

REACTION OF η^4 -DIENE- AND η^4 -HETERODIENE-IRON CARBONYL COMPLEXES WITH 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE: A ROUTE TO DICARBONYL TRISPHOSPHINE IRON COMPLEXES

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Summary

The reaction of 1,2-bis(diphenylphosphino)ethane with (η^4 -diene)- and (η^4 -heterodiene)- $\text{Fe}(\text{CO})_2\text{L}$ [$\text{L} = \text{CO}, \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$] complexes gives the complex $[\text{Fe}(\text{CO})_2(\text{diphos})_2]$. A mechanism for the formation of this complex is proposed on the basis of the reaction products and the kinetic results.

Introduction

The replacement of three CO ligands of iron pentacarbonyl by phosphine ligands does not occur by direct substitution owing to the high stability of the disubstituted complexes [1]. The trisubstituted complexes have been obtained from dicarbonyl-bisphosphine derivatives of iron(II), by reduction in the presence of excess of phosphine ligands [2,3].

The [$(\eta^4\text{-PhCH=CHCH=NPh})\text{Fe}(\text{CO})_2\text{L}$] complexes ($\text{L} = \text{Group V ligands}$) do not undergo further substitution [4], even when L is very basic, e.g. $\text{P}(\text{n-Bu})_3$ or under drastic conditions ($\sim 100^\circ\text{C}$). On the other hand, they react with the much less basic CO, even under mild conditions, to give [$(\eta^4\text{-PhCH=CHCH=NPh})\text{Fe}(\text{CO})_3$]. These results are easily explainable if the reaction is controlled by thermodynamic rather than kinetic factors, and this has been confirmed by a study of the equilibria and mechanism of the reaction with CO [5].

In the light of those findings, we decided to take advantage of the chelation effect of 1,2-bis(diphenylphosphino)ethane (diphos) to obtain trisubstituted complexes of iron pentacarbonyl, which are very reactive and show interesting catalytic properties [6].

Experimental

The IR and NMR spectra were recorded on a 257 Perkin Elmer spectrophotometer and a Jeol G60HL Spectrometer, respectively.

All the experiments were carried out in deaerated and anhydrous solvents.

a) Preparation of the complexes and reactions with 1,2-bis(diphenylphosphino)ethane

The complexes $[(\eta^4\text{-PhCH=CHCH=NPh})\text{Fe}(\text{CO})_2\text{L}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$) were prepared as previously described [4].

Preparation of $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]^$.* The reaction is described for $\text{L} = \text{PPh}_3$; it takes place similarly with $\text{L} = \text{AsPh}_3$ and SbPh_3 . 0.4 g of $[(\eta^4\text{-PhCH=CHCH=NPh})\text{Fe}(\text{CO})_2\text{PPh}_3]$ and 0.56 g of diphos (molar ratio 1/2) were suspended in 60 cc of anhydrous ethyl alcohol, and the stirred suspension was kept at to 68°C for 4 hours. Both the complex and diphos dissolved, and a some of the product precipitated out as a woolly solid. When the reaction was complete, as indicated by the IR spectrum of the solution, the temperature was lowered to 40°C and the solution was allowed to crystallize for 5 hours. The precipitate was filtered off at this temperature. It is a yellow solid, soluble in many organic solvents, but only very slightly soluble in n-hexane; it is decomposed by solvents containing halogens. Even though the reaction is quantitative, the yield of the product is very low (20%), because the separation of the $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ from the free diphos and from the Schiff base is difficult. $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ shows in the IR two strong CO stretching bands at 1847, 1904 cm^{-1} in n-hexane. Analysis: found: C, 72.3; H, 4.78. $\text{C}_{54}\text{H}_{48}\text{FeO}_2\text{P}_4$ calcd.: C, 71.37; H, 5.32%.

$[(\eta^4\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_3]$. This complex was prepared by irradiation of a solution of $[\text{Fe}(\text{CO})_5]$ and *trans,trans* PhCH=CHCH=CHPh (molar ratio 1/2) in benzene, using a medium pressure Hg Hanovia lamp. During the irradiation, the formation of the complex $[(\eta^2\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_4]$ was observed, as described in literature for the reaction of $[\text{Fe}(\text{CO})_5]$ with buadiene [7]; this complex was not isolated but the CO stretching bands was found to be at 2080, 2016, 2005 and 1985 cm^{-1} in n-pentane. After two days, the reaction was stopped and the solution was dried. The solid was purified by crystallization with a n-hexane/ CH_2Cl_2 mixture. The complex $[(\eta^4\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_3]$ is a yellow solid with m.p. $158\text{--}162^\circ\text{C}$ and CO stretching bands in n-hexane at 2945, 1988 and 1980 cm^{-1} . Anal. Found: C, 64.50; H, 3.93. $\text{C}_{19}\text{H}_{14}\text{FeO}_3$ calcd.: C, 65.92; H, 4.08%.

$[(\eta^4\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_2\text{PPh}_3]$. Irradiation of $[(\eta^4\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_3]$ and PPh_3 (molar ratio 1/1) in benzene with a medium pressure Hg Hanovia lamp for three days at room temperature gave the complex $[(\eta^4\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_2\text{PPh}_3]$. The solution was dried, and the solid was crystallized from a CH_2Cl_2 /n-hexane mixture. The complex shows two stretching CO bands at 1973 and 1914 cm^{-1} in CH_2Cl_2 ; m.p. $180\text{--}184^\circ\text{C}$. Anal.: found: C, 73.80; H, 4.91. $\text{C}_{35}\text{H}_{29}\text{FeO}_2\text{P}$ calcd.: C, 74.49; H, 5.04%.

* Here and elsewhere, (diphos) denotes the chelated ligand and diphos the singly bound ligand.

$[(\eta^2\text{-CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2)\text{Fe}(\text{CO})_4]$: a mixture of $[\text{Fe}_2(\text{CO})_9]$ (5 g) and isoprene (1 g) (molar ratio 1/5) was dissolved in benzene and stirred for 5 hours at 10°C . The formation of $[(\eta^2\text{-CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2)\text{Fe}(\text{CO})_4]$ and small quantities of $[(\eta^4\text{-CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2)\text{Fe}(\text{CO})_3]$ was observed. The solution was filtered and distilled. The product is a yellow liquid, which shows four CO stretching bands in n-pentane at 2082, 2009, 2005, 1984 cm^{-1} . The NMR spectrum is discussed below.

$[(\eta^4\text{-CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2)\text{Fe}(\text{CO})_3]$. This complex, already described in the literature [8], was prepared in the same way as the dihapto complex $[(\eta^2\text{-CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2)\text{Fe}(\text{CO})_4]$, but operating at 40°C . The purification was performed by distillation under vacuum and the red liquid shows the characteristics indicated by the literature [8].

Reaction of $[(\eta^4\text{-diene})\text{Fe}(\text{CO})_3]$ and $[(\eta^4\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_2\text{PPh}_3]$ with diphos. This reaction was carried out in mesitylene at $135\text{--}140^\circ\text{C}$. The formation of $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ was revealed by recording the IR spectrum after three hours. The reaction was not taken to completion because at this temperature the $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ decomposed.

Reaction of $[(\eta^4\text{-PhCH=CHCH=NPh})\text{Fe}(\text{CO})_3]$ and diphos. A mixture of $[(\eta^4\text{-PhCH=CHCH=NPh})\text{Fe}(\text{CO})_3]$ (0.7 g) and diphos (1 g) was allowed to react in benzene at 60°C . The reaction was complete after 4 hours. The formation of $[\text{Fe}(\text{CO})_3(\text{diphos})]$ [9] and $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ was observed. The ratio $[\text{Fe}(\text{CO})_3(\text{diphos})] : [\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ was 0.6, and this did not change after standing at 80°C for a day.

b) Kinetic measurements

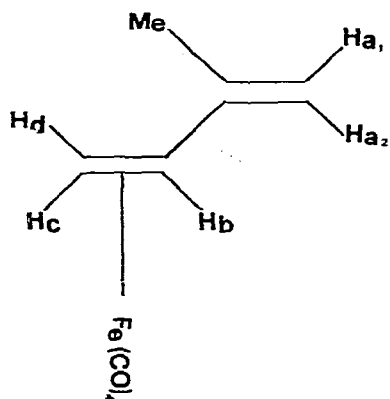
The kinetic runs were carried out in deaerated anhydrous toluene (by distillation over Na) in thermostated ($\pm 0.1^\circ\text{C}$) vessels, fitted with a rubber cup through which small portions were withdrawn at chosen time intervals with a hypodermic syringe.

The rate constants were measured in the presence of a large excess of diphos (>10 fold) in order to ensure pseudo-first order conditions. These constants were calculated both from the disappearance of the reagent complex (by plotting $\ln D_0/D_t$ against t , where D_0 and D_t are the initial absorbance and that at time t , respectively, of the CO stretching at higher frequency) and the appearance of the final complex (by plotting $\ln D_\infty/(D_\infty - D_t)$ against t , in which D_∞ and D_t are the absorbances of the lower CO stretching frequency of the complex $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ at the end of the reaction and at time t). The values of the rate constants obtained for the appearance of the product and the disappearance of the reagent complex are the same within 5%. The kinetics were followed for at least four half-lives, at temperatures between 50 and 70°C .

Results and discussion

a) Structure of $[\eta^2(\text{CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2)\text{Fe}(\text{CO})_4]$

The structure of this complex can be easily obtained from the NMR spectrum in CS_2 . This spectrum is very rich in resonances, and in discussing it, we refer to the following representation (Scheme 1):



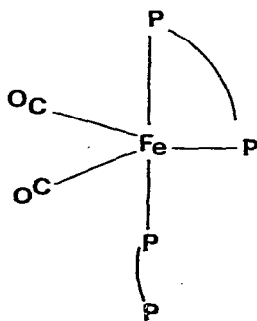
SCHEME 1

The Ha_1 and Ha_2 proton show two bands at $\tau(\text{Ha}_1) = 5.48$ ppm and $\tau(\text{Ha}_2) = 5.24$ ppm; the Ha_1 band is coupled with the methyl protons ($\tau = 8.06$ ppm) ($J(\text{Ha}_1-\text{CH}_3) = 1.1$ Hz). These bands are not much shifted with respect to the bands in the free isoprene [10]; this is in accord with the structure depicted, which indicates a bond between the iron and the double bond not bearing the methyl group.

The Hb proton shows a band at 6.25 ppm (double doublet), coupled with the Hd ($J(\text{Hb}-\text{Hd}) = 12.5$ Hz) in the *trans* position and with Hc ($J(\text{Hb}-\text{Hc}) = 8$ Hz) in the *cis* position. The protons Hc and Hd also show 8 double doublet structure due to the coupling with Hb and with each other: $\tau(\text{Hc}) = 7.63$ ppm, $J(\text{Hc}-\text{Hd}) = 1.5$ Hz; $\tau(\text{Hd}) = 7.24$ ppm; $J(\text{Hd}-\text{Hc}) = 1.5$ Hz. The chemical shift of the protons Hb, Hc and Hd are shifted to a higher magnetic field due to the bond with the iron atom [11].

b) Structure of the complex $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$

The trisubstituted complex $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$ shows two stretching bands of the CO ligand of equal intensity in the range $1800-1900$ cm^{-1} as does the trisubstituted $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_3]$ complex [2,3]. As for the latter complex, which contains two PPh_3 ligands in the apical and one PPh_3 in the planar position of a trigonal bipyramid, the proposed structure is the following ($\text{P}-\text{P} = \text{diphos}$):



The chelating ligand increases the stability of the complex, which is also stable at 80–90°C in toluene as opposed to the $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_3]$ complex, which decomposes in solution at room temperature to give $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$.

c) Mechanism of formation of $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$

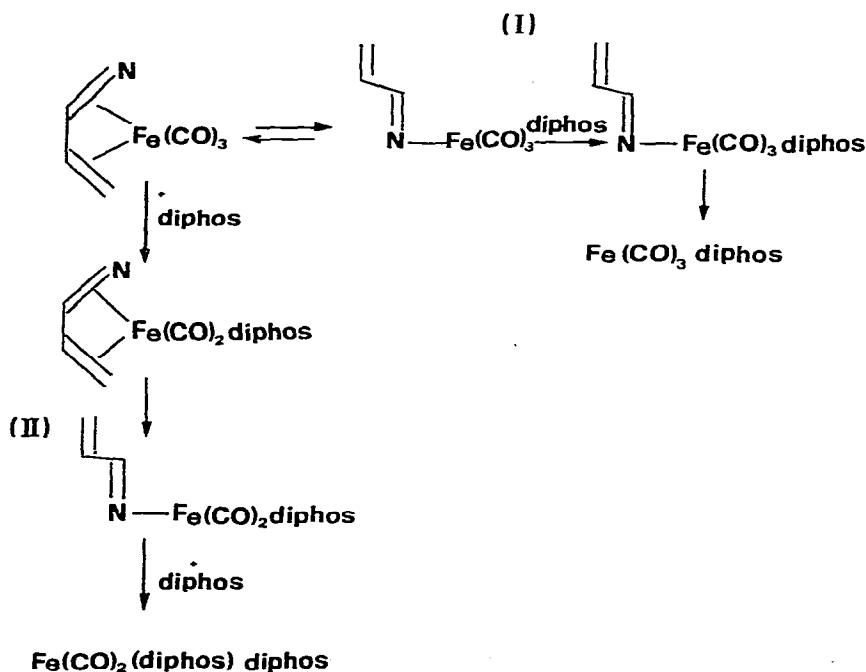
The reaction between $[(\eta^4\text{-heterodiene})\text{Fe}(\text{CO})_3]$ and diphos gives a mixture of $[\text{Fe}(\text{CO})_3(\text{diphos})]$ and $[\text{Fe}(\text{CO})_2(\text{diphos})\text{diphos}]$: as the complex $[\text{Fe}(\text{CO})_3(\text{diphos})]$ does not react with diphos to form the trisubstituted complex, a mechanism which can explain these results is as shown in Scheme 2.

There are two ways for the reaction to occur: (i) involving predissociation of a bond of the heterodiene ligand, followed by the association of the diphos; because of the weak Fe–N bond, chelation of diphos occurs to give $[\text{Fe}(\text{CO})_3(\text{diphos})]$; (ii) involving substitution of a CO ligand, chelation of diphos, and, finally, the substitution of the Schiff base.

With the complexes $[(\eta^4\text{-diene})\text{Fe}(\text{CO})_3]$, $[(\eta^4\text{-diene})\text{Fe}(\text{CO})_2\text{L}]$ and $[(\eta^4\text{-heterodiene})\text{Fe}(\text{CO})_2\text{L}]$, the reaction occurs only by the second route. This is in accord with the mechanism of reaction of $[(\eta^4\text{-diene})\text{Fe}(\text{CO})_3]$, which proceeds through CO dissociation [12].

d) Kinetic results

The kinetic results for the reaction between $[(\eta^4\text{-PhCH}=\text{CHCH}=\text{NPh})\text{Fe}(\text{CO})_2\text{PPh}_3]$ and diphos in toluene at different temperatures, are given in Table 1. The pseudo first order rate constants (k_{obs}) show a linear dependence on



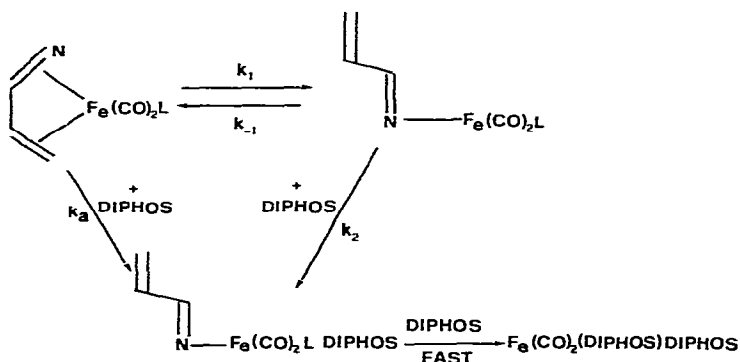
SCHEME 2

TABLE 1

KINETIC DATA FOR THE REACTION BETWEEN $[(\eta^4\text{-PhCH=CHCH=CHPh})\text{Fe}(\text{CO})_2\text{PPh}_3]$ AND DIPHOS IN TOLUENE AT VARIOUS TEMPERATURES

T (°C)	$10^2 \times [\text{diphos}]$ (M)	$10^4 \times k_{\text{obs}}$ (sec ⁻¹)	$10^3 \times k_a^a$ (M ⁻¹ sec ⁻¹)	$10^4 \times k_1^b$ (sec ⁻¹)
50	2.47	0.64	1.39	0.36
	4.99	1.11		
	7.01	1.37		
	10.05	1.82		
	15.11	2.45		
	20.02	3.11		
	28.04	4.07		
60	2.50	2.37	4.10	1.40
	5.11	3.51		
	10.09	5.54		
	20.50	9.96		
68	2.57	5.72	6.92	4.01
	5.04	7.27		
	10.05	11.20		
	14.73	13.80		

^a $\Delta H_a^\ddagger = 20.4$ kcal $\Delta S_a^\ddagger = -11$ e.u. ^b $\Delta H_1^\ddagger = 30.3$ kcal $\Delta S_1^\ddagger = +17$ e.u.



SCHEME 3

the diphos concentration as shown in Fig. 1 and represented by equation 1.

$$k_{\text{obs}} = k_1 + k_a[\text{diphos}] \quad (1)$$

The results can be interpreted on the basis of Scheme 3.

Applying the steady state approximation to the intermediates of Scheme 3, eqn. 2 is obtained:

$$k_{\text{obs}} = k_a[\text{diphos}] + \frac{k_1 k_2 [\text{diphos}]}{k_{-1} + k_2 [\text{diphos}]} \quad (2)$$

when $k_2[\text{diphos}] \gg k_{-1}$, eqn. 2 changes into eqn. 1. The simultaneous operation of two mechanisms of reaction, one associative and the other disassociative, is not unexpected, since such behaviour has been observed for other reactions of tetrahapto-heterodiene iron tricarbonyl complexes.

Exchange of ligand L with diphos in the first step of the reaction is excluded, because the Fe-L bond is very strong in the monosubstituted com-

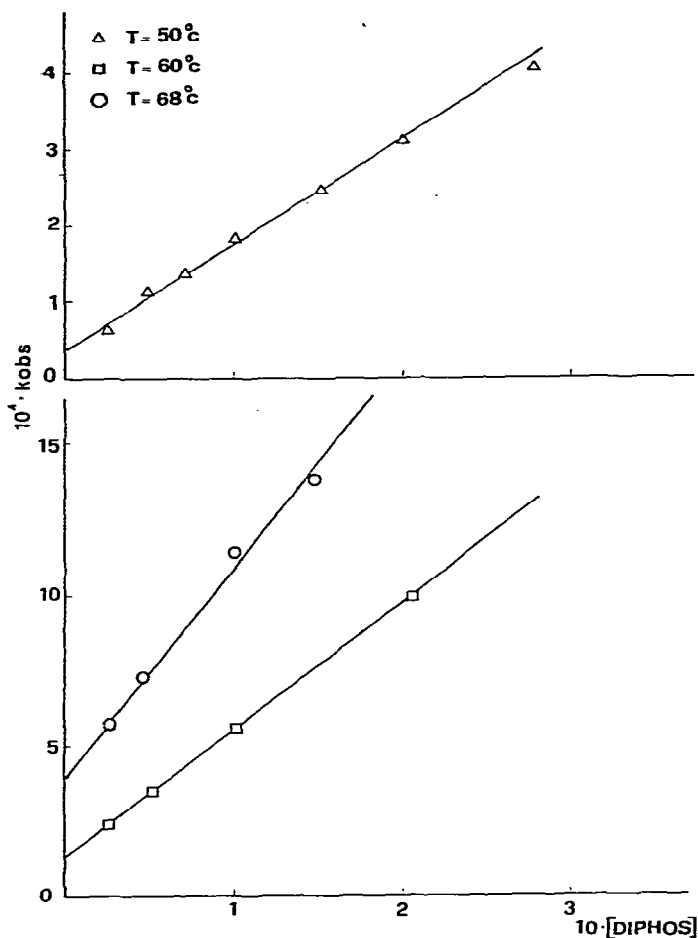


Fig. 1. k_{obs} vs [diphos] for the reaction of $[(\eta^4\text{-heterodiene})\text{Fe}(\text{CO})_2\text{PPh}_3]$ with diphos in toluene at various temperatures.

plexes of iron with Group V ligands.

On the other hand, it is not possible to decide the sequence of substitution of the Schiff base and ligand L in the intermediate complex by chelation of diphos.

On the basis of eqn. 1, the rate constants of the associative (k_a) and dissociative (k_1) processes are calculated (Table 1) at various temperatures. The activation enthalpy and entropy (Table 1) are in accord with the proposed mechanism.

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