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Synthesis of dinuclear alkenyl-bridged iron–nickel and diiron complexes. The crystal structure of $[Fe_2(CO)_4(C_5H_5)(\mu\text{-CO})(\mu\text{-CPh=CPhH})]$

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Abstract

The reaction of the anions $[Fe(\eta^3\text{-}R^1HC{=}CR^2CO)(CO)_3]^-$ ($R^1 = H$, $R^2{=}CO_2Me$ and CO_2Et; $R^1 = R^2 = CO_2Me$) with $[Ni(C_5H_5)(PPh_3)Br]$ gives the complexes $[FeNi(CO)_3(C_5H_5)(PPh_3)(\mu\text{-}R^2C{=}CH_2)]$ ($R^2 = CO_2Me$ (**1**) and CO_2Et(**2**)) and $[FeNi(CO)_2(C_5H_5)(PPh_3)(\mu\text{-}MeO_2CC{=}C(H)CO_2Me)]$ (**3**). Complexes **1** and **2** have been also obtained by heating mixtures of $[PPh_4][HFe(CO)_4]^-$, $R^1C{\equiv}CR^2$, and $[Ni(C_5H_5)(PPh_3)Br]$ in THF. Use of the $[HFe(CO)_4]^-/PhC{\equiv}CPh/M(C_5H_5)L_xX$ ($M = Ni$, $L_x = PPh_3$ and $M = Fe$, $L_x = (CO)_2$) system was successful for the synthesis of $[FeNi(CO)_3(C_5H_5)(PPh_3)(\mu\text{-CPhC=CPhH})]$ (**4**) and $[Fe_2(CO)_4(C_5H_5)(\mu\text{-CO})(\mu\text{-PhC=CPhH})]$ (**5**) complexes. The structure of **5** was determined by an X-ray diffraction study.

Introduction

In recent years interest in hetero bi- and poly-metallic complexes has led to development of a great variety of synthetic methods and observation of many reactions [1,2]. In most cases the heterobimetallic complexes are bridged by strong ligands such as chelating phosphines or three-electron groups such as phosphide [1].

Organic ligands have been less studied as bridges perhaps because of the difficulty of developing rational syntheses [3]. Our studies have been directed toward the synthesis and study of dinuclear vinyl-bridged complexes, and have for example, provided new methods of synthesis of Fe–Co complexes [4,5]. Very recently, a method was discovered for making dinuclear vinyl-bridged complexes from equimolar mixtures of $Fe_2(CO)_9$ and acetylene and subsequent reaction with hydrides [6]; it seems to involve activation of the acetylene by coordination to a $Fe(CO)_4$ fragment, followed by insertion into an H–M bond. In view of the limited information available on Fe–Ni complexes [1] compared with that on other mixed complexes, and in order to find other routes to heterobimetallic complexes, we decided to examine the reactions of the anions $[Fe(\eta^3\text{-}R^1HC{=}CR^2CO)(CO)_3]^-$ (R^1=H, R^2=CO_2Me and CO_2Et; R^1=R^2 = CO_2Me) with $[Ni(C_5H_5)(PPh_3)Br]$ and $[Fe(C_5H_5)(CO)_2I]$. The products formed by heating mixtures of $[HFe(CO)_4]^-$, PhC≡CPh and $M(C_5H_5)L_xX$ (M = Ni, L_x = PPh_3 and M = Fe, L_x = $(CO)_2$) have also been investigated; some new Fe–Ni vinyl bridged complexes were isolated, as well as $[Fe_2(CO)_4(C_5H_5)(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]$.

Results and discussion

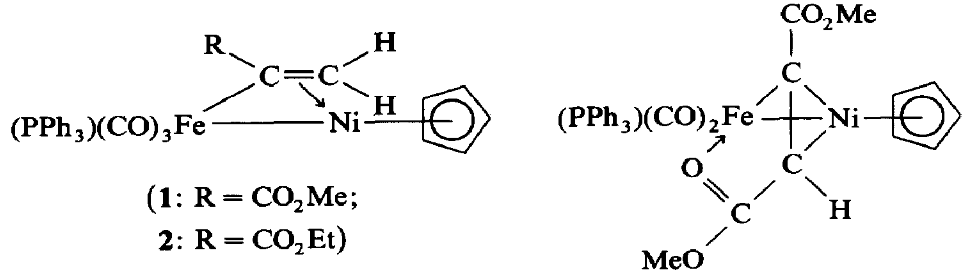
Mitsudo [7] showed that activated acetylenes $R^1C{\equiv}CR^2$ (R^1 = R^2 = CO_2Me; R^1 = CO_2Me, CO_2Et and R^2 = H) react readily with $[HFe(CO)_4]^-$ to give acryloyl complexes $[Fe(\eta^3\text{-}R^1HC{=}CR^2CO)(CO)_3]^-$ in which R^1 and R^2 are in a *trans* disposition. The reactions of tetraphenylphosphonium salts of these anions with $[Ni(C_5H_5)(PPh_3)Br]$ in refluxing THF solutions has been found to give crystalline green products for which the elemental analyses (C and H) and spectroscopic data are consistent with the formulations:

$[FeNi(CO)_3(C_5H_5)(PPh_3)(\mu\text{-}MeO_2CC{=}CH_2)]$ (**1**);
$[FeNi(CO)_3(C_5H_5)(PPh_3)(\mu\text{-}EtO_2CC{=}CH_2)]$ (**2**);
$[FeNi(CO)_2(C_5H_5)(PPh_3)(\mu\text{-}MeO_2CC{=}C(H)CO_2Me)]$ (**3**).

The products are soluble in dichloromethane, diethyl ether, and ethyl acetate, but only very slightly soluble in hydrocarbons and alcohols. The infrared spectra of **1–3** in the $\nu(CO)$ region recorded with dichloromethane solutions show bands corresponding to terminal carbonyls and with a band from the ester group at ca. 1680 cm^{-1}. Complex **3** also gives a medium band at 1560 cm^{-1} attributable to a C=O ligand coordinated to metal through oxygen [5]. The ^1H NMR spectra of **1** and **2** contain signals from geminal hydrogens, with weak couplings, together with signals from the ester, phosphine and C_5H_5 groups. Complex **3** also gives characteristic signals from the vinyl bridge and the other organic groups.

The same products were obtained when a solution of $[PPh_4][HFe(CO)_4]$, $R^1C{\equiv}CR^2$ and $[Ni(C_5H_5)(PPh_3)Br]$ in THF solution was refluxed, except that when PhC≡CPh was used the green complex $[FeNi(CO)_3(C_5H_5)(PPh_3)(\mu\text{-}CPhC{=}CPhH)]$ (**4**) was obtained. This complex shows resemblance to **1–3**, but gives a different pattern for the infrared spectrum recorded under the same conditions. The ^1H NMR spectra show the signals from diphenylethenyl, phosphine, and C_5H_5 ligands.

The position of the PPh_3 ligand in **4** was deduced from the $\{^1H\}^{31}P$ NMR spectra of complexes. Thus, **1–3** exhibit singlets at 63.7, 64.0, and 58.2 ppm respectively, indicating coordination of PPh_3 at the same metal. Complex **4** shows a peak at 31.5 ppm, suggesting that the ligands probably coordinated to the other



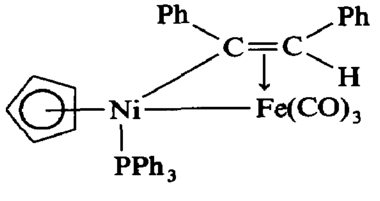
(**1**: R = CO_2Me;
2: R = CO_2Et)

(**3**)

Fig. 1

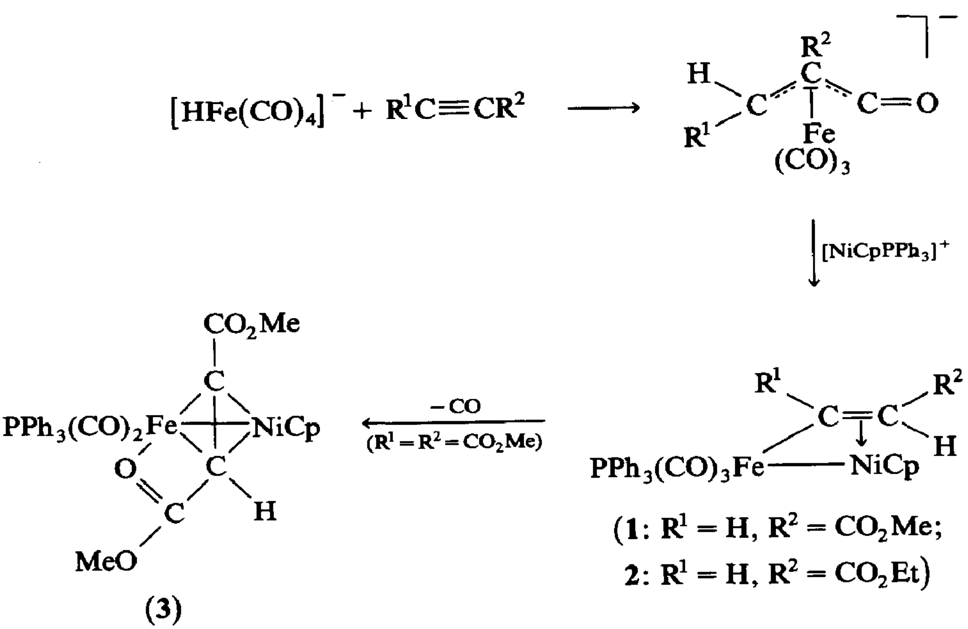
metal. The ^{31}P NMR spectrum of $[Ni(C_5H_5)(PPh_3)Br]$ was recorded for comparison, and showed one signal, at 32.4 ppm. From these data we conclude that PPh_3 is coordinated to Fe in complexes **1**–**3** but to Ni in complex **4**. The proposed structures for complexes **1**–**4** are shown in Figs. 1 and 2. The suggested structures for complexes **1** and **2** involve $Fe(CO)_3PPh_3$ and $Ni(C_5H_5)$ groups bonded by an α-substituted-ethenyl bridging ligand and a metal–metal bond. The vinyl ligand is σ-bonded to Fe and π-bonded to Ni. Complex **3** is essentially similar to **1** and **2** but with the additional coordination of an ester group to Fe, such as has been observed in Fe–Co complexes [5]. The coordination of PPh_3 to Ni prompts us to propose a different structure for **4**. We suggest that in this case the 1,2-diphenylethenyl bridge is σ-bonded to Ni and π-bonded to Fe. This 36-electron complex is probably electronically unbalanced in the manner observed for other mixed vinyl-bridged compounds [8].

In an extension of the method, the reaction of $[Fe(CO)_3(\eta^3\text{-}R^1HC{=}CR^2C{=}O)]^-$ with $[Fe(C_5H_5)(CO)_2I]$ and the products obtained from the $[HFe(CO)_4]^-$/acetylene/$[Fe(C_5H_5)(CO)_2I]$ mixtures in THF were investigated. The known $[Fe_2(C_5H_5)_2(CO)_4]$ complex was the only product formed in the most of reactions, except that involving PhC≡CPh. From the mixture of products obtained by reaction with PhC≡CPh the $[Fe_2(CO)_4(C_5H_5)(\mu\text{-}CO)(\mu\text{-}PhC{=}CPhH)]$ (**5**) complex was isolated in poor yield by chromatography on silica. Complex **5** was identified from elemental analyses (C and H), spectroscopic data and an X-ray diffraction study. It belongs to a family of products described by Nesmeyanov [9], and obtained recently by our group by a different route [14].



(**4**)

Fig. 2

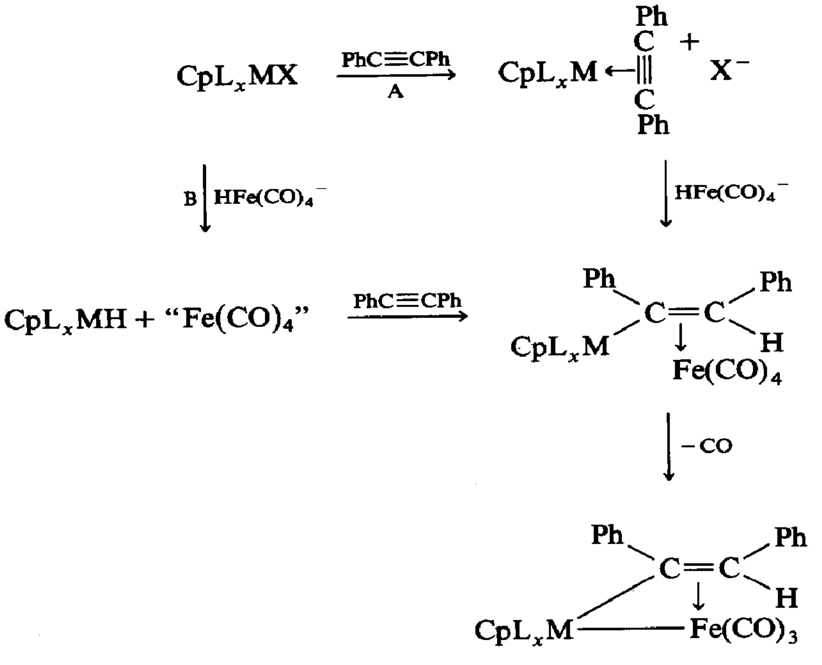


Scheme 1

The results described above allow us to suggest mechanisms of formation for complexes 1–5. The complexes 1–3 are formed by coupling of $[Fe(CO)_3(\eta^3\text{-}R^1HC{=}CR^2C{=}O)]^-$ and $[Ni(C_5H_5)(PPh_3)]^+$ fragments and elimination of one molecule of CO, in a sequence analogous to that involved in formation of related Fe–Co complexes [5] (see Scheme 1). When $R^1{=}R^2{=}CO_2Me$, there is an additional coordination to Fe and the loss of one molecule of CO. The complexes 4 and 5 seemed to be formed in a similar way since they contain the same bridging ligand σ-bonded to a metal which is also coordinated to C_5H_5 ligand (see Scheme 2). The proposed mechanism involves two methods of activation of $PhC{\equiv}CPh$. In the route A, the acetylene is activated by $[Ni(C_5H_5)(PPh_3)]^+$ and $[Fe(C_5H_5)(CO)_2]^+$ fragments. It is known that $[HFe(CO)_4]^-$ does not react with $PhC{=}CPh$ under conditions used for the synthesis of products 1–5, whereas the activated alkynes are very reactive. After coordination of $PhC{\equiv}CPh$ to metal, there is an insertion of the alkyne into the M–H bond. Route B involves the displacement of the halide by H^-. The $PhC{\equiv}CPh$ ligand may be complexed to the $Fe(CO)_4$ fragment and then insert into the H–M bond to give the same vinyl intermediate as that involves in route A. The loss of one molecule of CO leads to formation of complexes 4 and 5. Route B is proposed in the light of the fact that reactions of $[HFe(CO)_4]^-$ with $[Fe(C_5H_5)L_2(\eta^2\text{-}PhC{\equiv}CPh)]^+$ complexes were unsuccesful, probably because of the rapid reduction of $[Fe(C_5H_5)(CO)_2]^+$ cation to give the very stable complex $[Fe_2(C_5H_5)_2(CO)_4]$ [10].

Description of the structure of complex 5

Crystals of 5 were obtained from a dichloromethane/methanol mixture at −10 °C. A view of the molecule is presented in Fig. 3. Table 1 lists the atomic coordinates with standard deviations and Table 2 lists some relevant bond lengths and angles. The crystals of 5 consist of $[Fe_2(CO)_4(C_5H_5)(\mu\text{-}CO)(\mu\text{-}PhC{=}CPhH)]$ units linked by Van der Waals forces. The molecules are essentially similar to that



(**4**: $x = 1$, M = Ni, L = PPh_3;
5: $x = 2$, M = Fe, L = CO)

Scheme 2

described by Andrianov [11], and consist of $Fe(C_5H_5)(CO)$ and $Fe(CO)_3$ fragments linked by a 1,2-diphenylethenyl and CO bridges and a metal–metal bond. The Fe1–Fe2 distance of 2.585(3) Å is in the usual range of the values for single Fe–Fe

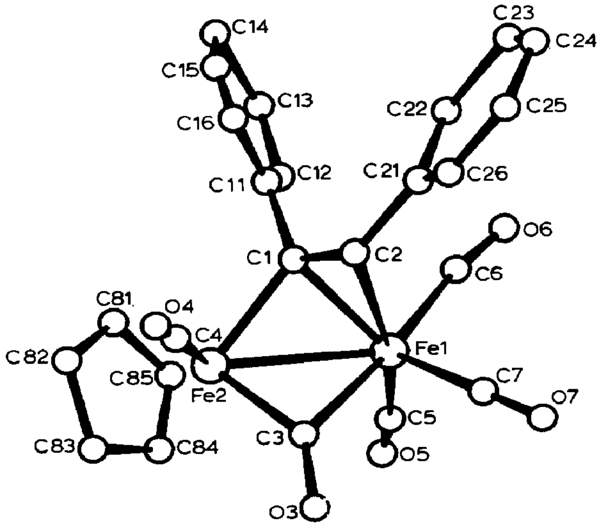


Fig. 3. Structure of complex $Fe_2(CO)_4(C_5H_5)(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)$ (**5**) showing the atomic numbering scheme.

Table 1

Fractional atomic coordinates ($\times 10^4$) for complex **5** with esd in parentheses

Atom	*x*	*y*	*z*
Fe1	3506(1)	1178(1)	10307(2)
Fe2	2934(1)	1806(1)	7864(2)
C1	2348(8)	1810(10)	9432(13)
C2	2097(10)	895(9)	9862(16)
C3	3604(10)	669(11)	8446(15)
O3	3971(7)	42(8)	8008(11)
C4	2044(11)	1059(11)	7030(17)
O4	1469(8)	627(9)	6428(12)
C5	4575(11)	1719(12)	10480(16)
O5	5279(22)	2128(74)	10580(84)
C6	3489(9)	1734(11)	11930(16)
O6	3539(7)	2058(9)	12976(11)
C7	3735(10)	−85(12)	10913(15)
O7	3848(9)	−854(8)	11254(12)
C81	2808(11)	3332(11)	7352(19)
C82	2603(12)	2730(13)	6147(18)
C83	3387(14)	2192(13)	6076(19)
C84	4060(12)	2429(13)	7246(20)
C85	3699(11)	3139(11)	8013(16)
C11	1950(9)	2732(9)	9805(13)
C12	2436(9)	3514(9)	10465(14)
C13	2034(10)	4333(10)	10779(15)
C14	1132(11)	4405(11)	10428(17)
C15	627(10)	3635(12)	9747(18)
C16	1043(9)	2826(10)	9444(15)
C21	1604(8)	660(10)	10937(14)
C22	1487(9)	1308(11)	11946(14)
C23	999(10)	1029(14)	12865(16)
C24	611(11)	143(16)	12792(22)
C25	707(11)	−492(12)	11810(20)
C26	1192(10)	−233(10)	10891(17)

bonds [12]. The alkenyl bridge is σ-bonded to Fe2 (Fe2–C1: 1.994(13) Å) and asymmetrically π-bonded to Fe1 (Fe1–C1: 2.018(12) and Fe1–C2: 2.171(15) Å). The CO bridge is also slightly asymmetric (Fe2–C3: 1.845(15) and Fe1–C3: 2.044(15) Å). The shorter Fe2–C3 distance is the result of the inductive effect of C_5H_5 ligand. The phenyl groups of the ethenyl bridge are in a *cis* configuration, forming a dihedral angle of 15.2°. As in other phenylethenyl bridged molecules, the Fe2, C1, C2 and C21 atoms lie in a plane [13]. The recently obtained complex $[FeRu(CO)_4(C_5H_5)(\mu\text{-}CO)(\mu\text{-}CPh{=}CPhH)]$ shows very similar molecular parameters [14].

Experimental

Reactions were carried out under nitrogen by Schlenk-tube techniques. ^1H NMR spectra were recorded on a Bruker WP80 spectrometer with $CDCl_3$ solutions. The ^1H-decoupled ^{31}P NMR spectra were recorded on a Bruker AM400 spectrometer with CD_2Cl_2 solutions, with aqueous 85% H_3PO_4 as external reference. Infrared

Table 2

Selected bond distances (Å) and angles (°) for complex **5**

Fe2–Fe1	2.585(3)	C1–Fe1	2.018(12)
C2–Fe1	2.171(15)	C3–Fe1	2.044(15)
C5–Fe1	1.792(18)	C6–Fe1	1.815(16)
C7–Fe1	1.844(17)	C1–Fe2	1.994(13)
C3–Fe2	1.895(15)	C4–Fe2	1.779(18)
C81–Fe2	2.151(14)	C82–Fe2	2.199(15)
C83–Fe2	2.144(15)	C84–Fe2	2.157(16)
C85–Fe2	2.165(14)	C2–C1	1.409(18)
C11–C1	1.491(17)	C21–C2	1.496(20)
O3–C3	1.170(16)	O4–C4	1.133(17)
O5–C5	1.214(84)	O6–C6	1.133(16)
O7–C7	1.111(17)		
C1–Fe1–Fe2	49.5(4)	C2–Fe1–Fe2	75.0(4)
C2–Fe1–C1	39.1(5)	C3–Fe1–Fe2	46.5(4)
C3–Fe1–C1	88.9(6)	C3–Fe1–C2	91.3(6)
C5–Fe1–Fe2	94.2(5)	C5–Fe1–C1	125.7(6)
C5–Fe1–C2	164.8(6)	C5–Fe1–C3	88.7(6)
C6–Fe1–Fe2	130.9(4)	C6–Fe1–C1	91.7(6)
C6–Fe1–C2	92.9(6)	C6–Fe1–C3	174.1(6)
C6–Fe1–C5	86.2(7)	C7–Fe1–Fe2	129.2(5)
C7–Fe1–C1	129.5(6)	C7–Fe1–C2	90.8(6)
C7–Fe1–C3	86.5(6)	C7–Fe1–C5	104.4(7)
Fe2–C1–Fe1	80.2(5)	C2–C1–Fe1	76.3(8)
C2–C1–Fe2	116.6(10)	C11–C1–Fe1	129.2(9)
C11–C1–Fe2	119.3(9)	C11–C1–C2	121.2(12)
C1–C2–Fe1	64.6(8)	C21–C2–Fe1	122.8(10)
C21–C2–C1	129.5(13)	Fe2–C3–Fe1	81.9(6)
O3–C3–Fe1	137.7(12)	O3–C3–Fe2	140.0(12)
O4–C4–Fe2	175.3(14)	O5–C5–Fe1	176.9(43)
O6–C6–Fe1	175.0(13)	C7–Fe1–C6	97.6(6)
C1–Fe2–Fe1	50.3(4)	C3–Fe2–Fe1	51.5(5)
C3–Fe2–C1	94.0(6)	C4–Fe2–Fe1	109.3(5)
C4–Fe2–C1	86.3(6)	C4–Fe2–C3	89.5(6)
O7–C7–Fe1	177.8(16)		

spectra in the ν(CO) region were recorded on a Perkin-Elmer IR 1710FT spectrophotometer with hexane solutions. Elemental analyses (C and H) were performed with a Perkin-Elmer 240-B analyzer. $[PPh_4][Fe(CO)_3(\eta^3\text{-}R^1HC{=}CR^2C{=}O)]$ [7], $[Ni(C_5H_5)(PPh_3)Br]$ [15] and $[Fe(C_5H_5)(CO)_2I]$ [16] complexes were prepared by published procedures.

Synthesis of 1 and 2 by method A

A solution of equimolar amounts (1.12 mmol) of $[PPh_4][Fe(CO)_3(\eta^3\text{-}R^1HC{=}CR^2C{=}O)]$ and $[Ni(C_5H_5)(PPh_3)Br]$ in 20 cm^3 of freshly distilled THF was stirred for 4 h, during which it turned green. The solvent was evaporated in vacuo and the residue extracted with diethyl ether. The extract was chromatographed on silica with a 20:1 hexane/ethyl acetate mixture as eluent. The green products isolated were recrystallized from a dichloromethane/pentane mixture at −12 °C. The yield was 50%.

*Synthesis of **1** and **2** by method B and of **4***

A mixture of 1 g (1.97 mmol) of [PPh_4][$HFe(CO)_4$], and the acetylene ($R^1C{\equiv}CR^2$) (1.97 mmol) and [$Ni(C_5H_5)(PPh_3)Br$] (1.97 mmol) in 20 cm^3 of freshly distilled THF was stirred at room temperature for 5 h. The green solution formed was evaporated to dryness and the residue extracted with diethyl ether. The crude product was chromatographed on silica with 20 : 1 hexane/ethyl acetate mixture as eluent. After recrystallization from a dichloromethane/pentane mixture at −12 °C green crystalline products were obtained in a total yield of 50%.

1: IR ν(CO): 1989s, 1929vs, 1883m and 1696 cm^{-1}. ^1H NMR δ (ppm): 3.6(s,3H + 1H), 3.72(s,1H), 5.05(s,5H) and 7.56(m,15H). $^{31}P\{^1H\}$ NMR δ (ppm): 63.71(s). Anal. Found: C,58.24; H,3.91. $C_{30}H_{25}FeNiO_5P$ calcd.: C, 58.96; H, 4.09%.

2: IR ν(CO): 1999s, 1942vs, 1870m and 1685m cm^{-1}. ^1H NMR δ (ppm): 1.2(t, *J* 6.5, 3H), 2.78(s, 1H), 3.72(s, 1H), 4.10(q, *J* 6.5, 2H), 5.05(s, 5H) and 7.56(m, 15H). $^{31}P\{^1H\}$ NMR δ (ppm): 64.3(s). Anal. Found: C, 59.54; H,4.30. $C_{21}H_{27}FeNiO_5P$ calcd.: C,59.59; H,4.32%.

(**4**): IR ν(CO): 2021vs, 1967s and 1953m cm^{-1}. ^1H NMR δ (ppm): 3.5(s, 1H), 5.21(s, 5H) and 7.4(m, 10H). $^{31}P\{^1H\}$ NMR δ (ppm): 58.16(s). Anal. Found: C, 68.15; H, 4.32. $C_{41}H_{30}FeNiO_3P$ calcd.: C, 68.09; H, 4.40%.

*Synthesis of **3***

A solution of 0.73 g (1.12 mmol) of [PPh_4][$Fe(CO)_3(\eta^3$-$MeO_2C(H)C{=}C(CO_2Me)$-$C{=}O)$] and 0.5 g (1.12 mmol) of [$Ni(C_5H_5)(PPh_3)Br$] in 20 cm^3 of freshly distilled THF was refluxed for 6 h and the resulting green solution then evaporated to dryness. The residue was then extracted with diethyl ether, the extract was evaporated, and the residue crystallized from methanol at −12 °C during 12 h. The yield was 60%.

3: IR ν(CO): 1985vs, 1931vs, 1670m and 1560m cm^{-1}. ^1H NMR δ (ppm): 3.16(s, 3H), 3.55(s, 3H) 3.67(s, 1H), 5.27(s, 5H) and 7.37(m, 15H). $^{31}P\{^1H\}$ NMR δ (ppm): 31.5(s). Anal. Found: C,59.54; H,4.29. $C_{31}H_{27}FeNiO_6P$ calcd.: C,58.10; H, 4.21%.

*Synthesis of **5***

To a solution of 0.57 g (1.12 mmol) of [PPh_4][$HFe(CO)_4$] in 15 ml of distilled THF were added 0.2 g (1.12 mmol) of $PhC{\equiv}CPh$ and 0.5 g (1.12 mmol) of [$Fe(C_5H_5)(CO)_2I$]. The mixture was stirred for 8 h at room temperature then evaporated to dryness. The residue was extracted with diethyl ether and subjected to chromatography on silica with a 20 : 1 mixture of hexane/ethyl acetate mixture as eluent. Recrystallization from dichloromethane/methanol at −12 °C gave a green product in 5% yield.

5: IR ν(CO): 2046s, 1988vs, 1966m and 1813m cm^{-1}. ^1H NMR δ (ppm): 2.6(s, 1H), 4.71(s, 5H) and 6.9–6.6(m, 10H). Anal. Found: C,58.65; H,3.32. $C_{24}H_{16}Fe_2O_5$ calcd.: C,58.15; H,3.22%.

*X-ray diffraction study of [$Fe_2(CO)_4(C_5H_5)(\mu$-$CO)(\mu$-$CPhC{=}CPhH)$] (**5**)*

Crystal data. $C_{24}H_{16}Fe_2O_5$. $F_w = 496.08$, monoclinic, $P2_1/n$, $a = 15.535(3)$, $b = 13.700(3)$, $c = 10.115(2)$ Å, $\beta = 102.59(3)°$. $V = 2101(1)$ Å^3, $D_x = 1.568$ g cm^{-3}, $Z = 4$, $F(000) = 1008.0$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$Å, $\mu(\text{Mo-}K_\alpha) = 14.51$ cm^{-1}. $T = 298$ K.

Data collection and processing. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($4 \leq \theta \leq 12$) and refined by least-squares method. Intensities were collected with graphite monochromated Mo-K_α radiation, by the ω-scan technique, scan width 0.8°, scan speed 0.03° s^{-1}. 2786 reflections were measured in the range $2 \leq \theta \leq 25°$, 1873 of which were measured as observed applying the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control, and no significant intensity decay was observed. Lorentz-polarization were made but no absorption correction.

Structure solution and refinement. The structure was solved by direct methods using the MULTAN system of computer programs [17] and refined by full-matrix least-squares method, using the SHELX76 computer program [18]. The function minimized was $\Sigma w \| F_o | - | F_c \|^2$, where $w = \sigma^{-2}(F_o)$, f, f' and f'' were taken from the International Tables of X-ray Crystallography [19]. The O5 atom was located in disordered positions; the occupancy factor for this atom was refined with a final result of 0.9(3) for the O5 and 0.1(3) for the O5′ position. The hydrogen atoms were placed in calculated positions, except for H2 which was located from a difference synthesis. All the hydrogen atoms were refined with an overall isotropic temperature factor, using a riding model for computed H, and the remaining atoms were refined anisotropically. The final R factor was 0.055 ($R_w = 0.056$) for all observed reflections. Number of refined parameters: 295. Residual electron density in difference map: 0.5 and -0.5 eÅ^{-3}, respectively.

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References

1 D.A. Roberts and G.L. Geoffroy in G. Wilkinson and F.G.A. Stone (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Ch. 40.

2 Reactivity of Metal–Metal Bonds, M.H. Chisholm (Ed.), American Chemical Society, Washington D.C., A.C.S. Symp. Ser., No 155, 1981.

3 J. Holton, M.F. Lappert, R. Pearce and P.I.W. Yarrow, Chem. Rev., 83 (1983) 135.

4 J. Ros and R. Mathieu, Organometallics, 2 (1983) 771.

5 I. Moldes, J. Ros, R. Mathieu, X. Solans and M. Font-Bardía, J. Chem. Soc., Dalton Trans., (1987) 1619.

6 R. Yañez, J. Ros and R. Mathieu, J. Organomet. Chem., 389 (1990) 219.

7 T. Mitsudo, Y. Watanabe, H. Nakanishi, I. Morishima, T. Inubushi and Y. Takegami, J. Chem. Soc., Dalton Trans., (1978) 1298.

8 I. Moldes, J. Ros, R. Yañez, R. Mathieu, X. Solans and M. Font-Bardía, J. Chem. Soc., Dalton Trans., (1988) 1417.

9 A.N. Nesmeyanov, M.I. Rybinskaya, L.V. Rybin, V.S. Kaganovich and P.V. Petrovskii, J. Organomet. Chem., 31 (1971) 257.

10 D.L. Reger, Acc. Chem. Res., 21 (1988) 229.

11 V.G. Andrianov and Y.T. Struchkov, J. Chem. Soc., Chem. Commun., (1968) 1590.

12 B.L. Kruger, L. Barnett and D. Brauer in E.A.K. von Gustorf, F.W. Grevels and I. Fisher (Eds.), The Organic Chemistry of Iron, Academic Press, 1978, Vol. 1.

13 I. Moldes, J. Ros, R. Yañez, R. Mathieu, X. Solans and M. Font-Bardía, J. Organomet. Chem., 315 (1986) C22.

14 R. Yañez, J. Ros, R. Mathieu, X. Solans and M. Font-Bardía, J. Chem. Soc., Dalton Trans., in press.

15 J.W. Faller and B.V. Johnson, J. Organomet. Chem., 110 (1976) 235.

16 J. Kleinberg (Ed.), Inorg. Synth., Vol. VII, 1963, p. 110.

17 P. Main, S.E. Fiske, S.L. Hull, L. Lessinger, G. Germain, J.P. Declercq and M.M. Woolfson, MULTAN80. A Computer program for crystal structure determination from X-Ray diffraction data, Univ. of York (England) and Univ. of Louvain (Belgium), 1980.

18 G.M. Sheldrick, SHELX. A computer program for crystal structure determination, Univ. of Cambridge (England), 1976.

19 International Tables for X-Ray Crystallography, Vol. 4, Birmingham, Kynock Press, 1974.