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FORMATION OF HYDRIDOIRON TETRACARBONYL ANION FROM IRON PENTACARBONYL UNDER CARBON MONOXIDE PRESSURE

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SUMMARY

Formation of hydridoiron carbonyl anions in methanol from $Fe(CO)_5$ in the presence of a tertiary amine and water or hydrogen under carbon monoxide pressure was investigated. Under carbon monoxide pressure above ca. 15 kg/cm^2, the most stable hydrido species from $Fe(CO)_5$ proved to be the hydridoiron tetracarbonyl anion, $HFe(CO)_4^-$ (I). The reaction below 150°C in the presence of water proceeded rapidly to yield a mixture consisting of I and $Fe(CO)_5$, in which the content of I (27 mol% at 50°C) decreased with increase of the reaction temperature and fell to nearly zero at 150°C. At 170°C, hydrogen was found to become an effective hydrogen source to form I, and nearly complete conversion of $Fe(CO)_5$ could be realized within 10 h with mixtures of hydrogen and carbon monoxide of the ratio between 0.5 and 5. The stability of I under the present conditions and the roles of tertiary amines, carbon monoxide and two hydrogen sources in the reaction are discussed.

INTRODUCTION

Hydroxymethylation of olefins in the presence of $Fe(CO)_5$, a base (preferably a tertiary amine) and water under carbon monoxide pressure was first reported by Reppe and Vetter[1] in 1953, and they suggested that the reaction was catalyzed by a hydridoiron carbonyl produced by the well known base reaction of $Fe(CO)_5$. After some discussions[2] on the structure of the catalytic species, the trinuclear anion salt, $[HFe_3(CO)_{11}]^-H\overset{+}{N}R_3$ (II), postulated by Kutepow and Kindler[3] in the synthesis of butanol from propylene under moderate reaction conditions*, has been generally accepted as the active catalytic species in the reaction. The proposal seems to be in line with the available information[2b,4] that the trinuclear anion salt is produced in the reaction of $Fe(CO)_5$ with tertiary amine in aqueous alcohol (Eq. 1).

$$3\ Fe(CO)_5 + NR_3 + 2\ H_2O \rightarrow [HFe_3(CO)_{11}]^-H\overset{+}{N}R_3 + 2CO_2 + 2CO + H_2 \quad (1)$$

However, in our series of studies on the hydroxymethylation of higher olefins

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* They noted that higher olefins required a higher reaction temperature and higher pressure to effect hydroxymethylation.

and related compounds[5] at 150–175°C, we have been repeatedly confronted with the following observations that suggest that the mononuclear hydrido anion, $HFe(CO)_4^-$ (I), is the active catalyst under our reaction conditions. An aliquot taken from the reaction vessel during the reaction shows a pale yellowish color and an infrared absorption at 1880 cm^{-1} of considerable intensity, but in a short time under atmospheric pressure the color turns pink and the absorption is replaced by one at 1995 cm^{-1}, both indicative of conversion of I to II.

The reaction of iron carbonyls with Lewis bases and the behavior of the resultant mono- and di-negative carbonylferrate anions in protic solvents have been extensively investigated by Hieber[6] and other investigators[2b]. In addition to the reaction with aqueous and alcoholic alkaline solution, considerable attention has been devoted to the reaction of various amines with iron carbonyls to form carbonylferrate anions, in which polynuclear anions are the most frequently encountered products. However, most of the previous studies seem to be confined to reactions at ordinary pressure and little has been published on the behavior of $Fe(CO)_5$ in these reactions under carbon monoxide pressure.

This paper deals with the formation of mononuclear hydrido anion (I) in the reaction of $Fe(CO)_5$ or the trinuclear anion salt (II) with water or hydrogen in the presence of tertiary amine under carbon monoxide pressure and presents an insight into the behavior of the iron carbonyl species under conditions comparable to those used in the hydroxymethylation of olefins. This work is not concerned directly with the active species in the hydroxymethylation, but forms a basis of mechanistic discussion for such a catalytic process.

RESULTS AND DISCUSSION

A mixture of $Fe(CO)_5$, trimethylamine and water in 70 ml of methanol was heated at 100°C for 3 h under an initial carbon monoxide pressure of 100 kg/cm^2. An aliquot taken into a pressure glass sampler from the reaction vessel was pale yellow and its infrared spectrum showed a new band at 1880 cm^{-1}, along with that for $Fe(CO)_5$ at 1995 cm^{-1} (Fig. 1a). The reported data[7,8] in Table 1 and the comparison

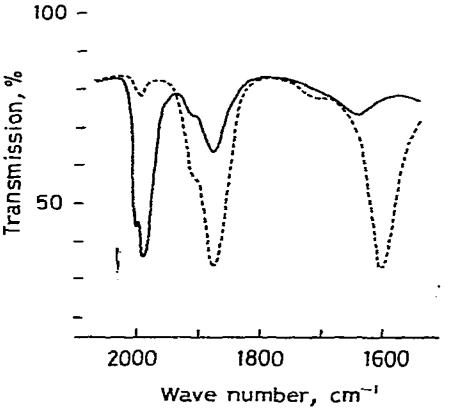

Fig. 1. Infrared spectra of reaction mixtures, ——— $Fe(CO)_5$–$N(CH_3)_3$–H_2O system at 50°C, ------- $Fe(CO)_5$–$N(CH_3)_3$–H_2 system at 170°C.

TABLE 1

CHARACTERISTIC CARBONYL ABSORPTIONS OF THE RELATED IRON CARBONYL ANIONS

Species	*Carbonyl absorptions in methanol* (cm^{-1})
$Fe(CO)_4^{2-}$	(1730s)[a], (1761s,br)[b]
$HFe(CO)_4^-$	2000w, 1915m, 1880s (2008w, 1914m, 1880s)[a], (2008w, 1910sh, 1848s,br)[b]
$HFe_2(CO)_8^-$	(1998w, 1980m, 1930s, 1906m, 1873w)[a] (2068w, 2045w, 1997m, 1923m, 1860s, 1778m, 1750s)[b]
$Fe_2(CO)_8^{2-}$	(1916m, 1866s, 1842w)[a], (1920s,br, 1852s,br)[b]
$HFe_3(CO)_{11}^-$	2070vw, 1995s, 1978m, 1950w (2070vw, 2004s, 1980m, 1950w)[a], (2068vw, 2009s, 1980s, 1957m, 1748w)[b]
$Fe(CO)_5$	2020s, 1995s

[a] Ref. 7, in DMF solution.

[b] Ref. 8, in solid state (Nujol mull) except for $HFe_3(CO)_{11}^-$ in methanol solution. Absorptions for two tetrairon carbonyl species are also presented in the paper.

with the spectra of $K^+HFe(CO)_4^-$ in methanol both in the 2000 cm^{-1} region and between 550 and 700 cm^{-1}[7] (699s*, 614s, and 586w cm^{-1} for the reaction mixture and 699s*, 619s, and 586w cm^{-1} for a methanolic $K^+HFe(CO)_4^-$) strongly suggested that the new absorption could be attributable to the formation of I. The absence of absorptions at 1930 and 1978 cm^{-1} for binuclear and trinuclear hydrido anions, as well as those for dinegative carbonylferrates in the spectrum excluded the presence of these species. The formation of the $Ni(o\text{-Phen})_3[HFe(CO)_4^-]_2$ adduct[7,9] and the pale yellow color of the sample at the time of withdrawal afforded additional evidence for the conclusion that the stable hydrido species under these conditions is the mononuclear hydrido anion (I), because the trinuclear hydridoiron carbonyl anion (II) can easily be distinguished by its characteristic deep-red color even in a low concentration of 0.5% in methanol. A similar treatment of triethylammonium salt of II in place of $Fe(CO)_5$ at 100°C afforded nearly the same result and showed that II was completely converted to a mixture of I and $Fe(CO)_5$ under these conditions.

Determination of I

After some preliminary examination for quantitative estimation of I and $Fe(CO)_5$ in the reaction mixture, infrared measurement in the 2000 cm^{-1} region seemed to be the most promising analytical technique. However, it was soon found that dilution of the sample with 20 to 30 times its volume of methanol to a concentration appropriate for use in a sealed cell with a CaF_2 window of 0.05 mm thickness led to the decomposition of I to II even when the dilution was carried out under a carbon monoxide pressure of 10 kg/cm^2. This fact also excluded the feasibility of using

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* This absorption appeared as a shoulder in the strong solvent absorption at 725 cm^{-1}.

ordinary ultraviolet and visible light. An additional problem raised in the analysis was the relatively facile transformation of I to II under atmospheric pressure even under nitrogen or carbon monoxide. The yellowish color of the initial sample gradually turned red after 1 h when the carbon monoxide pressure in the sampler was released. One of the major factors for the conversion seemed to be the partial pressure of carbon monoxide, since I formed under pressure was found to readily change into II by heating at 70°C under atmospheric carbon monoxide. Another important factor would be the basicity of the medium. This behavior of the tertiary amine salt of I in weakly basic solution seems to contrast with that of the alkali metal salt prepared in caustic solution, which was much less prone to decompose.

Nevertheless, $Fe(CO)_5$ and I were found to be the only stable species existing under the present reaction conditions up to a temperature of 175°C, and did not change to any other type of iron compound, except for the cases specified. Taking account of these facts, infrared spectra of reaction mixtures were measured in the range between 2500 and 1600 cm^{-1} as fast as possible using a demountable cell with NaCl windows, and the content of I was calculated from the relative intensity of the absorptions at 1995 and 1880 cm^{-1} for $Fe(CO)_5$ and I, respectively, using the absorption coefficients determined separately for each species. Gravimetric estimation of I by formation of $Ni(o\text{-}Phen)_3[HFe(CO)_4^-]_2$ proved to be in good agreement with the results obtained by the infrared technique within $\pm 2\%$ for the samples obtained with either water or hydrogen as a hydrogen source.

Formation of I in the system of $Fe(CO)_5$–NR_3–H_2O–CO

The time and temperature dependences of the molar content of I in the reaction mixture are illustrated in Figs. 2 and 3. The amounts of water and tertiary

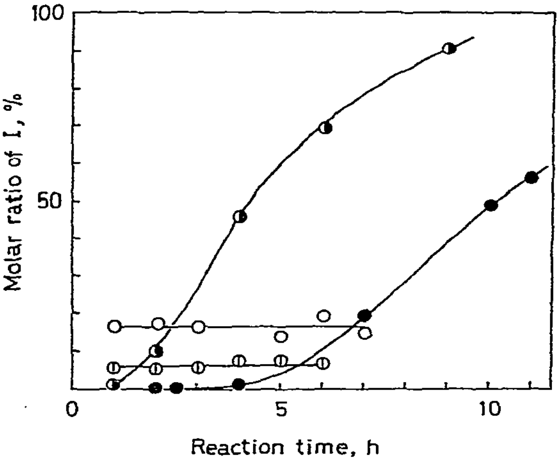


Fig. 2. Time and temperature dependence of the formation of I. –○– $N(CH_3)_3$, 100°C, p(CO) 15 kg/cm², –⦶– $N(CH_3)_3$, 125°C, p(CO) 50 kg/cm², –◑– $N(CH_3)_3$, 175°C, p(CO) 100 kg/cm², –●– $N(C_2H_5)_3$, 175°C, p(CO) 100 kg/cm².

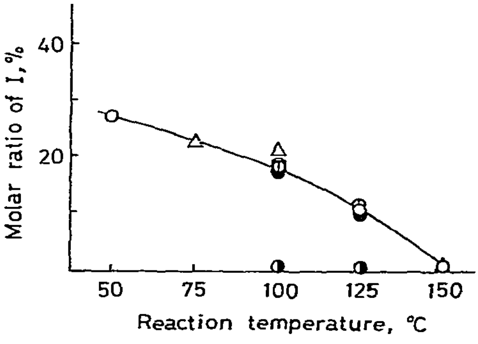


Fig. 3. Temperature dependence of the formation of I in the presence of water. Trimethylamine (p(CO), kg/cm²): △ (100), ○ (50), □ (15). ● *N*-ethylpiperidine (50). ⦶ *N,N*-diethylcyclohexylamine (50). ◑ *N*-ethylmorpholine (50).

amine were arbitrarily chosen to match those which proved to be optimal in the hydroxymethylation of higher olefins at 170 to 175°C. Below 150°C, I formed rapidly and an equilibrium mixture consisting of $Fe(CO)_5$ and a relatively small amount of I was obtained within 1 h. The content of I decreased with increasing reaction temperature and at 150°C $Fe(CO)_5$ became the only stable species in the reaction mixture. The equilibrium nature of the reaction was confirmed by the fact that the content of I returned to a previous value within 1 h on lowering the reaction temperature. Other tertiary amines of comparable basicity but of more bulkiness gave similar results, but less basic *N*-ethylmorpholine proved to be less effective in the formation of I as shown in Fig. 2.

At 170°C, the formation of I again took place at a rather slower rate with a small induction period, and most of the $Fe(CO)_5$ was converted into I. With triethylamine the reaction proceeded in a similar manner but with a longer induction period. A notable feature of this reaction at 170°C was that the formation of I was preceded by a pressure increase of about 20 kg/cm^2 in the initial induction stage, which was shown to be due to the formation of hydrogen and carbon dioxide and thus attributable to catalytic decomposition of water by $Fe(CO)_5$ and a base (see below, Eqns. 2, 3 and 4). The periods for the pressure increase, 2 h with trimethylamine and ca. 5 h with triethylamine, seemed to be closely related to the induction period.

Formation of I in the system of $Fe(CO)_5$–NR_3–H_2–CO

The results in the preceding section strongly suggested that at 170°C, the hydrogen source for formation of I is replaced by molecular hydrogen rather than water itself, and are in good accordance with the previous observations[5] that the hydroxymethylation of higher olefins was very sluggish below 160°C, but proceeded at reasonable rates after the initial pressure increase of about 20–25 kg/cm^2 ceased at 170°C. In order to determine the role of hydrogen in the formation of I, a mixture of $Fe(CO)_5$ and trimethylamine in 70 ml of anhydrous methanol was allowed to react at 170°C with mixtures of various ratios of carbon monoxide and hydrogen under an initial total pressure of 120 kg/cm^2. For the H_2/CO ratio range between 0.5 and 5, the time profiles for the formation of I were nearly the same and all $Fe(CO)_5$ was converted into I after 6 to 7 h. A rate depressing effect of other bulkier tertiary amines similar to that described in the previous section was observed in this case. Further increase or decrease in H_2/CO ratio seemed to affect mainly the initial rate of formation of I as shown in Fig. 4. Methanol might serve as the hydrogen source in the formation of I in the absence of hydrogen, although it seems to be a much poorer source than water. When only hydrogen was used in the reaction, the reaction mixture in the initial stage was found to consist of $Fe(CO)_5$ and a small amount of II. After 5 h, I began to form slowly at the expense of II, and after 10 h, the conversion was complete. A considerable amount of metallic iron found in the reaction vessel after the reaction indicated that a part of $Fe(CO)_5$ had decomposed and the resulting carbon monoxide had been utilized to convert II into I.

The role of water and hydrogen in the formation of I.

The apparent equilibrium formation of I from $Fe(CO)_5$ and its temperature dependence in the presence of water below 150°C is noteworthy in view of the fact that nearly all the $Fe(CO)_5$ can be converted to I in the presence of hydrogen at 170°C.

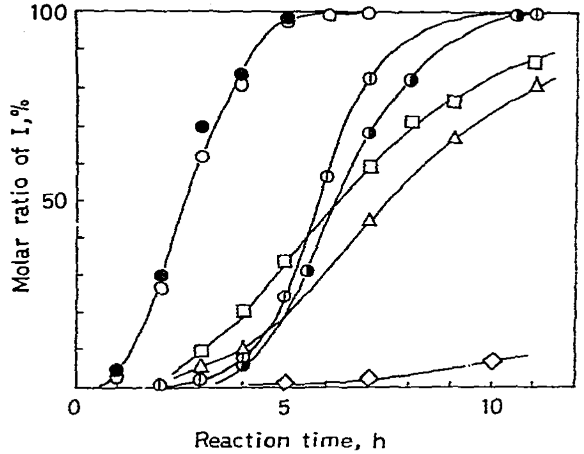


Fig. 4. Time dependence of the formation of I in the presence of hydrogen at 170°C. Trimethylamine: -○- ($H_2/CO=4$), -●- ($H_2/CO=1$), -◐- ($H_2/CO=1/23$), -◑- (CO only). Triethylamine: -△- ($H_2/CO=2$); *N*-ethylpiperidine: —□—($H_2/CO=2$); *N,N*-diethylcyclohexylamine: —◇—($H_2/CO=2$).

The formation of I in aqueous basic solution can be explained by the well known base reaction[10] (Eqns. 2 and 3).

$$NR_3+H_2O \rightleftarrows HN^+R_3+OH^- \qquad (2)$$

$$Fe(CO)_5+OH^- \rightarrow HFe(CO)_4^- +CO_2 \qquad (3)$$

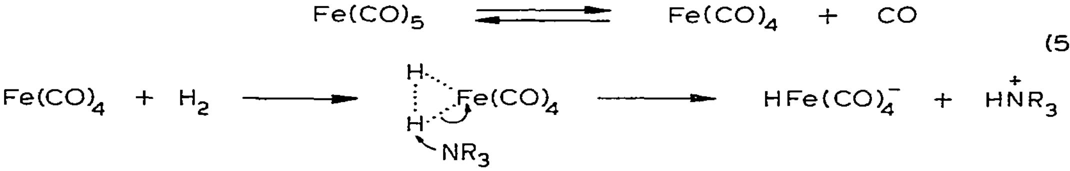
Hydroxide ion concentration, which is known to affect the interconversion of carbonylferrate species under atmospheric conditions[9,11], can be reasonably assumed to be one of the major factors determining the present equilibrium between I and $Fe(CO)_5$. Weak basicity of tertiary amines and a buffer action of trialkylammonium salts would limit the hydroxide ion concentration to a low value and thus prevent the complete formation of I. This explanation is consistent with the observed effects of bulkiness and basicity of tertiary amines on the equilibrium. It is also supported by the fact that $Fe(CO)_5$ in methanolic potassium hydroxide reacts completely to give I (potassium salt) in a solution of sufficiently high concentration of the base, but remained partially unreacted in a solution of much lower base concentration.

Although a pressure increase in the reaction of $Fe(CO)_5$ with water and a base under carbon monoxide pressure became evident at temperatures above 160°C, formation of hydrogen in the gas phase was found to take place at 100°C to a small degree and appreciably increased at 150°C. This observation seems to be closely related to the temperature dependence of the equilibrium and can be accounted for by the following reaction sequence which constitutes conversion of I to $Fe(CO)_5$.

$$\begin{aligned} &HFe(CO)_4^- +HN^+R_3 \rightarrow H_2Fe(CO)_4+NR_3 \\ &H_2Fe(CO)_4 \rightarrow Fe(CO)_4+H_2 \qquad (4) \\ &Fe(CO)_4+CO \rightarrow Fe(CO)_5 \end{aligned}$$

Thus, the observed equilibrium can be explained as a result of the combination of the base reaction of $Fe(CO)_5$ controlled by a low hydroxide ion concentration and the decomposition of I which is accelerated with increasing reaction temperature.

At temperatures lower than 150°C, $Fe(CO)_5$ in methanolic tertiary amine solution did not react with a mixture of hydrogen and carbon monoxide. However, hydrogen, alone or formed by the decomposition of water, was found to become an effective hydrogen source to form I at 170°C. This would imply that the pathway of the formation of I sharply changes around 160°C. It has been suggested[12] that the relatively inert saturated d^8 complex, $Fe(CO)_5$, becomes a hydrogenation catalyst[13] only at temperatures above 160°C because such temperatures are required to extrude carbon monoxide and form the unsaturated intermediate, $Fe(CO)_4$, which then can undergo oxidative addition with hydrogen. Although the previous papers were not concerned with the formation of I in the presence of a base, the present results can be explained by a scheme involving the oxidative addition of hydrogen. Proton abstraction by a tertiary amine concerted with the incorporation of hydrogen into $Fe(CO)_4$ could be reasonably accepted as a major factor to afford I in view of the retarding effect of bulkier tertiary amines (Eqn. 5).



(5)

The concentration of I in the resulting mixtures is not changed by lowering the temperature to 100°C, or by replacement of the original atmosphere (H_2 and CO) by carbon monoxide, provided that enough carbon monoxide pressure is maintained. Thus, the partial pressure of carbon monoxide above ca. 15 kg/cm² would be the principal requirement for the stable existence of I formed at 170°C, since a lower carbon monoxide partial pressure favors the formation of II from I (Eqn. 6).

$$3\mathrm{I} \underset{H_2 \text{ or } H_2O}{\overset{-H_2}{\rightleftharpoons}} \mathrm{II}+\mathrm{CO} \qquad (6)$$

It should be noted that although hydridoiron carbonyl formed from $Fe(CO)_5$ in caustic solution and related species have been used in stoichiometric amounts for the reduction of α, β-unsaturated carbonyl compounds[14], Schiff bases[15] and nitro compounds[16], the equilibrium nature of the formation of I under the present conditions affords the possibility of a catalytic reduction of these compounds[2a]. Studies of the chemical behavior of I thus formed under a variety of conditions are in progress.

EXPERIMENTAL

Iron pentacarbonyl was a commercial product (Strem Chemicals, U.S.A.) and distilled prior to use. The triethylamine salt of II, $HFe_3(CO)_{11}^-$ $HN^+(C_2H_5)_3$, was prepared by the standard method[4]. Methanol and tertiary amines were dried by treatment with magnesium and two distillations over potassium hydroxide, respectively.

Molar absorption coefficients.

Methanol solutions of $Fe(CO)_5$ and the freshly prepared salt of II in concentrations that would give absorbances between 0.05 and 0.4 were prepared and their molar absorption coefficients of the bands at 1995 and 1880 cm^{-1} were determined by the standard method using a 0.05 mm CaF_2 sealed cell. Calculated amounts of $Fe(CO)_5$ were allowed to react with methanol solutions containing three molar equivalents of potassium hydroxide at room temperature under nitrogen, and the resulting $K^+HFe(CO)_4^-$ solutions of approximate absorbances between 0.15 and 0.4 were directly used for the determination of the absorption coefficient of I. As described in the previous section, a portion of $Fe(CO)_5$ remained unreacted in dilute solutions lower than 0.16×10^{-2} $mol \cdot l^{-1}$. The amount of $Fe(CO)_5$ remaining unchanged was taken into account in the calculation of the absorption coefficient of I. The following values were used in the infrared analysis of the reaction mixtures.

$Fe(CO)_5$	(1995 cm^{-1})	3.66×10^4 $l \cdot mol^{-1} \cdot cm^{-1}$
$HFe(CO)_4^-$	(1880 cm^{-1})	3.54×10^4 $l \cdot mol^{-1} \cdot cm^{-1}$
$HFe_3(CO)_{11}^-$	(1995 cm^{-1})	7.20×10^4 $l \cdot mol^{-1} \cdot cm^{-1}$

An attempt to differentiate $Fe(CO)_5$ from II by using the band at 2020 cm^{-1} for $Fe(CO)_5$ gave unreproducible results. The difficulty in determining the concentration of II in the presence of $Fe(CO)_5$ or vice versa did not significantly disturb the present analytical technique, since II is easily discernible by its characteristic deep-red color and could not be detected in most of the reaction mixtures under the conditions of this study.

Reaction procedure

A mixture of $Fe(CO)_5$ (0.05 mol), trimethylamine (0.25 mol) and water (0.4 mol) in 70 ml methanol was placed in a 300 ml autoclave equipped with a glass liner, a 2 mm Teflon tubing that extended to the bottom of the vessel and a Teflon stirring rod. After air in the vessel was flushed out with carbon monoxide, the desired pressure of carbon monoxide (15 to 100 kg/cm^2) was introduced and the mixture was heated to the reaction temperature within 1 h. In another series, various mixtures of hydrogen and carbon monoxide (total pressure of 120 kg/cm^2) were used in place of water. An aliquot was taken into a pressure glass sampler from the reaction vessel under the reaction conditions at intervals, and the infrared spectrum of the sample was measured in the range of 2500–1600 cm^{-1} as fast as possible (within 5 min) using a demountable cell with NaCl windows. The concentration of I was calculated from the relative intensity of the absorbances at 1995 and 1880 cm^{-1}. The calculation was based on the assumption that the sum of the amounts (in molar base) of $Fe(CO)_5$ and I is equal to the initial amount of $Fe(CO)_5$ utilized. As a proof of the correctness of this assumption, gravimetrical determination of I by precipitation of $Ni(o\text{-Phen})_3[HFe(CO)_4^-]_2$ was performed according to the method described by Edgell *et al*[7,9]. Weights of the precipitate and those calculated from the infrared analysis for representative samples (5–10 g) were as follows.

$N(C_2H_5)_3$–H_2O series	Found(g)	Calcd.(g)	$N(C_2H_5)_3$–H_2 series	Found(g)	Calcd.(g)
at 50°C	1.64	1.67	at 170°C	2.63	2.67
at 125°C	1.84	1.85			

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