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PREPARATION AND PROPERTIES OF ETHYLENE- AND 1,3-BUTADIENE-COORDINATED COMPLEXES OF IRON(0) HAVING DIMETHYLPHENYLPHOSPHINE LIGANDS

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Summary

Bis(ethylene)tris(dimethylphenylphosphine)iron(0), I, has been prepared by the reaction of tris(2,4-pentanedionato)iron(III) with diethylaluminum ethoxide in the presence of dimethylphenylphosphine at low temperature. Coordinated ethylene is easily displaced by 1,3-butadiene to give (1,3-butadiene)tris(dimethylphenylphosphine)iron(0). These complexes are characterized by IR and NMR spectroscopy and elemental analysis as well as by chemical reactions.

Introduction

The importance of iron-olefin complexes has been well established in the organometallic chemistry of iron [1]. In contrast to a number of iron-olefin complexes containing carbonyl ligand [1] the isolated examples of iron-olefin complexes containing tertiary phosphine ligands are quite limited. Kruck has prepared a variety of Fe(olefin)$(PF_3)_n$ by the photolysis of $Fe(PF_3)_5$ in the presence of olefins [2]. Muetterties briefly reported the preparation of Fe(diene)$(PMe_3)_3$, the only diene-iron(0) complex having monodentate tertiary phosphines, by the reduction of $FeCl_2$ with Na/Hg [3]. Ittel recently applied the metal vapor technique in order to prepare a series of diene complexes of iron having phosphite ligands [4]. Bidentate ligands such as 1,2-bis(diphenylphosphino)ethane (dpe) [5] and 1,2-(dimethylphosphino)ethane (dmpe) [6], are also known to stabilize the iron–olefin bond.

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In the course of our continued study on the preparation of transition metal alkyl complexes from Ziegler-type catalyst systems in the presence of suitable ligands [7], we came across a new zero-valent iron-ethylene complex having dimethylphenylphosphine ligands. We wish to report here the preparation of bis(ethylene)tris(dimethylphenylphosphine)iron(0) and (1,3-butadiene)tris(dimethylphenylphosphine)iron(0).

Results and discussion

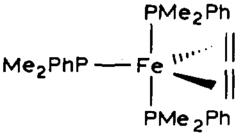
Preparation of $Fe(C_2H_4)_2(PPhMe_2)_3$, I

Treatment of tris(2,4-pentanedionato)iron(III) ($Fe(acac)_3$) with diethylaluminum ethoxide in the presence of dimethylphenylphosphine in dry diethyl ether below 0°C gave an orange, zerovalent iron complex formulated as $Fe(C_2H_4)_2(PPhMe_2)_3$ (I).

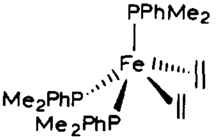
$$Fe(acac)_3 + AlEt_2(OEt) + PPhMe_2 \rightarrow \underset{(I)}{Fe(C_2H_4)_2(PPhMe_2)_3}$$

The extremely air sensitive complex I was carefully recrystallized from dry diethyl ether under argon and characterized by elemental analysis, IR and NMR spectroscopy as well as by chemical reactions. The IR spectrum of I showed mainly bands due to dimethylphenylphosphine ligands except for a weak band at 1475 cm^{-1} assignable to $\nu(C=C)$ of the coordinated ethylene. The ^1H NMR spectrum of I in toluene-d_8 at -50°C showed a broad signal at 2.6 ppm (8H) and two broad signals at 0.5(12H) and 1.6 ppm (6H) due to the coordinated ethylene and dimethylphenylphosphine ligands, respectively.

As a configuration consistent with the NMR data the following trigonal bipyramidal Ia [8] and square pyramidal Ib structures are conceivable.



(Ia)



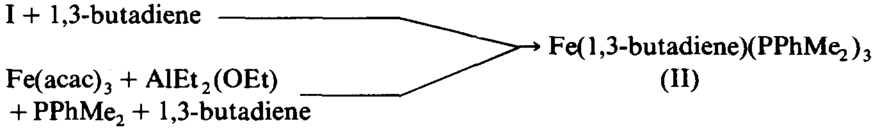
(Ib)

By analogy with the butadiene-coordinated complex (vide infra) the square pyramidal structure Ib seems most probable.

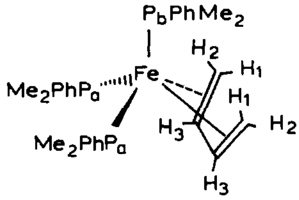
Complex I released ca. 1.5 mol of ethylene per Fe upon heating at 70°C for 30 min in the solid state. Acidolysis of I with sulfuric acid afforded a roughly 3 : 2 mixture of ethylene and ethane, the total yield of the gases being roughly 2 equivalents per Fe atom. Ligand exchange reaction of I with dpe in toluene gave the known complex, $Fe(C_2H_4)(dpe)_2$ [5] accompanying loss of one mole of the coordinated ethylenes.

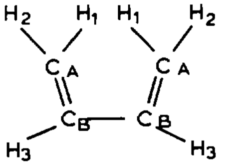
Preparation and NMR spectra of $Fe(1,3\text{-butadiene})(PPhMe_2)_3$, II

The coordinated ethylene ligands in I were easily displaced by 1,3-butadiene in ether below 0°C giving $Fe(1,3\text{-butadiene})(PPhMe_2)_3$ (II). Complex II was also prepared directly from the reaction of $Fe(acac)_3$ with $AlEt_2(OEt)$ in the presence of both dimethylphenylphosphine and 1,3-butadiene.



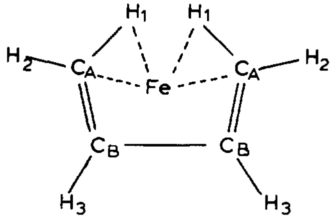
Complex II, which was recrystallized as yellow needles from diethyl ether, has a considerably higher thermal stability than complex I. The following square pyramidal structure of II is proposed on the basis of the ^{1}H, ^{31}P{^{1}H} and ^{13}C NMR analyses as well as by analogy with other known iron-diene complexes [1–4]:





The ^{31}P{^{1}H} NMR spectrum of II in acetone-d_6 at −40°C shows a sharp triplet and a doublet in a 1 : 2 ratio with a coupling constant of 3 Hz, suggesting that II contains two equivalent P$_a$'s and a unique P$_b$. In the ^{1}H NMR spectrum of II, two sets of methyl signals assignable to PPh*Me*$_2$ were observed at 1.92 and 1.20 ppm in a 1 : 2 ratio; the former is due to P$_b$ and the latter to P$_a$. Although the methyl ^{1}H signal of P$_b$ appears as a doublet due to coupling with P$_b$, the methyl proton signal of P$_a$ is further split into two sets of doublets, indicating that the two methyl groups in one P$_a$ are magnetically non-equivalent. These observations are consistent with the above square pyramidal structure of II.

Signals attributable to protons of the coordinated 1,3-butadiene are observed at −2.13 (2H, H(1)), 0.50(2H, H(2)), and 4.43 ppm (2H, H(3)) as broad singlets probably due to couplings with neighboring protons as well as phosphorus nuclei. This type of coupling pattern has been observed for several *cis*-butadiene complexes of transition metals [1–4,6,9]. We note the observed extraordinarily high field chemical shift of the anti proton (H(1)) in II, which is the highest chemical shift among the reported 1,3-butadiene complexes. The observation may indicate a strong metal diamagnetic anisotropy [10] and/or a fairly short Fe–H(1) bond distance which consequently leads to high shielding influence of Fe on H(1). The ^{13}C{^{1}H} NMR spectrum of II shows terminal and internal carbons (C$_A$ and C$_B$) of the coordinated 1,3-butadiene at 33.5 and 79.0 ppm from TMS as a doublet (J(C–P) = 11 Hz) and a singlet, respectively. The presence of the ^{13}C–^{31}P coupling only for the signal of C$_A$ suggests that the iron atom does not interact with the C$_B$ atom but mainly with the C$_A$ atom, if the coupling between carbon and phosphorus arises through C–Fe–P bonds. One might take this ^{13}C{^{1}H} NMR result as an indication of formation of an iron-containing cyclopentene similar to metallacyclopentene complexes which are reported to be formed by reactions of an iron carbonyl with perfluoro-1,3-butadiene and a platinum(0) complex with dienes [11]. However, formation of the σ-bond between Fe and C$_A$ seems unlikely in complex II, since the C–H coupling constants in C$_A$ and C$_B$ are observed as 154 and 163 Hz, respectively, these values being consistent with sp^2 hybridization of these carbon atoms [12]. We thus believe that 1,3-butadiene is still coordinated to Fe through olefinic double bonds. The stronger interaction of C_A with Fe probably arises from the tilted (or slid) plane of the 1,3-butadiene ligand toward Fe to make the distance from Fe to C_A shorter than that to C_B.



Similar reasoning applies to the interpretation of the ^1H NMR spectrum. However, a simple anisotropic influence of Fe on the coordinated 1,3-butadiene may still play important role in the large upfield shift of H(1) and C_A in ^1H and ^{31}P NMR spectra. Thus, such an interaction between Fe and 1,3-butadiene possibly involves the coordination of the C_A–H(1) bond to Fe without changing the sp^2 hybridization of C_A and C_B. Such an interaction might reflect the activation in the C–H bond of the coordinated butadiene. Some examples of extraordinarily short distance between transition metal and a C–H bond have been reported as a model for C–H bond activation of hydrocarbons [13].

Temperature dependence of $^{31}P\{^1H\}$ NMR

On raising temperature, the sharp signals of P_A and P_B in the $^{31}P\{^1H\}$ NMR of II gradually broaden, suggesting that a facile intra- and/or inter-molecular exchange of phosphine ligands is taking place in II. At a constant temperature the addition of free $PPhMe_2$ into the solution of II does not cause further broadening of P_A and P_B signals, ruling out the simple associative ligand exchange process involving Fe(1,3-BD)L_4. On the other hand, both signals due to the coordinated and uncoordinated $PPhMe_2$ extensively broaden with increasing temperature. These observations are consistent at least with the following mechanism involving fast dissociative ligand exchange process.

$$\mathrm{Fe(1,3\text{-}butadiene)(PPhMe_2)_3} \rightleftharpoons \mathrm{Fe(1,3\text{-}butadiene)(PPhMe_2)_2 + PPhMe_2}$$

However, a facile intramolecular exchange of the phosphine ligand in II (pseudo rotation) and intermolecular ligand exchange via a prior partial dissociation of 1,3-butadiene ligand may also be involved at the same time. Such fluxional behavior in FeL_3(diene) complexes having a phosphite ligand has been reported [4].

Experimental

All manipulations were carried out under deoxygenated Ar. Solvents were purified by the usual methods and stored under Ar before use. Dimethylphenylphosphine was prepared from $PPhCl_2$ and MeMgI. $AlEt_2(OEt)$ was obtained by alcoholysis of $AlEt_3$ with absolute ethanol. $Fe(acac)_3$ obtained from Tokyo Kasei Co-Ltd was used after recrystallization. Gases evolved in the reactions were analyzed by GC after collecting them by a Toepler pump. IR spectra were recorded on a

Hitachi-295 spectrometer. The ^{1}H, ^{31}P{^{1}H}, and ^{13}C NMR were recorded on a JEOL-FX-100 spectrometer. Chemical shifts are referred to TMS for ^{1}H and ^{13}C{^{1}H} NMR and to H_3PO_4 for ^{31}P{^{1}H} NMR. *J*(C–H) was estimated from the non-decoupled ^{13}C NMR spectrum.

Preparation of $\mathit{Fe(C_2H_4)_2(PPhMe_2)_3}$ *(I)*

An ether solution (25 ml) of Fe(acac)$_3$ (3 g, 8.6 mmol) and $\mathrm{PPhMe_2}$ (4.9 ml, 35 mmol) was treated with $\mathrm{AlEt_2OEt}$ (4.9 ml) at −39°C. On raising the temperature to −5°C, a vigorous reaction took place to give a dark red homogeneous solution. After stirring for 30 min at −5°C, the volume of the solution was reduced to ca. 15 ml. Cooling the solution to −78°C afforded red-brown crystals, which were recrystallized from ether below 0°C. Yield, 0.88 g (16%). Microanalysis of the complex was not feasible due to its thermal instability and air sensitivity. Anal: Fe, 11.1%. $\mathrm{C_{28}H_{41}P_3Fe}$: calcd. Fe, 10.6%. m.p. 58–60°C (dec.). ^{1}H NMR (in toluene-d_8, −50°C), 0.5 ppm (br, 12H) and 1.6 (br, 6H) for $\mathrm{PPh}\mathit{Me}_2$. 2.6 (br, 8H) for $\mathrm{C_2}\mathit{H}_4$. 6.8–7.5 (br, 15H) for $\mathrm{P}\mathit{Ph}\mathrm{Me_2}$.

Preparation of Fe(1,3-butadiene)$\mathit{(PPhMe_2)_3}$ *(II)*

When an excess of 1,3-butadiene was introduced into an ether (15 ml) solution of I (1.29 g, 2.45 mmol) below 0°C, the color changed from deep red to pale yellow. Cooling the solution to −78°C gave yellow crystals of II which were recrystallized from ether as yellow needles. Yield, 372 mg (35%); m.p. 116–117°C (180°C dec.). Anal. Found: C, 63.8; H, 8.0; Fe, 11.3. $\mathrm{C_{28}H_{39}P_3Fe}$ calcd.: C, 64.1; H, 7.5; Fe, 10.7%. ^{1}H NMR (in acetone-d_6, −40°C): −2.13 (br, 2H) for *anti* H(1), 0.50 (br, 2H) for *syn* $\mathrm{H_2}$, 1.20 (d, *J*(P–H) 6.4 Hz, 6H), 1.23 (d, *J*(P–H) 6.4 Hz, 6H) and 1.92 (d, *J*(P–H) 5.9 Hz, 6H) for $\mathrm{PPh}\mathit{Me}_2$, 4.43 (br, 2H) for $\mathrm{C_B}\mathit{H}_3$, 6.8–7.5 (m, 15H) for $\mathrm{P}\mathit{Ph}\mathrm{Me_2}$. ^{31}P{^{1}H} NMR (in acetone-d_6, −40°C): 33.7 (d, *J*(P–P) 3 Hz, 2P) for $\mathrm{P_a}$. 38.0 (d, 1P) for $\mathrm{P_b}$. ^{13}C{^{1}H} NMR (in $\mathrm{CD_2Cl_2}$, −40°C): 20.5 (m, *J*(C–H) 123 Hz(q)) and 23.5 (d, *J*(C–P) 20 Hz, *J*(C–H) 129 Hz(q)) for $\mathrm{PPh}\mathit{Me}_2$, 33.5 (d, *J*(C–P) 11 Hz, *J*(C–H) 154 Hz (t)) for $\mathrm{C_A}$. 79.0 (s, *J*(C–H) 163 Hz(d)) for $\mathrm{C_B}$. 128–130(m) for $\mathrm{P}\mathit{Ph}\mathrm{Me_2}$. Complex II was also obtained by the reaction of Fe(acac)$_3$ (1 g) with $\mathrm{AlEt_2(OEt)}$ (1.5 ml) in the presence of $\mathrm{PPh_2Me}$ (1.6 ml) and excess 1,3-butadiene at 0°C. Yield, 784 mg (52%).

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