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# Oxidative versus Electrophilic Chemistry of an Anionic Phosphido- and Vinylidene-Bridged Triiron Cluster: Oxidation-Induced P–C and C–C Bond Formation

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Electrochemical or chemical oxidation with CuCl, $[Cp_2Fe][PF_6]$, or $[Ph_3C][BF_4]$ of $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)]$ (1) leads to unstable radicals which rearrange mainly to neutral dinuclear complexes, the major product being $Fe_2(CO)_6[\mu\text{-}\eta^4\text{-}PPh_2CH{=}C(^tBu)C(OH)]$ (4), the structure of which has been established by an X-ray structure determination: monoclinic; space group $C_{2h}^5\text{-}P2_1/c$; $a = 10.669$ (2), $b = 12.716$ (2), $c = 18.436$ (2) Å; $\beta = 98.60$ (1)°; $Z = 4$. The structure was solved and refined to $R$ and $R_w$ values of 0.0361 and 0.0390, respectively, with use of 3598 reflections. The dinuclear $Fe_2(CO)_6$ unit is bridged by a ligand resulting from the coupling of the diphenylphosphido and the vinylidene ligands, migration of hydrogen from the C$\beta$ to the C$\alpha$ carbon of the vinylidene group, and coupling of the C$\beta$ carbon with a protonated carbonyl group. Minor products from the reaction are $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}C^tBu)$, $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}CH{=}CH^tBu)$, and the trinuclear cluster $Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)(H)$ (3). 3 can be obtained quantitatively by protonation of 1 with trifluoroacetic acid. $[NO][BF_4]$ behaves with 1 either as an oxidant generating 4 in 25% yield or as an electrophile leading to $Fe_3(CO)_7(NO)(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)$ (5) in 18% yield. The structure of 5 has been established by an X-ray structure determination: monoclinic; space group $C_{2h}^5\text{-}P2_1/c$; $a = 14.588$ (5), $b = 14.434$ (2), $c = 13.274$ (2) Å; $\beta = 99.58$ (2)°; $Z = 4$. The structure was solved and refined to $R$ and $R_w$ values of 0.0395 and 0.0396, respectively, with use of 3128 reflections.

## Introduction

We,[1] and others,[2,3] have shown that chemical reduction of a cluster containing one or several organic fragments can induce carbon–carbon bond formation between these fragments. Generally, these rearrangements have the effect of reequilibrating the electronic structure of the cluster leading to a fully saturated structure.

During the course of the study of electrochemical properties of the $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)]$ (1) cluster,[4] we have observed that 1 is oxidized quasi reversibly on the time scale of cyclic voltammetry but that electrolysis, or chemical oxidation, leads to cluster degradation to dinuclear species. Analysis of the reaction shows that the main product is a dinuclear complex, identified by an X-ray diffraction determination, in which a $Fe_2(CO)_6$ unit is bridged by a ligand resulting from the coupling of the phosphido and vinylidene bridges together with a protonated carbonyl group. We also describe in this paper how $[NO][BF_4]$ gives two types of reactions, oxidation or electrophilic attack leading to $Fe_3(CO)_7(NO)(\mu\text{-}C{=}CH^tBu)$, characterized by X-ray diffraction.

## Results and Discussion

**Electrochemical Oxidation.** Cyclic voltammetry experiments ($CH_2Cl_2$, $Bu_4N^+PF_6^-$, Pt electrode) indicate that the phosphido- and vinylidene-bridged cluster[4] $[PPh_4][Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)]$ (1) is oxidized quasi reversibly in a one-electron process ($E_{1/2} = 0.01$ V vs Ag/AgCl, $\Delta E_p = 75$ mV, $i_{p_c}/i_{p_a} = 0.8$, $v = 0.1$ V s$^{-1}$). Another irreversible oxidation occurs at $E_p = 0.73$ V, but it is not considered in this study. Attempts to generate the sought 47-electron cluster $[Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)]^\bullet$ have been conducted electrochemically or chemically.

Controlled-potential electrolysis of a dichloromethane solution of 1 at a potential of 0.10 V vs Ag/AgCl leads to consumption of 1 faraday/mol of 1 and to a zero electrolytic current. However, an IR spectrum of the electrolyzed solution in the CO absorption region shows a complicated pattern indicating that several species are formed. An electrolysis run at −20 °C did not give significant differences. An ESR examination of this solution at room temperature shows a single doublet signal centered at $g = 2.046$. The doublet pattern is ascribed to the superhyperfine coupling to a phosphorus nucleus ($^{31}P$, $I = {}^1/_2$, $A(^{31}P) = 33$ G). The $g$ and $A(^{31}P)$ values indicate this species is a phosphido-bridged cluster, since they compare well with values of isolated phosphido-bridged diiron radicals.[5] This radical is in no case a major component of the electrolyzed solution since the IR spectrum of the solution shows that several neutral species are present in comparable amount (see below).

Column chromatography after extraction of this solution with hexanes (after extraction the same ESR signal is recorded) only leads to several diamagnetic complexes, isolated in low yield (Scheme I). Among these, we have succeeded in characterizing two trinuclear clusters, Fe3-

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(1) de Montauzon, D.; Mathieu, R. *J. Organomet. Chem.* **1983**, *252*, C83. Dahan, F.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1984**, 432. Suades, J.; Dahan, F.; Mathieu, R. *Organometallics* **1988**, *7*, 47.

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(5) Baker, R. T.; Krusic, P. J.; Calabrese, J. C.; Roe, D. C. *Organometallics* **1986**, *5*, 1506.

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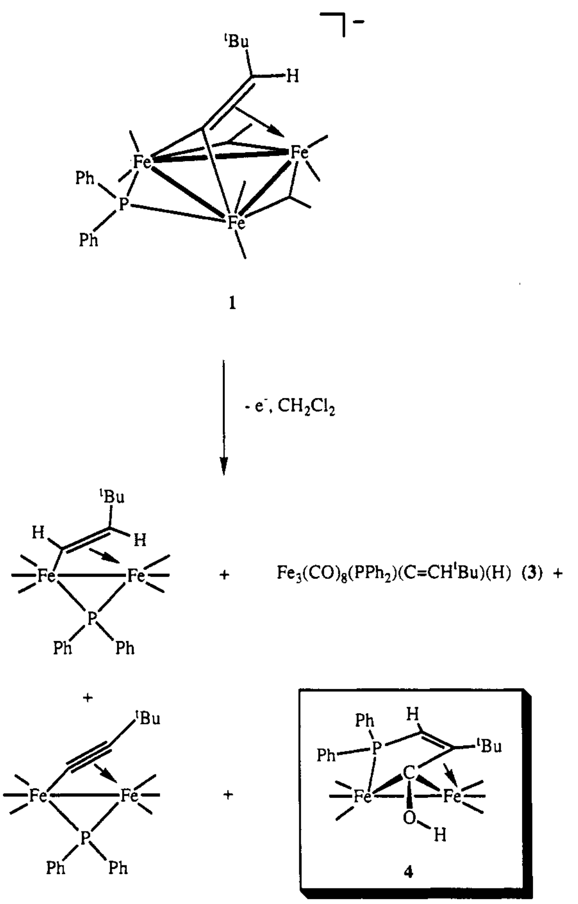
Scheme I



(CO)$_{12}$ (traces) and the new hydrido vinylidene $Fe_3(CO)_8(\mu\text{-}PPH_2)(\mu\text{-}C{=}CH^tBu)(H)$ (3) (ca. <5%), and some dinuclear species, namely, the $\mu$-vinyl complex $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}CH{=}CH^tBu)$ (ca. <5%), a new member of the $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}vinyl)$ family,[6] an as yet not fully characterized complex corresponding to the formula $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C_2H_2{}^tBu)$ (ca. <5%), the $\mu$-alkynyl $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}C^tBu)$ (ca. <5%),[7] and an interesting alcohol-containing product $Fe_2(CO)_6[\mu\text{-}\eta^4\text{-}PPh_2CH{=}C(^tBu)C(OH)]$ (4) (ca. <20%). Other compounds in trace amounts were not identified. Known complexes are identified by comparison of their IR and $^1H$ and $^{31}P$ NMR spectra with literature data and in some cases with mass spectra. The new complexes are characterized by spectroscopic methods, elemental analyses, and mass spectrometry (see below). An X-ray diffraction analysis has been carried out on complex 4.

The main conclusion of this electrochemical study is that the 47-electron complex generated by single oxidation of 1 is not stable under the experimental conditions and gives a variety of products, only one of which remains trinuclear. In hope of understanding more of these processes, chemical oxidants were used to achieve the single-electron oxidation.

**Chemical Oxidations.** The chemical oxidants used are $[Cp_2Fe^+][PF_6^-]$, CuCl, and $[Ph_3C^+][BF_4^-]$. Oxidations were run in dichloromethane at room temperature or 0 °C with a slight excess (ca. 10%) of the oxidizing species with respect to cluster 1. All reactions were monitored by IR and $^{31}P$ NMR spectroscopies and, in some cases, by ESR spectroscopy. Basically, the same spectra are observed in the three cases. According to IR and $^{31}P$ NMR the major product formed is the dinuclear complex 4. Formation of small amounts of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}C^tBu)$ and $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}CH{=}CH^tBu)$ is also noted. These complexes can be isolated after column chromatography. Complex 4 is obtained in 40% yield (Scheme I). Hence, the 47-electron species again appears not to be stable, and this is also deduced from ESR spectroscopy. ESR spectra of reaction mixtures do not show the same signal as the one observed after electrolysis. A singlet is observed at $g = 2.041$, among other ill-defined signals: it decreases erratically to leave, after ca. 2 h, a doublet ($g = 2.049$, $A = 15.5$ G) of very low intensity. The only really interesting observation is found in the case of the $[Ph_3C^+]$ oxidation: the produced triphenylmethyl radical is observed ($g = 2.002$, 16 lines with $A(^1H) = 1.30$ G) together with the other previously described signals. An estimation of the signals integration shows that the concentration of the $g = 2.041$ signal is never higher than that of the triphenylmethyl radical, i.e. in the order of 2% considering the equilibrium with its dimer form.[8]

It thus becomes obvious that the 47-electron radical cluster formed upon oxidation of 1 is not stable and rearranges in a somewhat intriguing manner. The pathway leading to 4 is unknown, but it is noteworthy that this rearrangement results from the coupling of the phosphido and vinylidene bridges together with carbonyl incorporation and a 1,2-hydrogen migration from the $\beta$-carbon to the $\alpha$-carbon of the vinylidene ligand. Adventitious hydrogen atoms also need to be trapped to give the alcohol fragment. Recall that deprotonated 4, namely the anion $[Fe_2(CO)_6(\mu\text{-}PPh_2CH{=}C(^tBu)C(O))]^-$, is obtained as one of the products of the reaction between $[PPh_4]^+[HFe_3(CO)_{11}]^-$ and $PPh_2C{\equiv}C^tBu$, a reaction also leading to cluster 1.[4]

**Electrophilic Reactions.** We next sought to compare the oxidative and electrophilic chemistry of 1. The nitrosonium cation was chosen in a first approach, since it may behave as an oxidant or an electrophile. Mixing 1 and 10% excess [NO][BF$_4$] in dichloromethane at room temperature gives a deep green solution. IR monitoring in the CO absorption region shows that dinuclear complex 4 is again formed, together with a nitrosyl-containing product since a broad band at 1760 cm$^{-1}$ is observed. After solvent removal and extraction of the residue with dichloromethane/hexanes (1/3 by volume) mixtures, column chromatography affords a green band (hexanes elution) and an orange band (dichloromethane/hexane, 1/2 by volume). Recrystallization of the latter gives complex 4 in 25% yield. From the green band, recrystallization from hexanes gives, in 18% yield, yield, the cluster $Fe_3(CO)_7(NO)(PPh_2)(C{=}CH^tBu)$ (5) (Scheme II). It has been characterized by elemental analysis, mass spectrometry, and IR and $^1H$, $^{31}P$, and $^{13}C$ NMR spectroscopies (see below). An X-ray crystal structure, as well as variable-temperature NMR studies, has been carried out on cluster 5.

Isolation of 5 can be regarded as a direct consequence of NO$^+$ behaving as an electrophile while, as suggested in the previous sections, formation of 4 is related to the fact

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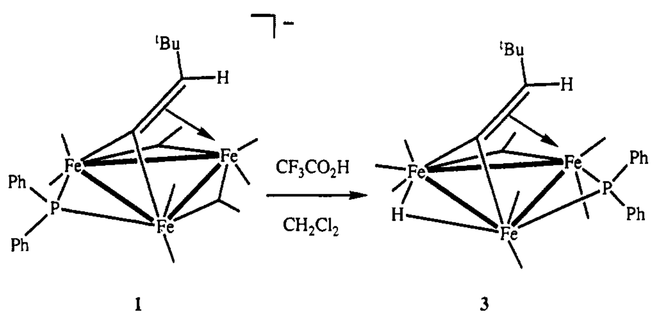
[6] Yanez, R.; Ros, J.; Mathieu, R.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **1990**, *389*, 219.

[7] Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726. Smith, W. F.; Yule, J.; Taylor, N. J.; Paik, H. N.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 1593.

[8] March, J. R. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 164.

Scheme II



that $NO^+$ may act as a one-electron oxidant. Furthermore, the condensate from the reaction mixture exhibited a distinct reddish color upon exposure to air due to $NO_2$, indicating that $NO^•$ is indeed produced in an electron-transfer reaction with **1**.

In a final experiment, we reacted cluster **1** with a protonic acid, a reaction considered as purely electrophilic. In addition to mechanistic consideration, it was of interest to know whether $\mu_3$-alkylidyne species were to be formed via protonation of a $\mu_3$-vinylidene precursor,[9] in the case of a phosphido-bridged cluster. Treatment of **1** with a slight excess of trifluoroacetic acid in $CDCl_3$ in an NMR tube gives, in a 100% spectroscopic yield ($^1H$ NMR), the green hydrido derivative $Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)(H)$ (**3**). It is noteworthy that no trace of the hypothetical $\mu_3$-alkylidyne $Fe_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}CCH_2{}^tBu)$ is observed, even in cases when the protonation is carried out under a CO atmosphere. The $\mu_3$-ethylidyne $Fe_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}CCH_3)$ has previously been obtained following a different route.[10,11] In a preparative experiment, **3** can be isolated in 70% yield after column chromatography and recrystallization from hexanes. It has been characterized by elemental analysis, mass spectrometry, and IR and $^1H$, $^{31}P$, and $^{13}C$ NMR spectroscopies. It is noteworthy that protonation of **1** generates no dinuclear complex **4**. Thus, the emerging pattern of reactivity previously described finds here a final argument: formation of **4** is a direct consequence of the single-electron oxidation of cluster **1** and of the instability or reactivity of the generated radical. It is interesting to note that carbon–carbon and carbon–phosphorus bonds are formed in this process.

**Characterization of Complexes.** We only detail here the characterization of complexes **3**–**5**. The data for other complexes are found in the Experimental Section.

**$Fe_2(CO)_6[\mu\text{-}PPh_2CH{=}C(^tBu)C(OH)]$ (4).** The mass spectrum (EI) of **4** has been somewhat intriguing to us, at least before we completed the X-ray crystal structure of **4**, since it shows the parent ion $M^+$ ($m/z$ 576) and the consecutive loss of *seven* CO groups. The IR spectrum of **4** exhibits absorptions typical of the $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}X)$ family. Complex **4** is only slightly soluble in hexanes in contrast to other $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}X)$ compounds. $^{31}P$ NMR shows a peak at $\delta$ 52.5, close to the $\delta$ 57.5 value observed[4] for $[PPh_4][Fe_2(CO)_6(PPh_2CH{=}C(^tBu)C(O))]$. In the $^1H$ NMR spectrum of **4**, apart from the Ph and $^tBu$ protons, two signals integrating for one proton each are observed. In benzene-$d_6$, a doublet with $^2J_{HP} = 2$ Hz centered at $\delta$ 3.04 is ascribed to the $PPh_2CH{=}$ proton. The high-field resonance is characteristic of the double carbon–carbon bond coordination. A broader signal at $\delta$ 5.41 is assigned to the alcoholic hydrogen, this signal being shifted to $\delta$ 10.03 in acetone-$d_6$. Relevant $^{13}C$ data ($CDCl_3$) are the $\delta$ 207.3 signal appearing as a pseudotriplet (doublet of doublets) in the gated $^1H$ spectrum with $J_{PC} = {}^2J_{CH} = 16$ Hz for the $\mu$-C(OH) carbon and the $\delta$ 106.8 (d, $J_{PC} = 21$ Hz) and $\delta$ 35.6 (dd, $J_{PC} = 36$ Hz, $J_{CH} = 165$ Hz) signals attributable respectively to the $^tBu$ and H bound carbons of the $PPh_2C(^tBu){=}C(H)C(OH)$ fragment. The last two values compare well to those found[4] in the anion $[Fe_2(CO)_6(PPh_2CH{=}C(^tBu)C(O))]^-$. An X-ray crystal structure has been obtained for **4** (see below).

**$Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)(H)$ (3).** The mass spectrum (EI) of complex **3** shows the parent ion ($m/z$ 660) as well as ions corresponding to loss of eight CO groups. The IR spectrum (hexanes) indicates the presence of both terminal and semibridging carbonyl groups. The presence of a phosphido group bridging an iron–iron bond can be inferred[4,12] from the $\delta$ 298.3 signal observed in the $^{31}P$ NMR spectrum of **3**. More surprising is the $^1H$ NMR of the complex. In dichloromethane-$d_2$ at room temperature, two slightly broad doublets are observed at $\delta$ 5.64 and −11.77 assigned respectively to the H$\beta$ vinylidene hydrogen and the hydride. At lower temperature (193 K), two well-resolved doublets are observed at $\delta$ 5.63 and −11.98 with a 9-Hz coupling constant. These couplings are not phosphorus–proton couplings since, upon broad-band phosphorus decoupling, the doublets remained unaffected (only for the high-field resonance is each peak of the doublet narrower). Upon irradiation of the hydride resonance in a homodecoupling experiment, the doublet signal at $\delta$ 5.63 becomes a singlet. Obviously, these observations should have direct structural consequences especially if one considers the data[4] for the anionic cluster **1** and the NO-containing product $Fe_3(CO)_7(NO)(PPh_2)(\mu\text{-}C{=}CH^tBu)$ (**5**) (see below for full characterization of **5**). In the case of **1** and **5**, the $^{31}P$ chemical shifts ($\delta$ 274 and 263, respectively) indicate the phosphido group bridges an iron–iron bond as in **3**, and the H$\beta$ vinylidene protons give doublets at $\delta$ 4.98 ($J_{PH} = 4.4$ Hz) and $\delta$ 5.6 ($J_{PH} = 4.3$ Hz), respectively, doublets obviously due to phosphorus–proton coupling and with comparable coupling constant magnitude. Considering the X-ray structures of **1** and **5** (the case of **5** is more complicated, however; see below) where the phosphido and vinylidene groups bridge the same iron–iron bond, we propose for **3** a structure in which the vinylidene and the phosphido groups bridge different metal–metal bonds. This is also supported by $^{13}C$ NMR spectra data. For complexes **1** and **5**, the vinylidene C$\alpha$ carbon gives a doublet at $\delta$ 232.6 ($J_{PC} = 57$ Hz)[4] and between $\delta$ 256.6 and 259.3 ($40 < J_{PC} < 44$ Hz) for the three isomers of **5** (see below), respectively. In complex **3**, the C$\alpha$ carbon of the vinylidene ligand gives a doublet of doublet at $\delta$ 210.5 with a $J_{PC}$ value of only 14 Hz and an additional $J_{CH}$ coupling of 4 Hz. The C$\beta$ carbon of the vinylidene ligand in **3** gives a doublet at $\delta$ 149.2 ($^1J_{CH} = 162$ Hz). Similarly, two different $J_{PC}$ values (29 and 46 Hz) have been observed[13] for the interconverting symmetric and asymmetric isomers of the bis(phosphido)(vinylidene)triiron

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(9) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(10) Yanez, R.; Ros, J.; De Gea, J.; Mathieu, R.; Torres, M. R.; Perales, A. *Inorg. Chim. Acta* **1990**, *168*, L1.

(11) Further studies aimed at understanding this isomerization problem are in progress.

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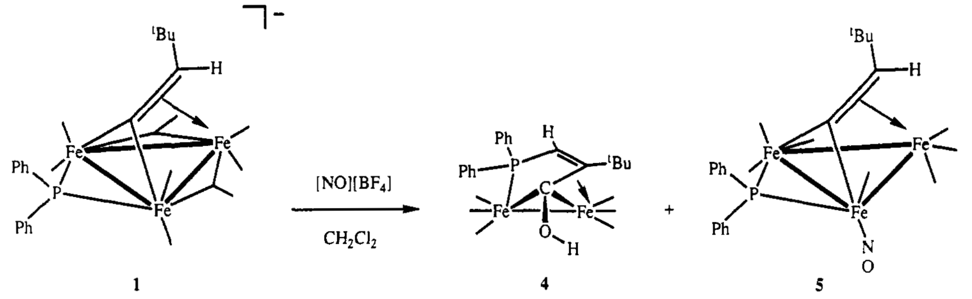
(13) Grist, N. J.; Hogarth, G.; Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 673.

Scheme III

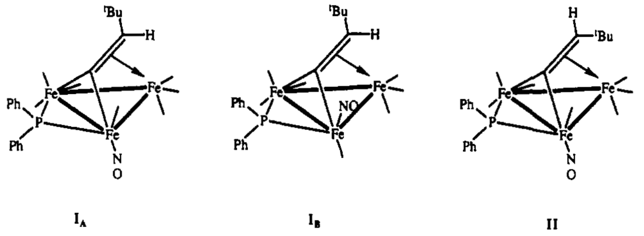


cluster $Fe_3(CO)_7(\mu\text{-}PPh_2)_2(\mu\text{-}C{=}CH_2)$. A likely structure of complex 3 is presented in Scheme II.

**$Fe_3(CO)_7(NO)(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)$ (5).** The mass spectrum (FAB$^+$) of 5 shows a parent ion ($m/z$ 661) with successive loss of seven CO groups. According to the IR spectrum of 5 in hexanes, terminal CO ligands as well as a terminal NO ligand acting as a three-electron donor are present. Dynamic behavior of the molecule is evidenced by the observation, in the $^{31}P\{^1H\}$ NMR spectrum at room temperature, of two signals at $\delta$ 265.3 (v br) and $\delta$ 249.8 (br) attributed to phosphido groups. These two isomers are also observed by $^1H$ and $^{13}C$ NMR at room temperature. From integration in the $^1H$ NMR spectrum in $CD_2Cl_2$, the ratio of the two isomers is ca. 2/1. The H$\beta$ vinylidene protons are observed at $\delta$ 5.65 ($J_{PH}$ = 4.1 Hz, isomer I) and $\delta$ 5.56 ($J_{PH}$ = 4.3 Hz, isomer II), the signal at $\delta$ 5.65 being broad but still resolved in a doublet, at room temperature. In the $^{13}C$ NMR spectrum ($CDCl_3$), only one doublet is observed for the C$\alpha$ carbon of the vinylidene ligand whereas the C$\beta$ carbons each give a doublet. We have not been able to observe the coalescence of these two sets of signals upon heating solutions of 5 in an NMR probe because of its decomposition at elevated temperatures, but we believe the observed ratio reflects a thermodynamic equilibrium since the same ratio is always observed whatever the crystals and the synthesis they come from.

Variable-low-temperature $^1H$, $^{31}P$, and $^{13}C$ NMR experiments have been carried out on complex 5 in $CD_2Cl_2$. These experiments are briefly summarized as follows. The spectra of the isomer II do not undergo pronounced changes when the temperature is lowered from 306 K to 193 K; the signals tend to be narrower in the intermediate temperature range. The broad major isomer resonances experience decoalescence when the temperature is lowered. In $^1H$ NMR spectroscopy, H$\beta$ decoalesces around 283 K to give at 193 K two peaks at $\delta$ 5.75 and 5.41. The low-field signal appears to be more populated (1.3/1). Similarly, in the $^{31}P$ NMR spectrum, the $\delta$ 265.3 signal decoalesces below ca. 283 K and splits into two signals at $\delta$ 269.5 (minor, $P_A$) and $\delta$ 262.6 (major, $P_B$). In the same way, the low temperature limiting $^{13}C\{^1H\}$NMR spectrum (213 K) gives signals, for the C$\alpha$ vinylidene carbon, at $\delta$ 259.3 ($J_{PC}$ = 42 Hz) coupled to $P_B$ and $\delta$ 256.6 ($J_{PC}$ = 40 Hz) coupled to $P_A$. These assignments have been made possible by selective $^{31}P$ site decoupling. At this temperature the noninterconverting isomer II gives a doublet at $\delta$ 258.4 ($J_{PC}$ = 44 Hz) coupled to $P_C$ ($\delta$ 252.2 in the $^{31}P$ NMR spectrum). Other resonances attributable to the C$\beta$ vinylidene carbon and $^t$Bu quaternary and methyl carbons are also observed. The CO resonances are too complicated to be attributed to each of three isomers, and this prevents us from safely ascribing their structure. Nevertheless, the $^{13}C$ and $^{31}P$ NMR data are consistent with the same relative positions for the phosphido and the vinylidene ligands in the three isomers. Furthermore taking into account the X-ray structure determination in which a statistical distribution between two positions was found for the CO and NO ligands on the same iron atom (see below), we can propose that two isomers $I_A$ and $I_B$ differ by the relative position of this two ligands. A third possibility II would be one in which the $^t$Bu group is directed toward the Fe(CO)(NO) entity. These three possibilities are presented in Chart I. So we are in presence of two phenomena, the change in the orientation of the vinylidene ligand and the fluxionality of the CO and NO ligands. From the literature data[14] it is expected that the first phenomenon should be slow, and so we propose that the major isomers are $I_A$ and $I_B$. It cannot be excluded that the third isomer has fluxional CO and NO ligands but with a lower barrier of energy.

Chart I



**X-ray Crystal Structure of $Fe_2(CO)_6[PPh_2CH{=}C(^tBu)C(OH)]$ (4).** A summary of crystal data and atomic coordinates can be found in Tables I and II, respectively. Table III provides relevant bond distances and angles, and an ORTEP plot of 4 is shown in Figure 1. 4 consist of two $Fe(CO)_3$ units at bonding distance[15] (Fe(1)–Fe(2) = 2.625 (1) Å), bridged by a six-electron donor ligand $PPh_2CH{=}C(^tBu)C(OH)$. This ligand is bound to Fe(1) through phosphorus and to Fe(2) via double carbon–carbon bond (C(8)–C(9)) coordination. In addition, the C(7) carbon bearing the alcohol functionality bridges, slightly asymmetrically, the two iron atoms (Fe(1)–C(7) = 1.984 (3) Å; Fe(2)–C(7) = 2.110 (4) Å). This C(OH) group represents the most peculiar feature of the structure and is relatively unusual in anhydrous organometallic chemistry. The ferrole-type compounds $Fe_2(CO)_6[\mu\text{-}C(OH){=}CRCR{=}C(OH)]$ have been synthesized by treating aqueous alkaline solution of $H_2Fe(CO)_4$ or $Fe(CO)_5$ with alkynes.[16] The

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[14] (a) Boyar, E.; Deeming, A. J.; Felix, M. S. B.; Kabir, S. E.; Adiata, T.; Bhusate, R.; McPartlin, M.; Powel, H. R. *J. Chem. Soc., Dalton Trans.* 1989, 5. (b) Green, M.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* 1989, 1333.

[15] Kruger, C.; Barnett, B. L.; Brauer, D. *The Organic Chemistry of Iron*; Koerner Von Gustorf, E. A., Grevels, F. W., Fischler, I., Eds.; Academic Press: New York, 1978; Vol. 1, p 1.

[16] (a) Hübel, W. *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; John Wiley: New York, 1968; Vol. 1, p 273 and references therein. (b) Aime, S.; Milone, L.; Sappa, E.; Tiripicchio, A.; Lanfredi, A. M. *J. Chem. Soc., Dalton Trans.* 1979, 1664.

**Table I. Experimental Data for the X-ray Study of Compounds 4 and 5**

| | compd | |
|---|---|---|
| | **4** | **5** |
| formula | $C_{25}H_{21}Fe_2O_7P$ | $C_{25}H_{20}Fe_3NO_8P$ |
| fw | 575.10 | 660.96 |
| $a$, Å | 10.669 (2) | 14.588 (5) |
| $b$, Å | 12.716 (2) | 14.434 (2) |
| $c$, Å | 18.436 (2) | 13.274 (2) |
| $\beta$, deg | 98.60 (1) | 99.58 (2) |
| $V$, Å$^3$ | 2473 (1) | 2756 (2) |
| $Z$ | 4 | 4 |
| $\rho_{calcd}$, g·cm$^{-3}$ | 1.544 | 1.593 |
| space group | $C_{2h}^5$-$P2_1/c$ | $C_{2h}^5$-$P2_1/c$ |
| $t$, °C | 22 | 22 |
| radiation | graphite monochrom, Mo K$\alpha$, $\lambda$(Mo K$\alpha_1$) = 0.7093 Å | |
| linear abs coeff, cm$^{-1}$ | 12.77 | 16.61 |
| transm factors[a] | 0.72–0.99 | 0.96–0.99 |
| receiving aperture, mm | 4.0 × 4.0 | 4.0 × 4.0 |
| take off angle, deg | 3.0 | 4.0 |
| scan speed, deg min$^{-1}$ | variable, 1–8 | fixed, 3 |
| scan mode | $\omega/2\theta$ | $\omega$ |
| scan range, deg | 0.9 below K$\alpha_1$ to 0.8 above K$\alpha_2$ | 0.8 below K$\alpha_1$ to 0.9 above K$\alpha_2$ |
| $2\theta$ limit, deg | 2–50 | 2–50 |
| no. of collcd data | 5180 ($0 \le h \le 17, 0 \le k \le 17, -15 \le l \le 15$) | 4801 ($0 \le h \le 12, 0 \le k \le 15, -21 \le l \le 21$) |
| no. of data used in final refinement, $F_o^2 > 3\sigma(F_o^2)$ | 3598 | 3128 |
| final no. of variables | 235 | 259 |
| $R$ (on $F_o$, $F_o^2 > 3\sigma(F_o^2)$)[b] | 0.0361 | 0.0395 |
| $R_w$ (on $F_o$, $F_o^2 > 3\sigma(F_o^2)$)[c] | 0.0390 | 0.0396 |
| error in observn of unit weight, e$^2$ | 1.5 | 1.7 |

[a] $\psi$-scan method. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum_w|F_o|^2)]^{1/2}$, unit weights.

C(7)–O(7) bond order is one.[17] This structure may be compared to that of the parent anion $Fe_2(CO)_6[PPh_2CH{=}C(^tBu)C(CO)]^-$ obtained previously.[1] The major difference, as may be expected, if found in the bonding of the C(OH) and C(O) groups. Whereas the C(O) group in the anion is bound in a $\eta^1$-fashion to a single iron atom (the one also bound to phosphorus), the C(OH) group in 4 bridges the two iron atoms. This additional bridge undoubtedly contributes to the shortening of the iron–iron bond (2.625 (1) Å in 4; 2.6795 (7) Å for the anion). The coordinated double bonds have comparable lengths in both compounds (1.420 (5) Å for the anion; 1.438 (5) Å for 4). The elongation of these "double" carbon–carbon bonds is nicely observed when these two structures are compared to a structure[18] of the mononuclear complex $CpMo(CO)_2[PPh_2CH{=}C(Ph)C(O)]$ containing a very similar ligand but where the double carbon–carbon bond is not involved in coordination (C–C = 1.337 (4) Å).

**Table II. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å$^2$ × 100) with Esd's in Parentheses ($U_{eq}$ = $^1/_3$ Trace $U$) for Compound 4**

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| Fe(1) | 0.16734 (5) | 0.29068 (4) | –0.11420 (3) | 3.23 (8) |
| Fe(2) | 0.13485 (5) | 0.22515 (4) | 0.01670 (3) | 2.98 (8) |
| P(1) | 0.30725 (8) | 0.16102 (7) | –0.08405 (5) | 2.8 (1) |
| O(1) | –0.0560 (3) | 0.3770 (2) | 0.0468 (2) | 7.0 (7) |
| O(2) | 0.1280 (3) | 0.1242 (3) | 0.1586 (2) | 6.0 (6) |
| O(3) | –0.0360 (3) | 0.0735 (2) | –0.0677 (2) | 5.0 (5) |
| O(4) | 0.0177 (3) | 0.1684 (3) | –0.2316 (2) | 6.4 (6) |
| O(5) | 0.3136 (4) | 0.4203 (3) | –0.2025 (2) | 7.6 (7) |
| O(6) | –0.0539 (3) | 0.4297 (3) | –0.1249 (2) | 8.0 (8) |
| O(7) | 0.2477 (3) | 0.4528 (2) | –0.0015 (2) | 4.2 (5) |
| H(7) | 0.190 (3) | 0.489 (3) | –0.038 (2) | 5.00 (0) |
| C(1) | 0.0184 (4) | 0.3186 (3) | 0.0343 (2) | 4.4 (7) |
| C(2) | 0.1327 (3) | 0.1629 (3) | 0.1034 (2) | 3.9 (7) |
| C(3) | 0.0333 (4) | 0.1314 (3) | –0.0364 (2) | 3.6 (6) |
| C(4) | 0.0772 (4) | 0.2133 (3) | –0.1858 (2) | 4.2 (7) |
| C(5) | 0.2576 (4) | 0.3684 (3) | –0.1690 (2) | 4.7 (7) |
| C(6) | 0.0341 (4) | 0.3782 (3) | –0.1193 (2) | 4.8 (8) |
| C(7) | 0.2467 (3) | 0.3470 (3) | –0.0178 (2) | 3.2 (6) |
| C(8) | 0.3206 (3) | 0.2834 (3) | 0.0359 (2) | 3.0 (5) |
| C(9) | 0.3210 (3) | 0.1758 (3) | 0.0120 (2) | 3.0 (5) |
| C(11) | 0.3985 (3) | 0.3221 (3) | 0.1075 (2) | 3.7 (6) |
| C(12) | 0.3199 (4) | 0.3882 (4) | 0.1542 (2) | 5.4 (8) |
| C(13) | 0.5078 (4) | 0.3891 (4) | 0.0873 (3) | 5.4 (8) |
| C(14) | 0.4556 (4) | 0.2304 (3) | 0.1550 (2) | 4.7 (7) |
| C(21) | 0.2645 (2) | 0.0249 (2) | –0.1052 (1) | 3.05 (8) |
| C(22) | 0.2328 (2) | –0.0053 (2) | –0.1784 (1) | 3.91 (9) |
| C(23) | 0.2019 (2) | –0.1098 (2) | –0.1958 (1) | 4.7 (1) |
| C(24) | 0.2026 (2) | –0.1841 (2) | –0.1400 (1) | 4.6 (1) |
| C(25) | 0.2342 (2) | –0.1538 (2) | –0.0668 (1) | 4.36 (9) |
| C(26) | 0.2652 (2) | –0.0493 (2) | –0.0494 (1) | 3.68 (8) |
| C(31) | 0.4659 (2) | 0.1739 (2) | –0.1112 (1) | 3.34 (8) |
| C(32) | 0.5271 (2) | 0.0908 (2) | –0.1407 (1) | 4.22 (9) |
| C(33) | 0.6481 (2) | 0.1052 (2) | –0.1592 (1) | 5.3 (1) |
| C(34) | 0.7077 (2) | 0.2027 (2) | –0.1482 (1) | 5.5 (1) |
| C(35) | 0.6465 (2) | 0.2858 (2) | –0.1187 (1) | 5.6 (1) |
| C(36) | 0.5256 (2) | 0.2714 (2) | –0.1002 (1) | 4.45 (9) |

**Table III. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for Compound 4**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Fe(2)–C(1) | 1.784 (4) | Fe(1)–C(7) | 1.984 (3) |
| Fe(2)–C(2) | 1.787 (4) | C(7)–C(8) | 1.422 (5) |
| Fe(2)–C(3) | 1.799 (4) | C(8)–C(9) | 1.438 (5) |
| Fe(2)–C(7) | 2.110 (4) | C(8)–C(11) | 1.532 (5) |
| Fe(2)–C(8) | 2.096 (3) | P(1)–C(9) | 1.764 (3) |
| Fe(2)–C(9) | 2.097 (3) | P(1)–C(21) | 1.817 (2) |
| Fe(2)–Fe(1) | 2.625 (1) | P(1)–C(31) | 1.842 (3) |
| Fe(1)–C(4) | 1.804 (4) | O(7)–C(7) | 1.378 (4) |
| Fe(1)–C(5) | 1.793 (5) | O(7)–H(7) | 0.96 (4) |
| Fe(1)–C(6) | 1.797 (4) | Fe(1)–P(1) | 2.238 (1) |
| Bond Angles | | | |
| C(7)–Fe(1)–Fe(2) | 52.3 (1) | C(7)–C(8)–C(11) | 126.2 (3) |
| C(8)–Fe(2)–C(7) | 39.5 (1) | C(9)–C(8)–C(11) | 122.9 (3) |
| C(8)–Fe(2)–C(9) | 40.1 (1) | C(11)–C(8)–Fe(2) | 129.5 (3) |
| C(8)–Fe(2)–Fe(1) | 77.9 (1) | C(7)–C(8)–Fe(2) | 70.8 (2) |
| C(9)–Fe(2)–Fe(1) | 78.5 (1) | C(9)–C(8)–Fe(2) | 70.0 (2) |
| C(9)–Fe(2)–C(7) | 68.0 (1) | C(7)–C(8)–C(9) | 110.8 (3) |
| C(7)–Fe(2)–Fe(1) | 48.0 (1) | C(8)–C(9)–Fe(2) | 69.9 (2) |
| O(7)–C(7)–C(8) | 114.7 (3) | C(8)–C(9)–P(1) | 113.9 (3) |
| O(7)–C(7)–Fe(1) | 122.4 (2) | P(1)–C(9)–Fe(2) | 97.8 (2) |
| C(8)–C(7)–Fe(1) | 122.4 (3) | C(21)–P(1)–C(31) | 103.7 (1) |
| Fe(1)–C(7)–Fe(2) | 79.7 (1) | H(7)–O(7)–C(7) | 110 (2) |

**X-ray Crystal Structure of $Fe_3(CO)_7(NO)(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)$ (5).** A summary of crystal data and atomic coordinates can be found in Tables I and IV, respectively. Table V provides relevant bond distances and angles, and an ORTEP plot of 5 is shown in Figure 2. 5 consists of a triangle of iron atoms with Fe(1)–Fe(2) bridged by a diphenylphosphido ligand lying approximately in the triangle plane. Fe(1) is bonded to three carbonyl groups, one C(3)–O(3) being in a semibridging position on the Fe(1)–Fe(3) bond. Fe(2) is bonded to one carbonyl and the nitrosyl group, and Fe(3), to three terminal carbonyl groups. On the Fe(2) atom there is a statistical distribution of the CO and NO groups on the two possible positions. The vinylidene ligand bridges the Fe(1)–Fe(2) bond and is $\pi$ bonded to Fe(3). Comparison of the main bond distances and angles of 5 and of the anionic precursor 1[4]

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(17) See ref 8, p 18 and 19.

(18) Adams, H.; Bailey, N. A.; Day, A. N.; Morris, M. J.; Harrison, M. M. *J. Organomet. Chem.* **1991**, *407*, 247.

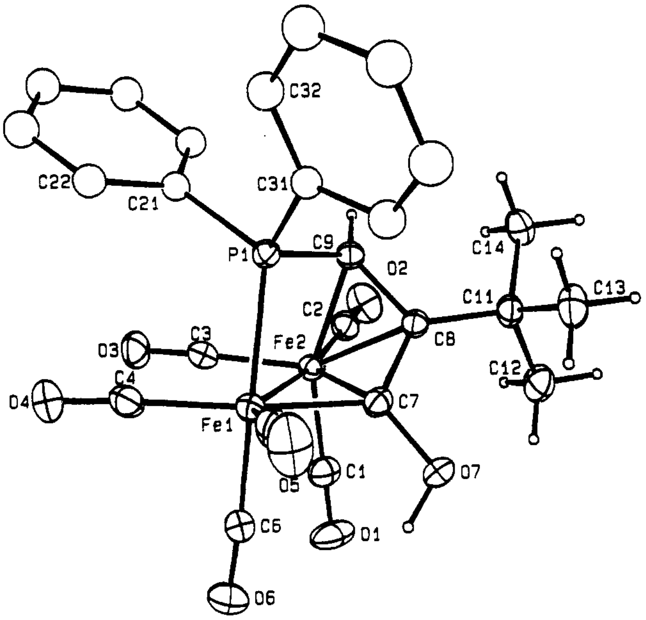

**Figure 1.** Perspective view of complex $Fe_2(CO)_6[PPh_2CH{=}C(^tBu)C(OH)]$. Thermal ellipsoids are shown at the 30% probability level.

**Table IV. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å² × 100) with Esd's in Parentheses for Compound 5 ($U_{eq}$ = $^1/_3$ Trace $U$)**

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| Fe(1) | 0.16616 (5) | 0.01550 (5) | 0.11877 (5) | 3.92 (4) |
| Fe(2) | 0.32884 (5) | 0.05494 (6) | 0.21155 (6) | 4.77 (4) |
| Fe(3) | 0.19207 (5) | 0.11466 (6) | 0.28567 (7) | 5.69 (5) |
| P(1) | 0.30285 (9) | –0.02803 (9) | 0.07328 (9) | 3.81 (7) |
| C(1) | 0.1161 (4) | –0.0940 (4) | 0.0823 (4) | 4.8 (3) |
| C(2) | 0.1459 (4) | 0.0915 (4) | 0.0069 (5) | 6.0 (4) |
| C(3) | 0.0598 (4) | 0.0633 (4) | 0.1536 (4) | 5.8 (4) |
| C/N (4) | 0.4115 (3) | –0.0020 (4) | 0.2946 (4) | 5.0 (3) |
| C/N(5) | 0.3769 (3) | 0.1579 (4) | 0.1715 (4) | 5.3 (3) |
| C(6) | 0.1023 (5) | 0.1442 (5) | 0.3560 (7) | 10.3 (6) |
| C(7) | 0.1877 (5) | 0.2194 (5) | 0.2133 (6) | 8.0 (5) |
| C(8) | 0.2877 (5) | 0.1524 (5) | 0.3792 (6) | 8.5 (5) |
| O(1) | 0.0864 (3) | –0.3346 (3) | 0.5630 (3) | 7.4 (3) |
| O(2) | 0.1333 (4) | 0.1400 (4) | –0.0600 (4) | 10.3 (4) |
| O(3) | –0.0157 (3) | 0.0843 (3) | 0.1540 (3) | 7.5 (3) |
| O(4) | 0.4639 (3) | –0.0443 (4) | 0.3504 (4) | 8.3 (3) |
| O(5) | 0.4131 (4) | 0.2242 (3) | 0.1540 (4) | 9.4 (4) |
| O(6) | 0.0462 (5) | 0.1669 (5) | 0.4004 (6) | 18.2 (7) |
| O(7) | 0.1823 (4) | 0.2845 (4) | 0.1660 (5) | 11.3 (5) |
| O(8) | 0.3442 (4) | 0.1786 (5) | 0.4408 (4) | 12.1 (5) |
| C(11) | 0.2273 (3) | –0.0125 (4) | 0.2532 (4) | 3.9 (3) |
| C(12) | 0.2103 (4) | –0.0342 (4) | 0.3487 (4) | 5.0 (3) |
| C(13) | 0.1355 (4) | –0.0945 (5) | 0.3839 (4) | 6.1 (4) |
| C(14) | 0.0372 (4) | –0.0836 (5) | 0.3266 (5) | 6.9 (4) |
| C(15) | 0.1366 (5) | –0.0764 (7) | 0.4969 (5) | 10.9 (6) |
| C(16) | 0.1656 (5) | –0.1954 (5) | 0.3707 (6) | 9.0 (5) |
| C(21) | 0.3204 (2) | 0.0076 (2) | –0.0526 (3) | 4.0 (1) |
| C(22) | 0.2582 (2) | –0.0229 (2) | –0.1375 (3) | 5.6 (1) |
| C(23) | 0.2688 (2) | 0.0060 (2) | –0.2352 (3) | 6.6 (2) |
| C(24) | 0.3414 (2) | 0.0653 (2) | –0.2480 (3) | 6.5 (2) |
| C(25) | 0.4036 (2) | 0.0958 (2) | –0.1631 (3) | 6.1 (2) |
| C(26) | 0.3931 (2) | 0.0669 (2) | –0.0654 (3) | 5.2 (1) |
| C(31) | 0.3391 (2) | –0.1483 (2) | 0.0806 (2) | 4.1 (1) |
| C(32) | 0.3850 (2) | –0.1868 (2) | 0.0065 (2) | 5.2 (1) |
| C(33) | 0.4185 (2) | –0.2773 (2) | 0.0176 (2) | 7.0 (2) |
| C(34) | 0.4061 (2) | –0.3294 (2) | 0.1028 (2) | 7.9 (2) |
| C(35) | 0.3602 (2) | –0.2909 (2) | 0.1769 (2) | 7.7 (2) |
| C(36) | 0.3267 (2) | –0.2003 (2) | 0.1658 (2) | 5.8 (2) |

**Table V. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for Compound 5**

| Bond Distances | | | |
|---|---|---|---|
| Fe(1)–C(1) | 1.774 (6) | Fe(3)–C(7) | 1.787 (7) |
| Fe(1)–C(3) | 1.827 (6) | Fe(3)–C(8) | 1.790 (7) |
| Fe(1)–C(2) | 1.830 (6) | Fe(3)–C(11) | 1.973 (5) |
| Fe(1)–C(11) | 1.901 (4) | Fe(3)–C(12) | 2.306 (6) |
| Fe(1)–P(1) | 2.266 (2) | Fe(3)–C(3) | 2.494 (5) |
| Fe(1)–Fe(2) | 2.549 (1) | P(1)–C(21) | 1.807 (4) |
| Fe(1)–Fe(3) | 2.612 (1) | P(1)–C(31) | 1.812 (4) |
| Fe(2)–C/N(4) | 1.704 (5) | C(3)–O(3) | 1.142 (7) |
| Fe(2)–C/N(5) | 1.762 (5) | C/N(4)–O(4) | 1.147 (6) |
| Fe(2)–C(11) | 1.928 (5) | C/N(5)–O(5) | 1.136 (7) |
| Fe(2)–P(1) | 2.171 (1) | C(8)–O(8) | 1.126 (9) |
| Fe(2)–Fe(3) | 2.519 (1) | C(11)–C(12) | 1.368 (7) |
| Fe(2)–C(8) | 2.781 (8) | C(12)–C(13) | 1.528 (8) |
| Fe(3)–C(6) | 1.781 (9) | | |
| **Bond Angles** | | | |
| Fe(2)–Fe(1)–Fe(3) | 58.41 (3) | O(8)–C(8)–Fe(3) | 176.0 (7) |
| C(3)–Fe(1)–Fe(3) | 65.6 (2) | C(12)–C(11)–Fe(1) | 142.1 (4) |
| C(11)–Fe(1)–Fe(2) | 48.7 (2) | C(12)–C(11)–Fe(2) | 130.4 (4) |
| C(11)–Fe(1)–Fe(3) | 48.8 (2) | C(12)–C(11)–Fe(3) | 85.2 (3) |
| P(1)–Fe(1)–Fe(2) | 53.21 (4) | Fe(1)–C(11)–Fe(2) | 83.5 (2) |
| P(1)–Fe(2)–Fe(1) | 56.70 (4) | Fe(1)–C(11)–Fe(3) | 84.8 (2) |
| Fe(2)–Fe(3)–Fe(1) | 59.56 (3) | Fe(2)–C(11)–Fe(3) | 80.4 (2) |
| C(11)–Fe(3)–C(12) | 36.3 (2) | C(11)–C(12)–C(13) | 131.5 (4) |
| C(21)–P(1)–C(31) | 103.7 (2) | C(14)–C(13)–C(12) | 116.8 (5) |
| O(3)–C(3)–Fe(1) | 163.9 (5) | C(15)–C(13)–C(12) | 108.2 (5) |
| O(4)–C/N(4)–Fe(2) | 176.4 (5) | C(12)–C(13)–C(16) | 105.8 (5) |
| O(5)–C/N(5)–Fe(2) | 173.7 (4) | | |

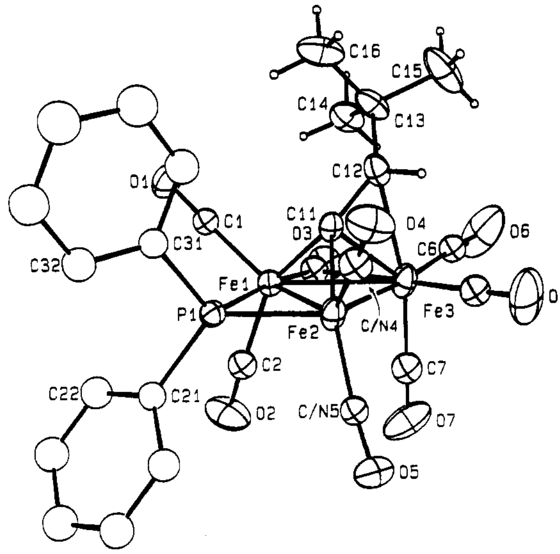

**Figure 2.** Perspective view of complex $Fe_3(CO)_7(NO)(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH^tBu)$. Thermal ellipsoids are shown at the 30% probability level.

shows that the main differences induced by the replacement of a negative charge and a CO group by a nitrosyl ligand affect essentially the metallic triangle. We observe a net lengthening of the Fe(1)–Fe(3) bond (2.4803 (7) Å in 1) even though it was, as in 1, supported by a semibridging carbonyl group. Moreover in 5 the shortest Fe–P bond is the Fe(2)–P(1) bond and not Fe(1)–P(1) as in 1. The bonding of the vinylidene ligand is not significantly modified by the introduction of the nitrosyl ligand.

## Experimental Section

All reactions were performed under a nitrogen atmosphere with use of standard Schlenk techniques. Dichloromethane and hexanes were dried by refluxing over $CaH_2$ under nitrogen. Column chromatography was conducted on silica gel. IR spectra were recorded on a Perkin-Elmer 225 spectrometer. NMR spectra were recorded on Bruker AC 80 ($^{31}P$), WH 90 ($^{31}P$, $^1H$), AC 200 ($^1H$, $^{13}C$), and WM 250 ($^1H$, $^{13}C$, $^{31}P$) instruments. Variable-temperature and selective decoupling experiments were carried out on the WM 250 machine. ESR spectra were obtained with a Bruker ER200 in the X-band mode at room temperature.

Elemental analyses were performed in our laboratory. Mass spectra were obtained at the Service Commun de Spectrométrie de Masse at the Université Paul Sabatier in Toulouse, France. $[PPh_4][Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH{}^tBu)]$ (1)[4] and $[Cp_2Fe][PF_6]$[19] have been prepared according to published procedures.

**Electrochemical Studies.** A homemade microcomputer-controlled instrument with ohmic resistance compensation was used for cyclic voltammetry studies. A platinum auxiliary electrode and an Ag/AgCl (0.1 M KCl) reference electrode were used in conjunction with a platinum disk electrode (Tacussel EDI rotating electrode). All voltammograms were recorded at room temperature at 0.1 V/s. All solutions were degassed with argon for 10 min before measurements. The cell used for coulometry was a two-compartment vessel with a sintered glass disk separating anode and cathode chambers. Coulommetry was conducted at a platinum-gauze working electrode with a platinum-wire auxiliary electrode. The supporting electrolyte $Bu_4NPF_6$ (Aldrich analytical grade) was used as received. Dichloromethane (SDS purex) was passed over alumina prior to use.

**Chemical Oxidations.** Chemical oxidations of 1 were run with either CuCl, $[Cp_2Fe][PF_6]$, or $[Ph_3C][BF_4]$ in dichloromethane following identical experimental procedures. Since they lead to the same results, only one type of reaction is detailed.

Complex 1 (0.280 g, 0.28 mmol) and $[Ph_3C][BF_4]$ (0.110 g, 0.33 mmol) were stirred in dichloromethane (20 mL) at 0 °C for 1 h and 30 min to give a brownish green solution. The volatiles were removed under vacuum, and the residue was extracted with a dichloromethane/hexanes mixture (1/3 by volume). The extracts were filtered through Celite, and the resulting solution was evaporated to dryness. Silica gel was poured into the flask and dichloromethane (15 mL) added. The slurry was stirred for a few minutes and the solvent removed. The residue was placed on the top of a chromatography column. Elution with hexanes gave orange bands containing small amounts of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}CH{=}CH{}^tBu)$ and $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}C{}^tBu)$ (<15 mg, ca. 10%). Elution with dichloromethane/hexanes (1/9 by volume) yielded a green band from which $Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH{}^tBu)(H)$ (3) was isolated (<15 mg, ca 8%). Elution with dichloromethane/hexanes (1/2 by volume) gave an orange band from which microcrystals of 4 were isolated after recrystallization from dichloromethane/hexanes (0.060 g, 37%).

**$Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}$*trans*-$CH{=}CH{}^tBu)$.** MS (EI, 70 eV): *m/z* 548 ($M^+$), 520 ($[M - CO]^+$), 492 ($[M - 2CO]^+$), 464 ($[M - 3CO]^+$), 436 ($[M - 4CO]^+$), 408 ($[M - 5CO]^+$), 380 ($[M - 6CO]^+$). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): $\delta$ 173.7. $^1H$ NMR ($CDCl_3$) (except phenyl resonances): $\delta$ 7.88 (dd, $J_{PH}$ = 5.6 Hz, $J_{HH}$ = 13.9 Hz, 1H, $\mu$-C*H*=CH$^t$Bu), 3.36 (dd, $J_{PH}$ = 5.3 Hz, $J_{HH}$ = 13.9 Hz, 1H, $\mu$-CH=C*H*$^t$Bu), 0.79 (s, 9H, C(C*H*$_3$)$_3$). IR (hexanes, cm$^{-1}$): $\nu_{CO}$ 2059 (s), 2022 (s), 1993 (s), 1979 (s), 1967 (sh).

**$Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}C{}^tBu)$.**[7] MS (EI, 70 eV): *m/z* 546 ($M^+$), 518 ($[M - CO]^+$), 490 ($[M - 2CO]^+$), 462 ($[M - 3CO]^+$), 434 ($[M - 4CO]^+$), 406 ($[M - 5CO]^+$), 378 ($[M - 6CO]^+$). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): $\delta$ 146.5. $^1H$ NMR ($CDCl_3$) (except phenyl resonances): $\delta$ 0.80 (s, C(CH$_3$)$_3$). IR (hexanes, cm$^{-1}$): $\nu_{CO}$ 2067 (s), 2028 (s), 2005 (s), 1985 (s), 1968 (m).

**$Fe_2(CO)_6[\mu\text{-}\eta^4\text{-}PPh_2CH{=}C({}^tBu)C(OH)]$ (4).** Anal. Calcd for $C_{25}H_{21}Fe_2O_7P$: C, 52.1; H, 3.65. Found: C, 51.8; H, 3.63. MS (EI, 70 eV): *m/z* 576 ($M^+$), 548 ($[M - CO]^+$), 520 ($[M - 2CO]^+$), 492 ($[M - 3CO]^+$), 464 ($[M - 4CO]^+$), 436 ($[M - 5CO]^+$), 408 ($[M - 6CO]^+$), 380 ($[M - 7CO]^+$). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): $\delta$ 52.5. $^1H$ NMR ($C_6D_6$) (except phenyl resonances): $\delta$ 5.41 (br s, 1H, C(O*H*)), 3.04 (d, $J_{PH}$ = 2 Hz, 1H, PPh$_2$C*H*=), 1.29 (s, 9H, C(C*H*$_3$)$_3$). $^1H$ NMR (acetone-$d_6$): $\delta$ 10.03 (br, 1H, C(O*H*)), 3.70 (d, $J_{PH}$ = 2.0 Hz, 1H, PPh$_2$ C*H*=), 1.45 (s, 9H, C(CH$_3$)$_3$). $^{13}C$ NMR ($CDCl_3$) (except phenyl resonances): $\delta$ 212.8 (d, $J_{PC}$ = 3 Hz, Fe–CO), 209.7 (br, Fe–CO), 207.3 (t, $J_{PC}$ = $J_{CH}$ = 16 Hz, $\mu$-*C*(OH)), 106.8 (d, $J_{PC}$ = 21 Hz, PPh$_2$CH=*C*(tBu)), 35.6 (dd, $J_{PC}$ = 36 Hz, $J_{CH}$ = 165 Hz, PPh$_2$*C*H=C), 33.8 (d, $J_{PC}$ = 5 Hz, *C*(CH$_3$)$_3$), 29.9 (q, $J_{CH}$ = 126 Hz, CH$_3$). IR ($CH_2Cl_2$, cm$^{-1}$): $\nu_{CO}$ 2052 (vs), 2009 (vs), 1984 (s br), 1950 (m br).

**Reaction of 1 with [NO][BF$_4$].** This reaction was run as previously described for $[Ph_3C][BF_4]$. The color of the solution obtained by mixing 1 (1.15 g, 1.15 mmol) and $[NO][BF_4]$ (0.170 g, 1.45 mmol) is deep green. Chromatography yielded a green band (hexanes elution) from which $Fe_3(CO)_7(NO)(\mu\text{-}PPh_2)(\mu\text{-}C{=}CHtBu)$ (5) was obtained in 18% yield (0.140 g, 0.2 mmol) after recrystallization from hexanes at −20 °C. Elution with dichloromethane/hexanes (1/2 by volume) yielded complex 4 in 25% yield (0.170 g, 0.3 mmol) after recrystallization from a dichloromethane/hexanes mixture.

**$Fe_3(CO)_7(NO)(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH{}^tBu)$ (5).** Anal. Calcd for $C_{25}H_{20}Fe_3NO_8P$: C, 45.4; H, 3.0; N, 2.1. Found: C, 45.4; H, 2.9; N, 2.1. MS (FAB$^+$): *m/z* 661 ($M^+$), 643 ($[M - CO]^+$), 605 ($[M - 2CO]^+$), 577 ($[M - 3CO]^+$), 549 ($[M - 4CO]^+$), 521 ($[M - 5CO]^+$), 493 ($[M - 6CO]^+$), 465 ($[M - 7CO]^+$). $^{31}P\{^1H\}$ NMR: $CD_2Cl_2$, 306 K, $\delta$ 265.3 (v br), 249.8 (br); $CD_2Cl_2$, 213 K, $\delta$ 269.5 ($P_A$), 262.6 ($P_B$), 252.2 ($P_C$). $^1H$ NMR ($CD_2Cl_2$, 306 K) (except phenyl resonances): $\delta$ 5.56 (d, $J_{PH}$ = 4.3 Hz, 1H, $\mu$-C=C*H*$^t$Bu), 1.05 (s, 9H, C(C*H*$_3$)$_3$) (isomer II): $\delta$ 5.65 (d, $J_{PH}$ = 4.1 Hz, 1H, $\mu$-C=C*H*$^t$Bu), 1.10 (s, 9H, C(C*H*$_3$)$_3$) (isomer I). $^1H$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 5.75, 5.54 (isomer II), 5.41 (br, $\mu$-C=C*H*$^t$Bu), 1.07, 1.17 (C(C*H*$_3$)$_3$). $^{13}C$ NMR ($CDCl_3$, 298 K) (except phenyl resonances): $\delta$ 258.9 (d, $J_{PC}$ = 41 Hz, $\mu$-*C*=CH$^t$Bu), 217.1, 215.5, 212.5, 211.6 (s, Fe–CO), 124.3 (d, $J_{CH}$ = 158 Hz, $\mu$-C=*C*H$^t$Bu, isomer I), 122.8 (d, $J_{CH}$ = 149 Hz, $\mu$-C=*C*H$^t$Bu, isomer II), 37.8 (s, *C*(CH$_3$)$_3$, isomer I), 37.2 (s, *C*(CH$_3$)$_3$, isomer II), 30.4 (q, $J_{CH}$ = 126 Hz, *C*H$_3$, isomer I), 30.1 (q, $J_{CH}$ = 126 Hz, *C*H$_3$, isomer II). $^{13}C$ NMR ($CDCl_3$, 213 K) (except phenyl resonances): $\delta$ 259.3 (d, $J_{P_BC}$ = 42 Hz), 258.4 (d, $J_{P_CC}$ = 44 Hz), 256.6 (d, $J_{P_AC}$ = 40 Hz) (all $\mu$-*C*=CH$^t$Bu), 221.7–202.1 (Fe–CO), 123.9 (A), 122.5 (B), 121.5 (C) (all $\mu$-C=*C*H$^t$Bu), 38.6 (C), 37.4 (B), 37.3 (A) (all *C*(CH$_3$)$_3$), 30.7 (C), 30.1 (B), 29.9 (A) (CH$_3$). IR (hexanes, cm$^{-1}$): $\nu_{CO}$ 2055 (vs), 2017 (vs), 2008 (s), 1998 (sh), 1992 (s), 1988 (s), 1968 (sh), 1935 (w); $\nu_{NO}$ 1765 (m), 1755 (sh).

**Reaction of 1 with $CF_3CO_2H$ To Give $Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH{}^tBu)(H)$ (3).** To a well-stirred dichloromethane solution (15 mL) of 1 (0.68 g, 0.68 mmol was added neat $CF_3CO_2H$ (0.1 mL, 100% excess) dropwise. The solution remained green but became brighter. After 15 min of stirring, the solution was pumped to dryness, extracted with a dichloromethane/hexanes mixture (1/3 by volume), and then chromatographed as described above. Elution with dichloromethane/hexanes (1/9 by volume) gave a green band from which $Fe_3(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH{}^tBu)$(H) (3) was obtained in 70% yield (0.310 g, 0.47 mmol) after recrystallization from hexanes at −20 °C. Anal. Calcd for $C_{26}H_{21}Fe_3NO_8P$: C, 47.3; H, 3.2. Found: C, 47.3; H, 2.8, MS (EI, 70 eV): *m/z* 660 ($M^+$), 632 ($[M - CO]^+$), 604 ($[M - 2CO]^+$), 576 ($[M - 3CO]^+$), 548 ($[M - 4CO]^+$), 520 ($[M - 5CO]^+$), 492 ($[M - 6CO]^+$), 436 ($[M - 8CO]^+$). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, $CDCl_3$): $\delta$ 298.3. $^1H$ NMR ($CD_2Cl_2$, 193 K) (except phenyl resonances): $\delta$ 5.6 (d, $J_{HH}$ = 9 Hz, 1H, $\mu$-C=C*H*$^t$Bu), 0.74 (s, 9H, C(C*H*$_3$)$_3$), −11.98 (d, $J_{HH}$ = 9 Hz, 1H, Fe–*H*). $^{13}C$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 217 (br, *C*O), 211.3 (s, *C*O), 210.5 (dd, $J_{PC}$ = 14 Hz, $J_{CH}$ = 4 Hz, $\mu$-*C*=CH$^t$Bu), 149.2 (d, $J_{CH}$ = 162 Hz, $\mu$-C=*C*H$^t$Bu), 38.8 (s, *C*(CH$_3$)$_3$), 30.0 (q, $J_{CH}$ = 126 Hz, CH$_3$). IR (hexanes, cm$^{-1}$): $\nu_{CO}$ 2050 (vs), 2012 (vs), 2000 (vs), 1989 (s), 1978 (sh), 1968 (sh), 1900–1850 (w br).

**Crystal Data Collection and Reduction.** Crystals of 4 suitable for X-ray diffraction were obtained from dichloromethane/hexanes solution. Crystals of 5 suitable for X-ray diffraction were obtained from hexanes solution. Data were collected on an Enraf-Nonius CAD4 diffractometer. The unit cells were obtained by the least-squares refinement of the setting angles of 25 reflections in the range 24° < 2$\theta$(Mo K$\alpha_1$) < 28°. Crystals and intensity data for the compounds 4 and 5 are summarized in Table I. The space groups were determined by careful examination of systematic extinctions in the listings of the measured reflections. Data reductions were carried out using the SDP crystallographic computing package.[20] The intensities were corrected for absorption by using empirical $\psi$-scan method.[21]

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**Solution and Refinement of the Structures.** All calculations were performed on a Micro Vax 3400. The structures were solved by using the SHELXS-86 program[22] and refined by using the SHELX-76 program.[23] The positions of the Fe and P atoms were determined by direct methods. All remaining nonhydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. Atomic scattering factors were taken from the usual tabulations.[24] Anomalous dispersion terms for Fe and P atoms were included in $F_C$.[25] All non-hydrogen atoms were allowed to vibrate anisotropically, except carbon atoms of the phenyl rings, which were refined as isotropic rigid groups in order to reduce the number of variable parameters ($C_6H_5$ ring: imposed $D_{6h}$ symmetry, C–C = 1.395 Å, C–H = 0.97 Å). All hydrogen atoms attached to carbon atoms were entered in ideal position (C–H = 0.97 Å) and were held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart et al.[26] For compound 4, the hydrogen atom attached to O(7) has been located on a final Fourier difference map, and its position has been refined with an isotropic thermal parameter fixed to 0.5 Å$^2$. For compound 5 at a first glance, a nitrosyl group could not be differentiated from any of the carbonyl groups; thus, it was first entered as a carbonyl group. A closer examination of the isotropic thermal parameters of the carbon atoms of the two carbonyl groups attached to Fe(2) showed these atoms to be more likely a statistical distribution of carbon or nitrogen atoms on these two positions. The atoms occupying the two sizes C/N(4) and C/N(5) were thus refined with 50% contribution of carbon and nitrogen.

Final atomic coordinates and $100U_{eq}$ (or $100U_{iso}$) values for non-hydrogen atoms in compounds 4 and 5 are given in Tables II and IV, respectively. Selected bond distances and angles for compounds 4 and 5 are listed in Tables III and V, respectively.

Tables of anisotropic thermal parameters and hydrogen coordinates, for the two structures are available as supplementary material.

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**Supplementary Material Available:** Final anisotropic thermal parameters and hydrogen atomic positional and thermal parameters for compounds 4 and 5 (2 pages). Ordering information is given on any current masthead page.

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