Reaction and Coordination Chemistry of Ferrocenylaminophosphines with Iron Carbonyls

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The reaction and coordination chemistry of chiral ferrocenylaminophosphines such as 2-(diphenylphosphino)-1-(N,N-dimethylaminoethyl) ferrocene (PPFA), and 1',2-bis(diphenylphosphino)-1-(N,N-dimethylaminoethyl) ferrocene (BPPFA), with various iron carbonyls have been investigated. PPFA reacted with iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$ to give an iron complex of the type (η^1-PPFA-*P*)$Fe(CO)_4$ (**1**) as a single product regardless the choice of the iron carbonyls. The bisphosphine ligand BPPFA afforded two products (η^1-BPPFA-*P*)$Fe(CO)_4$ (**2**) and (μ, η^1-BPPFA-*P,P*)$Fe_2(CO)_8$ (**3**) in which BPPFA acts as a monodentate and a bridging ligand, respectively. In all cases coordination to the -$Fe(CO)_4$ moiety is made through the phosphine rather than the amino group and, in the case of **2**, the coordination is made through the phosphine substituted at the C_5H_4 ring to reduce the steric congestion.

Introduction

It is now well established that ferrocenylphosphines are very efficient ligands for metal complexes in a wide range of homogeneous catalysis.[1-10] Of various chiral and achiral ferrocenylphosphine ligands those that have been most widely and effectively used in the catalytic reactions are 1,1'-bis(diphenylphosphino) ferrocene (BPPF), 2-(diphenylphosphino)-1-(N,N-dimethylaminoethyl) ferrocene (PPFA), and 1',2-bis(diphenylphosphino)-1-(N,N-dimethylaminoethyl) ferrocene (BPPFA).

We have recently reported the synthesis and catalytic properties of (η^2-BPPF)$Fe(CO)_3$, (η^1-BPPF)$Fe(CO_4)$, and (μ, η^2-BPPF)$Fe_2(CO)_8$. They were proved to be very efficient catalyst precursors for the synthesis of carbamates from the reaction of propargyl alcohol with secondary amines in the presence of CO_2.[11] We have found further that the ligand BPPF reacts with $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ to give a series of iron carbonyl derivatives with various coordination modes. It can act not only as a typical chelating bidentate but as a monodentate diphosphine, or a bridging ligand in di- and trimetallic species.[11,12]

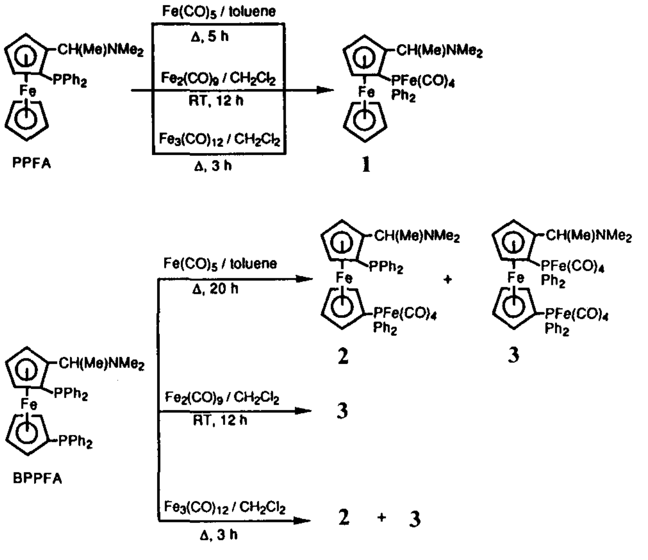
Prompted by these findings we decided to look further into the reactivity and coordination modes of the well-known chiral PN donor ligands PPFA and BPPFA because of their potential as catalysts. In such complexes these ligands can also act as a chelating bidentate, a monodentate coordinated through the phosphorus atom(s), or a bridging ligand. In this paper we report the synthesis and characterization of new iron complexes incooporating PPFA and BPPFA.

Experimentals

Reagents and Instruments. All Manipulations were conducted under an argon atmosphere using a double manifold vacuum system and Schlenk techniques. All commercial reagents were used as received. Solvents were purified by standard methods,[13] and were freshly distilled prior to use. Microanalyses were performed by Ms. T. Y. Park of this department. ^1H, ^{13}C, ^{31}P-NMR spectra were recorded on a Bruker Am-300 spectrometer operating at 300 MHz, 80.15 MHz, and 121.5 MHz, respectively. Infrared spectra were recorded on a FT-IR:Bio-RADFTS 20/30 spectrometer. The ligands PPFA and BPPFA were prepared according to the literature methods.[14]

Preparation of (η^1-PPFA-*P*)$Fe(CO)_4$ (1). PPFA (1.29 g, 2.94 mmol) and $Fe_3(CO)_{12}$(0.52 g, 1.47 mmol) were dissolved in CH_2Cl_2 (100 m*l*) in a 250 m*l* two necked, round bottom flask equipped with a condenser, a magnetic stirrer, and an argon inlet. The solution was refluxed with stirring for 3 h after which the solution filtered on a celite to remove solid impurities. The filtrate was evaporated under vacuo, and the remaining oily residue taken up in a small volume of THF to be chromatographed on silica gel. The single orange band was eluted with ether to give **1** as orange crystals after crystallization from a mixture of CH_2Cl_2 and hexane (1/3) at 0℃. Yield: 0.81 g, 46%. Anal. Calcd for (PPFA) $Fe(CO)_4$:C, 59.15; H, 4.63; N, 2.19. Found: C, 59.16; H, 4.66; N, 2.15. This same complex was also obtained as a single product either by refluxing a toluene solution of $Fe(CO)_5$/PPFA (5/1) or by stirring at room temperature a dichloromethane solution of $Fe_2(CO)_9$ and PPFA (1/1) for 12 h. The yields from these reactions ranged 40-50%.

Preparation of (η^1-BPPFA-*P*)$Fe(CO)_4$ (2) and (μ, η^2-BPPFA-*PP*)$Fe_2(CO)_8$ (3). The title complexes **2** and **3** were isolated as products of the same reaction between BPPFA and $Fe_3(CO)_{12}$. BPPFA (1.5 g, 2.4 mmol) and $Fe_3(CO)_{12}$ (1.21 g, 2.4 mmol) were dissolved in CH_2Cl_2 (30 m*l*) in a 100 m*l* two necked, round bottom flask equipped with a condenser, a magnetic stirrer, and an argon inlet. The solution was refluxed with stirring for about 4 h, filtered on a celite tube, and the filtrate evaporated under vacuo. The oily residue was dissolved in a small volume of CH_2Cl_2 and chromatographed on alumina (neutral). After the first green band of $Fe_3(CO)_{12}$ was removed on elution with hexane, the remaining three bands were eluted as follows: (1) band 2 eluted with ether to give **3** as orange powder after removal of solvent, (2) band 3 eluted with ether/acetone (5/1) to give **2** as yellow powder, (3) band 4 eluted with acetone to give purple solid to small an amount to be characterized. Yield



Scheme 1.

of **2**: 0.3 g, 16%, Anal. Calcd for (BPPFA)Fe(CO)$_4$: C, 63.60; H, 4.70; N, 1.77. Found: C, 63.93; H, 5.17; N, 1.89. Yield of **3**: 1.05, 46%. Anal. Calcd for (BPPFA)Fe$_2$(CO)$_8$: C, 56.96; H, 3.93; H, 1.48. Found: C, 56.98; H, 4.06; N, 1.42. When Fe$_2$(CO)$_9$ was employed in stead of Fe$_3$(CO)$_{12}$ the tetracarbonyl derivative **2** was obtained as a sole product (50%).

Table 1. Infrared Data for **1-3**[a]

Compound	ν(CO) (cm^{-1})
1	2048 (vs), 1987 (vs), 1952 (vs), 1917 (vs)
2	2048 (vs), 1971 (s), 1932 (vs)
3	1983 (vs), 1909 (vs), 1878 (vs), 1848 (s)

[a] Key: s=strong; vs=very strong.

Table 2. NMR Data for **1-3**[a, b, c]

Compound	^{1}H-NMR	^{31}P-NMR	^{13}C-NMR (CO region)
1	7.65-7.38 (m, C_6H_5) 4.61, 4.45, 4.25 (b, C_5H_3), 4.02 (s, C_5H_5), 3.86 (q, CH), 1.92 (s, NMe_2), 1.20 (d, $^3J_{HH}=6$, CMe)	59.1 (s)	213.9 (d, $^2J_{PC}=18$)
2	7.68-7.38 (m, C_6H_5) 4.72-3.91 (m, C_5H_3), 3.71, 3.46 (b, C_5H_4) 3.01 (b, CH), 1.50 (s, NMe_2) 1.10 (d, $^3J_{HH}=5.7$, CMe)	64.1 (s) 23.8 (s)	212.8 (d, $^2J_{PC}=19$)
3[d]	7.36 (m, C_6H_5) 4.84, 4.56 (b, C_5H_3), 4.10-3.67 (m, C_5H_4) 1.65 (s, NMe_2), 1.26 (d, $^3J_{HH}=5.7$, CMe)	64.9 (s) 59.3 (s)	213.7 (d, $^2J_{PC}=18$) 212.9 (d, $^2J_{PC}=19$)

[a] In CDCl$_3$. [b] Chemical shifts are in ppm and coupling constants in Hz. [c] Key: s=singlet; d=doublet; m=multiplet; q=quartet; b=broad, [d] Methyne proton concealed in the Cp region.

Results and Discussion

As one of our research objectives was to investigate the coordination chemistry of the chiral analogues of BPPF such as PPFA and BPPFA these ligands were reacted with Fe(CO)$_5$, Fe$_2$(CO)$_9$, and Fe$_3$(CO)$_{12}$. Since they possess both soft (phosphorus) and hard (nitrogen) donor sites, there exhibits more than one possibility of coordination mode; a chelating bidentate through P-N or P-P, a bridging bidentate, or a monodentate through nitrogen or phosphorus.

Scheme 1 shows various reaction conditions that lead to the synthesis of a new series of chiral iron carbonyl derivatives **1-3** demonstrating only one possibility, namely, coordination through phosphorus in a monodentate fashion. Thus, in the case of PPFA, the only observable product formed was **1** regardless the choice of iron carbonyls.

This can be confirmed by its spectroscopic data listed in Tables 1 and 2. The pattern of carbonyl stretching bands is quite similar to those found for (FcNP)Fe(CO)$_4$[15] (FcNP=2-(diphenylphosphino)-1-(N,N-dimethylaminomethyl)ferrocene) and (η^1-BPPF)Fe(CO)$_4$.[11] The coordination through phosphorus can be best identified by the ^{1}H-NMR spectrum showing only a single resonance line for the uncoordinated -NMe$_2$ protons, which has virtually the same chemical shift as the corresponding protons in the free ligand.[14,15] The ^{13}C

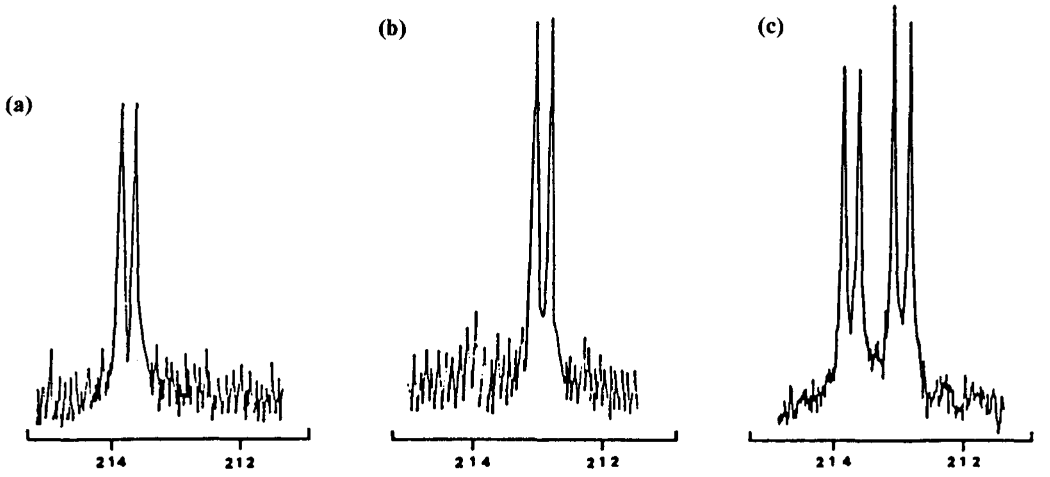


Figure 1. ^{13}C-NMR (80.15 MHz) spectra of (a) **1**, (b) **2**, and (c) **3** in the carbonyl region.

and ^{31}P-NMR patterns are as expected.

The reaction of BPPFA with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ afforded two major products **2** and **3**, while the reaction with $Fe_2(CO)_9$ gave **3** alone. The purple unidentified compound that was formed in a trace amount from the reaction with $Fe_3(CO)_{12}$ (see Experimental) may be considered as a trinuclear iron complex of BPPFA analogous to (μ, η^2-BPPF)$Fe_3(CO)_{10}$ judging from the same color.[12] The spectral data provided in Tables 1 and 2 are all in a good agreement with the formulation of each compound. An interesting aspect to be noted concerning the coordination behavior of BPPFA is that in **2** this ligand acts as a monodentate through a single phosphorus like that shown in (η^1-BPPF)$Fe(CO)_4$, while in **3** it acts as a bridge employing both phosphorus atoms as seen in (μ, η^2-BPPF)$Fe_2(CO)_8$. This is evidenced by the presence of two ^{31}P signals and of the singlet for the free -NMe_2 group in each compound. Even more supportive is the ^{13}C-NMR pattern for the carbonyl groups as shown in Figure 1. Table 2 shows a doublet for the -$Fe(CO)_4$ moiety in **2** and a pair of doublets for the two non-equivalent -$Fe(CO)_4$ groups in **3**, Finally, an important question concerning the point of attachment of BPPFA in **2** can be answered by comparing both the ^{31}P and ^{13}C-NMR patterns of the three compounds **1-3**. Thus, for example, as shown in Figure 1., the chemical shift of the doublet at $\delta=212.8$ ppm in **2** is closer to that of the one at $\delta=212.9$ ppm which is arising from the -$Fe(CO)_4$ moiety attached to the -PPh_2 group in the singly substituted cyclopentadienyl ring in **3**.

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A Statistical Termodynamic Study of Phase Equilibria in Microemulsions

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To investigate the phase equilibria and structural properties of microemulsions, we study a simple phenomenological model on the basis of the cubic lattice cell with which the oil- and water-filled cells are connected one another, respectively. The surfactant is assumed to be insoluble in both oil and water, and to be adsorbed at the oil-water interface. The Schulman condition, according to which the lateral pressure of the surfactant layer is compensated by the oil-water interfacial tension, is found to hold to good approximation in the middle-phase microemulsion. Our results show that the oil- and water-filled domains in that microemulsion are about 50-150 Å across, and depend sensitively on the curvature parameters. The phase diagram is not symmetric in this model. It may be asymmetrized intrinsically by non-equivalency of oil and water. The two- and tree-phase equilibria including critical points and critical endpoints are found.

Introduction

Mixtures of oil and water are naturally unstable, but they can be stabilized by addition of suitable surfactants, which optimize their interactions by standing at the oil-water interface and decrease drastically the interfacial energy. With