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Synthesis and structure of diiron compounds containing both diphenylphosphido and ethenyl bridges. Crystal structure of $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CPh=CPhH})]$

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Abstract

Treatment of $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR=CR'H})]^-$ ($\text{R} = \text{R}' = \text{Ph}$, H an $\text{R}=\text{Ph}$, $\text{R}' = \text{Me}$) with PPh_2Cl in CH_2Cl_2 in the presence of TlBF_4 gives complexes of the type $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CR=CR'H})]$, containing both phosphido and ethenyl bridges. Similar products were isolated from the reaction of $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]^-$ with CF_3COOH and acetylenes. The crystal structure of the complex $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CPh=CPhH})]$ is reported.

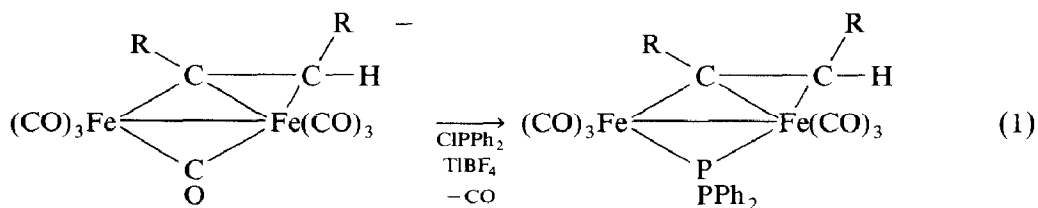
Introduction

Dinuclear transition-metal complexes containing organic bridges have been shown to undergo interesting reactions [1,2]. In most cases the dinuclear structure is maintained by ligands which contain coordinating heteroatoms, such as PR_2 , SR , or halides, which probably have different influences on the reactivity of the organic ligands also coordinated to metals. The phosphido group is the most commonly used bridging ligand in dinuclear complexes because its bridging strength and flexibility allow a study of reactions at the metal centres without breaking of the bridge [3]. We recently showed that the anionic vinyl-bridged diiron complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR=CR'H})]^-$ readily take up heteroatom-bridging ligands to give complexes of the type $\text{Fe}_2(\text{CO})_6(\mu\text{-X})(\mu\text{-CR=CR'H})$ where $\text{X} = \text{Cl}$ [4] at SR [5], the structures of which have been resolved. The chloro-bridged complexes were

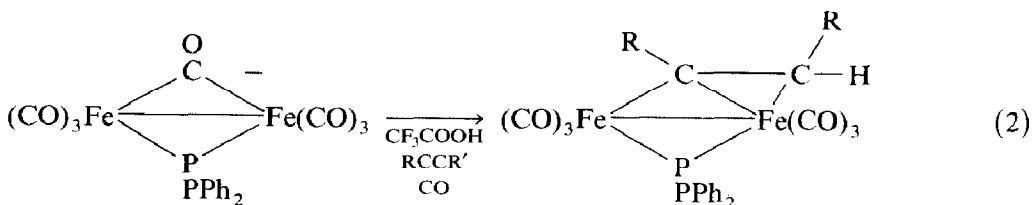
obtained by treatment of the anionic vinyl-bridged complexes with $[\text{Me}_3\text{O}][\text{SbCl}_6]$, and the thiolato-bridged compounds by similar treatment with LiSR . In this paper we describe two methods of synthesis of dinuclear vinyl and phosphido-bridged complexes involving (a) treatment of $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}=\text{CR}'\text{H})]^-$ complexes with PPh_2Cl , and (b) treatment of $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]^-$ with trifluoroacetic acid and alkynes. The structures of the complexes were deduced from spectroscopic techniques, and in the case of diphenylethenyl derivative by an X-ray diffraction study.

Results and discussion

The successful synthesis of $\text{Fe}_2(\text{CO})_6(\mu\text{-SR})(\mu\text{-CR}=\text{CR}'\text{H})$ from $\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})(\mu\text{-CR}=\text{CR}'\text{H})$ and LiSR [5] prompted us to examine the reactions of such chloro-bridged species with NaPPh_2 , with a view to preparing a new family of complexes phosphido containing both and ethenyl bridges (referred to subsequently for convenience as phosphido-ethynyl bridged complexes), but these led to the complete breakdown of the complexes. A better method was found to involve the reaction of the anionic complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}=\text{CR}'\text{H})]^-$ with PPh_2Cl (Method A). Thus the reaction of the anionic vinyl-bridged complexes with PPh_2Cl in dichloromethane solution at room temperature in the presence of a stoichiometric amount of TlBF_4 gave, in 60% yields complexes for which elemental analyses and IR and NMR spectra were in accord with the formulation $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CR}=\text{CR}'\text{H})$ ($\text{R} = \text{R}' = \text{Ph}$ **1**, $\text{R} = \text{R}' = \text{H}$ **2** and $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$ **3**) (eq. 1).



We recently devised a new simple method of making the anions $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CR}=\text{CR}'\text{H})]^-$ from $[\text{HFe}(\text{CO})_4]^-$, $\text{Fe}_2(\text{CO})_6$ and acetylenes [6], and we decided to use the anion $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]^-$ as the starting point for the preparation of phosphido-vinyl bridged complexes. When the anion $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]^-$ was treated with equimolar amounts of CF_3COOH and acetylenes $\text{RC}\equiv\text{CR}'$ ($\text{R} = \text{R}' = \text{Ph}$ and H ; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$ and $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$) at room temperature in dichloromethane (Method B), new products containing phosphido and vinyl bridges $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CR}=\text{CR}'\text{H})]$ ($\text{R} = \text{R}' = \text{Ph}$ **1**, $\text{R} = \text{R}' = \text{H}$ **2**, $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$ **3** and $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$ **4**) were obtained in 75% yield (eq. 2).



All the new complexes are crystalline air-stable orange solids, soluble in hydrocarbons, ethers, and dichloromethane but insoluble in alcohols, and can be recrystallized from dichloromethane/methanol mixtures. The IR spectra of all the complexes in the $\nu(\text{CO})$ region in cyclohexane solution are very similar, and show the established pattern for the neutral diiron complexes containing two bridges [7]. The ^1H NMR spectra show the signals from the ethenyl bridge and the phenyl groups of the diphenylphosphido ligand. The ^{31}P NMR spectrum of the complex with $\text{R} = \text{R}' = \text{Ph}$ showed a signal at 165.7 ppm characteristic of PPh_2 bridges, confirming the proposed formulation [3]. From the ^1H NMR spectra of products obtained by method A we conclude that the geometry of the ethenyl ligand is maintained in the reaction. The ^1H NMR spectra of the complexes with $\text{R} = \text{R}' = \text{Ph}$, H and $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$, obtained by method B were identical with those made by method A. However, the reaction of $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)]^-$ with CF_3COOH and $\text{PhC}\equiv\text{CH}$ gave a complex whose ^1H NMR spectrum displayed signals characteristic of a μ, η^2 -phenylethenyl bridge with geminal hydrogens. This geometry contrasts with the *trans* disposition of the hydrogens observed in the complex $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH=CPhH})]^-$ made from $[\text{HFe}_3(\text{CO})_{11}]^-$ and $\text{PhC}\equiv\text{CH}$, but is consistent with that of the sole product from the reaction of $[\text{HFe}(\text{CO})_4]^-$ or $\text{Fe}_2(\text{CO})_6$ with $\text{PhC}\equiv\text{CH}$ in THF. Method B involves protonation of the anionic phosphido complex and subsequent insertion of the alkyne, and the stereochemistry of the reaction is similar to that involved in the recently reported synthesis of anionic vinyl-bridged diiron complexes [6].

Description of the structure of $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CPh=CPhH})]$

Table 1 gives details of the data collection and structure refinement. Tables 2 and 3, respectively, list the final atomic coordinates and some selected bond lengths and angles. The structure is shown in Fig. 1 and consists of two $\text{Fe}(\text{CO})_3$ units linked by a single metal-metal bond and σ, π -diphenylethenyl and diphenylphosphido bridges. The $\text{Fe}(1)\text{-Fe}(2)$ bond of 2.597(1) Å is longer than $\text{Fe}\text{-Fe}$ distances found in some other diphenylethenyl-bridged complexes [4,5,8]; e.g. in $\text{Fe}_2(\text{CO})_6(\mu\text{-Cl})(\mu\text{-CPh=CPhH})$ [4] the $\text{Fe}\text{-Fe}$ distance is 2.533(1) Å, and in $\text{Fe}_2(\text{CO})_6(\mu\text{-SCH}_2\text{Ph})(\mu\text{-CPh=CPhH})$ [5] it is 2.569(2) Å. The 1,2-diphenylethenyl bridge is η^1 -bonded to $\text{Fe}(2)$ with a $\text{C}(1)\text{-Fe}(2)$ distance of 2.04(1) Å, and unsymmetrically η^2 -bonded to $\text{Fe}(1)$ and $\text{Fe}(2)$ ($\text{C}(1)\text{-Fe}(1)$: 2.099(7) and $\text{C}(2)\text{-Fe}(1)$: 2.223(11) Å), as in the related complexes just mentioned. The μ -phosphido bridging ligand is almost symmetrically linked to iron atoms, with bond lengths of $\text{Fe}(1)\text{-P}$ 2.260(3) and $\text{Fe}(2)\text{-P}$ 2.223(2) Å. The small difference between the two $\text{Fe}\text{-P}$ distances is similar to that observed for the related complex $\text{Fe}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-CCPh})(\mu\text{-PPh}_2)$ [9], indicating that the three-electron phosphido bridge behaves as two-electron donor to $\text{Fe}(2)$ and a one-electron donor to $\text{Fe}(1)$. Such asymmetry has been found with other heteroatom-bridging ligands, such as chloride or thiolate. The $\text{Fe}(1)\text{-P}\text{-Fe}(2)$ angle of 70.8° is normal for μ -diphenylphosphido diiron complexes [3]. The co-planarity of the $\text{Fe}(2)$, $\text{C}(1)$, $\text{C}(2)$, $\text{H}(2)$ atoms and the phenyl group bonded to $\text{C}(2)$ is similar to that of the diphenylethenyl complexes [4,5,10], and is indicative of a π -electron delocalisation through the vinyl ligand. The mean $\text{Fe}\text{-CO}$ distance is 1.78 Å, with the seemingly shortest distances that for $\text{Fe}(1)\text{-C}(5)$ (1.77(1) Å), i.e. to the CO ligand *trans* to the phosphorus atom (with a $\text{C}\text{-Fe}\text{-P}$ angle of 177.6°). All the

Table 1

<i>Crystal data</i>	
Formula	C ₃₂ H ₂₁ Fe ₂ O ₆ P
Crystal habit	yellow prisms
Crystal size (mm)	0.1 × 0.1 × 0.15
Symmetry	triclinic, P $\bar{1}$
Unit cell dimensions (Å)	<i>a</i> 14.788(3), <i>b</i> 12.853(2) <i>c</i> 9.780(2); α 111.32(2), β 107.52(2), γ 104.21(2)
Packing: <i>V</i> (Å ³)	1513.8(8), <i>Z</i> = 2
<i>D_c</i> (gcm ⁻³), <i>M</i> , <i>F</i> (000)	1.413, 64419, 656
<i>Experimental data</i>	
Technique	Four circle diffractometer: Philips PW-1100, bisecting geometry graphite oriented monochromator: Mo-K α , $\omega/2\theta$ scans, scan width: 0.8°
Scanning range for	2 < θ < 25°
Number of reflections:	
measured	2157
observed	2025
Standard reflections	3 reflections every 2 h, no variation I
<i>Solution and refinement</i>	
Solution mode [14]	direct methods
Refinement mode [15]	full matrix least squares, observed reflections only, anisotropic for non-hydrogen (except H2) and isotropic for fixed H atoms
Final <i>R</i> and <i>R_w</i>	0.046, 0.046
Atomic factors	taken from International Tables for X-Ray Crystallography
Computer and programs	IBM 3090/170, MULTAN80 [14], SHELX76 [15]

carbonyl ligands are linear, with Fe–C–O angles averaging 176.1°, in contrast with the geometry of complex Mn₂(CO)₇(μ -PPh₂)(μ -CH=CH₂) [11] in which an imbalance in the electron density distribution gives rise to an incipiently semibridging CO (Mn(1)–Mn(2)–CO angle of 69.8(2)°). This suggests the complete delocalization of the charge in the complex [Fe₂(CO)₆(μ -PPh₂)(μ -CPh=CPhH)] through the ligands and the metal–metal bond. As in related complexes, the two bridging ligands are in a cisoid configuration [5].

Experimental

All reactions were performed under nitrogen. The ¹H NMR spectra were recorded on a Bruker WH90 spectrometer in CDCl₃ solutions and the ³¹P NMR spectrum on a Bruker WP80 apparatus in CDCl₃ solution relative to P(OMe)₃. Infrared spectra in the ν (CO) stretching region were recorded on a Perkin Elmer FT-1710 spectrophotometer for solutions in hexane.

The complexes [PPh₄][Fe₂(CO)₆(μ -CO)(μ -CR=CR'H)] (R = R' = Ph, H; R = Ph, R' = Me) and [NEt₄]₂[Fe₂(CO)₇(μ -PPh₂)] were prepared by published procedures [12,13]. Elemental analysis (C and H) were carried out with a Perkin Elmer 240-B analyzer.

Preparation of complexes 1, 2 and 3

Method A. To a solution of [PPh₄][Fe₂(CO)₆(μ -CO)(μ -CR=CR'H)] (R = R' = Ph, R = R' = H and R = Ph, R' = Me) (1 g) in dichloromethane (10 cm³) were added

Table 2

Atomic coordinates ($\times 10^4$) for $C_{32}H_{21}O_6PFe_2$ (hydrogen atoms excluded) ($B_{eq} = \frac{8}{3}\eta^2(U_{ij}a_i^2a_j^2 \times a_i \times a_j)$)

Fe(1)	15694(8)	16120(10)	-4362(13)	4.05(6)
Fe(2)	35722(8)	25807(10)	13721(13)	4.36(6)
C(1)	2703(5)	3388(7)	497(11)	4.45(42)
C(2)	2171(6)	2910(7)	-1246(11)	4.26(43)
C(11)	2822(6)	4630(8)	1707(11)	5.21(46)
C(12)	3303(6)	5631(8)	1540(11)	6.82(51)
C(13)	3459(8)	6861(10)	2715(15)	8.97(72)
C(14)	3136(10)	6999(13)	3952(17)	10.82(85)
C(15)	2664(9)	6002(13)	4092(14)	9.64(73)
C(16)	2515(7)	4830(9)	2988(12)	6.97(53)
C(21)	1481(6)	3358(7)	-2130(13)	4.96(47)
C(22)	903(7)	3944(7)	-1488(12)	5.88(50)
C(23)	223(8)	4232(9)	-2418(16)	7.48(64)
C(24)	120(8)	3978(9)	-3969(16)	8.11(70)
C(25)	723(9)	3450(9)	-4581(13)	7.86(66)
C(26)	1427(7)	3111(8)	-3650(12)	6.47(54)
P	2693(2)	845(2)	-1107(3)	3.95(11)
C(31)	2654(6)	-615(7)	-1223(9)	4.14(41)
C(32)	1860(6)	-1416(7)	-1169(10)	5.29(48)
C(33)	1886(7)	-2518(8)	-1224(12)	6.43(56)
C(34)	2716(7)	-2797(8)	-1298(11)	6.21(57)
C(35)	3484(7)	-2019(9)	-1368(11)	6.33(58)
C(36)	3461(6)	-928(8)	-1327(11)	5.58(51)
C(41)	2786(6)	582(7)	-3030(10)	4.21(43)
C(42)	2032(6)	-501(8)	-4528(12)	4.93(48)
C(43)	2110(7)	-773(9)	-5988(11)	5.82(56)
C(44)	2940(9)	-6(11)	-5981(13)	6.90(68)
C(45)	4685(8)	1074(11)	-4511(15)	7.51(67)
C(46)	3612(7)	1363(8)	-3044(12)	6.31(55)
C(3)	532(6)	428(8)	-2439(12)	4.86(50)
O(3)	-128(5)	-315(6)	-3723(8)	7.30(39)
C(4)	1547(6)	1020(8)	933(12)	5.49(54)
O(4)	1443(5)	634(7)	1782(9)	7.91(47)
C(5)	734(6)	2272(7)	164(10)	4.94(46)
O(5)	140(5)	2607(6)	528(9)	7.63(41)
C(6)	4161(6)	1732(8)	2113(11)	5.22(49)
O(6)	4570(5)	1202(6)	2597(7)	6.58(38)
C(7)	3843(7)	3521(8)	3503(13)	6.30(55)
O(7)	4045(6)	4040(7)	4898(9)	9.06(46)
C(8)	4626(6)	3539(8)	1286(10)	4.96(48)
O(8)	5284(5)	4177(6)	1221(8)	7.12(38)

stoichiometric amounts of PPh_2Cl and $TiBF_4$. The solution was stirred for 30 min at room temperature then evaporated to dryness, and the residue was extracted with hexane. The extract was evaporated, and the residue dissolved in a minimum of dichloromethane, and methanol was added. Cooling at $-20^\circ C$ gave orange crystals of **1**, **2** or **3** in ca. 60% yield.

$[Fe_2(CO)_6(\mu-PPh_2)(\mu-CPh=CPhH)]$ (**1**). IR $\nu(CO)$: 2056s, 2024vs, 1990s and 1979vs cm^{-1} . 1H NMR: δ (ppm) 7 (m, 20H), 3.75 (d, J 13.75 Hz, 1H). $^{31}P\{^1H\}$ NMR: δ (ppm) 165.7. Anal. Found C, 59.24; H, 3.29. $C_{32}H_{21}Fe_2O_6P$ calcd.: C, 59.63; H, 3.3%.

Table 3

Selected bond lengths (Å) and angles (°) for $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CPh=CPhH})]$ with e.s.d.'s in parentheses

Fe(2)–Fe(1)	2.597(1)	C(1)–Fe(1)	2.099(7)
C(2)–Fe(1)	2.223(7)	P–Fe(1)	2.260(11)
C(3)–Fe(1)	1.786(7)	C(4)–Fe(1)	1.787(13)
C(5)–Fe(1)	1.775(10)	C(1)–Fe(2)	2.038(10)
P–Fe(2)	2.223(2)	C(6)–Fe(2)	1.785(12)
C(7)–Fe(2)	1.797(11)	C(8)–Fe(2)	1.781(10)
C(2)–C(1)	1.424(13)	C(11)–C(1)	1.490(12)
C(21)–C(2)	1.507(15)	C(31)–P	1.819(9)
C(41)–P	1.830(11)	O(3)–C(3)	1.139(8)
O(4)–C(4)	1.151(17)	O(5)–C(5)	1.156(13)
O(6)–C(6)	1.157(14)	O(7)–C(7)	1.154(14)
O(8)–C(8)	1.145(13)		
C(1)–Fe(1)–Fe(2)	50.1(3)	C(2)–Fe(1)–Fe(2)	77.2(2)
C(2)–Fe(1)–C(1)	38.3(3)	P–Fe(1)–Fe(2)	53.9(1)
P–Fe(1)–C(1)	87.2(3)	P–Fe(1)–C(2)	83.3(3)
P–Fe(2)–Fe(1)	55.3(1)	P–Fe(2)–C(1)	89.7(2)
Fe(2)–C(1)–Fe(1)	77.7(3)	C(2)–C(1)–Fe(2)	120.4(6)
C(1)–C(2)–Fe(1)	66.1(6)		

$[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CH=CH}_2)]$ (**2**). IR $\nu(\text{CO})$: 2065s, 2029vs, 1998s and 1983s cm^{-1} . ^1H NMR: δ (ppm) 8.54(ddd, $J(\text{PH})$ 2.9 Hz, J_{trans} 13.2 Hz, J_{cis} 9.4 Hz, 1H), 7.25(m, 10H), 3.41(ddd, J_{gem} 2.1 Hz, J_{trans} 13.1 Hz, $J(\text{PH})$ 6.2, 1H), 2.53(m, 1H). Anal. Found C, 48.82; H, 2.61. $\text{C}_{32}\text{H}_{21}\text{Fe}_2\text{O}_6\text{P}$ calcd.: C, 48.78; H, 2.64%.

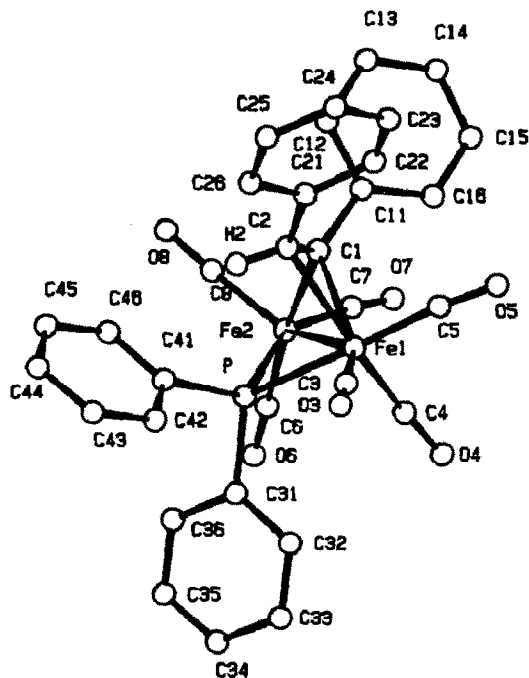


Fig. 1. The molecular structure of $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-CPh=CPhH})$.

[Fe₂(CO)₆(μ-PPh₂)(μ-CPh=CMeH)] (3). IR ν(CO): 2054s, 2020vs, 1988s and 1976s cm⁻¹. ¹H NMR: δ (ppm) 7.3(m, 15H), 3.09(dq, *J*(PH) 7.9 Hz, *J*(HH) 6.3 Hz, 1H), 1.2(d, *J*(HH) 6.3 Hz, 3H). Anal. Found C, 55.71; H, 3.26. C₂₇H₁₈Fe₂O₆P calcd.: C, 55.67; H, 3.26%.

Method B. To a solution of complex [NEt₄]₂[Fe₂(CO)₇(μ-PPh₂)] (1 g) in dichloromethane (10 cm³) were added stoichiometric amounts of the alkyne RC≡CR' (R = R' = Ph, H; R = Ph, R' = Me; R = Ph, R' = H) and CF₃COOH. The solution was stirred for 30 min at room temperature then evaporated to dryness. The residue was extracted with hexane and the extract evaporated to dryness. The residue was dissolved in a minimum of dichloromethane and methanol was added. Cooling at -20 °C gave orange crystals of 1, 2, 3, or 4 in ca. 75% yield.

[Fe₂(CO)₆(μ-PPh₂)(μ-CPh=CH₂)] (4). IR ν(CO): 2056s, 2024vs, 1990s and 1979vs cm⁻¹. ¹H NMR δ (ppm) 7.3(m, 20H), 3.3 (d, *J* 7 Hz, 1H), 2.8(d, *J* 13 Hz, 1H). Anal. Found C, 55.2; H, 3.2. C₂₈H₁₇Fe₂O₆P calcd.: C, 54.92; H, 2.99%.

X-ray analysis of Fe₂(CO)₆(μ-PPh₂)(μ-CPh=CPhH)

Details of the crystal data, data collection, and structure refinement are given in Table 1.

The structure was solved by direct methods by use of the MULTAN 80 program [14] and refined by full-matrix least squares with the SHELX 76 program [15]. The function minimized was $\sum w \| F_o - |F_c| \|^2$, where $w = [\sigma^2 |F_o| + 0.0005 |F_c|^2]^{-1}$; values of *f*, *f'* and *f''* were taken from International Tables for X-Ray Crystallography [16]. H atoms were placed in calculated positions except for H(2) which was located from a difference synthesis and refined freely. The other H atoms were refined with an overall isotropic temperature factor and the remaining atoms anisotropically.

Tables of thermal parameters, calculated H positions, and structure factors are available from the authors.

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