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## PREPARATION AND PROPERTIES OF METHYLIRON COMPLEXES WITH TERTIARY PHOSPHINE LIGANDS AND THEIR DECOMPOSITION PATHWAYS THROUGH THE FORMATION OF CARBENOID INTERMEDIATES

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### Summary

Reaction of  $\text{Fe}(\text{acac})_3$ ,  $\text{AlMe}_2(\text{OEt})$  and 1,2-bis(diphenylphosphino)ethane (dpe) gives a new dimethyliron complex,  $\text{Fe}(\text{CH}_3)_2(\text{dpe})_2$  (I). Complex I is unstable in solution and gives a methyliron complex containing an *ortho*-metallated ring,  $\text{Fe}(\text{CH}_3)(\text{dpe})\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}(o\text{-C}_6\text{H}_4)\}$  (II) with liberation of methane. On thermal decomposition and treatment with  $\text{CH}_2\text{Cl}_2$  compound I liberates ethylene, the formation of which suggests the intermediacy of carbenoid complexes. Reactions of I with  $\text{H}_2$  or  $\text{D}_2$ , carbon dioxide and phenylacetylene yield  $\text{FeH}_2(\text{dpe})_2 \cdot \text{C}_6\text{H}_6$  (IV) or  $\text{FeD}_2(\text{dpe})_2 \cdot \text{C}_6\text{H}_6$  (VI),  $\text{Fe}(\text{OOCCH}_3)(\text{CO}_2)_m(\text{py})_n$  (VII) and  $\text{FeH}(\text{C}\equiv\text{CPh})(\text{dpe})_2$  (VIII), respectively. I initiates the polymerization of acrylonitrile. Employment of  $\text{PPhMe}_2$  instead of dpe in the reaction of  $\text{Fe}(\text{acac})_3$  and  $\text{AlMe}_2(\text{OEt})$  gave a new methylbis(acetylacetonato)iron(III) complex,  $\text{Fe}(\text{CH}_3)(\text{acac})_2(\text{PPhMe}_2)$  (V). I and V react with carbon monoxide to yield acetone.

### Introduction

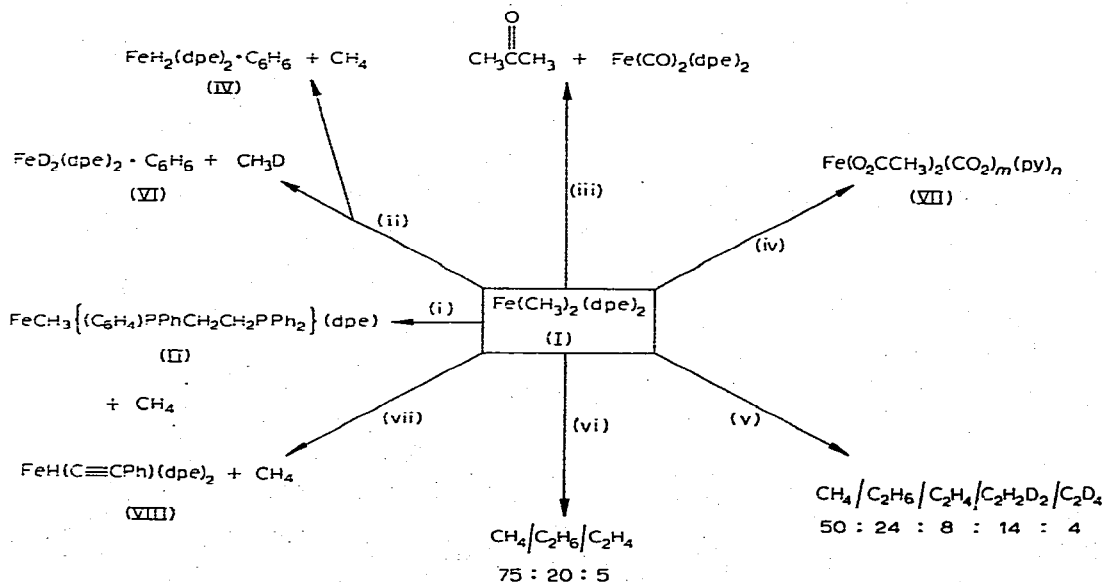
Many alkyliron complexes having cyclopentadienyl or carbonyl ligands are known [1], but much less is known about alkyliron complexes having other ligands. We have previously observed a pronounced stabilization effect of 2,2'-bipyridine [2] and a somewhat weaker stabilizing effect of triphenylphosphine [3,11b,c] and prepared various alkyltransition metal complexes having these ligands. A bidentate ditertiary phosphine ligand, 1,2-bis(diphenylphosphino)ethane (dpe) often serves as an excellent stabilizing ligand in alkyl- and hydrido-transition metal complexes and some stable alkyl-nickel [4,5] and -cobalt [6] and hydridocobalt [7] complexes have been isolated. We now describe the

preparation of dimethylbis[1,2-bis(diphenylphosphino)ethane]iron(II),  $\text{Fe}(\text{CH}_3)_2(\text{dpe})_2$  (I), by reaction of iron(III) acetylacetonate, dimethylaluminium monoethoxide and dpe. Hata et al. previously reported the preparation of an ethylene-coordinated iron(0) complex,  $\text{Fe}(\text{CH}_2=\text{CH}_2)(\text{dpe})_2$  by the reaction of  $\text{Fe}(\text{acac})_3$ ,  $\text{AlEt}_2(\text{OEt})$  and dpe [8]. The ethylene-iron complex is considered to be derived through formation of an ethyliron intermediate obtained by alkylation with  $\text{AlEt}_2(\text{OEt})$ . The dimethyliron complex I is thermally stable and decomposes on pyrolysis at elevated temperatures and on reaction with dichloroalkanes at room temperature, forming ethylene in addition to methane and ethane. The decomposition pathway presumably involves the formation of carbenoid intermediates as we reported in a preliminary note [9]. This paper also describes other chemical properties of I such as the reactions with  $\text{H}_2$  and  $\text{D}_2$ , phenylacetylene, carbon monoxide and carbon dioxide.

In attempts to examine the stabilizing effect of other tertiary phosphines we have isolated another methyliron complex, methylbis(acetylacetonato)(dimethylphenylphosphine)iron(III),  $\text{FeCH}_3(\text{acac})_2(\text{PPhMe}_2)_2$  in the reaction of  $\text{Fe}(\text{acac})_3$ ,  $\text{AlMe}_2(\text{OEt})$  and  $\text{PPhMe}_2$ . This complex may be regarded as the intermediate alkylation product of  $\text{Fe}(\text{acac})_3$  with alkylaluminium compounds. Similar transition metal complexes containing alkyl, acetylacetonato and tertiary phosphine ligands have been prepared in reaction systems using  $\text{Fe}(\text{acac})_3$  [3a],  $\text{Co}(\text{acac})_3$  [3a,10] and  $\text{Ni}(\text{acac})_2$  [11].

## Results and discussion

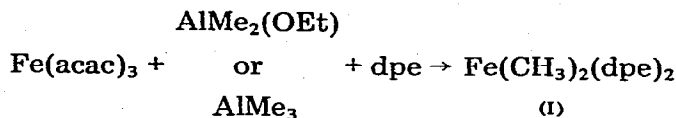
The reactions carried out in the present study are summarized in Scheme 1.



SCHEME 1. (i) Recrystallization from toluene; (ii)  $\text{H}_2$  or  $\text{D}_2$  at room temperature; (iii)  $\text{CO}$ , at room temperature; (iv)  $\text{CO}_2$ , in pyridine; (v) thermolysis in  $\text{CD}_2\text{Cl}_2$ ; (vi) thermolysis in the solid state; (vii)  $\text{PhC}\equiv\text{CH}$  at room temperature.

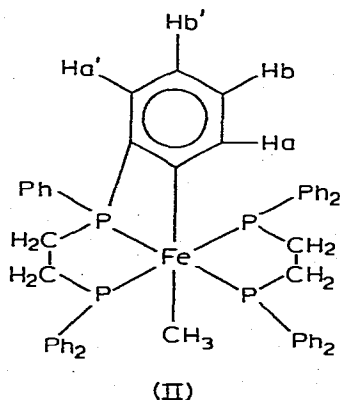
### 1. Preparation and properties of methyliron complexes

The dimethyliron complex I was prepared as orange crystals by the reaction of  $\text{Fe}(\text{acac})_3$ , dpe and dimethylaluminum monoethoxide or trimethylaluminum in ether at  $-30$  to  $0^\circ\text{C}$  under nitrogen.



Since the complex is insoluble in any common organic solvents and decomposed in others such as pyridine and  $\text{CH}_2\text{Cl}_2$ , recrystallization and NMR measurement were not feasible, but elemental analysis and chemical characterization of I supported its formulation as  $\text{Fe}(\text{CH}_3)_2(\text{dpe})_2$ . Complex I is stable in air for 10–15 min and decomposes slowly releasing  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . Acidolysis with concentrated  $\text{H}_2\text{SO}_4$  released 1.8 mol of  $\text{CH}_4$  per Fe. Iodolysis in benzene liberated methane and ethane in a 1/2.5 ratio and yielded  $\text{FeI}_2(\text{dpe})$ . Complex I is stable in the solid state under nitrogen at room temperature and decomposes at  $130$ – $135^\circ\text{C}$  releasing methane, ethane and ethylene in a ratio of 75 : 20 : 5, the amount of the gases liberated accounting for 75% of the methyl groups bonded to iron on assumption that the hydrocarbon source is the methyl groups (*vide infra*).

In attempts to recrystallize complex I from toluene, methane was liberated and a yellow to orange solution was obtained. On cooling it to  $-70^\circ\text{C}$ , orange crystals (II) were deposited. The IR spectrum of II shows new bands at  $1555$  and  $730\text{ cm}^{-1}$ , which were absent in the original complex I. The new band which appeared at  $1555\text{ cm}^{-1}$  may be assigned to the metallated phenyl ring stretching vibration, and the intense band at  $730\text{ cm}^{-1}$  to the C–H out-of-plane deformation of the *ortho*-disubstituted benzene ring, respectively. The recovered dpe ligand after acidolysis of II with  $\text{D}_2\text{SO}_4$  was found to have a C–D bond in the dpe ligand as revealed by mass spectroscopic examination of water produced on oxidative degradation of the dpe ligand with  $\text{CuO}$ . Evidence supporting the *ortho*-metallated structure as shown below also was obtained by examination of the NMR spectrum of II in  $\text{CD}_2\text{Cl}_2$ . The NMR spectrum of II at  $-20^\circ\text{C}$  shows a broad peak due to the methyl group bonded to iron at  $\tau$  10.8 ppm



(3H), two sets of broad peaks due to the methylene groups of the dpe ligand at  $\tau$  7.8 (4H) and 8.2 ppm (4H), broad peaks due to  $H_b$  and  $H_b'$  protons in structure II at 4.2 ppm (2H), broad peaks due to  $H_a$  and  $H_a'$  protons at  $\tau$  3.6 ppm (2H), and two sets of complex multiplets at  $\tau$  2.5–3.4 ppm due to the phenyl protons, except for  $H_a$ ,  $H_a'$ ,  $H_b$  and  $H_b'$  protons. Acidolysis of II gave methane.

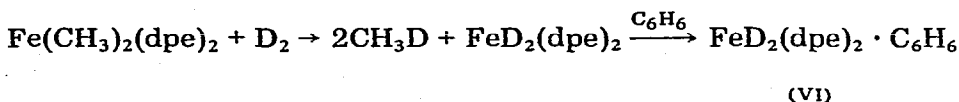
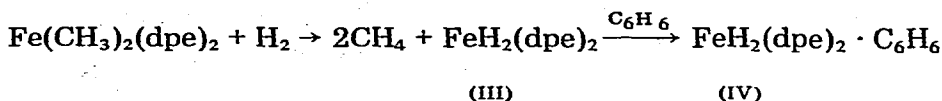
There are many examples of *ortho*-metallation involving the loss of hydrogen from an aromatic ring of a ligand with the concomitant formation of a metal-carbon bond as reviewed recently [12]. *Ortho*-metallation reactions similar to the present case promoted by recrystallization of alkyl complexes have been demonstrated by Keim and Kaesz et al. in an alkylrhodium [13], and an alkylmanganese complex [14], and by Hata et al. who observed the *ortho*-metallation in an ethylene-iron complex producing  $HFe(dpe)(C_6H_4PPhCH_2CH_2PPh_2)$  [8]. However, no precedent for this type of complex having an alkyl group and an *ortho*-metallated ring has been reported.

In contrast to the methyliron complex, the similar reaction of  $Fe(acac)_3$  with  $AlEt_2(OEt)$  instead of  $AlMe_2(OEt)$  in the presence of dpe in ether gives the ethylene-coordinated complex,  $Fe(CH_2=CH_2)(dpe)_2$  [8]. Alkylation with  $Al-n-Pr_3$  and  $Al-i-Bu_3$ , on the other hand, afforded the known hydride,  $FeH_2(dpe)_2$  (III) [15], which on recrystallization from benzene was recovered as  $FeH_2(dpe)_2 \cdot C_6H_6$  (IV) [8]. These results suggest that higher alkyl homologs of  $FeR_2(dpe)_2$  are less stable than I and prone to decompose via a  $\beta$ -elimination process affording III. The reaction carried out under similar conditions using  $AlEt_3$  instead of  $AlEt_2(OEt)$  also gave the dihydride complex III, but the ethylene complex was obtained only when the reaction was conducted by carefully controlling the reaction temperature and the product was contaminated with III. The variation of the reduction product depending upon the use of either  $AlEt_2(OEt)$  or  $AlEt_3$  implies that the decomposition pathway of an ethyliron complex which is formed as an intermediate alkylation product may be influenced by the kind of the ethylating agents which exist in some excess in the reaction system. We have previously observed that alkyltransition metal complexes once isolated are susceptible to further attack by alkylaluminum compounds [16].

The intermediate alkylation product of  $Fe(acac)_3$  with  $AlMe_2(OEt)$  was isolated as  $FeCH_3(acac)_2(PPhMe_2)$  (V) when dimethylphenylphosphine was employed. V is thermally stable at room temperature under nitrogen but sensitive to air. It is soluble in ether and other organic solvents and can be recrystallized as red crystals from ether. The paramagnetism of V precludes NMR measurements, but its IR spectrum indicates the presence of the acac and  $PPhMe_2$  ligands and of an iron-bonded methyl group as observed in the  $\nu(C-H)$  bands at 2900 and 2850  $cm^{-1}$ . Complex V decomposes with melting at 55–58°C, evolving methane, ethane and ethylene in a ratio of 75 : 14 : 11, the total amount of the gases accounting for 100% of the iron-bonded methyl group on the assumption that the  $PPhMe_2$  ligand is not thermolyzed at the temperature to produce these hydrocarbons (vide infra). Acidolysis of V released 0.92 mol of methane per Fe. Attempts to prepare a methyliron complex containing no acetylacetonato ligand by further methylation of V did not lead to any isolable product.

The reaction of I with dihydrogen in a toluene suspension at room temperature liberates methane to produce  $FeH_2(dpe)_2$  from the resultant solution. The similar reaction of I with  $D_2$  released  $CH_3D$  as the sole gaseous product and gave

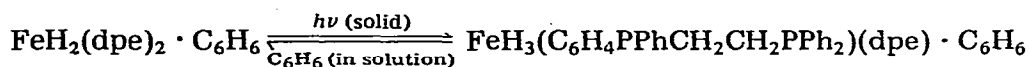
$\text{FeD}_2(\text{dpe})_2$ , which on recrystallization from benzene afforded yellow crystals of composition  $\text{FeD}_2(\text{dpe})_2 \cdot \text{C}_6\text{H}_6$  (VI).



The IR spectrum of the iron dideuteride complex VI showed a  $\nu(\text{Fe}-\text{D})$  band at  $1330 \text{ cm}^{-1}$  in comparison with  $\nu(\text{Fe}-\text{H})$  band of IV at  $1840 \text{ cm}^{-1}$ , the  $\nu(\text{Fe}-\text{H})/\nu(\text{Fe}-\text{D})$  ratio being 1.4. The presence of the single  $\nu(\text{Fe}-\text{H})$  or  $\nu(\text{Fe}-\text{D})$  band suggests the *trans*-configuration for the dihydride and dideuteride complexes [15]. Similar hydrogenolysis of other methyltransition metal complexes such as  $\text{CoCH}_3(\text{dpe})_2$  [6], and  $\text{RhCH}_3(\text{PPh}_3)_3$  [13] under mild conditions to afford the deuteride complexes are known.

Complex IV showed peculiar photochemical behavior in sunlight; the color of the solid complex changed from yellow to red without evolution of hydrogen upon irradiation with sunlight. The IR spectrum of the red complex shows a new  $\nu(\text{Fe}-\text{H})$  band at  $1890 \text{ cm}^{-1}$  and a new band at  $728 \text{ cm}^{-1}$  due to the *ortho*-metallated species. On recrystallization of the red complex from benzene IV was recovered.

The interconversion suggests either an isomerization between *trans* and *cis* configurations or hydrogen transfer involving the *ortho*-metallation. The hydrogen transfer from the dpe ligand to a transition metal hydride has precedents in  $\text{Ru}(\text{dmpe})_2$  (dmpe = 1,2-bis(dimethylphosphino)ethane) [17] and  $\text{Fe}(\text{C}_2\text{H}_4)(\text{dpe})_2$  [8]. In the latter case the hydrogen transfer took place on irradiating the iron complex. The IR band at  $728 \text{ cm}^{-1}$  appeared on UV irradiation of the solid complex was interpreted as an indication of the occurrence of the *ortho*-metallation, together with other supporting NMR evidence. The appearance of the IR band at  $728 \text{ cm}^{-1}$  on irradiation of the present complex is in line with the behavior of  $\text{Fe}(\text{C}_2\text{H}_4)(\text{dpe})_2$  and may be taken as an indication of intramolecular hydrogen transfer as shown below.



A similar hydrogen transfer involving the *ortho*-metallation has been observed on UV irradiation of  $\text{FeH}_2\text{N}_2(\text{PPh}_2\text{Et})_3$  [18].

In view of the recent growing interest on reactions of carbon dioxide with transition metal complexes having metal-carbon [19a-d] and metal-hydrogen [19c,e,f] bonds, I was treated with  $\text{CO}_2$  in pyridine. A very air-sensitive and thermally unstable yellow solid was obtained which was proved to be an iron(II) acetate containing pyridine and some coordinated  $\text{CO}_2$ . The dpe ligands in I were completely displaced by pyridine and went into the pyridine solution. We tentatively formulate the complex as  $\text{Fe}(\text{OOCCH}_3)_2(\text{CO}_2)_m(\text{py})_n$  (VII). The IR spectrum of VII shows the  $\nu(\text{OCO})$  bands of the acetato groups at 1610 and

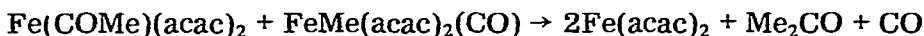
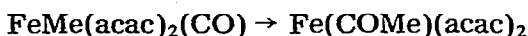
1380  $\text{cm}^{-1}$  and bands due to the coordinated  $\text{CO}_2$  at 2650, 1670, 1420, 1340, and 850  $\text{cm}^{-1}$  [19a,b,20] in addition to bands associated with the coordinated pyridine ligands. The formation of the iron acetate complex VII by  $\text{CO}_2$  insertion into  $\text{Fe}-\text{CH}_3$  bonds has been supported by comparison of the IR spectrum of VII with that of a complex obtained by the reaction of iron(II) acetate with  $\text{CO}_2$  in pyridine. A similar  $\text{CO}_2$  insertion into  $\text{Fe}-\text{H}$  bond to give a formate complex has been recently reported [21].

Phenylacetylene having an acidic hydrogen reacts with I evolving methane and small amounts of ethane and ethylene to produce a crystalline hydridoiron(II) acetylide,  $\text{FeH}(\text{C}\equiv\text{CPh})(\text{dpe})_2$  (VIII), which was characterized on the basis of elemental analysis and IR spectrum showing a  $\nu(\text{Fe}-\text{H})$  band at 1850,  $\nu(\text{C}\equiv\text{C})$  at 2035 and  $\nu(\text{Fe}-\text{C})$  at 560  $\text{cm}^{-1}$ . The hydrido acetylide complex VIII is considered to be formed by oxidative addition of  $\text{PhC}\equiv\text{CH}$  to an intermediate which was formed during dissolution of I in toluene. Similar oxidative addition reactions of mono-substituted acetylenes with several transition metal complexes have been observed [22].

Complex I reacted with carbon monoxide under mild conditions to produce acetone and an iron carbonyl complex containing the dpe ligand with a composition of  $\text{Fe}(\text{CO})_2(\text{dpe})_2$ . Since the reaction of I with carbon monoxide proceeds with partial decomposition of I, the yields of acetone and the iron carbonyl complex were low. On the other hand, a similar reaction of V with carbon monoxide gave quantitatively one equivalent of acetone per two iron atoms accompanied by formation of  $\text{Fe}(\text{acac})_2$ . We have previously observed a disproportionation of  $\text{FeEt}(\text{acac})(\text{PPh}_3)_3$  in acetone or tetrahydrofuran affording  $\text{Fe}(\text{acac})_2$  [3] and quantitative formation of 1 mol equivalent of ketone from 1 mol of  $\text{CoR}_2(\text{acac})\text{L}_2$  ( $\text{L}$  = tertiary phosphines) and carbon monoxide [10]. A further example of CO insertion into transition metal-alkyl bonds producing ketone is provided by the reaction of  $\text{NiMe}(\text{acac})(\text{PPh}_3)_2$  or  $\text{NiEt}(\text{acac})(\text{PPh}_3)$  with carbon monoxide to give acetone or diethyl ketone and  $\text{Ni}(\text{acac})_2$  [23]. The present reaction probably follows the similar pattern as shown below.



(v)

(or  $\text{FeMe}(\text{acac})_2(\text{PPhMe}_2)$ )(or  $\text{PPhMe}_2$ )

An acyliron complex related to the proposed intermediate in the present reaction has been obtained in the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  and a tertiary phosphine [24]. Kinetic study of the CO insertion was not feasible in the present case since the reaction proceeded too fast even at low temperature.

## 2. On thermal stability of the methyliron complex (I) and its decomposition pathways

The dimethyliron complex I having the bidentate dpe ligands exhibits pronounced thermal stability compared with the corresponding iron complex having

triphenyl] phosphine ligands [3a]. The much higher stability of methylbis(acetylacetonato)iron complex (V) containing the PPhMe<sub>2</sub> ligand than the ethyl(acetylacetonato)iron complex having the PPh<sub>3</sub> ligand [3] is also noted. The role of ligands such as tertiary phosphine, cyclopentadienyl, and CO for stabilization of a metal-carbon bond has been accounted for by Wilkinson [25] and other workers [26,27] as a blocking agent to hinder the  $\beta$ -elimination to take place.

We have observed the effect of the addition of tertiary phosphine ligands to hinder the occurrence of the  $\beta$ -elimination in Co(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>(acac)(PPhMe<sub>2</sub>)<sub>2</sub> in solution [28]. However, the same reasoning cannot be applied to the discussion on the stability of methyltransition metal complexes. Evidence supporting the occurrence of  $\alpha$ -elimination from the methyltransition metal complex is still scarce [29] but its importance is acquiring growing attention in connection with olefin metathesis catalysts using transition metal halides and alkylating agents [30]. We present below some evidence supporting that the  $\alpha$ -elimination is taking place. If the  $\alpha$ -elimination process provides a low-energy pathway for decomposition of methyltransition metal complexes, the tertiary phosphine ligands may be regarded, at least partly, as playing the role of blocking agents to prevent  $\alpha$ -elimination. The enhanced thermal stability of the hexacoordinated dimethyliron complex coordinated with the bidentate dpe ligands compared with the PPh<sub>3</sub>-coordinated methyliron complex may be accounted for as such. The PPhMe<sub>2</sub> ligand in the hexacoordinated complex FeCH<sub>3</sub>(acac)<sub>2</sub>(PPhMe<sub>2</sub>) may also play the role of a blocking agent, but other factors such as the electronic influence of the ligands and the oxidation state of the iron complex also may be important.

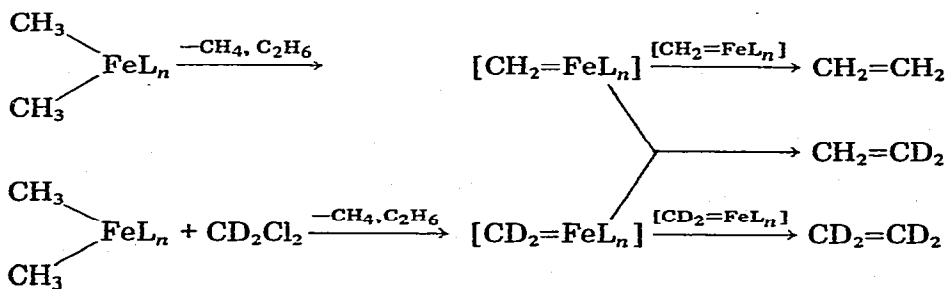
Thermolysis of the solid sample of I liberates methane, ethane and ethylene. Formation of methane may be accounted for as hydrogen abstraction by the methyl group in the process of homolysis of Fe-CH<sub>3</sub> bonds from the ligand (vide supra) or from the other methyl group and the formation of ethane may be explained as coupling of two methyl groups. By the term homolysis, however, we do not intend to suggest the formation of free methyl radicals, since some evidence against free radical formation in the reductive elimination of dialkyl transition metal complexes is known [2b]. The formation of ethylene may be accounted for either by decomposition of the dpe ligands or by coupling of a carbenoid species formed by an  $\alpha$ -elimination of the methyl complex. Since the formation of ethylene also was observed in thermolysis of Fe(CH<sub>3</sub>)(acac)<sub>2</sub>(PPhMe<sub>2</sub>), which contains no dpe ligand and is decomposed at relatively low temperature (55-58°C) and since no gas was detected on thermolysis of Ni(dpe)<sub>2</sub> [31] at 240-245°C, we regard the iron-bonded methyl group as the source of ethylene. The insolubility of I in organic solvents precluded a kinetic study to decide whether the  $\alpha$ -elimination is a unimolecular or bimolecular process. The following study, however, concerning the decomposition of I in dichloroalkanes lends support to the assumption of a bimolecular process involving coupling of intermediate iron-carbenoid species.

When I was treated with CH<sub>2</sub>Cl<sub>2</sub> at 20°C, the gas evolved contained a larger amount of ethylene and a lesser amount of methane than in thermolysis of I as shown in Table 1. In order to confirm the source of ethylene, I was treated with deuterated dichloromethane. The gas liberated on treatment of I with CD<sub>2</sub>Cl<sub>2</sub> of 99% isotopic purity consisted of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>2</sub>=CD<sub>2</sub>, and CD<sub>2</sub>=CD<sub>2</sub>

TABLE I  
THE COMPOSITION OF THE EVOLVED GAS ON THERMOLYSIS

Run	Complex	Solvent	Temperature (°C) (time (day))	Composition of the evolved gas (%)		
				CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>
1	Fe(CH <sub>3</sub> ) <sub>2</sub> (dpe) <sub>2</sub>	—	130—135	75	20	5
2	Fe(CH <sub>3</sub> ) <sub>2</sub> (dpe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	20 (1.5)	55	15	30
3	Fe(CH <sub>3</sub> ) <sub>2</sub> (dpe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	20 (1)	50	24	26
4	Fe(CH <sub>3</sub> ) <sub>2</sub> (dpe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> + styrene	20 (1)	51	21	28
5	Fe(CH <sub>3</sub> ) <sub>2</sub> (dpe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> + 1-hexene	20 (1)	57	16	29
6	Fe(CH <sub>3</sub> ) <sub>2</sub> (dpe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> + cyclohexene	20 (1)	55	16	27
7	Fe(CH <sub>3</sub> ) <sub>2</sub> (dpe) <sub>2</sub>	CCl <sub>4</sub>	20 (1)	0	0	0
8	Fe(CH <sub>2</sub> =CH <sub>2</sub> )(dpe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	20 (1)			100
9	FeCH <sub>3</sub> (acac) <sub>2</sub> (PPhMe <sub>2</sub> )	—	55—58	75	14	11
10	Ni(CH <sub>3</sub> ) <sub>2</sub> (dpe)	—	130—131	30	57	13
11	Ni(dpe) <sub>2</sub>	—	235—240	0	0	0

in a ratio of 50 : 24 : 8 : 14 : 4 as confirmed by IR and mass spectroscopy. The amount of the evolved gas with correction for the part of the deuterated ethylene components accounts for ca. 90% of the fate of the methyl groups in I. From the reaction mixture an off-white powder of composition FeCl<sub>2</sub>(dpe) was recovered. The absence of deuterated methane in the gaseous product produced on treatment of I with CD<sub>2</sub>Cl<sub>2</sub> excludes the dichloromethane as the hydrogen source for giving methane, indicating that this is not a radical process. The formation of C<sub>2</sub>D<sub>4</sub> in the reaction suggests the intermediacy of a carbenoid species formed by Cl<sub>2</sub>-abstraction by the iron complex. Similar dehalogenation from *gem*-dihalides by transition metal complexes to produce olefins are known [32]. The exclusive formation of CH<sub>2</sub>CD<sub>2</sub> and the absence of other deuterated ethylenes and ethanes suggests the formation of a carbenoid species, [CH<sub>2</sub>=Fe], produced by α-elimination from the iron-methyl group and its self-coupling and cross-coupling with another carbenoid species, [CD<sub>2</sub>=Fe], formed by dehalogenation of CD<sub>2</sub>Cl<sub>2</sub>.



The insertion of the carbenoid entity into the Fe—CH<sub>3</sub> bond followed by β-elimination to afford CH<sub>2</sub>=CD<sub>2</sub> seems unlikely because such a reaction would accompany the formation of a deuterated ethane which was not detected.

The nature of the "carbenoid" species assumed as the intermediate may be very different from that of a "free" carbene, since addition of olefins such as styrene, 1-hexene and cyclohexene to the reaction system of I with CH<sub>2</sub>Cl<sub>2</sub>



did not appreciably alter the gas composition nor the total amount of the gas produced as shown in Table 1.

Complex I does not react with  $\text{CCl}_4$  but attacks other dichloroalkanes and acts as a  $\text{Cl}_2$ -abstracting agent. Treatment of I with  $\text{ClCD}_2\text{CD}_2\text{Cl}$  liberated  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{D}_4$  and  $\text{C}_2\text{H}_3\text{D}_3$  in a ratio of 44 : 35 : 12 : 9 but no  $\text{C}_2\text{H}_4$  was detected. The reactions of I with  $\text{CH}_3\text{CHCl}_2$  and  $\text{CH}_3\text{CHClCH}_2\text{Cl}$  produced mainly methane and minor amounts of  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_6$ .

## Experimental

All manipulations were carried out under an atmosphere of oxygen-free nitrogen. Solvents were dried in usual manner, distilled and stored under nitrogen or argon. IR spectra were recorded on a Hitachi EPI-G3 spectrometer using KBr pellets prepared under an inert atmosphere. Microanalyses were carried out by Mr. T. Saito of our Research Laboratory. Gases evolved during the preparation of complexes and their chemical reactions were analysed by gas chromatography and/or mass spectrometry after collecting the gas by a Toepler pump, by which means the volume of the gas was also measured. Deuterated ethylenes were examined by observing the IR spectra of gas samples introduced into a gas cell of 4 cm path. This method proved useful in checking the presence of partially deuterated ethylenes [33].

Tris(acetylacetonato)iron, 1,2-bis(diphenylphosphino)ethane, (dpe) and dimethylphenylphosphine [34] were prepared according to the literature. The several chlorinated compounds were used as purchased from Tokyo Kasei Ltd. after dehydration.  $\text{CD}_2\text{Cl}_2$  and  $\text{CD}_2\text{ClCD}_2\text{Cl}$  were used as purchased from Stohler Isotope Chemicals without further purification.

### 1. Preparation of $\text{Fe}(\text{CH}_3)_2(\text{dpe})_2$ (I)

To an ethereal suspension of  $\text{Fe}(\text{acac})_3$  (1 g, 2.8 mmol) and 2 molar equivalents of dpe (2.25 g), 6 molar equivalents of dimethylaluminum monoethoxide or trimethylaluminum were added at  $-30^\circ\text{C}$  with stirring. The temperature was gradually raised to  $0^\circ\text{C}$  to give an orange to red microcrystalline powder deposited. The reddish orange crystals were filtered and washed with ether and hexane several times below  $0^\circ\text{C}$ , and dried in vacuo. Yield, 70%. (Found: C, 73.8; H, 6.4.  $\text{C}_{54}\text{H}_{54}\text{FeP}_4$  calcd.: C, 73.5; H, 6.1%. IR (KBr):  $\nu(\text{C}-\text{H})$  of  $\text{Fe}-\text{CH}_3$ , 2905 and  $2850\text{ cm}^{-1}$ ,  $\nu(\text{dpe})_{\text{max}}$ ; 3030, 1585, 1483, 1430, 1090, 875, 819, 745 and  $700\text{ cm}^{-1}$ .

### 2. Preparation of $\text{Fe}(\text{CH}_3)(\text{dpe})[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}(\text{C}_6\text{H}_4)]$ (II)

Complex I (1 g) was dissolved in toluene (10 ml) by warming slightly. The yellow to orange filtrate was separated by filtration, concentrated by evaporation, and cooled to  $-78^\circ\text{C}$  to produce orange crystals, which were washed with hexane at room temperature and dried in vacuo. Yield, 10%. (Found: C, 72.9; H, 5.7.  $\text{C}_{53}\text{H}_{50}\text{FeP}_4$  calcd., C, 73.5; H, 5.8%). Dec. p.:  $160-170^\circ\text{C}$ . NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-20^\circ\text{C}$ ):  $\tau$  (ppm) 10.8 (br), ( $\text{Fe}-\underline{\text{CH}}_3$ , 3H); 7.8 and 8.2 (br) (dpe, 8H), 4.2 (br) (2H), 3.6 (br) (2H) (*ortho*-metallated phenyl group in dpe ligand), 2.5-3.4 (complex multiplet, 35H). Acidolysis of II with  $\text{H}_2\text{SO}_4$  released methane. After acidolysis of II with  $\text{D}_2\text{SO}_4$ , the dpe ligand liberated was recovered by extraction with

ether. The dpe thus obtained was oxidatively degraded with CuO to give carbon dioxide and water and the deuterium content in the water was determined by mass spectrometry. The deuterium content in the water was 1.9% compared with the calculated value of 3.2% on the assumption that one phenyl group contains a deuterium per two dpe ligands.

### 3. Preparation of $FeH_2(dpe)_2$ (III) and $FeH_2(dpe)_2 \cdot C_6H_6$ (IV)

The similar reaction of  $Fe(acac)_3$ , dpe, and  $AlEt_3$  or  $Al-n-Pr_3$  or  $Al-i-Bu_3$  in ether under nitrogen at  $-5$  to  $0^\circ C$  gave yellow crystals which were separated by filtration and washed with ether and hexane. The yellow compound was recrystallized from benzene/hexane to give pure yellow crystals,  $FeH_2(dpe)_2 \cdot C_6H_6$  (IV), which were dried in vacuo. (Found: C, 75.0; H, 6.4.  $C_{58}H_{56}FeP_4$  calcd.: C, 74.7; H, 6.0%.) IR (KBr):  $\nu(Fe-H)$ ,  $1840\text{ cm}^{-1}$ ;  $\nu(dpe)_{max}$ ,  $3030$ ,  $1585$ ,  $1478$ ,  $1430$ ,  $1095$ ,  $870$ ,  $809$ ,  $740$  and  $690\text{ cm}^{-1}$ .

### 4. Preparation of $Fe(CH_3)(acac)_2(PPhMe_2)$ (V)

To an ethereal solution of  $Fe(acac)_3$  (1.0 g, 2.8 mmol) and  $PPhMe_2$  (1.4 ml, 11 mmol) dimethylaluminium monoethoxide (3 ml) was added at  $-30$  to  $-40^\circ C$  under nitrogen. The reaction mixture turned to a deep red solution at  $-10^\circ C$  and on stirring the mixture for 2 h at that temperature red crystals appeared. The reaction mixture was cooled to  $-78^\circ C$  and the red crystals which had deposited were filtered off, washed with ether and hexane at  $-78^\circ C$  and recrystallized from ether. Yield, 50%. V is sensitive to air, thermally stable at room temperature under nitrogen and soluble in ether. (Found: C, 55.4; H, 7.9.  $C_{19}H_{28}O_4PFe$  calcd.: C, 56.0; H, 6.9%.) IR (KBr):  $\nu(C-H)$  of  $Fe-CH_3$ ,  $2900$ ,  $2850\text{ cm}^{-1}$ ;  $\nu(Fe-C)$ ,  $550\text{ cm}^{-1}$ ;  $PPhMe_2$ ,  $3050$ ,  $1435$ ,  $925$ ,  $895$ ,  $740$ ,  $690$  and  $580\text{ cm}^{-1}$ ;  $\nu(acac)$ ,  $1570$ ,  $1510$ ,  $1390$ ,  $1270$ ,  $1050$  and  $790\text{ cm}^{-1}$ .

### 5. Reaction of I with $D_2$ and preparation of $FeD_2(dpe)_2 \cdot C_6H_6$ (VI)

Complex I (0.30 g, 0.34 mmol) was suspended in 5 ml of toluene and brought in contact at  $-10^\circ C$  with  $D_2$  of an atmospheric pressure in a closed system. With the rise of temperature the reaction mixture changed from the initial orange suspension to a deep yellow solution, which was stirred further for 1 day at room temperature. The gas evolved during the reaction was confirmed to be  $CH_3D$  by mass spectrometry. The solution on recrystallization from benzene/hexane gave 0.3 g of yellow crystals of composition  $FeD_2(dpe)_2 \cdot C_6H_6$  (VI). Yield, 90%. (Found: C, 74.0; H, 5.8.  $C_{58}H_{56}FeP_4$  calcd.: C, 74.7; H, 6.0%.) IR (KBr):  $\nu(Fe-D)$ ,  $1330\text{ cm}^{-1}$ .

### 6. Reaction of I with carbon dioxide

A dry  $CO_2$  stream was bubbled through a pyridine suspension containing I at  $-10^\circ C$ . After the gradual temperature rise to  $0^\circ C$  the reaction mixture changed from the initial orange-red suspension to a yellow solution and a yellow precipitate was deposited from the solution. The yellow solid VII was separated by filtration from the yellow solution, washed with hexane at  $-10$  to  $0^\circ C$  and dried in vacuo below  $0^\circ C$ . From the solution the dpe ligand was recovered. Because of the instability of the yellow complex microanalysis was not successful. IR (KBr):  $\nu(OCO)$  of  $CH_3COO$  groups,  $1610$  and  $1385\text{ cm}^{-1}$ ;  $CO_2$  (coordinat-

ed), 2650, 1670, 1420, 1340 and 850  $\text{cm}^{-1}$ ; pyridine(max) 1600, 1485, 1445, 1325, 1215, 1040, 765 and 705  $\text{cm}^{-1}$ .

Thermolysis of VII at 150°C released  $\text{CO}_2$  and pyridine and treatment of VII in benzene with dry HCl gas liberated  $\text{CO}_2$  and acetic acid as detected by gas chromatography.

Complex VII was prepared via another route by the reaction of  $\text{Fe}(\text{CH}_3\text{COO})_2 \cdot (\text{py})_n$  and  $\text{CO}_2$  in pyridine and was identified by comparison of the IR spectra.

### 7. Reaction of I with $\text{PhC}\equiv\text{CH}$

To complex I (0.20 g, 0.25 mmol) suspended in toluene (5 ml) was added phenylacetylene (0.1 ml) at  $-30^\circ\text{C}$  by means of a syringe. The reaction mixture was stirred at  $0^\circ\text{C}$  for 20 min and then further for 4 h at room temperature. The orange suspension turned to a brown solution evolving  $\text{CH}_4$  (0.2 mmol) and small amounts of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . The amount of the gases formed accounted for about 40% of the calculated value for I. On addition of hexane to the brown solution and subsequent cooling, brown crystals were deposited, which were washed with hexane after filtration and dried in vacuo. Yield, 45%. (Found: C, 75.2; H, 5.8.  $\text{C}_{60}\text{H}_{53}\text{FeP}_4$  calcd.: C, 75.5; H, 5.6%.) IR (KBr):  $\nu(\text{C}\equiv\text{C})$ , 2035  $\text{cm}^{-1}$ ,  $\nu(\text{Fe}-\text{H})$ , 1850  $\text{cm}^{-1}$ ;  $\nu(\text{Fe}-\text{C})$ , 560  $\text{cm}^{-1}$ ;  $\nu(\text{dpe})_{\text{max}}$ , 3050, 1480, 1435, 1090 and 690  $\text{cm}^{-1}$ .

### 8. Reactions of I and V with carbon monoxide

(a) A dry CO stream was bubbled through a toluene solution containing I (0.28 g, 0.32 mmol) at room temperature for 0.5 h. After bubbling of CO the system was closed under CO and was further stirred at room temperature for 1 day. The system changed from an orange suspension to a yellow solution. The amount of acetone formed in the reaction mixture was determined by VPC as 30% per iron. An iron carbonyl compound of composition,  $\text{Fe}(\text{CO})_2(\text{dpe})_2$  was recovered from the resultant solution as yellow crystals. Yield, 20%. (Found: C, 70.8; H, 5.5.  $\text{C}_{54}\text{H}_{48}\text{P}_4\text{FeO}_2$  calcd.: C, 71.4; H, 5.3%.) IR(KBr):  $\nu(\text{CO})$ , 1985, 1915(sh), 1895 and 1835  $\text{cm}^{-1}$ ;  $\nu(\text{dpe})$ , 3060, 1588, 1490, 1440, 1090, 740 and 698  $\text{cm}^{-1}$ .

(b) Complex V was dissolved in 2 ml of toluene and brought in contact with carbon monoxide at atmospheric pressure at  $-70^\circ\text{C}$  in a closed system. At this temperature the color of the system changed from red to green. This color change took place reversibly. On raising the temperature the green solution changed to a brownish yellow solution. At room temperature the system was stirred for 3 h. The amount of acetone formed in the reaction solution was determined by VPC as 90%. From the resultant solution an orange to brown complex  $\text{Fe}(\text{acac})_2$  was obtained. Its IR spectrum shows the presence of only acetylacetonato ligands [3]. IR(KBr):  $\nu(\text{acac})_{\text{max}}$ , 1575, 1525, 1360, 1275, 1020, and 930  $\text{cm}^{-1}$ .

### 9. Reactions of I with a few vinyl compounds

Acrylonitrile (2 g) was distilled into a flask containing complex I (0.1 g) in vacuum. As soon as the temperature was raised polymerization of acrylonitrile took place suddenly and poly(acrylonitrile) was obtained in 80% yield. No reaction of I with styrene was observed.

### 10. Thermolysis and $\text{CH}_2\text{Cl}_2$ treatment of I

On thermolysis of I (0.18 g, 0.21 mmol) in the solid state at 130–135°C  $\text{CH}_4$  (4.2 ml STP),  $\text{C}_2\text{H}_6$  (1.3 ml) and  $\text{C}_2\text{H}_4$  (0.3 ml) were evolved. The total amount of gas liberated was equivalent to 75% of the methyl groups bonded to iron. Table 1 shows the composition of gases evolved on treatment of I with  $\text{CH}_2\text{Cl}_2$ . A typical procedure is described below.  $\text{CH}_2\text{Cl}_2$  (1 ml) was added to complex I (0.15 g, 0.17 mmol) by a trap-to-trap distillation using a vacuum line and the reaction mixture was stirred at room temperature for 1 day. The initial orange suspension turned to a dark red solution and a white precipitate was deposited. The gas evolved in the process was examined by means of mass spectrometry and VPC. Using  $\text{CD}_2\text{Cl}_2$  (isotopic purity 99%) a similar treatment of I (0.23 g, 0.27 mmol) was carried out under the same conditions and the gas composition was determined.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_2=\text{CH}_2$ ,  $\text{CH}_2=\text{CD}_2$ ,  $\text{CD}_2=\text{CD}_2$  in a ratio of 50 : 24 : 8 : 14 : 4 were produced. Neither *cis*- or *trans*- $\text{CHD}=\text{CHD}$  nor  $\text{CH}_3\text{D}$  or  $\text{CHD}_2\text{CH}_3$  was detected. From the resultant solution free dpe ligand and an off-white compound with an approximate composition of  $\text{FeCl}_2(\text{dpe})$  were recovered. (Found: C, 61.1; H, 5.2; Cl, 12.5.  $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{FeP}_4$  calcd.: C, 59.5; H, 4.6; Cl, 13.5%.)

### 11. Treatment of I with several chlorinated compounds

Treatment of I with several chlorinated compounds such as  $\text{CD}_2\text{ClCD}_2\text{Cl}$ ,  $\text{CH}_2\text{ClCH}_2\text{Cl}$ ,  $\text{CH}_3\text{CHClCH}_2\text{Cl}$ , and  $\text{CH}_3\text{CHCl}_2$  were carried out similarly to that of I with  $\text{CH}_2\text{Cl}_2$  as described above.

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