

TRANSITION METAL-CYANOCARBON CHEMISTRY

VI *. INSERTIONS OF CYANO- AND DICYANO-ACETYLENES INTO THE IRON-HYDRIDE BONDS IN $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{LFeH}$ (L = CO, PPh_3) AND $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{FeH}]_2 [\mu\text{-(C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P(C}_6\text{H}_5)_2]$ COMPLEXES

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(Received December 30th, 1986)

Summary

Monocyanoacetylene ($\text{HC}\equiv\text{CCN}$, mca) and dicyanoacetylene ($\text{NCC}\equiv\text{CCN}$, dca) have been shown to insert into the Fe–H bonds of various mononuclear and dinuclear iron hydrides. In the presence of dca, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeH}]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeH}]$ give $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\sigma\text{-(Z)-C(CN)=CH(CN)})]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Fe}(\sigma\text{-(Z)-C(CN)=CH(CN)})]$ respectively. The reaction involving $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeH}]$ provides the first evidence for non-regioselectivity of an insertion of mca; the isomers $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Fe}(\sigma\text{-(Z)-CH=CH(CN)})]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Fe}(\sigma\text{-C(CN)=CH}_2)]$ being obtained in a 4/1 ratio. However regioselectivity is observed for insertion of mca into the Fe–H bonds of dinuclear $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{FeH}]_2(\mu\text{-dppe})$ (dppe = 1,2-bis(diphenylphosphido)ethane); in this case the CN groups are attached only to the C_α carbon atom. The reaction of dca with the dinuclear hydride gives products analogous to those from the mononuclear ones. The mechanisms of these various insertions are discussed in terms of the degree of hydridic nature of the hydridic hydrogen in the initial iron complexes.

Introduction

The insertion of unsaturated organic molecules into metal–hydrogen bonds is one of the key steps in many homogeneous catalytic systems [1]. Detailed studies of the stoichiometric reactions of alkenes and alkynes with hydrido complexes, thought to be relevant models for the intermediates involved in such processes, have

* For part V see Ref. 24.

contributed to knowledge of their mechanisms [1,2]. A survey of the literature indicates that surprisingly little work has been carried out in the field of alkynes containing cyano groups [3]. The nitrile-containing unsaturated molecules involve weak steric effects, so offer an easy approach to the metal center.

For some years we have been engaged in a systematic study of the behaviour of cyano-substituted alkynes towards organometallic hydrides, and have observed that the interactions of monocynoacetylene (mca) and dicyanoacetylene (dca) with mono- and bis-cyclopentadienyl hydrides of molybdenum and tungsten always lead to insertion of the alkyne into the metal hydride bonds [4]. An interesting feature of these reactions is their regio- and stereo-specificity. We note, however, that in the case of some dihydride platinum complexes which were examined, only one Pt-H bond is reactive towards cyano-alkyne insertion because of the steric effects of the bulky tricyclohexylphosphine ligands present [5].

We report here the results of reactions of mca and dca with mono- and di-nuclear iron hydrides of the type $[\text{Cp}(\text{CO})\text{LFeH}]$ ($\text{L} = \text{CO}, \text{PPh}_3$) and $[\text{Cp}(\text{CO})\text{FeH}]_2(\mu\text{-dppe})$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphido})\text{ethane}$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$).

Results and discussion

Reactions of mca and dca with cyclopentadienyliron hydrides involve insertion of the alkyne into the Fe-H bonds. Polymerisation of alkynes is indicated by the blackening of the reaction mixtures, which takes place in all reactions examined in the present study. In all cases, the insertion products were separated from the complex product mixtures by chromatography on Florisil. The results are summarized in Table 1, and the spectroscopic data for the resulting σ -alkenyl complexes are given in Table 2.

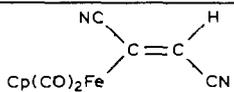
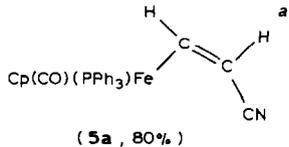
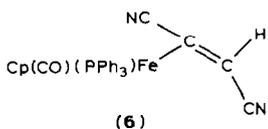
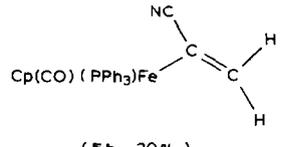
The reaction of $[\text{Cp}(\text{CO})_2\text{FeH}]$ (**1**) with mca gave, besides polymeric species, highly unstable organometallic products, and no defined compound could be isolated and characterized. A similar outcome was encountered previously in the case of the products of the reaction of $\text{Cp}(\text{CO})_3\text{MoH}$ with mca, although the insertion complex $\text{Cp}(\text{CO})_3\text{W}[\sigma\text{-CH=CH}(\text{CN})]$ formed in the analogous reaction of $\text{Cp}(\text{CO})_3\text{WH}$ was isolated and fully characterized [4a]. We note that in the case of 3,3,3-trifluoropropyne (tfp), complexes containing σ -alkenyl bonds, of the type $[\text{M}]\text{-CH=CH}(\text{CF}_3)$ and $[\text{M}]\text{-C}(\text{CF}_3)=\text{CH}_2$, to the metal centres of $\text{Cp}(\text{CO})_2\text{Fe}$ and $\text{Re}(\text{CO})_5$ entities, originating from the corresponding hydrides, were isolated and characterized [6].

The action of dca on $\text{Cp}(\text{CO})_2\text{FeH}$ (**1**) led to the formation of a well-defined red product (**4**) of formula $\text{Cp}(\text{CO})_2\text{Fe}[\sigma\text{-C}(\text{CN})=\text{CH}(\text{CN})]$. From comparison of the chemical shift value of the vinylic proton with other related structures [4a], we suggest that the insertion of dca is a *trans* process, so that the hydrogen atom on the σ -alkenyl ligand is *trans* to the metal. Similar insertions of dca into the Mo-H and W-H bonds of $\text{Cp}(\text{CO})_3\text{MH}$ hydrides have been observed previously [4a]. However, we note that hexafluorobutyne (hfb) gives no insertion product with $\text{Cp}(\text{CO})_3\text{MoH}$, and that such a product is obtained only in very low yield in the case of tungsten $\text{Cp}(\text{CO})_3\text{WH}$; the alkyne-bridged binuclear compounds $[\text{Cp}(\text{CO})_2\text{M}]_2(\text{F}_3\text{CC}\equiv\text{CCF}_3)$ mainly being formed [7].

The insertion σ -alkenyl (*Z* and *E* isomers) complexes of tungsten $\text{Cp}(\text{CO})_3\text{W}[\sigma\text{-C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})]$ were formed in the reaction of the hydride $\text{Cp}(\text{CO})_3\text{WH}$

TABLE 1

RESULTS OF THE REACTIONS OF *mca* AND *dca* WITH CYCLOPENTADIENYLIRON HYDRIDES

Compound	<i>mca</i>	<i>dca</i>
Cp(CO) ₂ FeH (1)	very unstable and intractable products	 (4)
Cp(CO)(PPh ₃)FeH (2)	 (5a, 80%)	 (6)
	 (5b, 20%)	
[Cp(CO)FeH] ₂ (μ-dppe) (3)	[Cp(CO)Fe(σ-C(CN)=CH ₂) ₂] (μ-dppe) (7a and 7b)	[Cp(CO)Fe(σ-C(CN)=CH(CN))] (μ-dppe) (8a and 8b)

^a The percentages do not refer to the yield, but to the isomer ratio based on the relative intensities of NMR resonances of Cp protons; a small amount of pure but poorly stable (a) was separated by fast chromatography on degassed and dried Florisil (CH₂Cl₂/5% THF).

with dimethylacetylenedicarboxylate (*dmad*) [2c]. Other hydrides such as Cp(CO)(PPh₃)RuH [8], Cp(PPh₃)₂RuH [9] and (CO)₅MnH [10] react with *hfb* and *dmad* to give σ -vinylic complexes, but other products, especially metallacyclic species, are also formed.

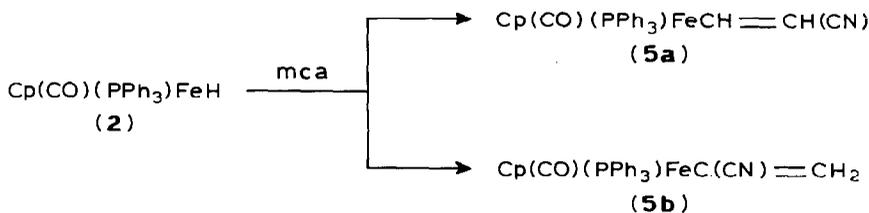
The phosphine-containing hydride Cp(CO)(PPh₃)FeH (2) was found to undergo insertion of *mca* and *dca*. The product complexes (5) (Scheme 1) were more stable than those of the products of the reaction of 1 with *mca*. The product mixture contains two isomers of σ -alkenyl complexes in 4/1 ratio, as determined from the relative intensities of the ¹H resonances of the C₅H₅ protons. These isomers differ in the position of the CN substituent on the σ -alkenyl ligand; the nitrile is on the C _{β} carbon atom (with respect to the metal) in the major isomer, which is so a β -metallated species (5a), but on the C _{α} carbon atom in the less stable minor isomer (5b) (Scheme 1).

In the major isomer (5a), the value of coupling constant ³J(HH) of 12 Hz indicates the *cis* positions of the protons and consequently the occurrence of *trans* insertion of *mca* into the Fe–H bond. The chemical shift as well as the coupling constant values are very close to those observed for Cp(CO)₃WCH_a=CH_b(CN) (H_a, δ 8.70 ppm, d, *J* 13.5 Hz; H_b, δ 6.45 ppm, d, in CDCl₃) [4a]. This result is closely

TABLE 2
NMR DATA (δ (ppm) and J (Hz)) FOR σ -ALKENYL COMPLEXES

Complex	Solvent	^1H		^{31}P		^{13}C		C_β	CO	CN
		C_5H_5	H_a	H_b	C_5H_5	C_a				
$\text{Cp}(\text{CO})_2\text{FeC}(\text{CN})=\text{CH}(\text{CN})$ (4)	CDCl_3	5.10(s)	6.55(s)			86.3	151.9	127.0	210.8	119.1
$\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{FeC}_\alpha\text{H}_a=\text{C}_\beta\text{H}_b(\text{CN})$ (5a)	CDCl_3	4.52 (d, $J(\text{PH})$ 1.5)	8.80 (dd, $J(\text{HH})$ 12, $J(\text{PH})$ 12)	6.10 (dd, $J(\text{HH})$ 12, $J(\text{PH})$ 4)	a			a		124.0
	C_6D_6	4.00	8.40	5.85	79.0			a		
	$(\text{CD}_3)_2\text{CO}$	4.60	8.83	6.03	83.2			a		
		(d, $J(\text{PH})$ 1.5)	(dd, $J(\text{HH})$ 12, $J(\text{PH})$ 12)	(dd, $J(\text{HH})$ 12, $J(\text{PH})$ 4)						
$\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{FeC}(\text{CN})=\text{C} \begin{matrix} \text{H}_a \\ \diagdown \\ \text{H}_b \end{matrix}$	C_6D_6	3.90	6.02	5.63	75.3			a		
(5b)										
$\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{FeC}_\alpha(\text{CN})=\text{C}_\beta\text{H}(\text{CN})$ (6)	CDCl_3	4.59 (d, $J(\text{PH})$ 1.4)	6.27 (d, $J(\text{PH})$ 1.4)	(br, d, $J(\text{HH})$ 4, $J(\text{PH})$ 3)	69.6	85.2	168.4	125.0	218.4	120.0
							(d, $J(\text{PC})$ 21.0)	(d, $J(\text{PC})$ 4.0)	(d, $J(\text{PC})$ 30.0)	126.3
$\left[\text{Cp}(\text{CO})\text{FeC}_\alpha(\text{CN})=\text{C} \begin{matrix} \text{H}_a \\ \diagdown \\ \text{H}_b \end{matrix} \right]_2$ (7a)	C_6D_6	4.09	6.41	5.75 (br)	72.9			a		
			(dd, $J(\text{HH})$ ~ 3, $J(\text{PH})$ ~ 4)							
$\left[\text{Cp}(\text{CO})\text{FeC}_\alpha(\text{CN})=\text{C} \begin{matrix} \text{H}_a \\ \diagdown \\ \text{H}_b \end{matrix} \right]_2$ (7b)	C_6H_6	4.05	6.30	5.91	72.4	86.0		144.2	221.5	b
			(dd, $J(\text{HH})$ 2.5, $J(\text{PH})$ 5.5)	(dd, $J(\text{HH})$ 2.5, $J(\text{PH})$ < 1)				(dd, $J(\text{CH})$ 155.1, $J(\text{CH})$ 159.7)	(d, $J(\text{PC})$ 29.5)	
$\left[\text{Cp}(\text{CO})\text{FeC}_\alpha(\text{CN})=\text{CH}(\text{CN}) \right]_2$ (8a)	CDCl_3	4.65	6.05 (br)		69.4			123.9	218.2(d, $J(\text{PC})$ 30)	119.7(br)
					85.5	168.4		124.5	217.8(d, $J(\text{PC})$ 30)	
$\left[\text{Cp}(\text{CO})\text{FeC}_\alpha(\text{CN})=\text{CH}(\text{CN}) \right]_2$ (8b)	CDCl_3	4.56	6.30 (br)		69.0					

a Not recorded. b Not observed.



SCHEME 1

related to that observed for the reaction of $\text{Cp(CO)}_2\text{FeH}$ with *tfp*, in which both α - and β -metallated isomers were formed, in a 7/3 ratio [6].

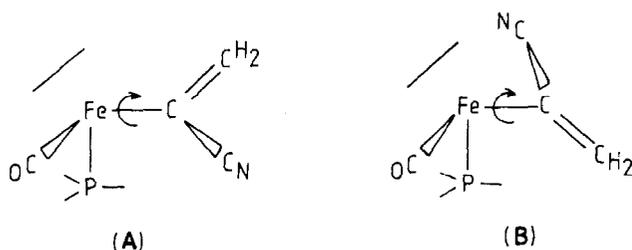
We note that the reaction of *mca* with $\text{Cp(CO)(PPh}_3\text{)FeH}$ is one of the few examples in which cyano- and trifluoromethyl-substituted alkynes behave similarly. Usually the cyanoalkynes give rise to regio- and stereo-selective reactions with restricted number of products, whereas *tfp* and *hfb* undergo more complex reactions. We think that the difference (e.g. the regio- and stereo-selectivity of reactions with the CN-containing alkynes) is mainly due to (i) the speed of the reactions, (ii) the supposed hardness of the conjugated $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$ system, and (iii) the low steric requirements of the cyanoalkynes.

The reaction of **2** with *dca* gave the insertion complex **6** as the sole isolable and detectable product. Similar results have been obtained in the reactions of $\text{Cp(CO)(PPh}_3\text{)RuH}$ with *hfb* and *dmad* [8]. However, Bruce and Stone proposed that the σ -alkenyl ligand $\text{C(CF}_3\text{)=CH(CF}_3\text{)}$ can have two different orientations with respect to the organometallic entity, giving rise to two conformational isomers in which the CF_3 substituents are close to or far from the PPh_3 ligand [8]. It was also observed that *hfb* insertion complexes of Cp_2MoH_2 [11] and of $\text{Cp}_2\text{Nb(CO)H}$ [12] exhibit a similar conformational isomerism.

In the course of this study we also used the dinuclear dihydride $[\text{Cp(CO)FeH}]_2(\mu\text{-dppe})$ (**3**) in order to examine the influence of a second metallic centre and especially to test the possibility of coupling between two molecules of alkyne arising from their proximity. The reaction of *mca* with **3** gives the two isomers, **7a** and **7b**, of $\{\text{Cp(CO)Fe}[\sigma\text{-C(CN)=CH}_2]\}_2(\mu\text{-dppe})$, in ca. 3/2 ratio. These isomers can be separated by crystallization. Each of the isomers exhibits one set of ^1H resonances of equivalent Cp and $\sigma\text{-C(CN)=CH}_2$ ligands, thus indicating the same arrangement of ligands at the metallic centre in both cases. It should be noted that in this case the insertion reaction is highly regioselective, the CN group being attached to C_α (with respect to Fe); the presence of the =CH_2 group is confirmed by ^1H NMR spectroscopy (Table 2).

The formation of two closely related isomers could be accounted for in two ways. First, it could be due to a different orientation of the σ -alkenyl ligands with respect to the " CpFe(CO)P " fragments; the suggestion shown in Scheme 2 is that the CN group is on the same side as the CO ligand in one of the isomers (**A**) but on the opposite side in the other (**B**).

The other possible explanation is based on the fact that **7** contains two chiral iron centers, so that two diastereoisomers should exist. The presence of two such isomers was proposed by Davies for **3** [13], but in that case fast exchange precluded their observation, but it seemed likely in the case of the analogous diruthenium dihydride



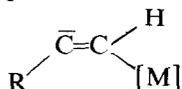
SCHEME 2

[14]. We think that substitution of the hydride in **3** by the σ -alkenyl ligand $C(CN)=CH_2$ in **7** could introduce sufficient rigidity (for steric and/or electronic reasons) to allow the observation and the separation of the diastereoisomers **7a** and **7b**. The results obtained in the present do not allow a decision between the two proposals.

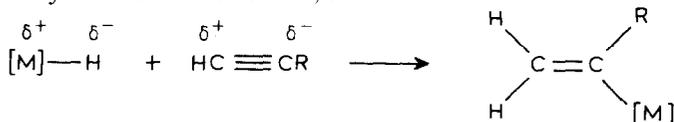
Insertion of dca into the Fe–H bonds in **3** gives two isomers, **8a** and **8b**, in ca. 3/2 ratio. Like **7a** and **7b**, these could not be separated. The spectroscopic data for **8a** and **8b** are similar to one another, and both sets very close to those observed for **6** (Table 2).

The most important aspect of this study is that the regioselectivity of the insertion reactions of mca with mononuclear hydrides **2** is different from that with the dinuclear hydrides **3**. In the major isomer of mononuclear insertion product (**5a**), the CN group is attached to the C_β carbon atom of the σ -alkenyl ligand, but it is bound to the C_α atom in the minor isomer (**5b**) as well as in the dinuclear adducts **7a** and **7b**. This difference is particularly surprising because the NMR parameters of the parent hydrides **2** and **3** are very close: 1H (C_6D_6), **2**: Fe–H δ –12.7 (d, $J(PH)$ 74 Hz), C_5H_5 δ 4.26 ppm; **3**: Fe–H δ –13.1 (d, $J(PH)$ 74 Hz), C_5H_5 δ 3.9 ppm. ^{31}P (C_6D_6), **2**: δ +89.7 ppm, **3**: δ +84.4 ppm [15].

The *Z*-configuration found in the major isomer (**5a**), i.e. the *cis*-substituted ethylene, has been often observed in the reactions of terminal alkynes $HC\equiv CR$ with hydrides of Fe, Re ($R = CF_3$) [6], Mn ($R = CO_2Me$) [16] ($R = CN$) [17] and W ($R = CN$) [4a] and with organometallic anions $Cp(CO)_2Fe^-$, $(CO)_5Re^-$ and $(CO)_5Mn^-$ ($R = CF_3$ and C_6F_5) [18]. It has been suggested that the reactions of ionic nucleophiles with acetylenes which result in *trans* nucleophilic addition may proceed via an intermediate configurationally-stable carbanion



in which the negative charge and the metal group are separated as far as possible [18]. In the case of hydrides, such a mechanism would account to the formation of β -metallated *cis* (*Z*) olefins if dissociation of hydride ligands could occur. On the other hand, nucleophilic attack of hydride H^- may also take place rather than that of the organometallic anion. In this case, the positively charged side of terminal alkyne should be attacked, as in



leading to formation of α -metallated products. This type of interaction can also be regarded as a concerted addition to the alkyne.

A theoretical molecular orbital treatment by Bursten showed the $\text{Cp}(\text{CO})_2\text{MH}$ ($\text{M} = \text{Fe}, \text{Ru}$) hydrides to be amphoteric species, and emphasized the importance of the energy of the HOMO which is the nonbonding orbital in the corresponding anions [19]. The amphoteric nature of $\text{Cp}(\text{CO})_2\text{FeH}$ suggests that dissociation of a proton, $[\text{Fe}]\text{H} \rightarrow [\text{Fe}]^- + \text{H}^+$, should be a ready process. Bursten also showed that the acidity of the hydride decreases upon the introduction of electron-releasing groups (e.g. PR_3) in place of CO [20].

It follows that the β -metallated olefins would be more easily formed the higher the acidity of the hydride, whereas the α -metallated species would predominate in the case of a greater hydridic nature. Thus, the β -metallated species $\text{Cp}(\text{CO})_2\text{FeCH}=\text{CH}(\text{CN})$ should be obtained with **1**, and some of the α -metallated $\text{Cp}(\text{CO})''\text{P}''\text{FeC}(\text{CN})=\text{CH}_2$ with **2** and **3**. Moreover the different behaviour of **2** and **3** could be related to the kinetic stabilities of the hydrides, which would complicate predictions based on energy changes. It is well-known that $\text{Cp}(\text{CO})_2\text{FeH}$ (**1**) is very difficult to manipulate and readily gives the corresponding dimer $[\text{Cp}(\text{CO})_2\text{Fe}]_2$, that $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$ (**2**) is relatively air-stable in the solid state, and that the dinuclear $[\text{Cp}(\text{CO})\text{FeH}]_2(\mu\text{-dppe})$ (**3**) is more stable in the solid state and in solution.

In the light of the above discussion it seems reasonable to draw the following conclusions:

(i) The high acidity and low stability of the dicarbonyl iron hydride (**1**) is responsible of the low stability of the σ -alkenyl complexes (presumably β -metallated $\text{FeCH}=\text{CH}(\text{CN})$) formed in the reaction of **1** with highly electrophilic and asymmetric mca; use of dca leads to a more stable complex owing to the symmetry of the new ligand and to the presence of CN on the carbon atom bound to the iron, so that the Fe–C bond is strengthened.

(ii) The more hydridic nature of the Fe–H bond in $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$ (**2**) may allow both hydride $[\text{Fe}]\text{H} \rightarrow \text{Fe}^+ + \text{H}^-$ and proton $[\text{Fe}]\text{H} \rightarrow \text{Fe}^- + \text{H}^+$ dissociations, and so permit formation of both the β -metallated (**5a**) and α -metallated (**5b**) species;

(iii) The dinuclear complex **3**, which has spectroscopic properties very close to those of **2** but which is much more stable than the latter, reacts with mca to give only α -metallated σ -alkenyl ligands as a result of hydride addition, probably via a concerted mechanism, to the more positive C_β atom of the polarized alkyne.

Experimental

All reactions were carried out under nitrogen by use of Schlenk-tube techniques. Solvents were purified by standard methods and purged with nitrogen before use. Monocarbonylacetylene and dicyanoacetylene were prepared as described by Moureu and Bongrand [21]. The complexes $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeH}$ [22], $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeH}$ [23] and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{FeH}]_2(\mu\text{-PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$ [15] were synthesised by published methods. All other products were reagent grade materials.

IR spectra were recorded on a Pye-Unicam SP 2000 spectrophotometer. NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer operated at 99.60 MHz for ^1H , 40.32 MHz for ^{31}P , and 25.05 MHz for ^{13}C . Chemical shifts are relative to internal SiMe_4 or external aqueous H_3PO_4 (85%).

All insertion reactions were carried out in the same way, 5 mmol of initial hydride (1–3) (calculated per one iron atom) in toluene or THF were frozen in liquid nitrogen and the alkynes (100% excess, from 1 g of monoamide and from 2.2 g of diamide) were condensed into the reaction tube. The mixtures were then stirred at room temperature for 6 to 40 h.

Work-up of the product mixtures

1 + dca. Solvent was removed in vacuo, and the residue was transferred in CH_2Cl_2 to a Florisil column. A yellow band eluted with $\text{CH}_2\text{Cl}_2/2\%$ THF gave the crude insertion complex **4**, which was further chromatographed on alumina to give pure **4** in ca. 15% yield. Anal. Found: C, 52.3; H, 2.3; Fe, 21.8; N, 11.1 $\text{C}_{11}\text{H}_6\text{FeN}_2\text{O}_2$ calc: C, 52.01; H, 2.38; Fe, 21.98; N, 11.03%.

2 + mca. The brown to black solution was evaporated and the residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on Florisil. Elution with $\text{CH}_2\text{Cl}_2/5\%$ THF gave a crude oil containing the insertion complexes **5**, PPh_3 and some unidentified impurities. A second chromatography on alumina gave a mixture of insertion compounds **5a** and **5b** (7/3 ratio), identified by ^1H NMR spectroscopy (Table 2). An elemental analysis of the mixture was not obtained.

2 + dca. The dark brown solution was evaporated and the residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on Florisil. Elution with $\text{CH}_2\text{Cl}_2/2\%$ THF gave the crude product **6**, which was recrystallized from a $\text{CH}_2\text{Cl}_2/\text{pentane}$ solution. Yield 30%. Anal. Found: C, 67.0; H, 4.5; Fe, 10.6; N, 5.7; P, 6.0. $\text{C}_{28}\text{H}_{21}\text{FeN}_2\text{OP}$ calc: C, 68.87; H, 4.33; Fe, 11.44; N, 5.74; P, 6.34%.

3 + mca. The dark brown toluene solution was concentrated and filtered through a Celite pad. At this stage ^{31}P NMR showed the presence of **7a** and **7b**. To the dark red solution was added an approximate equal volume of hexane, the resulting solution was allowed to stand overnight, during which time dark orange crystals of **7b** separated. The isomer **7a** was obtained by chromatography of the supernatant liquid (Florisil column). Elution with $\text{CH}_2\text{Cl}_2/2\%$ THF gave **7a**, which was recrystallized from toluene/hexane. Overall yield 35%. Analysis. **7b**: Found: C, 67.0; H, 5.0; N, 3.4; P, 7.2; $\text{C}_{44}\text{H}_{38}\text{Fe}_2\text{N}_2\text{O}_2\text{P}_2$ calc: C, 66.02; H, 4.75; N, 3.50; P, 7.75%. IR (cm^{-1} , Nujol, KBr) **7a**: $\nu(\text{CO})$ 1940vs; $\nu(\text{CN})$ 2175m; $\nu(\text{C}=\text{C})$ 1545m. **7b**: $\nu(\text{CO})$ 1940vs; $\nu(\text{CN})$ 2175m; $\nu(\text{C}=\text{C})$ 1545m.

3 + dca. The dark-red THF solution was filtered through a Celite pad and evaporated to dryness, and the residue chromatographed on Florisil. Elution with $\text{CH}_2\text{Cl}_2/5\%$ THF gave a dark red material, which was recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$. Yield 32%. Attempts to separate **8a** and **8b** by crystallization or further chromatography failed. Anal. Found: C, 64.4; H, 4.7; P, 7.1. $\text{C}_{46}\text{H}_{36}\text{Fe}_2\text{N}_4\text{O}_2\text{P}_2$ calc: C, 64.96; H, 4.24; P, 7.30%. IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{CO})$ 1960vs; $\nu(\text{CN})$ 2200–2180m, br.

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