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## Reactivity of phosphinoalkynes toward $[\text{HFe}_3(\text{CO})_9(\text{C}=\text{CH}_2)]^-$

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### Abstract

The reactions of triphenylphosphine and (diphenylphosphino)alkynes  $\text{Ph}_2\text{PC}\equiv\text{CR}$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{CH}_3, \text{C}(\text{CH}_3)_3$  or  $\text{C}(\text{O})\text{OCH}_3$ ) with  $[\text{PPh}_4][\text{HFe}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}=\text{CH}_2)]$  have been studied. The complexes  $[\text{PPh}_4][\text{Fe}_3(\text{CO})_9(\mu_3\text{-CCH}_3)\text{L}]$  ( $\text{L} = \text{PPh}_3$  or  $\text{Ph}_2\text{PC}\equiv\text{CR}$ ) were isolated in high yields. The reaction involves migration of hydride which transforms the vinylidene ligand into an ethylidyne ligand. (Diphenylphosphino)alkynes are coordinated to metal atoms only through the phosphine centre and the alkyne group remains uncoordinated. The reaction of the new complexes with  $\text{Co}_2(\text{CO})_8$  has been studied.

### Introduction

The reactions of (diphenylphosphino)alkynes  $\text{Ph}_2\text{PC}\equiv\text{CR}$  with polynuclear metal complexes have attracted much interest in recent years, and the studies have revealed some interesting rearrangement reactions, some involving breaking of the phosphorus–alkynyl bond [1,2].

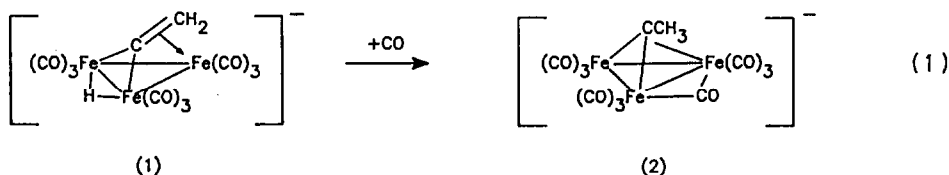
We recently showed that the cluster anion  $[\text{HFe}_3(\text{CO})_{11}]^-$  reacts with (diphenylphosphino)alkynes to give different compounds depending on the nature of the R group and the temperature of the reaction [3,4]. The first step of the reaction with  $[\text{HFe}_3(\text{CO})_{11}]^-$  is probably replacement of CO by the phosphorus atom of the phosphinoalkyne, though this intermediate would be very reactive and so has not been isolated. In all the characterized compounds there is coordination of the phosphorus atom, migration of hydride to the alkyne function having taken place. However in the literature there are some examples of neutral phosphinoalkyne complexes with coordination only through the phosphorus atom [5].

These facts led us to search for an iron anionic cluster which could react with phosphinoalkynes only through the phosphine function, leaving the alkyne group uncoordinated. The synthesis of such compounds is of interest for two reasons:

(a) they allow a study of the influence of phosphorus coordination on the reactivity of the alkyne function;

(b) they may provide an excellent starting point for the synthesis of mixed metal clusters by coordination of the alkyne to a different metal centre [6].

We thus chose for our study the iron anionic cluster  $[\text{HFe}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}=\text{CH}_2)]^-$  (**1**). This vinylidene compound reacts reversibly with carbon monoxide to yield the complex  $[\text{Fe}_3(\text{CO})_{10}(\text{CCH}_3)]^-$  (**2**) containing an ethylidyne ligand [7]. We reasoned that a similar reaction might occur with another two-electron ligand such as a phosphine.



## Results and discussion

### Reaction with $\text{PPh}_3$

First we studied the reaction of **1** with triphenylphosphine in order to see whether reaction 1 could occur with another two-electron ligand.

Complex **1** was found to react with triphenylphosphine in acetone solution at room temperature to give only one main product, in high yield. The elemental analysis is consistent with the formulation  $[\text{PPh}_4][\text{Fe}_3(\text{CO})_9(\text{PPh}_3)(\text{CCH}_3)]$  (**3**). In the proton NMR spectrum, in addition to the phenyl resonances, only one singlet at 4.1 ppm, attributed to the methyl group, is observed. The presence of the ethylidyne ligand is confirmed by the  $^{13}\text{C}$  NMR spectrum; one signal characteristic of the carbon of an alkylidyne ligand  $\mu_3$ -bond appears at 282.5 ppm and another signal, attributed to the  $\text{CH}_3$  group, at 43.2 ppm (the  $^{13}\text{C}$  NMR spectrum of complex **2** show resonances at 44.3 (C- $\text{CH}_3$ ) and 289 ppm (C- $\text{CH}_3$ ) assigned to ethylidyne ligand). Furthermore, the substantial downfield shift of phosphorus resonance (66.2 ppm) relative to that for free  $\text{PPh}_3$  is consistent with coordination of triphenylphosphine to the metal. The result confirmed that reaction 1 could be extended to phosphine ligands.

### Reaction with $\text{Ph}_2\text{PC}\equiv\text{CR}$ ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_6\text{H}_4\text{CH}_3, \text{C}(\text{CH}_3)_3$ or $\text{C}(\text{O})\text{OCH}_3$ )

Treatment of **1** with  $\text{Ph}_2\text{PC}\equiv\text{CR}$  as described for  $\text{PPh}_3$  gave as the main products **4a** ( $\text{R} = \text{Me}$ ), **4b** ( $\text{R} = \text{Ph}$ ), **4c** ( $\text{R} = \text{Tol}$ ), **4d** ( $\text{R} = \text{tBu}$ ) and **4e** ( $\text{R} = \text{CCOOMe}$ ) in high yields.

Solutions of the isolated products give similar IR spectra in the  $\nu(\text{CO})$  stretching region (Table 1), and these closely resemble that of **3**, the complex previously prepared from  $\text{PPh}_3$ . In addition, the characteristic peak of uncoordinated alkynes is observed in the  $\nu(\text{C}\equiv\text{C})$  (Table 1) region in the IR spectrum of the solid. From these results, it can be deduced that the alkynylphosphine is coordinated to the metal atom only through the phosphorus atom. This is consistent with the  $^{31}\text{P}$  NMR chemical shifts (Table 2); the relatively high field shift of the phosphorus resonance in **4a–4e** complexes relative to that for **3** may be attributed to the electron ring current of the two  $\pi$ -bonds of the alkynyl group [8].

Table 1

IR data for the isolated complexes

Compound	$\nu(\text{CO})^a$ ( $\text{cm}^{-1}$ )	$\nu(\text{C}\equiv\text{C})^{b,c}$ ( $\text{cm}^{-1}$ )	$\Delta\nu(\text{C}\equiv\text{C})^{b,d}$ ( $\text{cm}^{-1}$ )
<b>3</b>	2024m, 1978vs, 1956s, 1654b		
<b>4a</b>	2022m, 1972vs, 1956s, 1652b	2169(2158)	11
<b>4b</b>	2022m, 1972vs, 1956s, 1652b	2168(2156)	12
<b>4c</b>	2022m, 1972vs, 1956vs, 1652b	2168(2156)	12
<b>4d</b>	2022m, 1973vs, 1953s, 1652b	2173(2164)	9
<b>4e</b>	2025m, 1976vs, 1957s, 1713m 1656b	2177(2168)	9

<sup>a</sup> In solution. <sup>b</sup> In solid state. <sup>c</sup> Values for free phosphinoalkynes are in parenthesis. <sup>d</sup>  $\Delta\nu(\text{C}\equiv\text{C}) = \nu(\text{C}\equiv\text{C})$  (complex) –  $\nu(\text{C}\equiv\text{C})$  (free phosphinoalkyne).

The <sup>1</sup>H NMR data (Table 2) confirm the similarity to the phosphine complex **3**. A characteristic singlet near 4.1 ppm, which integrates for three protons, suggests the formulation [PPh<sub>4</sub>][Fe<sub>3</sub>(CO)<sub>9</sub>(CCH<sub>3</sub>)(Ph<sub>2</sub>PC≡CR)]. This is consistent with the chemical analysis and with the <sup>13</sup>C NMR spectrum, in which resonances assigned to ethylidyne ligand at 43.1–43.6 ppm (C–CH<sub>3</sub>) and 282.4–283.6 ppm (C≡C) are observed. In the light of the results we suggest the structure shown in Fig. 1 for complexes **3** and **4a–4e**. The triply bridging CO ligand is not firmly established, but it is consistent with an IR band near 1650 cm<sup>-1</sup> [7].

Table 2

NMR data for the isolated complexes

Compound	<sup>31</sup> P $\delta$ (ppm)	<sup>1</sup> H <sup>a</sup> $\delta$ (ppm)	<sup>13</sup> C <sup>a</sup> $\delta$ (ppm)
<b>3</b>	23.4(PPh <sub>4</sub> ), 62.2(PPh <sub>2</sub> )	4.1(3H, CH <sub>3</sub> CFe <sub>3</sub> )	43.2(CH <sub>3</sub> CFe <sub>3</sub> ), 224.5(CO) 282.5(CH <sub>3</sub> CFe <sub>3</sub> )
<b>4a</b>	23.6(PPh <sub>4</sub> ), 43.9(PPh <sub>2</sub> )	2.4(3H, CH <sub>3</sub> C≡C), 4.1(3H, CH <sub>3</sub> CFe <sub>3</sub> )	21.3(CH <sub>3</sub> C≡C), 43.1(CH <sub>3</sub> CFe <sub>3</sub> ) 85.6 (d, <i>J</i> = 72.4, C≡C–P), 106.3 (d, <i>J</i> = 14.1, C≡C–P), 225(CO), 282.5(CH <sub>3</sub> CFe <sub>3</sub> )
<b>4b</b>	23.9(PPh <sub>4</sub> ), 44.5(PPh <sub>2</sub> )	4.2(3H, CH <sub>3</sub> CFe <sub>3</sub> )	43.3(CH <sub>3</sub> CFe <sub>3</sub> ), 86.3(d, <i>J</i> = 72.4, C≡C–P), 106.5(d, <i>J</i> = 0.4, C=C–P), 225.1(CO), 283.6(CH <sub>3</sub> CFe <sub>3</sub> )
<b>4c</b>	23.5(PPh <sub>4</sub> ), 42.6(PPh <sub>2</sub> )	2.4(3H, CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ), 4.1(3H, CH <sub>3</sub> CFe <sub>3</sub> )	21.5(CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ), 43.6(CH <sub>3</sub> CFe <sub>3</sub> ), 86.1(d, <i>J</i> = 74.3, C≡C–P), 107.4 (d, <i>J</i> = 10, C≡C–P), 224.6(CO), 283.3(d, <i>J</i> = 7.4, CH <sub>3</sub> CFe <sub>3</sub> )
<b>4d</b>	23.5(PPh <sub>4</sub> ), 41.6(PPh <sub>2</sub> )	1.4(9H, (CH <sub>3</sub> ) <sub>3</sub> C), 4.1(3H, CH <sub>3</sub> CFe <sub>3</sub> )	30.6((CH <sub>3</sub> ) <sub>3</sub> C), 43.5(CH <sub>3</sub> CFe <sub>3</sub> ), 75.7(d, <i>J</i> = 75.7, C≡C–P), 117.7 (C≡C–P), 224.8(CO), 282.9 (CH <sub>3</sub> CFe <sub>3</sub> )
<b>4e</b>	23.6(PPh <sub>4</sub> ), 45.6(PPh <sub>2</sub> )	3.8(3H, COOCH <sub>3</sub> ), 4.1(3H, CH <sub>3</sub> CFe <sub>3</sub> )	43.4(CH <sub>3</sub> CFe <sub>3</sub> ), 53.1(COOCH <sub>3</sub> ), 86.3(d, <i>J</i> = 50.7, C≡C–P), 95.7 (C≡C–P), 153.7(COOCH <sub>3</sub> ), 226.7 (CO), 282.5(d, <i>J</i> = 9.0, CH <sub>3</sub> CFe <sub>3</sub> )

<sup>a</sup> Except phenyl resonances.

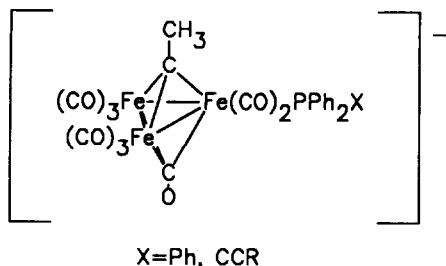


Fig. 1.

In summary, the addition of one molecule of alkynyl-diphenylphosphine to cluster **1** induces migration of hydride and consequent transformation of the vinylidene into an ethylidyne ligand. The alkynylphosphine is coordinated to the metal atom only through the phosphorus atom, and the alkynyl function remains uncoordinated.

In phosphinoalkyne metal complexes involving coordination of the ligand only through the phosphorus atom, the influence of the phosphorus coordination on the alkyne function may be estimated from IR and NMR data. The increase in the  $\nu(\text{C}\equiv\text{C})$  frequency ( $\Delta\nu$ ) on going from free phosphinoalkynes to their metal complexes has been related to the transfer of electron density from the filled  $d$ -orbitals of the transition metal to the empty  $d$ -orbitals of the phosphorus atom [9]. This retrodonative bonding from the transition metal atom to the phosphorus atom will lower the ability of the phosphorus  $d$ -orbitals to attract electron density from the filled  $\pi$ -orbitals of the carbon-carbon triple bond, and hence the  $\nu(\text{C}\equiv\text{C})$  frequency increases [10]. The  $\Delta\nu$  values (Table 1) are similar to those for the iron carbonyl complex  $(\text{PhC}\equiv\text{CPh})_2\text{Fe}(\text{CO})_3$  ( $\Delta\nu = 12 \text{ cm}^{-1}$ ) [9], and so relative to this neutral iron carbonyl complex there is no significant change when the diphenylphosphino alkyne is coordinated to the anionic iron complex.

If we assume, as others have done [11], that a change in  $\delta(^{13}\text{C})$  may be associated with a change in charge on the carbon atom, then the sum of the chemical shifts of the two acetylenic carbon atoms for different compounds  $\delta(\text{C}^1) + \delta(\text{C}^2)$  gives an idea of the charge changes in the triple bond, and the difference  $\delta(\text{C}^1) - \delta(\text{C}^2)$  is a measure of the polarisation of the charge in the triple bond [11]. Comparison of the values of  $\delta(\text{C}^1) + \delta(\text{C}^2)$  and  $\delta(\text{C}^1) - \delta(\text{C}^2)$  for the free phosphinoalkynes and their respective metal complexes **4a-4e**, can give some idea of the charge and polarisation changes as a result of the coordination to the metal. The analysis in Table 3 does not reveal significant differences in  $\delta(\text{C}^1) + \delta(\text{C}^2)$  and  $\delta(\text{C}^1) - \delta(\text{C}^2)$  values between each phosphinoalkyne and its respective metal complex, and in terms of these spectroscopic data the influence of phosphorus coordination in alkyne function in complexes **4a-4e** seems fairly unimportant.

*Reaction between complex  $[\text{PPh}_4][\text{Fe}_3(\text{CO})_9(\text{CCH}_3)(\text{Ph}_2\text{PC}\equiv\text{CPh})]$  and  $\text{Co}_2(\text{CO})_8$*

According to the IR and NMR data, alkyne function is uncoordinated in complexes **4a-4e**. We tried to prepare heteronuclear complexes by classical treatment of the alkyne with  $\text{Co}_2(\text{CO})_8$ . Unfortunately all attempts were unsuccessful, and the ethylidyne complex **2** was always recovered after the attempted reaction between **4b** and  $\text{Co}_2(\text{CO})_8$ . This rather surprising behaviour may be due to the loss

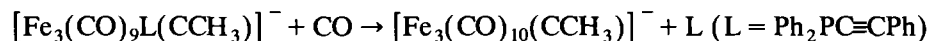
Table 3

Carbon-13 chemical shifts for the acetylenic atoms  $[\text{Fe}_3(\text{CO})_9(\text{CCH}_3)(\text{Ph}_2\text{PC}^1\equiv\text{C}^2\text{R})]^-$ 

Compound	$\delta(\text{C}^1)$	$\delta(\text{C}^2)$	$\delta(\text{C}^1) + \delta(\text{C}^2)$	$\delta(\text{C}^2) - \delta(\text{C}^1)$
<b>4a</b>	85.6(75.4) <sup>a</sup>	106.3(107.2)	191.9(182.6)	20.7(31.8)
<b>4b</b>	87.0(86.3)	107.1(108.7)	194.1(195.0)	20.1(22.4)
<b>4c</b>	86.1(85.4)	107.4(108.9)	193.5(194.3)	21.3(23.5)
<b>4d</b>	75.7(75.2)	117.7(119.5)	193.4(194.7)	42.0(44.3)
<b>4e</b>	86.3(87.0)	95.7(98.8)	182.0(185.9)	9.4(11.9)

<sup>a</sup> Values for free phosphinoalkynes are in parentheses.

of two molecules of carbon monoxide in the reaction between the alkyne and  $\text{Co}_2(\text{CO})_8$ . The carbon monoxide formed may replace the phosphine:



This suggestion is consistent with the fact that the complex **4b** reacts with carbon monoxide to give complex **2** as the main product.

## Experimental

All reactions were performed under nitrogen by standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 1710 FT spectrometer using dichloromethane solutions or KBr pellets. The NMR spectra were recorded by the *Servei de Ressonancia Magnètica Nuclear de la Universitat Autònoma de Barcelona* on a Bruker AM400 instrument.

Complex **1** and  $\text{Ph}_2\text{PCCR}$  (R=Me, Ph, <sup>t</sup>Bu, COOMe) were prepared by published procedures [4,7]. Microanalyses were performed in our laboratory.

### Preparation of $\text{Ph}_2\text{PCCTol}$

To a solution of 5.45 ml of  $\text{HC}\equiv\text{CTol}$  (Tol = *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ) in 100 ml of diethyl ether maintained at  $-60^\circ\text{C}$  was added 27 ml of 1.6 M solution of butyllithium in hexane. The solution was stirred for 30 min then a solution of 7.75 ml of  $\text{Ph}_2\text{PCl}$  in 20 ml of diethyl ether was slowly added at  $-60^\circ\text{C}$ . The temperature was slowly raised to ambient and the solution stirred for a further 2 h. After filtration through Celite to remove LiCl, the solution was evaporated to dryness, and the residue recrystallized from methanol to give 11.9 g (92%) of  $\text{Ph}_2\text{PCCTol}$  as white crystals.

Anal. Found: C, 84.00; H, 5.65.  $\text{C}_{21}\text{H}_{17}$  calc.: C, 84.05; H, 5.41%.

### Preparation of **3**

A solution of **1** (0.5 g) and  $\text{PPh}_3$  (0.17 g) in acetone (20 ml) was stirred at room temperature for 20 h then evaporated to dryness in vacuo. The residue was dissolved in a small amount of dichloromethane, methanol was added, and the resulting solution cooled to  $-20^\circ\text{C}$  to give 0.55 g (85%) of **3** as dark red crystals.

Anal. Found: C, 61.49; H, 3.78.  $\text{C}_{53}\text{H}_{38}\text{O}_9\text{P}_2\text{Fe}_3$  calc.: C, 62.50; H, 3.73%.

### Preparation of **4a-4e**

A solution of **1** (0.5 g) and a stoichiometric amount of the alkynylphosphine  $\text{Ph}_2\text{PCCR}$  in acetone was stirred at room temperature for 20 h then evaporated to

dryness *in vacuo*. The residue was dissolved in a small amount of dichloromethane, methanol was added, and the resulting solution cooled to  $-20^{\circ}\text{C}$  to give: **4a** (0.46 g, 72% yield) as dark red crystals. Anal. Found: C, 60.04; H, 3.65.  $\text{C}_{50}\text{H}_{36}\text{O}_9\text{P}_2\text{Fe}_3$  calc.: C, 59.64; H, 3.57%. **4b** (0.60 g, 88% yield) as dark red crystals. Anal. Found: C, 61.79; H, 3.69.  $\text{C}_{55}\text{H}_{38}\text{O}_9\text{P}_2\text{Fe}_3$  calc.: C, 61.59; H, 3.55%. **4c** (0.58 g, 84% yield) as dark red crystals. Anal. Found: C, 61.14; H, 3.84.  $\text{C}_{56}\text{H}_{40}\text{O}_9\text{P}_2\text{Fe}_3$  calc.: C, 61.90; H, 3.70%. **4d** (0.55 g, 83% yield) as dark red crystals. Anal. Found: C, 60.35; H, 4.11.  $\text{C}_{53}\text{H}_{42}\text{O}_9\text{P}_2\text{Fe}_3$  calc.: C, 60.48; H, 4.09%. **4e** (0.53 g, 79% yield) as dark red crystals. Anal. Found: C, 58.38; H, 3.44.  $\text{C}_{51}\text{H}_{36}\text{O}_{11}\text{P}_2\text{Fe}_3$  calc.: C, 58.09; H, 3.42%.

#### *Reaction of 4b with $[\text{Co}_2(\text{CO})_8]$*

To a solution of **4b** (0.50 g) in dichloromethane (15 ml) was slowly added a solution of  $[\text{Co}_2(\text{CO})_8]$  (0.16 g) in dichloromethane (15 ml). The solution was stirred for 8 h and then evaporated to dryness. Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  gave **2** as the main product.

#### *Reaction of 4b with CO*

Carbon monoxide was bubbled through a solution of **4b** (0.1 g) in 20 ml of dichloromethane for 5 min. The IR spectrum of the resulting solution in the  $\nu(\text{CO})$  stretching region showed the characteristic peaks of complex **2**.

#### **Acknowledgement**

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