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Journal of Organometallic Chemistry 508 (1996) 23–30

Journal of Organometallic Chemistry

Comparison of the oxidation of dinuclear cyclopentadienyl iron diphosphine complexes with the bridging ligands $-CN$ and $-C{\equiv}C(CH_2)_2CN$

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Received 10 February 1995

Abstract

The alkynyliron complex $[Fe(C{\equiv}C{-}CH_2CH_2{-}CN)(dppe)(C_5H_5)]$ (2) (dppe = $Ph_2PCH_2CH_2PPh_2$), prepared from $[Fe(C{\equiv}C{-}CH_2CH_2{-}CN)(CO)_2(C_5H_5)]$ (1) and dppe under UV irradiation, reacted with $HBF_4.Et_2O$ in tetrahydrofuran and with $NH_4[PF_6]$ in CH_2Cl_2 to give the cationic vinylidene derivative $[Fe(=C=CH{-}CH_2CH_2{-}CN)(dppe)(C_5H_5)][A]$ (A = BF_4 (**3a**) or PF_6 (**3b**)), which can be reconverted to **2** with K_2CO_3 in CH_2Cl_2. The compound $[(C_5H_5)(dppe)Fe{-}NC{-}CH_2CH_2{-}C{\equiv}CH][PF_6]$ (**4**), which is a tautomeric form of **3** was prepared by reaction of $[Fe(I)(dppe)(C_5H_5)]$ with the alkyne $HC{\equiv}C{-}CH_2CH_2CN$ in the presence of $NH_4[PF_6]$ in CH_2Cl_2. The dinuclear compound $[(C_5H_5)(dppe)Fe{-}C{\equiv}C{-}CH_2CH_2{-}CN{-}Fe(dppe)(C_5H_5)][PF_6]$ (**5**), which is unstable, can be formed by reaction of **2** with $[Fe(NCMe)(dppe)(C_5H_5)]\ PF_6$ in CH_2Cl_2. Its electrochemical oxidation shows that there is no electronic interaction between the two metal centres. Extended Hückel molecular orbital calculations have been carried out on the model complexes $[(C_5H_5)(PH_3)_2Fe{-}C{\equiv}C{-}CH_2CH_2{-}CN{-}Fe(PH_3)_2(C_5H_5)]^+$ (**7**) and $[(C_5H_5)(PH_3)_2Fe{-}CN{-}Fe(PH_3)_2(C_5H_5)]^+$ (**8**).

Keywords: Iron; Alkynyl; Cyanide; Ligand bridged; Electrochemistry; EHMO calculations

1. Introduction

In previous studies [1] we have shown that the binuclear cyanide-bridged complex $[(C_5H_5)(dppe)Fe{-}CN{-}Fe(dppe)(C_5H_5)][PF_6]$ undergoes two one-electron oxidations, the first affecting mainly the *N*-bonded Fe atom, with electrode potentials that suggested an extended electronic communication between the two iron atoms mediated by the CN bridge.

Here we wish to report how the electron delocalization in this species can be further shown by comparison with the oxidation behaviour of the related binuclear complex $[(C_5H_5)(dppe)Fe{-}C{\equiv}C{-}CH_2CH_2{-}CN{-}Fe(dppe)(C_5H_5)][PF_6]$ containing the asymmetric bidentate cyanoalkynyl $-C{\equiv}C{-}CH_2CH_2{-}CN$, which is an isolating bridging ligand, and by a molecular orbital (MO) study carried out on the model complexes $[(C_5H_5)(PH_3)_2Fe{-}C{\equiv}C{-}CH_2CH_2{-}CN{-}Fe(PH_3)_2(C_5H_5)]^+$ and $[(C_5H_5)(PH_3)_2Fe{-}CN{-}Fe(PH_3)_2(C_5H_5)]^+$.

2. Results and discussion

The orange iron alkynyl complex $[Fe(C{\equiv}CCH_2CH_2CN)(dppe)(C_5H_5)]$ (**2**) was prepared from the dicarbonyl precursor $[Fe(C{\equiv}CCH_2CH_2CN)(CO)_2(C_5H_5)]$ (**1**) and dppe under UV irradiation. Compound **2** can be stored under dinitrogen in the solid state for several months, but it decomposes in solution.

As might be expected [2], the neutral complex **2** can be protonated with HBF_4 in diethyl ether to give the cationic vinylidene complex $[Fe(=C=CH{-}CH_2CH_2{-}CN)(dppe)(C_5H_5)]\ BF_4$ (**3a**) (Scheme 1). The protonation can be also achieved in dichloromethane solution under very mild conditions using $NH_4[PF_6]$ to give the $[PF_6]$ salt (**3b**). The cationic complex **3** could be reconverted to **2** with K_2CO_3 in CH_2Cl_2.

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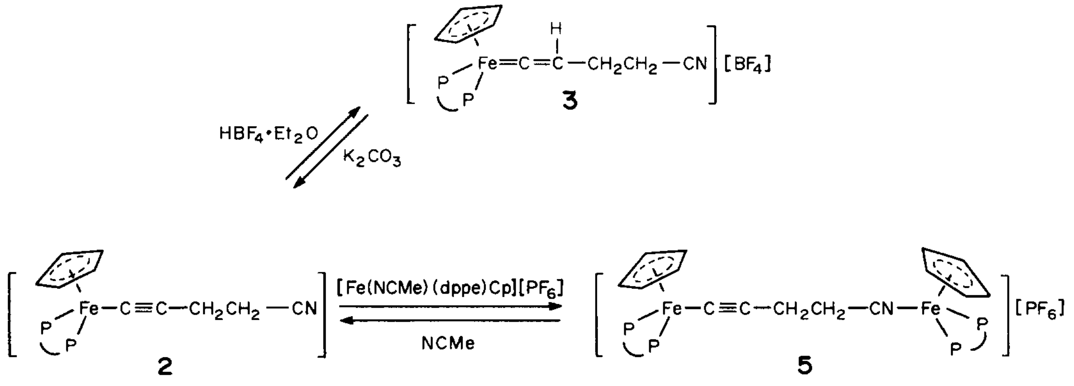
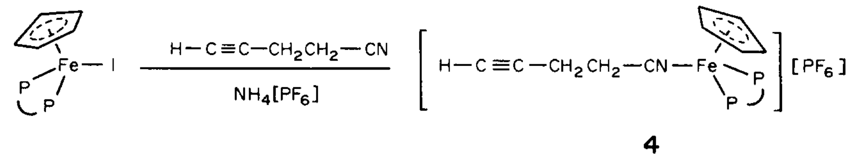
SSDI 0022-328X(95)05829-X



Scheme 1. (PP = dppe).



Scheme 2.

The alkyne H–C≡C–CH_2CH_2–CN reacted very easily with [FeI(dppe)(C_5H_5)] and $NH_4[PF_6]$ in CH_2Cl_2 or methanol (Scheme 2) to give the cationic nitrile complex [(C_5H_5)(dppe)Fe–NC–CH_2CH_2–C≡CH][PF_6] (**4**), which is a tautomeric form of **3b**.

These compounds were characterized by the analytical and spectroscopic data given in Tables 1 and 2 and Section 3.

The changes in ν(CN) and ν(CC), and the chemical shifts of the phosphorus atoms in the ^{31}P NMR spectra are consistent with the formulations proposed. For example, **2** had a very similar ν(CN) frequency to, but a significantly lower ν(CC) frequency than the free alkyne H–C≡C–CH_2CH_2–CN (2251 and 2134 cm^{-1} respectively), while for **4** both frequencies are slightly higher than in the alkyne.

The IR spectrum of the cationic vinylidene complex **3** did not show any absorption attributable to ν(H–C≡) stretching (the alkyne H–C≡C–CH_2CH_2–CN has a band at 3294 cm^{-1}, and **4** at 3293 cm^{-1}) but had an intense band at 1657 cm^{-1}, owing to the C=C double bond, and a ν(CN) band almost identical with that of **2**. More significantly, the ^{13}C NMR spectrum of **3** showed a triplet at 355.3 ppm (J(P–C) = 34 Hz), which corresponds to the α-vinylidene carbon atom.

In contrast, the ^{13}C NMR spectrum of **2** shows the signal of the –CN carbon atom at almost the same frequency as in the free alkyne, while for **4** the chemical

Table 1
Spectroscopic and voltammetric data for the compounds

Compound [a]	IR, ν(cm^{-1}) [b]		^{31}P NMR, δ [c] (ppm)		$E_{1/2}$ (V)	
	ν(CN)	ν(CC)			E_1	E_2
[Fe(C≡CCH$_2$CH$_2$CN)(CO)$_2$(C$_5$H$_5$)] (**1**)	2246	2134 [e]				
[Fe(C≡CCH$_2$CH$_2$CN)(dppe)(C$_5$H$_5$)] (**2**)	2243	2087	106.6 [f]		0.02	
[Fe(=C=CHCH$_2$CH$_2$CN)(dppe)(C$_5$H$_5$)][PF$_6$] (**3**)	2244	1657	95.9 [g]		> 1.2	
[Fe(NC–CH$_2$CH$_2$C≡CH)(dppe)(C$_5$H$_5$)][PF$_6$] (**4**)	2263	2153 [h]	98.0 [i]		0.77	
[{Fe(dppe)(C$_5$H$_5$)}$_2${μ-(C≡CCH$_2$CH$_2$CN)}][PF$_6$] (**5**)	2253	2085	106.5 [j]	97.7	0.05	0.73

[a] The free alkyne H–C≡C–CH_2CH_2–CN has IR absorptions at 3294 (CH), 2251 (CN) and 2134 (CC) cm^{-1}.
[b] Nujol mull.
[c] Measured in CD_2Cl_2 downfield to external 85% aqueous H_3PO_4.
[d] In CH_2Cl_2 with reference to a saturated calomel electrode.
[e] ν(CO) in THF at 2036s. 1987s cm^{-1}.
[f] In acetone 107.6.
[g] In acetone 96.7.
[h] ν(CH) at 3293 cm^{-1}.
[i] In $CDCl_3$ 98.4.
[j] In acetone 107.4, 98.6.

Table 2
^1H and ^{13}C NMR data for the compounds

Compound	^1H NMR, δ [a] (ppm)				^{13}C NMR, δ [a,b] (ppm)					
	P–CH_2CH_2–P	–CH_2CH_2–	C_5H_5	Other	P–CH_2CH_2–P	–CH_2CH_2–	C_5H_5	CN	Cα	Cβ
2	2.16 (m)	2.65 (m), 1.65 (t)	4.14 (t, J = 1.05 Hz)	7–8 (m, Ph)	28.4 (t, J_{CP} = 22.4 Hz)	20.3, 19.4	79.2	120.8	108.2 (t, J = 40 Hz)	113.6
3	3.00 (m)	2.00 (m), 1.52 (m)	5.13s	7–8 (m, Ph), 4.33 (CH)	30.0 (t, J_{CP} = 23 Hz)	20.99, 18.77	90.96	122.4	355.3 (t, J_{CP} = 34 Hz)	c
4	2.40 (m)	1.90 (m), 1.45 (m)	4.33	7–8 (m, Ph), 1.70 (m, CH)	28.3 (t, J_{CP} = 21.2 Hz)	20.3, 15.3	79.7	136.2	71.7 (=CH)	80.4 (–C=)
5	2.2–2.5		4.09, 4.26	7–8 (m, Ph)						

[a] In CD_2Cl_2 unless otherwise stated.

[b] Other signals from the C_6H_5 rings are between 129 and 134 ppm.

[c] Hidden by the C_6H_5 signals.

For the free alkyne HCC–CH_2CH_2CN: ^1H NMR: δ 2.59m(4H), 2.20m(1H) ppm. ^{13}C NMR: δ120.5(CN), 82.2 (–C–), 72.6 (CH), 18.48, 16.58(CH_2CH_2) ppm.

shift of the –CN carbon atom is to a higher field which is the expected effect of coordination to the iron [3]. The assignment of the signals corresponding to the C_α and C_β alkynyl carbon atoms was made by comparison with the literature data [4].

The formation of **4** by the reaction shown in Scheme 2 suggested to us the possibility of synthesizing the binuclear compound $[(C_5H_5)(dppe)Fe–C{\equiv}C–CH_2–CH_2–CN–Fe(dppe)(C_5H_5)][PF_6]$ (**5**) in a similar manner, using the iron-alkynyl derivative **2**. However, the reaction in the presence of $NH_4[PF_6]$ gave a mixture of the expected **5**, together with its protonated form **3b**, and another species having two ^{31}P NMR signals in a 1 : 1 ratio at 97.7 and 95.5 ppm, which most probably arose from the binuclear vinylidene derivative $[(C_5H_5)(dppe)–Fe{=}C{=}CH–CH_2CH_2–CN–Fe(dppe)(C_5H_5)][PF_6]_2$ (**6**). Monitoring the reaction by ^{31}P NMR spectroscopy revealed that the mononuclear vinylidene complex **3b** is formed first, and that the slow reaction of this latter with $[FeI(dppe)(C_5H_5)]$ and $NH_4[PF_6]$ gives **6**. The addition of K_2CO_3 to the mixture gave mainly **5**, but with other decomposition products.

The use of $Tl[PF_6]$ as iodine abstractor in place of $NH_4[PF_6]$ in the reaction of $[FeI(dppe)(C_5H_5)]$ with **2** was also accompanied by extended decomposition and could not be used to obtain pure **5**.

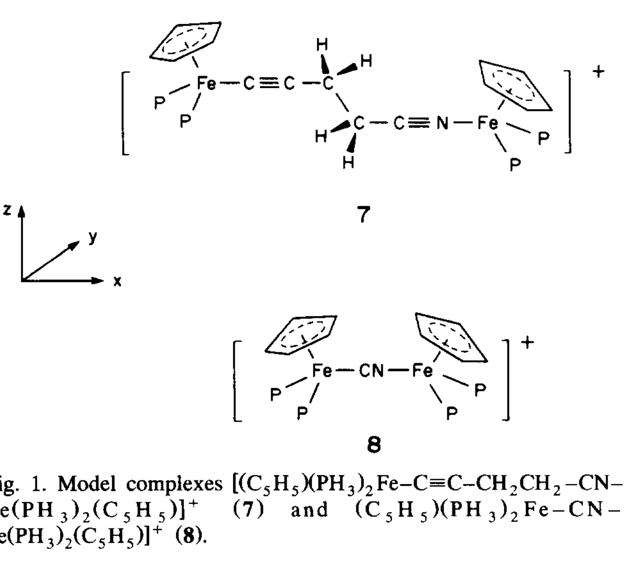
In another attempt to synthesize **5**, we observed that the alkynyl **2** reacts with the acetonitrile complex $[Fe(NCMe)(dppe)(C_5H_5)][PF_6]$ in CH_2Cl_2 with partial replacement of the coordinated acetonitrile, generating an equilibrium shown in Scheme 1. (We also observed that the cationic vinylidene complex **3** reacts similarly with $[Fe(NCMe)(dppe)(C_5H_5)]$, partially replacing the acetonitrile to give **6** but, in the reaction, **5** is also formed alongside other products.)

The formation of **5** in the equilibrium represented in Scheme 1 was shown by the appearance of a signal at 97.7 ppm in the ^{31}P NMR spectrum of the reaction mixture. In CH_2Cl_2 it is well separated from the signal corresponding to the complex $[Fe(NCMe)(dppe)(C_5H_5)][PF_6]$ (97.9 ppm). The equilibrium could be shifted to the species **5** by periodically evaporating the volatiles to remove the free acetonitrile. Unfortunately, all the attempts to isolate **5** from the final mixture failed, yielding red to brown solids that contained it together with $[Fe(NCMe)(dppe)(C_5H_5)][PF_6]$ and other mononuclear nitrile complexes of the type of **4**. However, the presence of **5** as the main product in the materials isolated was clearly demonstrated by the ^{31}P and ^{1}H NMR spectra (Tables 1 and 2). As expected, the ^{31}P NMR spectrum showed two signals at very similar positions to those of **2** and **4**, but the signal at 106.5 ppm was broad, and the relative intensities indicated an excess of 0.4–1 mmol of mononuclear nitrile complexes per millimole of **5**, increasing with the time in solution.

In order to examine the oxidation behaviour of the dinuclear compound **5**, we measured the cyclic voltammograms of the reaction products containing it (see Section 3). The voltammograms showed two thermodynamically controlled oxidation waves, with chemical irreversibility. The oxidation peak of the wave at higher potential was about 1.3–1.5 times more intense than that of the other, which is due to the presence of the mononuclear nitrile complexes $[Fe(NCR)(dppe)(C_5H_5)]^+$ (we checked that the electrode potential of the complex $[Fe(NCMe)(dppe)(C_5H_5)][PF_6]$ under the same experimental conditions was 0.77 V). We have observed repeatedly that the compound $[Fe(NCMe)(dppe)(C_5H_5)][PF_6]$, as similar nitrile complexes, decomposes slowly in dichloromethane solution with formation of an unidentified product that has an oxidation wave centred at 0.06 V. As a consequence, after a while the wave at 0.05 V may be mixed with the product wave of the decomposition of the iron cationic nitrile complexes. No other waves were detected in the voltammograms.

These results unambiguously confirmed that the binuclear cation $[(C_5H_5)(dppe)Fe–C{\equiv}C–CH_2CH_2–CN–Fe(dppe)(C_5H_5)]^+$ undergoes two one-electron oxidations with electrode potentials almost identical with those of the mononuclear compounds **2** and **4** (see Table 1). These were obtained by measuring their cyclic voltammograms and were as expected [4,5]. This coincidence indicates that the first oxidation of the binuclear monocation affects only the neutral Fe–C≡C– site, and the second the cationic –CN–Fe moiety, demonstrating that the electronic interaction between the two iron atoms is almost non-existent. This is to be expected considering that the two metallic centres are separated in the binuclear compound by an isolating CH_2CH_2 group.

The behaviour of **5** towards oxidation is markedly different to that of the diiron cyano-bridged cationic complex $[(C_5H_5)(dppe)Fe–CN–Fe(dppe)(C_5H_5)][PF_6]$



7

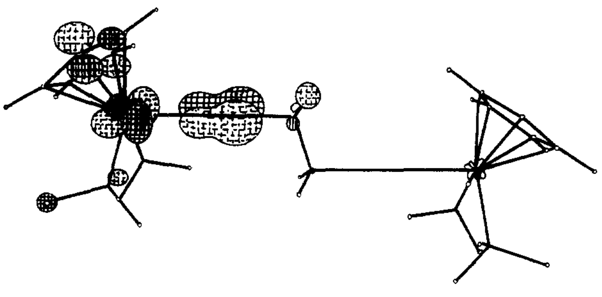
8

Fig. 1. Model complexes $[(C_5H_5)(PH_3)_2Fe–C{\equiv}C–CH_2CH_2–CN–Fe(PH_3)_2(C_5H_5)]^+$ (**7**) and $(C_5H_5)(PH_3)_2Fe–CN–Fe(PH_3)_2(C_5H_5)]^+$ (**8**).

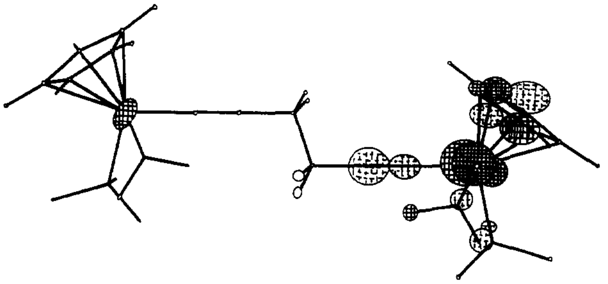
reported previously [1]. In the latter case the two electrode potentials (0.34 and 1.00 V) are significantly different from those of the non-interacting sites $(C_5H_5)(dppe)Fe-C$ and $N-Fe(dppe)(C_5H_5)$, as estimated from the electrode potentials of the mononuclear species $[MeCN-Fe(dppe)(C_5H_5)][PF_6]$(0.77 V), and $[(C_5H_5)(dppe)Fe-CNMe][PF_6]$ (1.15 V). For this work the methyl isocyanide complex was obtained by reaction of $[(C_5H_5)(dppe)Fe-CN]$ with MeI in tetrahydrofuran (THF) in the presence of $K[PF_6]$, and the cyclic voltammograms was recorded in CH_2Cl_2.

Although the differences between the isolated Fe(dppe)Cp fragments in **5** and the interconnected fragments in the μ-cyanide $[(C_5H_5)(dppe)Fe-CN-Fe(dppe)(C_5H_5)][PF_6]$ complex can be understood intuitively, we examined the electronic effects more quantitatively by carrying out MO calculations at the extended Hückel (EH) level on the model complexes $[(C_5H_5)(PH_3)_2Fe-C{\equiv}C-CH_2CH_2-CN-Fe(PH_3)_2(C_5H_5)]^+$ (**7**) and $[(C_5H_5)(PH_3)_2Fe-CN-Fe(PH_3)_2(C_5H_5)]^+$ (**8**) (Fig. 1).

As might be expected, the calculations (Table 3) showed that the highest occupied molecular orbital (HOMO) of the cation **7** (−11.87 eV), which is mainly formed by the Fe d_{xy} and the π-bonding combination of the p_y orbitals of the $-C{\equiv}C-$ group (Fig. 2), is totally located on the $Fe-C{\equiv}C-$ alkynyl moiety without significant participation of the other Fe atom orbitals. However, the second- and third-highest occupied MOs are also located in the $Fe-C{\equiv}C$ alkynyl fragment, and only the fourth-highest occupied MO (MO 65) with $\varepsilon = -12.02$ eV is totally localized on the −CN–Fe moiety. This might suggest that the second oxidation of the complex should also occur at the Fe-alkynyl fragment although, as indicated by the experimental results, it must be related to the MO 65 that is located on the CN–Fe moiety of the molecule. This is because, after the first oxidation, the d-orbital energies of the oxidized iron atom should be more negative, making the MOs 63 and 64 of the monocation lower in energy than the MO 65 of the dication.



MO 62 - HOMO



MO 65

Fig. 2. Selected MOs for **7**.

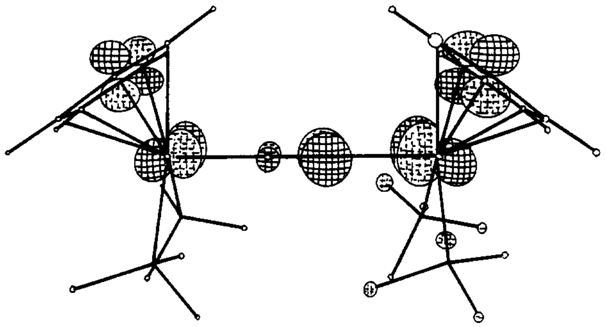
The ordering in the energy of the MOs localized at the $Fe-C{\equiv}C$, and Fe–NC– moieties in **7** were the same as those corresponding to the mononuclear models $[Fe(C{\equiv}CMe)(PH_3)_2(C_5H_5)]^+$ (ε(HOMO) = −11.87 eV) and $[Fe(NCMe)(PH_3)_2(C_5H_5)]^+$ (ε(HOMO) = −12.02 eV), which have also been studied by Fenske–Hall calculations with H in place of Me [6].

In the cyanide-bridged model **8** and in contrast with the alkynyl-cyano-bridged complex **2** the HOMO (−11.94 eV), which again is mainly formed by the combination of the Fe d_{xy} orbitals of both fragments, and the p_y component of the π occupied MO of the CN ligand (Fig. 3), is delocalized, although mainly located (62.55%) on the *N*-bonded $Cp(PH_3)_2Fe-$ fragment and significantly less (30.21%) on the other fragment. This is totally analogous to the case of the complex *trans-trans*-$[\{PH_3\}_3(CO)_2Mn-CN-Mn(CO)_2\{PH_3\}_3]^+$, where the HOMO is more localized on the *N*-bonded site [7]. In both cases the effect is due to the higher electronegativity of the N atom. However, in **8** the second-highest occupied orbital (−11.96 eV) is very delocalized, being located more on the *N*-bonded site (47.03%), but with a similar contribution of the *C*-bonded iron fragment

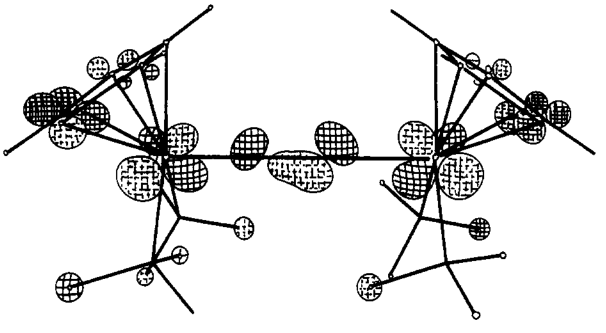
Table 3
Localization of selected molecular orbitals in the model molecules, as measured by the charge matrix elements

Model molecule	Orbital	ε (eV)	N–Fe(PH$_3$)$_2$Cp				C–Fe(PH$_3$)$_2$Cp				NC– (%)	CC (%)
			Fe (%)	(PH$_3$)$_2$ (%)	C$_p$ (%)	Total (%)	Fe (%)	(PH$_3$)$_2$ (%)	C$_p$ (%)	Total (%)		
7	1.HOMO	−11.87 [a]	1.31	0.06	0.14	1.51	53.93	4.70	11.86	70.49	0.25	25.08
	4.HOMO	−12.02	61.73	6.18	16.61	84.52	3.15	0.33	1.47	4.95	9.04	0.47
8	1.HOMO	−11.94	45.75	4.68	12.12	62.55	22.03	2.24	5.94	30.21	7.25	
	2.HOMO	−11.96	39.29	1.93	5.81	47.03	33.39	2.36	8.64	44.39	8.58	

[a] When the Fe–C distance ranged from 1.80 to 2.00 Å, the energy varied from −11.74 to −11.94 eV.



MO 52- HOMO



MO 53

Fig. 3. Selected MOs for **8**.

(44.39%). Therefore the first oxidation affects mainly the *N*-bonded iron atom, but the second may affect both metal atoms to nearly the same extent.

The two electrode potentials for the oxidations of $[(C_5H_5)(dppe)Fe{-}CN{-}Fe(dppe)(C_5H_5)][PF_6]$ differ by about 0.7 V, whereas the orbital energies of the MOs of the model **8** involved in each ionization process are almost the same. However, as observed in other cases [7], the potentials for the oxidation of **2**, **4**, **5**, $[Fe(CNMe)(dppe)(C_5H_5)]^+$, and the first $[(C_5H_5)(dppe)Fe{-}CN{-}Fe(dppe)(C_5H_5)]^+$ increase almost linearly with the orbital energies of the corresponding HOMOs of the models (for the molecule $[Fe(CNMe)(dppe)(C_5H_5)]^+$ the computed HOMO energy is -12.09 eV). Therefore the potential for the second oxidation of $[(C_5H_5)(dppe)Fe{-}CN{-}Fe(dppe)(C_5H_5)]^+$ appears to be much higher than the value expected for the orbital energy of the corresponding HOMO of this cation. This is due to the extended electron delocalization in the cyanide bridged species. It shows that, after the first oxidation of the molecule, not only the d-orbital parameters of the *N*-bonded iron atom, but also those of the *C*-bonded ion atom must become more negative to account for the second oxidation. In other words, the oxidation of the monocation markedly affects both Fe atoms.

It is unfortunate that the instability of the binuclear cyanide-bridged dications and trications prevents good experimental examination of its magnetic and spectroscopic properties.

3. Experimental part

All reactions were carried out under dry dinitrogen with standard Schlenk techniques. The IR spectra were recorded with a Perkin–Elmer FT 1720-X spectrometer. NMR spectra were recorded on a Bruker AC-300 instrument. Elemental analyses were performed with a Perkin–Elmer 240 microanalyser. The cyclic voltammograms were measured with a PAR M273 instrument. The auxiliary electrode was a platinum wire, and the working electrode was a platinum bead. The reference was a calomel electrode separated from the solution by a a fine-porosity frit and an agar–agar bridge saturated with KCl. Solutions were 0.5×10^{-3} M in the complexes and 0.1 M in $[^nNBu_4][PF_6]$ as supporting electrolyte. Under the same experimental conditions $E_{1/2}$ for the ferrocene–ferrocenium couple was 0.46 V, with a peak separation of 76 mV.

The alkyne $NC{-}CH_2CH_2{-}C{\equiv}C{-}H$ [8], and the complex $[FeI(dppe)(C_5H_5)]$ [1] were prepared as described. The two-step preparation of **2** (see below) is based on similar published methods for Fe alkynyls with CO or diphosphines [4,5,9]. The red complex $[Fe(NCMe)(dppe)(C_5H_5)[PF_6]$[10,11], was prepared with a good yield by reaction overnight at room temperature of the neutral complex $[FeI(dppe)(C_5H_5)]$ with an excess of NCMe in CH_2Cl_2 in the presence of $NH_4[PF_6]$ filtering and precipitating with ether. Anal. Found: C, 55.7; H, 4.29; N, 1.70, Calc.; C, 56.2; H, 4.54; N, 1.89%. The yellow $[Fe(CNMe)(dppe)(C_5H_5)][PF_6]$ was obtained also with a good yield by adding MeI and $K[PF_6]$ to a solution of $[Fe(CN)(dppe)(C_5H_5)]$ in THF and stirring overnight at room temperature, filtering and precipitating with ether. Anal. Found: C, 55.5; H, 4.47; N, 1.72. Calc.: C, 56.2; H, 4.54; N, 1.89%.

3.1. Preparation of *[Fe(C≡C–CH$_2$CH$_2$–CN)(dppe)(C$_5$H$_5$)] (2)*

A solution of $HC{\equiv}CCH_2CH_2{-}CN$ (0.33 ml, 4.17 mmol) in THF (20 ml) was cooled to -20°C, and 2.7 ml of 1.6 N LiBu in hexane (4.32 mmol) were added dropwise with stirring. Stirring was continued for $\frac{1}{2}$ h, and the mixture was cooled to -80°C. A solution of $[FeCl(CO)_2(C_5H_5)]$ (0.9 g, 4.24 mmol) in THF (25 ml) was added dropwise and, after 1 h, the mixture was allowed to reach room temperature, stirred for two more hours and filtered through 1 cm of alumina, to give a yellow solution of [FeC≡C–CH_2CH_2–CN)$(CO)_2$(C_5H_5)] (**1**) (IR: ν(CO) 2036s 1987s cm^{-1}) (occasionally mixed with some [$Fe_2(CO)_4(C_5H_5)_2$]). This solution was concentrated to 30 ml, dppe (1.73 g, 4.34 mmol) was added, and the mixture was irradiated at −20°C until no ν(CO) absorptions could be observed in the IR spectrum (about 5 h). The resulting red solution was filtered through Celite and evaporated to dryness. The residue was extracted with diethyl ether and the extracts were filtered through alumina (1 cm) and evaporated to dryness, to give a red solid that contained some dppe. This was washed five times with 20 ml of hot hexane to give **2** (Yield, 0.6 g, 1 mmol (23.7%). Anal. Found: C, 72.1; H, 5.53; N, 2.30. Calc. 72.4; H, 5.53; N, 2.35%.

3.2. Preparation of [(C_5H_5)(dppe)Fe=C=CH–CH_2–CH_2–CN][BF_4] (3)

A mixture of **2** (0.106 g, 0.177 mmol) in THF (15 ml) and $HBF_4 \cdot Et_2O$ (0.03 ml, 0.0286 g of solution of 85%, $d = 1.1$ g cm^{-3}, equivalent to 0.2 mmol of acid) was stirred for 30 min. The volatiles were evaporated in vacuo, and the residue was washed once with diethyl ether and dissolved in CH_2Cl_2. The solution was treated with dried K_2CO_3, filtered and concentrated. Addition of diethyl ether gave a red–orange precipitate of **3a** (yield, 0.08 g (66%)). Anal. Found: C, 62.9; H, 4.76; N, 1.56. Calc.: C, 631; H, 4.97; N, 2.00%.

3.3. Preparation of [(C_5H_5)(dppe)Fe–NC–CH_2CH_2–CCH][PF_6] (4)

A mixture of [FeI(dppe)(C_5H_5)] (0.2 g, 0.31 mmol), and the alkyne HC≡CCH_2CH_2CN (0.5 ml, 6.32 mmol) in CH_2Cl_2 (20 ml) was stirred overnight with solid $NH_4[PF_6]$ (0.2 g, 1.2 mmol) at room temperature. The mixture was filtered (Celite) and evaporated to dryness. The resulting solid was washed with ether and dried in vacuo to give **4** as a red microcrystalline powder (yield, 0.15 g (65%)). Anal. Found: C, 58.4; H, 4.47; N, 1.97. Calc.: C, 58.2; H, 4.58; N, 1.88%.

3.4. The formation of [(C_5H_5)(dppe)Fe–C≡C–CH_2–CH_2–CN–Fe(dppe)(C_5H_5)][PF_6] (5)

A mixture of **2** (0.09 g, 0.15 mmol) and [Fe(NCMe)(dppe)(C_5H_5)] (0.056 g, 0.1 mmol) in CH_2Cl_2 (15 ml) was stirred in the absence of light overnight and evaporated to dryness in vacuo. The residue was redissolved in 15 ml of CH_2Cl_2 and the treatment was repeated three more times. The final residue was dissolved in 20 ml of CH_2Cl_2, filtered and concentrated to 2 ml. Addition of a large excess of diethyl ether and stirring gave a red–brown solid that was repeatedly washed with diethyl ether until no neutral **2** was detected in the extracts (yields, about 0.07 g). This product was used for the cyclic voltammograms.

Table 4
Bonding distances used in the models

Model cation [a]	Fe–N (Å)	FeC (Å)	NC (Å)	C≡C (Å)
[Fe]–C≡C–CH_2CH_2–CN–[Fe]	1.946	1.920	1.130	1.181
[Fe]–NC–Me	1.946		1.130	
[Fe]–C≡C–Me		1.920		1.181
[Fe]–CN–Me		1.860	1.150	
[Fe]–CN–[Fe]	2.083	1.914	1.107	

[a] [Fe] = $Fe(PH_3)_2Cp$.

3.5. Computational details

EH MO calculations [12] were carried out using the modified Wolfsberg–Helmholz formula [13]. The atomic parameters were taken from the literature [14]. The bonding distances used in the models [15] are indicated in Table 4. Other distances were as follows: Fe–P, 2.214; P–H, 1.437; Fe–Cp–centre, 1.706; C_{Cp}–C_{Cp}, 1.500; CC–CH_2, 1.460; CH_2–CH_2, 1.514; CH_2–CN, 1.470; C–H, 1.080.

The angles around the CH_2 carbon atoms were 109.5° and between the Fe–CC vector and the Fe–PH_3 bonds, and between the two Fe–PH_3 bonds were 90°. The calculation showed that changing the last to 109° did not modify substantially the results. The HPH angles were the tetrahedral.

The calculations were carried out on a Micro VAX 3400 computer at the Scientific Computer Center of the University of Oviedo with a locally modified version of the program ICON. MO drawing were generated with the use of the program CACAO [16].

Acknowledgments

We are very grateful to the Spanish Instituto de Cooperacion Iberoamericana, to the Oficina de Relaciones Internacionales de la Universidad de Oviedo for a joint Project between Chile and Spain, and to FONDECYT (Chile)(Grant 1950305) for support.

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