbonyl (1 ml, 1.45 g, 7.5 mmol) and tin(IV) bromide (3.3 g, 7.5 mmol) in 10 ml of benzene were heated in a pressure bottle at 55° for 20 hr. All volatile material was then removed under reduced pressure and the dry residue was extracted with six 30-ml portions of petroleum ether. The approximate composition of the extracts (estimated from band intensities in its infrared spectrum) was 70% $(OC)_4Fe(SnBr_3)_2$ and 30% $(OC)_4BrFeSnBr_3$. The combined and concentrated extracts were heated again in a pressure bottle to 70° for about 3 min, when the infrared spectrum was again examined; after four or five of these brief heating periods the $(OC)_4BrFeSnBr_3$ was completely decomposed. The solution was then filtered and cooled to −80°, affording an orange-brown precipitate (0.8 g, 26%) which was dried under vacuum. An attempt to sublime the product at 60–80° (0.1 mm) resulted in decomposition, apparently to $(OC)_4BrFeSnBr_3$.

Preparation of $(C_6H_5)_3P(CO)_3ClFeSnCl_3$.—A solution of $(C_6H_5)_3PFe(CO)_4$ (0.43 g, 1 mmol) in 15 ml of dichloromethane was cooled to 0°. After addition of 1 ml of $SnCl_4$ (2.23 g, 8.5 mmol) the solution was slowly warmed to room temperature. After 24 hr the solution was filtered and concentrated to 5 ml under reduced pressure. Dropwise addition of petroleum ether afforded yellow crystals (0.6 g, 90%) which were recrystallized from CH_2Cl_2–petroleum ether, washed with pentane, and dried under vacuum. The compound is soluble in dichloromethane, chloroform, and benzene but insoluble in pentane and cyclohexane. It decomposes slowly in ether and rapidly in acetone. The same product is obtained from the reaction of $[(C_6H_5)_3P]_2Fe(CO)_3$ with $SnCl_4$.

The analogous **iodo derivative** was prepared by heating $(C_6H_5)_3PFe(CO)_4$ and SnI_4 in benzene for 2 hr at 50° and recrystallizing from benzene–petroleum ether. Solutions of the iodo derivative are rapidly decomposed by sunlight.

Preparation of $[(OC)_4FeGeCl_2]_2$.—Iron pentacarbonyl (2 ml, 2.9 g, 15 mmol) and $GeCl_4$ (2.2 ml, 4.0 g, 18.4 mmol) were heated with 6 ml of xylene in a 40-ml evacuated sealed tube at 90° for 4 days. Large orange crystals formed during this interval, in addition to dark material, evidently decomposition products. The tube was opened and washed with hexane to remove starting materials and some $(OC)_4Fe(GeCl_3)_2$ (recognized by infrared analysis). The tube was then extracted with warm chloroform until all of the orange crystals had dissolved. After concentration of the chloroform extracts to 10 ml and addition of a few milliliters of pentane, cooling produced yellow crystals of product (0.5 g, 14%) which were recrystallized from dichloromethane–pentane and vacuum dried. The compound is stable to air and light, soluble in dichloromethane, chloroform, and benzene, and slightly soluble in cyclohexane and pentane. The bromo derivative, $[(OC)_4FeGeBr_2]_2$, was prepared in the same fashion.

Preparation of $[(OC)_4FeGeI_2]_2$.—The readily available (see above) compound $(OC)_4IFeGeI_3$ (0.4 g, 0.52 mmol) and iron pentacarbonyl (0.2 ml, 0.29 g, 15 mmol) were heated in cyclohexane at reflux for 4 hr. Intermittent sampling and infrared examination showed the formation of $(OC)_4Fe(GeI_3)_2$ at an early stage in the reaction. Solvent was removed under vacuum and the reaction product was extracted with dichloromethane.

A residue of FeI_2, ~0.2 g, remained. The combined extracts were concentrated to 4 ml and cooled to −80° until crystallization began. Addition of 3 ml of pentane afforded 0.12 g (90%) of purple-red crystals. The analytical sample was obtained by sublimation at 120° (0.1 mm).

Discussion

The reactions investigated in this work suggest that the oxidative elimination reaction of halides of germanium(IV) and tin(IV) with metal carbonyls may be a rather general one. The reaction has now been fairly thoroughly delineated for iron pentacarbonyl, and a number of compounds have been produced which are of considerable structural and spectroscopic interest. A qualitative discussion of the infrared spectrum will be given at the end of this section.[13] It may be noted, however, that the infrared evidence is entirely consistent with the reasonable assumption that all of the compounds reported here involve octahedral iron with the germanium- or tin-containing groups bonded directly to the iron atom. Also, in the cases

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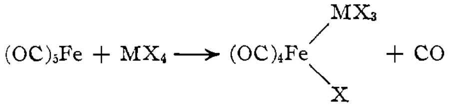
(13) A more quantitative discussion, in particular approximate force constant calculations for these and related molecules, is at present under way in collaboration with Mr. R. S. Gay.

of *cis–trans* isomerism encountered, the infrared spectrum makes an unambiguous distinction between the two forms.

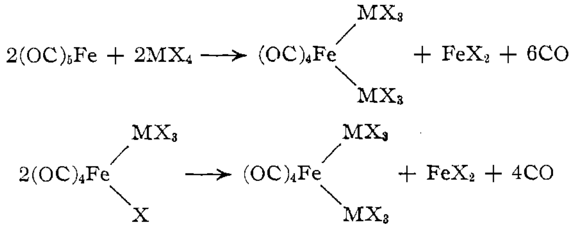
The products of these reactions contain one or more metal–metal bonds, depending upon reaction conditions and the nature of the reactants. When the reaction is carried out below or only slightly above room temperature (depending upon the tetrahalide), compounds with one Fe–M bond (M = Ge or Sn) are formed



$$(OC)_5Fe + MX_4 \longrightarrow (OC)_4Fe(MX_3)(X) + CO$$

I

Reactions at higher temperatures or heating type I products in an appropriate solvent form products with a sequence of M–Fe–M bonds[14]



$$2(OC)_5Fe + 2MX_4 \longrightarrow (OC)_4Fe(MX_3)_2 + FeX_2 + 6CO$$

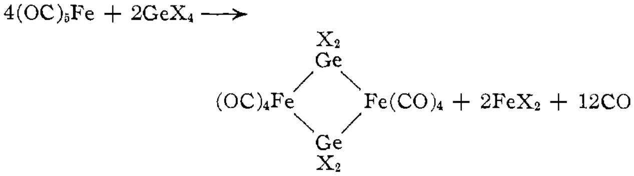
$$2(OC)_4Fe(MX_3)(X) \longrightarrow (OC)_4Fe(MX_3)_2 + FeX_2 + 4CO$$

II

Compounds of types I and II are crystalline substances, very susceptible to attack by moist air. They range in color from white (*trans*-$(OC)_4Fe(GeCl_3)_2$) to red-brown ($(OC)_4IFeSnI_3$). Type I compounds have been observed only in the *cis* form; these unsymmetrical derivatives are not very stable thermally, tending to rearrange or disproportionate to the symmetrical type II, especially in solution. In relation to the parent iron tetracarbonyl dihalides, the order of increasing thermal stability is clearly $(OC)_4FeX_2 < I < II$. Such a stability order may well be a consequence of the π-acceptor character of the MX_3 ligand in relation to the π-donor character of the halide ligand.[12,15]

For compounds of type II, *cis* and *trans* forms are observed. In the two cases where both isomers of a particular compound were isolated, $(OC)_4Fe(GeCl_3)_2$ and $(OC)_4Fe(SnCl_3)_2$, the *cis* form was the more stable and the *trans* form isomerized in solution in a short time; it was nevertheless possible to obtain satisfactory solution infrared spectra on both forms. For the tribromogermanium and triiodogermanium compounds, *only the trans isomer was detected.* Extensive efforts were not made to produce the *cis* forms of these compounds, but it should be noted that the triiodogermanium derivative was formed in 4-hr reaction in benzene at 70–80°, conditions which would certainly have converted *trans*-$(OC)_4Fe(SnCl_3)_2$ to the *cis* form. These facts are perhaps best accommodated by regarding the *cis* form as the electronically preferred structure, since it avoids as nearly as possible a condition in which mutually *trans*-carbonyl groups are competing for π-electron density of the iron. Steric hindrance may then be invoked to explain the "anomalous" stability of *trans*-$(OC)_4Fe(GeI_3)_2$. These compounds are among the first *trans*-disubstituted derivatives of the iron group carbonyls to be reported. Very recently, *trans*-$(OC)_4Fe(SiCl_3)_2$ has been mentioned,[16] although it was apparently not isolated. In an even more recent communication,[17] the ruthenium compounds *trans*-$(OC)_4Ru(SnR_3)_2$ ($R = C_6H_5, C_6H_5CH_2$) have been reported.

Under more vigorous conditions (80–90°, sealed tubes), iron pentacarbonyl reacts with germanium tetrahalides (but not those of tin) to form compounds of type III, having a four-membered ring of metal atoms

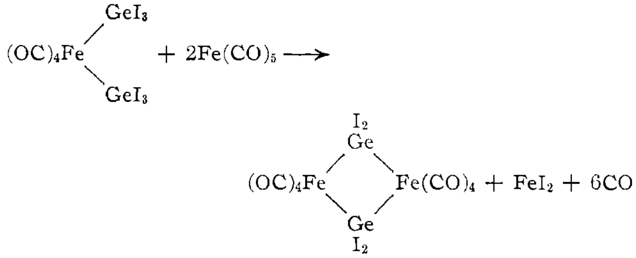


$$4(OC)_5Fe + 2GeX_4 \longrightarrow [(OC)_4FeGeX_2]_2 + 2FeX_2 + 12CO$$

III

Compounds of this type involving R_2Sn[18] or R_2Pb[19] groups have been known for some time, although the dimeric character and structure were more recently recognized.[20] Compounds of type III with bridging dimethyl- and diethylgermanium groups have also been reported.[21] The usual preparative methods for these compounds are apparently not suitable for the preparation of halo derivatives such as $[(OC)_4FeGeX_2]$ ($X = Cl, Br, I$); the compounds reported here, together with the previously reported $[(OC)_4FeSiCl_2]_2$,[22] are the first such halogen derivatives to be described.

Compounds of type III were also prepared in this work, as reported for the iodo derivative, by allowing compounds of type II to react with iron pentacarbonyl at higher temperatures



$$(OC)_4Fe(GeI_3)_2 + 2Fe(CO)_5 \longrightarrow [(OC)_4FeGeI_2]_2 + FeI_2 + 6CO$$

In this particular case, it was convenient to start with $(OC)_4IFeGeI_3$ (a type I compound) which was shown to produce $(OC)_4Fe(GeI_3)_2$ in the first stage of the reaction. *The particular significance of this reaction is that it*

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[14] The high yields of iron(II) halides in these reactions make it unnecessary to postulate phosgene as one of the products, as is usually done in the formally analogous reaction of $Fe(CO)_5$ with $HgCl_2$.[3] This apparent difference between SnX_4 and HgX_2 systems requires further examination.

[15] W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968); G. W. Parshall, *J. Am. Chem. Soc.*, **88**, 704 (1966).

[16] O. Kahn and M. Bigorgne, *J. Organometal. Chem.* (Amsterdam), **10**, 137 (1967).

[17] J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *Chem. Commun.*, 965 (1967).

[18] W. Hieber and R. Breu, *Ber.*, **90**, 1270 (1957).

[19] F. Hein and H. Pobloth, *Z. Anorg. Allgem. Chem.*, **248**, 84 (1941).

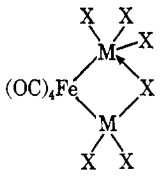
[20] R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 3833 (1960).

[21] O. Kahn and M. Bigorgne, *Compt. Rend.*, **262**, 906 (1966).

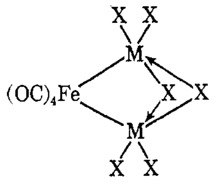
[22] W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2772 (1967).

appears to represent a ring-closure process. The mechanism by which this occurs is a matter for speculation at the present time. Investigations of the scope of this process are currently under way in this laboratory.

The order of decreasing solubility in nonpolar organic solvents of the compounds reported here is *cis*-$(OC)_4Fe(MX_3)_2$ > *trans*-$(OC)_4Fe(MX_3)_2 \sim (OC)_4XFeMX_3 \gg [(OC)_4FeMX_2]_2$. The greater solubility of *cis*-type I than that of the *trans* form is surprising. A possible explanation may be found in an intramolecular coordination process suggested on other grounds for the compound π-$C_5H_5(CO)Co(SnCl_3)(SnRCl_2)$.[23] This process, which might be formulated as IV or V, would reduce polarity and the number of "free inorganic groups" of the molecule. X-Ray crystallographic investigations have recently revealed the presence of such an intramolecular tin–halogen coordination in quite a different molecule,[24] lending support to the suggestions made here. Such an interaction would also tend to stabilize the *cis* isomer of these molecules.

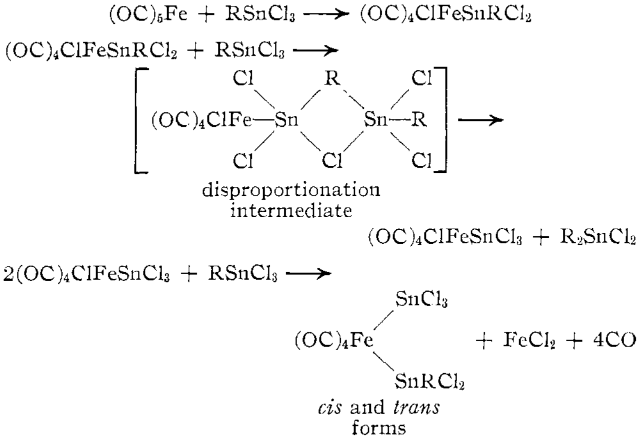


IV



V

The unusual reaction of $C_6H_5SnCl_3$ with $Fe(CO)_5$ to produce *trans*-$(OC)_4Fe(SnCl_3)_2$ requires comment, and the intramolecular coordination process just discussed is thought to play some part in the reaction. The reaction sequence suggested is



$$(OC)_5Fe + RSnCl_3 \longrightarrow (OC)_4ClFeSnRCl_2$$

$$(OC)_4ClFeSnRCl_2 + RSnCl_3 \longrightarrow$$

disproportionation intermediate

$$\longrightarrow (OC)_4ClFeSnCl_3 + R_2SnCl_2$$

$$2(OC)_4ClFeSnCl_3 + RSnCl_3 \longrightarrow$$

$$+ FeCl_2 + 4CO$$

cis and *trans* forms

In the *cis* isomer of the "mixed" product, intramolecular coordination as in IV or V would prevent further disproportionation; this mixed *cis* isomer was not isolated although a set of infrared bands was observed that could reasonably be attributed to it.[25] In *trans*-$(OC)_4Fe(SnCl_3)(SnRCl_2)$, disproportionation is not precluded and proceeds to form the observed product.

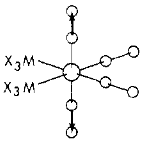
The reaction of iron pentacarbonyl with $RSnI_3$ ($R = C_6H_5$, CH_3; the methyl derivative could not be obtained crystalline nor satisfactorily characterized and is not reported in the tables) afforded only $(OC)_4IFeSnRI_2$. Disproportionation to the triiodotin compound does not occur, owing presumably to the lower acceptor properties of the $-SnRI_2$ group.

Reaction of the substituted carbonyl $(C_6H_5)_3PFe(CO)_4$ with tin(IV) halides is straightforward, leading to the stable derivatives $(C_6H_5)_3P(OC)_3XFeSnX_3$. Unexpectedly, the same products were obtained starting with the bis(triphenylphosphine) complex

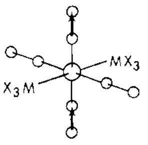
$$L_2Fe(CO)_3 + SnX_4 \longrightarrow L(OC)_3XFeSnX_3 + L \quad [L = (C_6H_5)_3P]$$

In this case, triphenylphosphine is eliminated, marking the first time a group other than carbon monoxide has been eliminated in a reaction of this type. Reaction of the phosphine complexes with $GeCl_4$ and $GeBr_4$ afforded a mixture of two very unstable compounds (presumably $L(OC)_3XFeGeX_3$ and $L(OC)_3Fe(GeX_3)_2$) which could not be separated by the usual methods.

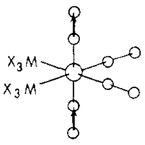
Infrared Spectra.—If C_{2v} symmetry is assumed for the *cis*-$(OC)_4Fe(MX_3)_2$ molecules, four infrared-active carbonyl stretching fundamentals are predicted ($2A_1 + B_1 + B_2$). Four well-resolved bands are observed in the spectra of these molecules, as shown in Table II and Figure 1. The medium-intensity band at highest frequency can be taken with some assurance[26,27] to be the symmetric stretching vibration of the pair of carbonyl groups *trans* to one another; this is designated $A_1^{(2)}$, and is shown crudely in VI. The relative positions and intensities of the other three modes cannot be so readily predicted, and none of the six possible assignments that result from permuting the three remaining modes over the three observed bands can be ruled out *a priori.*



VI($A_1^{(2)}$)



VII(E_u)



VIII(B_1)

The availability of the corresponding *trans* isomer in two cases may permit some reduction in the number of possible assignments, however. A single strong band is observed for the *trans*-$(OC)_4Fe(MX_3)_2$ compounds, which must be the E_u fundamental.[28] If one compares the conventional representation of the E_u mode (VII), with that of the B_1 mode of the *cis* isomer (VIII), the qualitative similarity of the two modes is

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[23] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 523 (1968).

[24] F. P. Boer, J. J. Flynn, H. H. Freedman, S. V. McKinley, and V. R. Sandel, *J. Am. Chem. Soc.*, **89**, 5068 (1967). Note Added in Proof.—Halogen bridges of the type postulated here have been found in a very recent X-ray structure determination on bipy$(OC)_3ClMoSnCH_3Cl_2$; *cf.* M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *ibid.*, **90**, 2189 (1968).

[25] In a very closely related case, the mixed derivative $(\pi$-$C_5H_5)(OC)Co(SnCl_3)(SnRCl_2)$ has been isolated, and its failure to undergo further disproportionation has been rationalized in similar terms.[23]

[26] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[27] L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

[28] In spectra of the *trans* derivatives, two very weak bands are observed at higher frequencies than the main band. These could be due to A_{1g} and B_{1g} fundamentals, which gain some intensity because the true molecular symmetry is less than C_{4v} owing to the threefold axis of the MX_3 groups. It seems more likely that they stem from a very small amount of the *cis* isomer, however.

TABLE II

INFRARED CARBONYL STRETCHING FREQUENCIES[a]

Compound	ν, cm^{-1}			
$(OC)_4IFeGeI_3$	2125 s	2088 s	2078 vs	2064 s
$(OC)_4ClFeSnCl_3$	2141 m	2106 m	2092 vs	2070 s
$(OC)_4BrFeSnBr_3$	2133 s	2098 ms	2084 vs	2066 svs
$(OC)_4IFeSnI_3$	2120 svs	2085 s	2071 vs	2060 s
$(OC)_4IFeSnC_6H_5I_2$	2114 svs	2075 s	2057 vs	2051 s
cis-$(OC)_4Fe(GeCl_3)_2$	2135 m	2095 m	2089 vs	2082 s
trans-$(OC)_4Fe(GeCl_3)_2$[b]			2088 vs	
trans-$(OC)_4Fe(GeBr_3)_2$[c]			2084 vs	
trans-$(OC)_4Fe(GeI_3)_2$[d]			2076 vs	
cis-$(OC)_4Fe(SnCl_3)_2$	2127 m	2087 m	2080 vs	2071 s
cis-$(OC)_4Fe(SnCl_3)_2(CH_2Cl_2)$	2135 m	2096 m, sh	2085 vs	2078 s, sh
trans-$(OC)_4Fe(SnCl_3)_2(CH_2Cl_2)$			2084 vs	
cis-$(OC)_4Fe(SnBr_3)_2$	2120 ms	2082 m	2074 vs	2066 s
$[(OC)_4FeGeCl_2]_2$	2094 s	2059 m, sh	2055 s, sh	2052 vs
$[(OC)_4FeGeBr_2]_2$	2093 vs	2058 m, sh	2054 s, sh	2052 vs
$[(OC)_4FeGeI_2]_2$	2090 vs	2054 m, sh	2051 s	2048 vs
$(C_6H_5)_3P(OC)_3ClFeSnCl_3(CHCl_3)$	2102 mw	2054 vs	2035 s	
$(C_6H_5)_3P(OC)_3IFeSnI_3(CHCl_3)$	2083 m	2034 vs	2024 s, sh	

[a] In cyclohexane solution except as noted; values in cm^{-1}. Intensity designations: w, weak; m, medium; s, strong; v, very; sh, shoulder; svs indicates an intensity between strong and very strong. [b] $C^{13}O$ band at 2052 cm^{-1} vw. [c] $C^{13}O$ band at 2048 cm^{-1} vw. [d] $C^{13}O$ band at 2039 cm^{-1} vw.

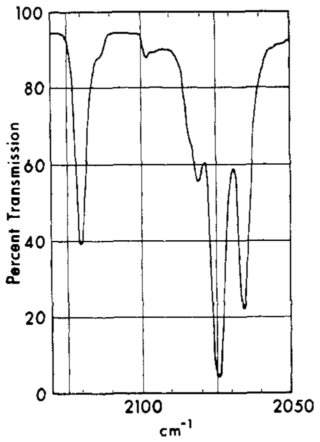

Figure 1.—Carbonyl stretching region of the infrared spectrum of *cis*-$(OC)_4Fe(SnBr_3)_2$ in cyclohexane solution.

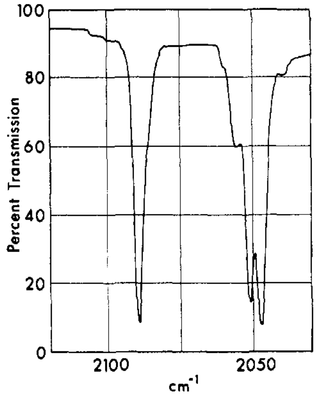

Figure 2.—Carbonyl stretching region of the infrared spectrum of $[(OC)_4FeGeI_2]_2$ in cyclohexane solution.

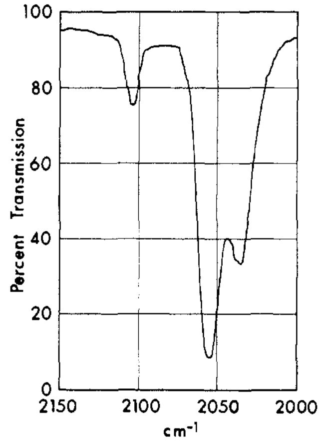

Figure 3.—Carbonyl stretching region of the infrared spectrum of $(C_6H_5)_3P(OC)_3ClFeSnCl_3$ in chloroform solution.

apparent.[29] One of the bands in the *cis* isomer should compare closely in position with the strong band of the analogous *trans* isomer. This is exactly what has been observed for *cis*- and *trans*-$[(OC)_4Fe(GeCl_3)_2]$ (2089 *vs.* 2088 cm^{-1}) and *cis*- and *trans*- $[(OC)_4Fe(SnCl_3)_2]$ (2085 *vs.* 2084 cm^{-1}). If this identification is correct, the number of reasonable assignments is reduced to two; only the $A_1^{(1)}$ and B_2 modes are then in doubt.

Four bands are expected for the compounds *cis*-$(OC)_4XFeMX_3$ of C_s symmetry. Four well-resolved bands are observed in all cases. An interesting feature is the great intensity of the highest frequency band; it is in some cases only slightly less intense than the most intense band of the spectrum, an unexpected feature for a band that presumably arises from the "almost forbidden" A′ mode similar to VI.

Four carbonyl stretching bands are also expected for the dimeric germanium–iron compounds of presumed molecular symmetry D_{2h}. In the chloro and bromo compounds, two of the bands are observed only as shoulders, while the iodo derivative (Figure 2) shows four resolved bands.

An examination of the infrared spectrum permits

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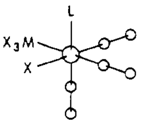
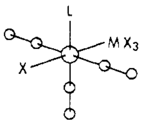
(29) Algebraically, a similar conclusion may be reached by examining the secular equations for the E_u and B_1 modes, which are,[25] respectively, $\lambda = \mu(k - k_t)$ and $\lambda = \mu(k_2 - k_t)$. If substituent effects are additive on the carbonyls in question, the k and k_2 should be the same.

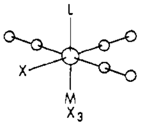
some tentative conclusions about the nature of the triphenylphosphine adducts $(OC)_3LXFeMX_3$. Four isomers are possible (IX–XII), each with three infrared-active carbonyl stretching modes. Three bands are seen in the compounds reported here (Figure 3).



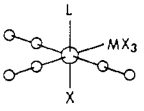
IX



X



XI



XII

Intensity considerations similar to those previously used in a related instance[30] lead us to expect one strong band and two bands of approximately equal intensity for isomer IX; in isomers X–XII, the mutually *trans* arrangement of two carbonyls should give rise to a weak A′ mode (also at highest frequency) and a very strong A″ mode, while the third carbonyl group should produce a strong A′ mode. The observed intensities (Figure 3) certainly favor X, XI, or XII over IX but do not make possible an unambiguous choice. On other grounds, we tend to prefer XI or XII, with a *cis* placement of the X and SnX_3 ligands. Thus, these ligands are invariably *cis* in the $(OC)_4XFeSnX_3$ derivatives, and the fact that *trans*-$L_2Fe(CO)_3$ gives the same product as $LFe(CO)_4$ would tend to favor an isomer in which one of the new ligands (X or MX_3) is *trans* to the remaining L.

Acknowledgment.—We thank the National Research Council of Canada for financial support.

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[30] R. C. Taylor and W. D. Horrocks, Jr., *Inorg. Chem.*, **3**, 584 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Organosulfur Derivatives of the Metal Carbonyls. XI. Some *cis*-1,2-Ethylenedithiolate Derivatives of Manganese Carbonyl and Related Compounds[1,2]

BY R. B. KING[3] AND C. A. EGGERS[4]

Received November 1, 1967

Reaction between $Mn(CO)_5Br$ and disodium *cis*-1,2-ethylenedithiolate in a mixture of acetone and methanol gives the deep red volatile complex $H_2C_2S_2Mn_2(CO)_6$. This compound reacts with various Lewis base ligands in inert solvents to form products of two types: (a) dark red-brown substitution products of the type $H_2C_2S_2Mn_2(CO)_4L_2$ ($L = (C_6H_5)_3P$ or $[(CH_3)_2N]_3P$); (b) yellow addition products of the type $H_2C_2S_2Mn_2(CO)_6L$ ($L = (C_6H_5)_3P$, $0.5(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, or NH_3). Reaction between $Fe_2(CO)_9$ and disodium *cis*-1,2-ethylenedithiolate in methanol solution results in hydrogenation of the carbon–carbon double bond giving the saturated derivative $C_2H_4S_2Fe_2(CO)_6$ previously obtained from $Fe(CO)_5$ and 1,2-ethanedithiol.

Introduction

The previous paper of this series[2] discusses reactions between cyclopentadienylmetal halides and disodium *cis*-1,2-ethylenedithiolate. Reactions between metal carbonyl halides and disodium *cis*-1,2-ethylenedithiolate have also been investigated. This paper describes the reaction between disodium ethylenedithiolate[5] and bromopentacarbonylmanganese, $Mn(CO)_5Br$. This reaction was found to give a novel type of organosulfur derivative of manganese carbonyl, $H_2C_2S_2Mn_2(CO)_6$. This paper also describes some unusual reactions of this manganese complex.

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations were carried out with a Mechrolab vapor pressure osmometer in benzene solution by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were taken in either potassium bromide pellets or appropriate organic solvents and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton nmr spectra were taken in chloroform-*d* or acetone solutions and recorded on either a Varian A-60 or a Varian HA-100 spectrometer. Melting and decomposition points were determined in capillaries and are uncorrected.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated vessels.

Reagents.—Sodium ethylenedithiolate, first reported by Schroth and Peschel,[6] was obtained by the procedure described in the previous paper.[2] Bromopentacarbonylmanganese was obtained from decacarbonyldimanganese[7] by the usual bromination procedure.[8] The phosphorus derivatives $[(CH_3)_2N]_3P$

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[1] Portions of this work were presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] Part X: R. B. King and C. A. Eggers, *Inorg. Chem.*, **7**, 340 (1968).

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[4] Postdoctoral Research Associate supported by the Air Force Office of Scientific Research, Jan–Oct 1967.

[5] For brevity the *cis*-1,2-ethylenedithiolate dianion will be hereafter designated simply as "ethylenedithiolate."

[6] W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).

[7] For a convenient preparation of decacarbonyldimanganese see R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometal. Chem.* (Amsterdam), **11**, 641 (1968).

[8] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959); R. B. King, *Organometal. Syn.*, **1**, 174 (1965).