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Pentakis(η^1-phosphinine)iron: Synthesis, Structure, and Mode of Formation[1]

Christoph Elschenbroich,* Mathias Nowotny, Andreas Behrendt, Klaus Harms, Sigrid Wocadlo, and Jürgen Pebler

Contribution from the Fachbereich Chemie, Philipps-Universität, D-35032 Marburg, Germany

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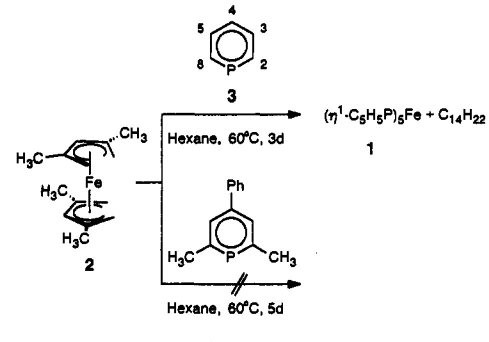
Abstract: In order to elucidate the preferred mode of coordination—$\eta^1(\sigma)$ or $\eta^6(\pi)$—we have reacted phosphinine (C_5H_5P) with the open ferrocene $(2,4\text{-Me}_2\text{-}\eta^5\text{-}C_5H_5)_2Fe$. The product, pentakis($\eta^1$-phosphinine)iron (**1**), was subjected to X-ray structural analysis: **1** crystallizes in the space group $P2/n$ with the cell parameters a = 16.010(3) Å, b = 9.727(2) Å, c = 16.193(3) Å, α = 90°, β = 102.11(3)°, γ = 90°, Z = 4, R = 0.056, R_w = 0.049. The structure of **1** is trigonal bipyramidal with a slight distortion toward square pyramidal. The bond distance Fe–P (2.155 Å) is probably influenced by interligand repulsion. Cyclic voltammetry reveals that oxidation and reduction of **1** are irreversible even at −45 °C. The likely intermediate in the formation of **1**, (2,4,7,9-tetramethyl-η^4:η^2-decatetraene)bis(η^1-phosphinine)iron (**5**) was also isolated and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

The group 15 heteroarenes C_5H_5E (E = N, P, As, Sb) are ambidentate ligands and as such pose the question of the preferred coordination mode—$\eta^1(\sigma)$ or $\eta^6(\pi)$—as a function of the nature of E and of the respective central metal. In order to obtain unequivocal answers, we set out to study homoleptic complexes of the unsubstituted heteroarenes. This endeavor has led us to the characterization of the species $(\eta^6\text{-}C_5H_5As)_2Ti$,[2] $(\eta^6\text{-}C_5H_5P)_2V$,[3] $(\eta^6\text{-}C_5H_5As)_2V$,[2] $(\eta^6\text{-}C_5H_5N)_2Cr$,[4] $(\eta^6\text{-}C_5H_5As)_2Cr$,[5] $(\eta^1\text{-}C_5H_5P)_6Cr$,[6] and $(\eta^1\text{-}C_5H_5P)_4Ni$.[7] Apparently, the early transition metals prefer the $\eta^6(\pi)$ coordination mode, whereas the $\eta^1(\sigma)$ fashion is favored by the late transition metals. In the center of the 3d series, both variants should be accessible. Here we report on the synthesis and X-ray crystallography of pentakis(η^1-phosphinine)iron (**1**), which complements the π-complex $[2,4,6\text{-}(t\text{-Bu})_3\text{-}\eta^6\text{-}C_5H_2P]_2Cr$ obtained by metal–vapor techniques.[6b] To our knowledge, this constitutes the first structure determination of a binary phosphane iron complex FeL_5.

The title compound **1** was prepared in analogy to the synthesis of $Fe(PF_3)_5$[8] from bis(2,4-dimethyl-η^5-pentadienyl)iron (**2**) and phosphinine (**3**).[9] Use of a phosphinine derivative, which bears ortho substituents, failed to yield an η^1- or η^6-phosphinine–iron complex (Scheme 1). In view of the high sensitivity of **3**, the stability of **1** to air (several hours as a solid) and heat (mp 173 °C) is remarkable. As opposed to $(\eta^1\text{-}C_5H_5P)_4Ni$,[7] in the case of **1**, neither the UV–vis nor the NMR spectra furnish evidence for a dissociation equilibrium $1 \rightleftarrows (C_5H_5P)_4Fe + 3$.

Scheme 1



The molecular structure of **1** was determined by X-ray diffraction;[12] an XP drawing is shown in Figure 1. The FeP_5 core displays trigonal-bipyramidal geometry which—as opposed to $Fe(CO)_5$[13]—is slightly distorted toward square pyramidal. In

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® Abstract published in *Advance ACS Abstracts*, June 1, 1994.

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[9] Procedure: a solution of compounds **2**[10] (116 mg, 0.47 mmol) and **3**[11] (314 mg, 3.27 mmol) in 20 mL of thoroughly degassed hexane was refluxed for 3 days under an N_2 atmosphere. Upon cooling of the solution to room temperature, brown crystals precipitated which were washed with three 2-mL portions of hexane and redissolved in 20 mL of THF. This solution was filtered through Celite, reduced to 5 mL, and covered with 5 mL of hexane. Within 2 days 33 mg (13% yield) of **1** were obtained as brown cubes (air-stable for several h, mp 173 °C, uncorrected). IR (Nujol) $\nu(FeP_{eq})$ 151 cm^{-1} (vw), $\nu(FeP_{ax})$ 123 cm^{-1} (w). $^1H\{^{31}P\}$ NMR (500 MHz, THF-d_8) δ 8.00 (d, J = 10.7 Hz, 2 H, $C_{2,6}$-H), 7.40 (dd, J = 10.7, 8.0 Hz, 2 H, $C_{3,5}$-H), 6.84 (d, J = 8.0 Hz, 1 H, C_4-H). ^{13}C NMR (125 MHz, THF-d_8) δ 148.1 ($C_{2,6}$, ^1J(CH) = 158.0 Hz), 137.2 ($C_{3,5}$, ^1J(CH) = 151.8 Hz), 120.7 (C_4, ^1J(CH) = 159.9 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ 242.9, UV–vis (THF) λ_{max} 245 nm (ϵ = 44 000 L/mol^{-1} cm^{-1}), 290 sh (22 000), 371 (24 000), 490 sh (13 000); (methylcyclohexane) λ_{max} 248, 379, 530 sh. Anal. Calcd for $C_{25}H_{25}FeP_5$: C, 56.00; H, 4.70. Found: C, 55.92; H, 4.81. The mother liquor of the initial precipitation of **1** was evaporated to dryness, and the residue was recrystallized from 2 mL of hexane. After 3 days at 4 °C, 106 mg (51% yield) of **5** was obtained as a dark red, microcrystalline air-stable material (mp 136 °C uncorrected) EI-MS (70 eV) m/e = 438 (1, M^+), 342 (3, $M^+ - L$), 246 (6, $M^+ - 2L$), 190 (17, $M^+ - 2L - Fe$), 175 (23, $M^+ - 2L - Fe - CH_3$), 121 (88, $C_9H_{13}^+$), 96 (100, L^+), 70 (28, $L^+ - C_2H_2$), L = C_5H_5P. $^1H\{^{31}P\}$ NMR (500 MHz, THF-d_8) δ 8.15 (d, ^3J = 10.5 Hz, $C_{15,19}$-H), 7.64 (d, ^3J = 11.0 Hz, $C_{16',18'}$-H), 7.49 (t, $C_{16,18}$-H), 7.30 (t, $C_{16',18'}$-H), 6.93 (t, ^3J = 8.0 Hz, C_{17}-H), 6.72 (t, ^3J = 8.0 Hz, $C_{17'}$-H), 4.51 (s, C_8-H), 3.21 (s, C_1-H), 2.45 (s, C_3-H), 2.39 (m, C_5-H), 2.05 (s, C_{11}-H), 2.0 (m, $C_{5'}$-H), 1.91 (s, $C_{1'}$-H), 1.56 (s, C_{13}-H), 1.52 (m, C_6-H), 1.21 (s, C_{14}-H), 1.04 (m, $C_{6'}$-H), 0.94 (d, C_{10}-H), 0.92 (s, C_{12}-H), 0.65 (d, ^2J = 15.7 Hz, $C_{10'}$-H). ^1H NMR $J(^1H_i, {}^{31}P)$ H_1 7.9, H_3 4.9, H_8 10.3, $H_{15,19}$ 21.1, H_{17} 6.4, $H_{17'}$ 4.3 Hz. ^{13}C NMR (100 MHz, THF-d_8) δ 150.6 (d, $C_{15,19}$, ^1J(C-H) = 159.1 Hz), 145.5 (d, $C_{15',19'}$, ^1J(C-H) = 156.3 Hz), 136.3 (d, $C_{16,18}$, ^1J(C-H) = 157.1 Hz), 136.0 (d, $C_{16',18'}$, ^1J(C-H) = 155.5 Hz), 121.4 (d, C_{17}, ^1J(C-H) = 159.8 Hz), 119.6 (d, $C_{17'}$, ^1J(C–H) = 160.6 Hz), 101.4 (s, C_2), 94.2 (d, C_8, ^1J(C-H) = 153.6 Hz), 82.3 (d, C_3, ^1J(C-H) = 142.4 Hz), 80.4 (s, C_9), 73.0 (s, C_7), 51.2 (t, C_1, ^1J(C-H) = 155.5 Hz), 48.5 (t, C_{10}, ^1J(C-H) = 124.8 Hz), 41.6 (t, C_5, ^1J(C-H) = 123.4 Hz), 38.5 (s, C_4), 35.8 (t, C_6, ^1J(C-H) = 122.0 Hz), 33.7 (q, C_{13}, ^1J(C-H) = 126.5 Hz), 33.2 (q, C_{12}, ^1J(C-H) = 125.2 Hz), 33.0 (q, C_{11}, ^1J(C-H) = 121.3 Hz), 28.6 (q, C_{14}, ^1J(C-H) = 124.5 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ 258.9, 258.6, $^2J(P,P')$ = 82.9 Hz. Anal. Calcd for $C_{24}H_{32}FeP_2$: C, 65.75; H, 7.36. Found: C, 65.65; H, 7.44.

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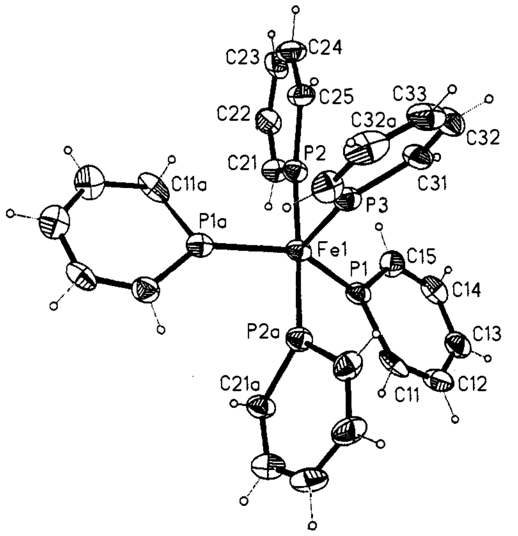

Figure 1. XP drawing of one of the two symmetry-independent molecules in the unit cell of **1** (50% probability ellipsoids). Average values of bond distances (Å) and angles (deg): Fe–P(eq), 2.153(2), Fe–P(ax), 2.157(2); P–C(*o*), 1.714(8); C(*o*)–C(*m*), 1.390(11), 1.377(11); C(*m*)–C(*p*), 1.380(11), 1.376(11); P(eq)–Fe–P(eq), 113.4(1)–133.3(1); P(eq)–Fe–P(ax), 87.6(1)–92.1(1); P(ax)–Fe–P(ax), 176.0(1)–178.7(1); Fe–P–C(*o*), 128.7(3), 129.8(3); C(*o*)–P–C(*o*), 101.3(4); P–C(*o*)–C(*m*), 124.6(6), 124.0(6); C(*o*)–C(*m*)–C(*p*), 124.3(8), 124.2(7); C(*m*)–C(*p*)–C(*m*), 122.1(8).

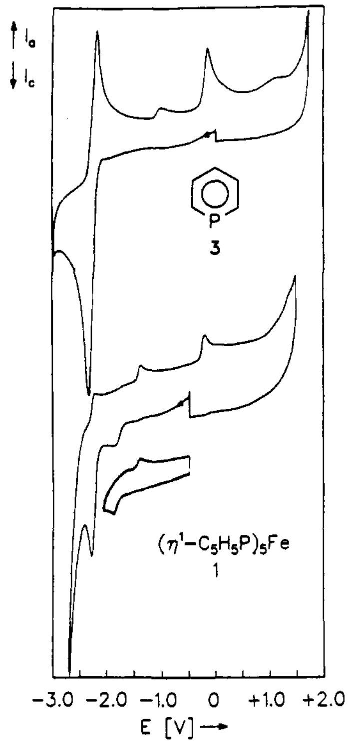

Figure 2. Cyclic voltammograms for the ligand **3** and the complex **1** in DME/Bu_4NClO_4 at −45 °C, 100 m s^{-1}.

the ensuing C_{2v} symmetry, Fe1–P3 and Fe2–P6 represent the C_2 axes. The distortion affects the bond angles only, the bond lengths Fe–P_{ax} and Fe–P_{eq} being nearly identical (difference of 0.4 pm). For lack of X-ray data on homoleptic FeL_5 complexes, the Fe–P bond lengths in **1** can be compared only with values observed for Fe complexes of chelating diphosphane ligands: [η^1-MeN(PF_2)-(PF_2)][η^2-MeN(PF_2)$_2$]$_2$Fe (2.11, 2.09 Å)[14a] and [η^1-CH_2(PMe_2)-(PMe_2)][η^2-CH_2(PMe_2)$_2$]$_2$Fe (2.16, 2.17 Å).[14b] Thus, the Fe–P bond length of 2.15 Å in **1** is unexceptional. If the phosphinine rings rather than just the P atoms are considered, the symmetry of **1** is lowered to C_2. This reflects the varying extents of torsion about the respective Fe–P–C_p axes. Even in the equilibrium conformations, the distances between the ortho hydrogen atoms of equatorial phosphinine ligands and the phosphorous atoms of axial phosphinines fall short of the sum of the van der Waals radii. Conceivably, this strain causes the gradation of bond distances Cr–P [2.26 Å, (η^1-C_5H_5P)$_6Cr^0$[6]] > Fe–P [2.16 Å, (η^1-C_5H_5P)$_5$Fe] > Ni–P [2.13 Å, (η^1-C_5H_5P)$_4Ni^0$[7]] which is much more pronounced than the covalent metal radii would suggest. The ligand dimensions are affected only marginally by η^1-coordination: while the C–C bond lengths and the C–P–C bond angle remain virtually constant, the P–C bonds are shortened by a mere 1.5 pm. Constancy of the C–P–C bond angle had also been observed upon homoleptic η^1-coordination of phosphinine to nickel[3] and chromium,[6a] whereas in the heteroleptic complex (η^1-C_5H_5P)Mo(CO)$_5$, slight enlargement of this angle to 103.1° has been reported.[6c]

As inferred from ^{31}P NMR, the structure of **1** in solution is dynamic, no decoalescence of the signal at δ 242.9 (coordination shift $\Delta\delta$ 36.4) being detectable down to $T = -100$ °C. Interestingly, no decoalescence is displayed by (PF_3)$_5$Fe,[15a] [Tolman cone angle Θ(PF_3) = 104° [16a]], whereas, at −104 °C, [P(OMe)$_3$]$_5$Fe [Θ = 107°;[16a] resp. 128° [16b]] exhibits an A_2B_3-type spectrum near the slow exchange limit.[15b] Considering the noncircular shape of the cone generated by the MPC_5H_5 segment, a weight-average cone angle for phosphinine of 108° can be derived (tangents in the ligand plane 120°, perpendicular to the ligand plane 96°) which explains the low barrier for Berry pseudorotation in **1**. A strong resemblance between C_5H_5P and CO or PF_3 as ligands is also suggested by the Mössbauer spectra, which yield the parameters (mm s^{-1}) $\delta = 0.02$, $\Delta E_Q = 1.74$ for (C_5H_5P)$_5$Fe, to be compared with $\delta = 0.035$, $\Delta E_Q = 2.57$ for Fe(CO)$_5$[17a] and $\delta = 0.062$, $\Delta E_Q = 2.62$ for Fe(PF_3)$_5$.[17b] Whereas the similarity of the isomer shifts δ points to almost identical σ-donor, π-acceptor character of C_5H_5P, CO, and PF_3, with regard to the quadrupole splitting ΔE_Q, **1** stands out. The considerably reduced value of ΔE_Q observed for **1** probably reflects the departure of **1** from ideal trigonal-bipyramidal symmetry (vide supra) and the fact that, due to more extensive electron delocalization in the ligand C_5H_5P, electric quadrupole interactions are attenuated. In order to test whether conjugation in the ligand C_5H_5P may stabilize the radical cation $1^{\bullet+}$ or the radical anion $1^{\bullet-}$, we subjected **1** to cyclic voltammetry (Figure 2). The redox behavior of five-coordinate Fe^0 complexes differs from totally irreversible in the case of Fe(CO)$_5$[18] to reversible for Fe(CO)$_3$(PPh_3)$_2$;[19] in the latter case, the highly reactive[19a] cation Fe(CO)$_3$(PPh_3)$_2^{\bullet+}$ is even accessible

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(12) Crystal data for **1** at −80 °C: $a = 16.010(3)$ Å, $b = 9.727(2)$ Å, $c = 16.193(3)$ Å, $\alpha = 90°$, $\beta = 102.11(3)°$, $\gamma = 90°$, $V = 2465.6(8)$ Å^3, monoclinic with space group *P*2/*n*, $Z = 4$, $\rho = 1.444$ g cm^{-3}. The structure was solved by direct methods, $R = 0.056$, $R_w = 0.045$ for 2358 reflections with $F > 4\sigma(F)$.

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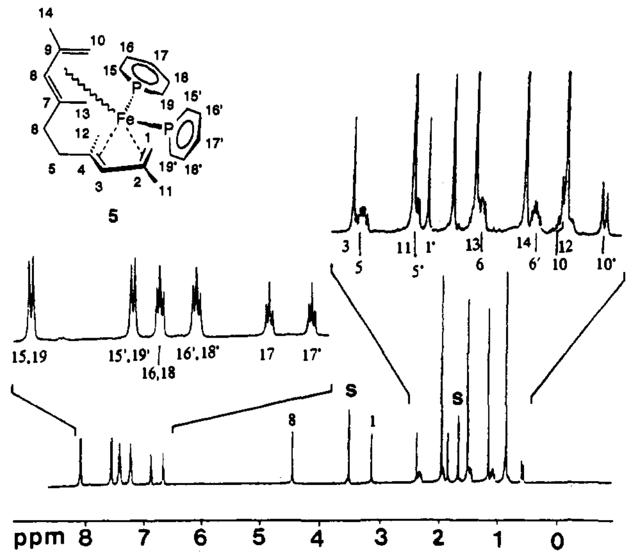
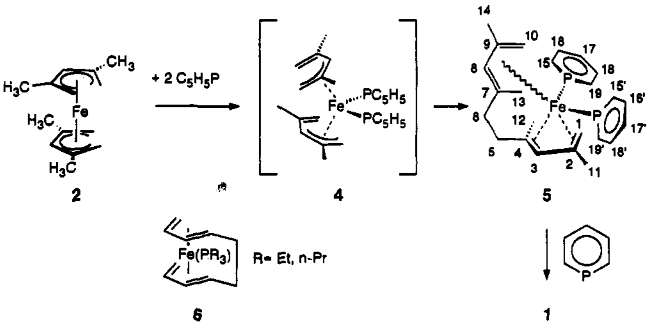


Figure 3. $^1H\{^{31}P\}$ NMR spectrum of the intermediate **5** in THF-d_8 at 30 °C. The assignment is based on *HH* NOESY experiments; s, solvent peak.

on a preparative scale.[19b] Electrochemical oxidation of **1** is irreversible even at –45 °C, and the reduction features an irreversible cathodic peak at –1.84 V which is followed by a trace which, based on a comparison with the CV of authentic material, is characteristic for the free ligand C_5H_5P. Thus, in analogy to $Fe(CO)_5$, metal–ligand bond cleavage occurs upon reduction of **1**.[20] If a cyclovoltammogram of **1** is recorded in the limited scan range $-2.0 < E < -0.5$ V, i.e., *before* reduction of free C_5H_5P (**3**) takes place, the anodic peak at $E = -1.37$ V also arises, which means that this peak represents oxidation of a metal-containing fragment formed during the decomposition of 1^- (ECE mechanism). Note that the anodic peak belonging to the ECE process of the free ligand **3** appears at E = –1.10 V.

It remains to elucidate the mode of formation of **1** from the open ferrocene **2**. A hint is provided by the isolation of a compound which we regard as (2,4,7,9-Me_4-η^4:η^2-$C_{10}H_{10}$)Fe(η^1-C_5H_5P)$_2$ (**5**) from the mother liquor of the precipitation of **1**. The structural proposal for **5** is based on ^1H NMR (Figure 3) and ^{13}C NMR (Experimental Section) spectroscopy. A key feature of **5** is the unsymmetrically coordinated decatetraene unit, formed by phosphinine-induced coupling of two pentadienyl ligands in the coordination sphere of **2** (Scheme 2). The formation of a 1,3,7,9-decatetraene unit follows from the observation of an ABCD spin system for an ethano bridge (H-5,5′6,6′), and its η^4:η^2 coordination serves to satisfy the 18 VE rule. The low symmetry of the species thus obtained manifests itself in the complete anisochrony of the ^1H and ^{13}C nuclei and the fact that the two η^1-C_5H_5P ligands are also inequivalent. An unequivocal choice between the coordination modes 1–4:7,8-η and 1–4:9,10-η would require a study of **5** by X-ray diffraction which, as yet, was impractical for lack of suitable single crystals. However, the NMR data favor the latter alternative, C_8–*H* appearing as a singlet in the shift range characteristic for a noncoordinated olefin unit and the vinylic protons at C_{10} displaying a pronounced upfield shift. The coupling constant $J(^{13}C_{10}–^1H_{10})$ of 124.8 Hz would suggest that C_{10} has aquired a hybridization ratio between sp^2 and sp^3, a phenomenon which is often encountered with coordinated alkenes.[21] The surprisingly small value for this coupling constant may be traced to the fact that distortion of the coordinated decatetraene ligand by the bulky $Fe(PC_5H_5)_2$ unit is much more severe than that caused by a $Fe(CO)_3$ moiety. Precedent for the metal-centered ligand coupling leading to **5** exists in the isolation of (η^8-1,3,7,9-decatetraene)Fe(PR_3) (**6**) from $FeCl_2(PR_3)_2$ and potassium pentadienide.[22] The presence of two phosphinine ligands in the stable intermediate **5** as opposed to one phosphane in compound **6** can be traced to the much smaller cone angle of C_5H_5P (108°) compared to those of PEt_3 and $P(n\text{-}Pr)_3$ (132°) and the strength of the phosphinine transition-metal bond.[3] Of course, an intermediacy of a phosphinine complex analogous to **6**, which subsequently accepts a second phosphinine ligand with accompanying hapticity change η^4:$\eta^4 \rightarrow \eta^4$:$\eta^2$, cannot at present be excluded.

Scheme 2



Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the NATO Scientific Affairs Division. We thank a reviewer for drawing our attention to an inconsistency in our original interpretation of the NMR data and to the revision of the cone angles for phosphite ligands.

Supplementary Material Available: Experimental details of the crystal structure determination of (η^1-C_5H_5P)$_5$Fe (**1**), stereoview of the structure, and tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths; complete ^1H, ^{13}C, and ^{31}P NMR data and *HH* NOESY diagram of (2,4,7,9-Me_4-η^4:η^2-$C_{10}H_{10}$)(η^1-C_5H_5P)$_2$Fe (**5**) (15 pages); listing of observed and calculated structure factors for **1** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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