

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 $\text{Fe}(\text{olefin})(\text{PF}_3)_n$ by the photolysis of $\text{Fe}(\text{PF}_3)_5$ in the presence of olefins [2]. Muetterties briefly reported the preparation of $\text{Fe}(\text{diene})(\text{PMe}_3)_3$, 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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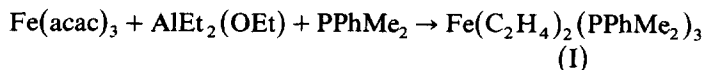
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In the course of our continued study on the preparation of transition metal alkyl complexes from Ziegler-type catalyst systems in the presence of suitable ligands [7], we came across a new zero-valent iron-ethylene complex having dimethylphenylphosphine 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

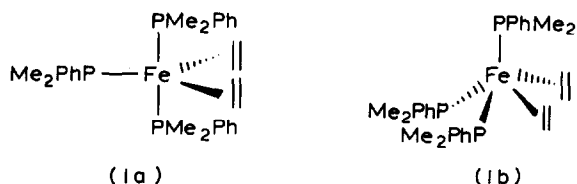
Preparation of $\text{Fe}(\text{C}_2\text{H}_4)_2(\text{PPhMe}_2)_3$, I

Treatment of tris(2,4-pentanedionato)iron(III) ($\text{Fe}(\text{acac})_3$) with diethylaluminum ethoxide in the presence of dimethylphenylphosphine in dry diethyl ether below 0°C gave an orange, zerovalent iron complex formulated as $\text{Fe}(\text{C}_2\text{H}_4)_2(\text{PPhMe}_2)_3$ (I).



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 $\nu(\text{C}=\text{C})$ 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.

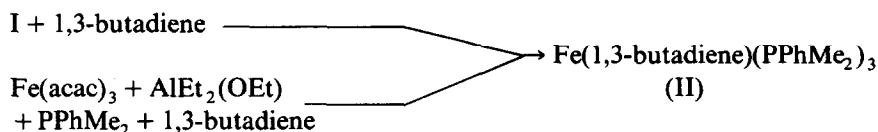


By analogy with the butadiene-coordinated complex (vide infra) the square pyramidal structure Ib seems most probable.

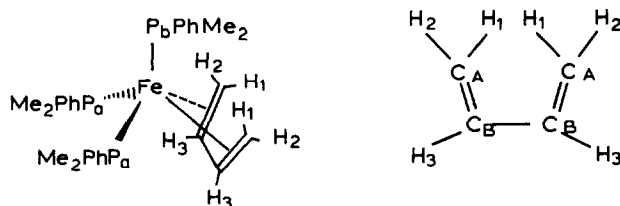
Complex I released ca. 1.5 mol of ethylene per Fe upon heating at 70°C for 30 min in the solid state. Acidolysis of I with sulfuric acid afforded a roughly 3:2 mixture of ethylene and ethane, the total yield of the gases being roughly 2 equivalents per Fe atom. Ligand exchange reaction of I with dpe in toluene gave the known complex, $\text{Fe}(\text{C}_2\text{H}_4)(\text{dpe})_2$ [5] accompanying loss of one mole of the coordinated ethylenes.

Preparation and NMR spectra of $\text{Fe}(\text{1,3-butadiene})(\text{PPhMe}_2)_3$, II

The coordinated ethylene ligands in I were easily displaced by 1,3-butadiene in ether below 0°C giving $\text{Fe}(\text{1,3-butadiene})(\text{PPhMe}_2)_3$ (II). Complex II was also prepared directly from the reaction of $\text{Fe}(\text{acac})_3$ with $\text{AlEt}_2(\text{OEt})$ in the presence of both dimethylphenylphosphine and 1,3-butadiene.



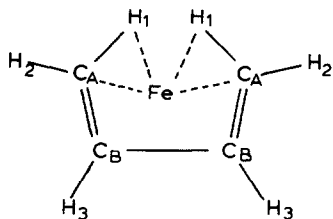
Complex II, which was recrystallized as yellow needles from diethyl ether, has a considerably higher thermal stability than complex I. The following square pyramidal structure of II is proposed on the basis of the ^1H , $^{31}\text{P}\{^1\text{H}\}$ and ^{13}C NMR analyses as well as by analogy with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



The $^{31}\text{P}\{^1\text{H}\}$ 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 ^1H NMR spectrum of II, two sets of methyl signals assignable to PPhMe_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 ^1H 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 $^{13}\text{C}\{^1\text{H}\}$ 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 ($J(\text{C-P}) = 11$ 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 $^{13}\text{C}\{^1\text{H}\}$ 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

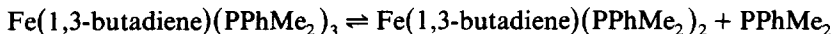
bonds. The stronger interaction of C_A with Fe probably arises from the tilted (or slid) plane of the 1,3-butadiene ligand toward Fe to make the distance from Fe to C_A shorter than that to C_B .



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 $C_A\text{--}H(1)$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR

On raising temperature, the sharp signals of P_A and P_B in the $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{Fe}(1,3\text{-BD})\text{L}_4$. 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.



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 $\text{FeL}_3(\text{diene})$ 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 . $\text{AlEt}_2(\text{OEt})$ was obtained by alcoholysis of AlEt_3 with absolute ethanol. $\text{Fe}(\text{acac})_3$ 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 ^1H , $^{31}\text{P}\{^1\text{H}\}$, and ^{13}C NMR were recorded on a JEOL-FX-100 spectrometer. Chemical shifts are referred to TMS for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR and to H_3PO_4 for $^{31}\text{P}\{^1\text{H}\}$ NMR. $J(\text{C}-\text{H})$ was estimated from the non-decoupled ^{13}C NMR spectrum.

Preparation of $\text{Fe}(\text{C}_2\text{H}_4)_2(\text{PPhMe}_2)_3$ (I)

An ether solution (25 ml) of $\text{Fe}(\text{acac})_3$ (3 g, 8.6 mmol) and PPhMe_2 (4.9 ml, 35 mmol) was treated with 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%. $\text{C}_{28}\text{H}_{41}\text{P}_3\text{Fe}$: calcd. Fe, 10.6%. m.p. $58-60^\circ\text{C}$ (dec.). ^1H NMR (in toluene- d_8 , -50°C), 0.5 ppm (br, 12H) and 1.6 (br, 6H) for PPhMe_2 . 2.6 (br, 8H) for C_2H_4 . 6.8–7.5 (br, 15H) for PPhMe_2 .

Preparation of $\text{Fe}(1,3\text{-butadiene})(\text{PPhMe}_2)_3$ (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. $116-117^\circ\text{C}$ (180°C dec.). Anal. Found: C, 63.8; H, 8.0; Fe, 11.3. $\text{C}_{28}\text{H}_{39}\text{P}_3\text{Fe}$ calcd.: C, 64.1; H, 7.5; Fe, 10.7%. ^1H NMR (in acetone- d_6 , -40°C): -2.13 (br, 2H) for *anti* H(1), 0.50 (br, 2H) for *syn* H₂, 1.20 (d, $J(\text{P}-\text{H})$ 6.4 Hz, 6H), 1.23 (d, $J(\text{P}-\text{H})$ 6.4 Hz, 6H) and 1.92 (d, $J(\text{P}-\text{H})$ 5.9 Hz, 6H) for PPhMe_2 , 4.43 (br, 2H) for $\text{C}_\text{B}\text{H}_3$, 6.8–7.5 (m, 15H) for PPhMe_2 . $^{31}\text{P}\{^1\text{H}\}$ NMR (in acetone- d_6 , -40°C): 33.7 (d, $J(\text{P}-\text{P})$ 3 Hz, 2P) for P_a . 38.0 (d, 1P) for P_b . $^{13}\text{C}\{^1\text{H}\}$ NMR (in CD_2Cl_2 , -40°C): 20.5 (m, $J(\text{C}-\text{H})$ 123 Hz(q)) and 23.5 (d, $J(\text{C}-\text{P})$ 20 Hz, $J(\text{C}-\text{H})$ 129 Hz(q)) for PPhMe_2 , 33.5 (d, $J(\text{C}-\text{P})$ 11 Hz, $J(\text{C}-\text{H})$ 154 Hz (t)) for C_A . 79.0 (s, $J(\text{C}-\text{H})$ 163 Hz(d)) for C_B . 128–130(m) for PPhMe_2 . Complex II was also obtained by the reaction of $\text{Fe}(\text{acac})_3$ (1 g) with $\text{AlEt}_2(\text{OEt})$ (1.5 ml) in the presence of PPh_2Me (1.6 ml) and excess 1,3-butadiene at 0°C . Yield, 784 mg (52%).

References and Notes

- 1 E.A. Koerner von Gustorf, F-W Grevels and I. Fischler (Eds.), *The Organic Chemistry of Iron*, Academic Press, New York, London, 1978
- 2 T. Kruck and L. Knoll, *Chem. Ber.*, 106 (1973) 3578.
- 3 J.W. Rathke and E.L. Muetterties, *J. Amer. Chem. Soc.*, 97 (1975) 3272.
- 4 S.D. Ittel, F.A. Van-Catledge, and J.P. Jesson, *J. Amer. Chem. Soc.*, 101 (1979) 3874.
- 5 G. Hata, H. Kondo, and A. Miyake, *J. Amer. Chem. Soc.*, 90 (1968) 2278.
- 6 C.A. Tolman, S.D. Ittel, A.D. English, and J.P. Jesson, *J. Amer. Chem. Soc.*, 100 (1978) 4080.
- 7 For example (a) A. Yamamoto and S. Ikeda, *J. Macromol. Sci.-Chem.*, A9 (1975) 931 and references cited therein; (b) T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, 118 (1976) 65, (c) T. Ito, H. Tsuchiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 50 (1977) 1319, (d) S. Komiya, M. Bundo, A. Yamamoto, and T. Yamamoto, *J. Organomet. Chem.*, 174 (1979) 343; (e) F. Ozawa, T. Ito, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc., Jpn.*, 54 (1981) 1868.
- 8 Olefins are reported to coordinate most likely to metal parallel with rather than perpendicular to the trigonal plane: F.R. Hartley, *J. Organomet. Chem.*, 216 (1981) 277.

- 9 For example, (a) S. Komiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 49 (1976) 2553, (b) C.F. Emerson, J.E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, 29 (1964) 3620, (c) W. Keim, *J. Organomet. Chem.*, 16 (1969) 191.
- 10 (a) M.L.H. Green, L. Paratt, and G. Wilkinson, *J. Chem. Soc.*, (1959) 3753, (b) E.A.K. von Gustorf, F.W. Grevels and I. Fishler, *The Chemistry of Iron*, Vol. 1, Academic Press, New York, London, 1978, p.114.
- 11 For example, (a) P.B. Hitchcock and R. Mason, *Chem. Commun.*, (1967) 242, (b) G.K. Baker, M. Green, J.A.K. Howard, J.L. Spencer, and F.G.A. Stone, *J. Amer. Chem. Soc.*, 98 (1976) 3373.
- 12 J.B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York and London, 1972.
- 13 For example, (a) O.W. Howarth, C.H. McAteer, P. Moore, and G.E. Morris, *J. Chem. Soc. Chem. Commun.*, (1981) 506. (b) R.K. Brown, J.M. Williams, A.J. Schultz, G.D. Stucky, S.D. Ittel, and R.L. Harlow, *J. Amer. Chem. Soc.*, 102 (1980) 981 and references cited therein. (c) K. Itoh and N. Oshima, *Chem. Lett.*, 8 (1980) 1219.