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Photoexcitation of iron-allyl complexes $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)Fe(CO)(\eta^1-CH_2CR=CH_2)$ (R = H, CH₃) which contains a tethered phosphine ligand

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Abstract

Photoexcitation of the phosphino ligand chelated iron-allyl complexes $(\eta^5:\eta'-C_5H_4CH_2CH_2PPh_2)Fe(CO)(\eta'-CH_2CR=CH_2)$ (1a: R = H; 1b: $R = CH_3$) gives a mixture of Fe-CO bond cleavaged compound $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)Fe(\eta^3-CH_2CRCH_2)$ (2) and Fe-allyl bond homolysis compounds $[\eta^4:\eta^1-(1-CH_2CR=CH_2)C_5H_4CH_2CH_2PPh_2]Fe(CO)_2$ (3) and $[\eta^4:\eta^1-(3-CH_2CR=CH_2)C_5H_4CH_2CH_2PPh_2]Fe(CO)_2$ (4) in a ratio of 20:5:1. Their structures were determined spectroscopically. No phosphine exchange products were observed when the reaction was conducted in the presence of triphenylphosphine. © 1997 Elsevier Science S.A.

Keywords: Iron; Chelate; Phosphine; Photochemistry; Cyclopentadiene; Allyl

1. Introduction

The photochemistry of $(\eta^5 - C_5 H_5)Fe(CO)_2 R$ derivatives (R = alkyl, benzyl, allyl) has been extensively investigated [1,2]. Four primary photochemical processes have been proposed: (1) cleavage of the Fe-CO bond; (2) CO insertion into the Fe-R bond; (3) Cp ring-slipage from η^5 to η^3 ; (4) homolysis of the Fe-R bond. Cleavage of the Fe--CO bond usually predominates under most experimental conditions. However, the photochemistry of related triphenylphosphine complex $(\eta^5-C_5H_5)Fe(CO)(PPh_3)R$ gave exclusive loss of triphenylphosphine either photochemically [3] or thermally instance, photolysis [4]. For of $(\eta^5$ - C_5H_5)Fe(CO)(PPh₃)CH₃ in the presence of tri-ptolylphosphine gave exclusive phosphine exchange product $(\eta^5-C_5H_5)Fe(CO)(P(p-Tol)_3)CH_3$ [3]. The allyl complex $(\eta^5-C_5H_5)Fe(PPh_3)(CO)(\eta^1-allyl)$ lost triphenylphosphine ligand to form (η^{5}) -

 C_5H_5)Fe(CO)(η^3 -allyl) when it was heated above 40°C [4].

$$(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}R \xrightarrow{h\nu} (\eta^{5}-C_{5}H_{5})Fe(CO)R + CO$$
(1)

$$(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}R \xrightarrow{h\nu} (\eta^{5}-C_{5}H_{5})Fe(CO)COR$$
 (2)

$$(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}R \xrightarrow{h\nu} (\eta^{3}-C_{5}H_{5})Fe(CO)_{2}R$$
 (3)

$$(\eta^5 - C_5 H_5) Fe(CO)_2 R \xrightarrow{h\nu} [(\eta^5 - C_5 H_5) Fe(CO)_2] + R^{-1}$$

(4)

We have been interesting in the chemistry of chelate iron phosphine complexes of the type $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)Fe(CO)R$ [5]. With the phosphino ligand connected to the cyclopentadienyl ring, the chemistry of these complexes relative to that of the non-chelate complexes is of interest. Here we describe the photochemistry of iron-allyl complexes $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)Fe(CO)(\eta^1-CH_2CR=CH_2)$ (1a:

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R = H; 1b: R = CH₃) which behave differently from that of the related, non-chelate complex (η^{5} -C₅H₅)Fe(PPh₃)(CO)(η^{1} -allyl) [4].

2. Results and discussion

2.1. Preparation of $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)$ -Fe(CO) $(\eta^1-CH_2CR=CH_2)(1a:R=H; 1b:R=CH_3)$

Preparation of chelate complex 1a has been illustrated in the report that described the general methodology for making this type of complexes [5]. The analogous methallyl complex 1b was prepared in a similar procedure. Addition of methallyl Grignard reagent to a green solution of $(\eta^5: \eta^1-C_5H_4CH_2CH_2PPh_2)Fe(CO)Cl$ resulted in an immediate change of color to orange. Upon column chromatography on neutral aluminum, 1b was isolated as orange powders in 63% yield. Carbonyl stretching of 1b appeared at 1899 cm⁻¹ is a typical value for this type of compounds [5]. In the ¹H NMR spectrum, the diastereotopic methylene protons of the methally ligand displayed at δ 1.82 and δ 0.47, as triplets (J = 7.4 Hz), respectively. The splittings are resulted from the geminal couplings $({}^{2}J_{HH})$ and the couplings between the methylene protons and the ${}^{31}P$



 $({}^{3}J_{HP})$, indicates that the phosphino and the methallyl groups are both ligated on the metal (Scheme 1).

2.2. Photoexitation of Ia and Ib

Irradiation of a THF solution of 1a at 0°C for 30 min resulted in almost disappearance of carbonyl stretchings in the infrared spectrum. Only a few, very weak peaks were observable and were assigned to two minor products. Irradiation of 1a in an acetone- d_6 solution in a NMR tube and examining the ³¹P NMR spectrum im-



Fig. 1. The significant part of the INADEQUATE spectrum of 3b.

mediately after invadiation showed that the resonance associated with **1a** disappeared and three new resonances at δ 90.5, 58.4 and 71.8 in a ratio of 20:5:1 appeared. Similar results were observed for the methallyl complex **1b** which gave three new resonances at δ 90.1, 59.3 and 71.8 in a ratio of 20:5:1 in the ³¹ P NMR spectrum.

The major components for both reactions are very air labile. They both displayed absence of CO absorptions in the infrared spectra and showed resonances assignable to the η^3 -allyl ligand in the ¹H NMR spectra. Therefore, the major products were assigned as 2a and 2b, respectively. The orientation of the η^3 -allyl group was deduced from the ¹H NMR spectral characteristics of the allyl group by comparison with the known exo and endo forms of $(\eta^{5}-C_{5}H_{5})Fe(CO)(\eta^{3}-allyl)$ [2]. The magnitude between the outer lines of an AA'BB' splittings of the anti and the syn protons was measured as 1.6 Hz for 2a, falls in the criterion of the exo conformation [2]. Broad resonances of the anti and the syn protons of **2b** prevented the measurement of the magnitude of splittings between the anti and the syn protons. However, the conformation of 2b was also assigned as exo based upon the similarities of the ¹H and ³¹P NMR spectra with those of 2a.

Two minor components 3 and 4, in a ratio of 5:1, could be separated and isolated by column chromatography. Chemical shifts of the phosphorous appeared at about δ 58.4–59.3 for 3 and δ 71.8 for 4 in the ³¹P NMR spectra, compared to $\delta - 14.7$ for the free phosphine ligand [5], suggests that the phosphine is coordinated on the metal for both 3 and 4. Both complexes showed two carbonyl strechings in the infrared spectra, 1971 and 1906 cm^{-1} for 3 and 1963 and 1904 cm^{-1} for 4, indicates that there are two terminal carbonyl groups for both complexes. Complex 3 showed symmetrical ¹H and ¹³C NMR spectra, therefore it was assigned as C₁-isomer. Assignment of the complex 4 as C₃-isomer was based upon the fact that the chemical shifts of the inner carbons of η^4 -dienyliron complexes appear relatively down-field than those of the outer carbons [6]. In the ¹³C NMR spectrum of 4b, resonance at δ 47.2 (CH) was assigned to the sp³ carbon, C₃. The resonance at δ 116.8 was assigned to the olefinic C₁. The other three olefinic CH carbons consists of one down-field resonance at δ 82.6 (C₅) and two up-field resonances at 55.6 and 60.7 (C_2 and C_4), consistent with the structure of C_3 -isomer. The corresponding C2-isomer should have two down-field olefinic CH carbons and one up-field olefinic CH carbon.

Although spectroscopic data of 3 and 4 are in accordance with our assignment, a definite answer should be required. Complexes 3 and 4 are both liquid, therefore preclude definite assignment by crystallography. Fortunately, we were able to collect enough materials of 3b for $^{13}C-^{13}C$ connectivity study (INADEQUATE). Fig. 1 showed the significant part of the INADEQUATE spectrum of **3b**. The methylene carbon of the methallyl group, C_8 (δ 60.5), showed cross peak with the ring carbon C_1 (δ 59.1, ${}^{3}J_{CP} = 15.4$ Hz), suggests that the methallyl group is attached on the C_1 position of the Cp ring.

3. Conclusion

From above results, it could be concluded that photoexcitation of the phosphino ligand chelated iron-allyl complexes $(\eta^5: \eta^1 - C_5 H_4 CH_2 CH_2 PPh_2)Fe(CO)(\eta^1 - \eta^2)$ $CH_2CR=CH_2$) (1a: R=H; 1b: $R=CH_3$) proceeded via majority (77%) of Fe-CO bond cleavage to give η^3 -allyl complex 2. About 23% of the reaction proceeded via homolysis of the Fe-allyl bond, followed by capture of a CO [7] and recombination with the allyl radical on the C₁ position or on the C₃ position to provide C1-isomer 3 or C3-isomer 4, respectively. Related Fe-R homolysis reaction has been reported for the photolysis of $(\eta^5 - C_5 R_5)$ Fe(CO)₂ $(\eta^1 - CH_2 C_6 H_5)$ (R = H, CH₃) under 2 atm of CO [7]. From that reaction, dienyliron complex $(\eta^4 - C_5 R_5 (CH_2 C_6 H_5))Fe(CO)_3$ was isolated as the major product. Irradiation of the chelate complex 1 under | atm of CO does not give significant change of the ratio of the products.

Different from the reactions of the photolysis of $(\eta^5-C_5H_5)Fe(CO)(PPh_3)CH_3$ and the thermolysis of $(\eta^5-C_5H_5)$ Fe(PPh₃)(CO) $(\eta^1$ -allyl), chelate complex 1 showed no loss of the phosphine ligand. When 1 was irradiated or heated (50°C) in the presence of triphenylphosphine, no phosphine exchange products could be observed. This may imply that the phosphine ligand with a two carbon tether on the cyclopentadienyl ring binds so tight as to escape dissociation or, alternatively, the phosphine ligand did dissociate, but the rate of recombination is so fast that other ligands can not compete with. The unique property of chelation effect [8] allowed us to observe Fe-R homolysis which are barely observable in the solution phase. However, irradiation of the chelate complex $(\eta^5:\eta^1-$ C₅H₄CH₂CH₂PPh₂)Fe(CO)(CH₃) provided recovery of the starting material along with the decomposition mixtures.

4. Experimental section

Infrared solution spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer using 0.1 mm cells with CaF₂ windows. UV spectra were recorded on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Melting points were determined by using a Yanaco model MP micro melting point apparatus and were uncorrected. ¹H NMR (300 MHz), ¹³C NMR (75 MHz) and ³¹P(¹H) NMR (121 MHz) were obtained with a Bruker AC-300 FT spectrometer. On the assignment of ¹H and ¹³C NMR data for 1, the carbon bound to the phosphorous was designated as C_1 and the hydrogens on C_1 were designated as H_{1a} and H_{1b} . Next carbon was designated as C_2 and the hydrogens on C_2 were designated as H_{2a} and H_{2b} . Elemental analyses were obtained on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were recorded on a VG 70-250S mass spectrometer.

4.1. Preparation of $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)$ -Fe(CO) $(\eta^1-CH_2CH=CH_2)$ (Ia)

Complex 1a was prepared according to the literature procedure [5]. UV (acetone): $\lambda_{max} = 389$ nm ($\epsilon = 272$), 483 (87).

4.2. Preparation of $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)$ -Fe(CO) $(\eta^1-CH_2C(CH_3)=CH_2)$ (1b)

Over a period of 5 min, a THF solution of methallylmagnesium chloride (13 ml \times 0.5 M, 6.5 mmol) was added to a stirred solution of $(\eta^5; \eta^1)$ - $C_5H_4CH_2CH_2PPh_2$)Fe(CO)Cl [5] (1.023 g, 2.58 mmol) in THF (30 ml) at 0°C. The original green solution turned to red solution immediately. The cold bath was removed and the solution was allowed to stir at room temperature for 10 min. The resulting red solution was concentrated under reduced pressure. The residue was then dissolved in CH_2Cl_2 (2 ml) and flash column chromatographed on neutral alumina (activity V) upon elution with 30% EtOAc in hexane. The first orange band was collected and concentrated to provide red liquid. The red liquid was dissolved in CH₂Cl₂ (2 ml) and added to a solution of hexane (80 ml) to effect the precipitation of 1b as orange powders (0.676 g, 63% yield). M.p., 75°C (decomp.). IR (CH₂Cl₂): 1899 cm⁻¹. UV (acetone): $\lambda_{max} = 392$ nm ($\epsilon = 212$), 482 (84). ³¹P(¹H) NMR (CD₃COCD₁): δ 92.3. ³¹P(¹H) NMR (CDCl₃): δ 94.4. ¹H NMR (CD₃COCD₃): δ 7.86–7.82 (2H, m, phenyl), 7.47-7.26 (8H, m, phenyl), 4.83-4.81 (1H, m, Cp), 4.40-4.38 (1H, m, Cp), 4.33-4.31 (1H, m, vinyl-H_a), 4.17-4.15 (1H, m, vinyl-H_b), 4.06-4.04(1H, m, Cp), 3.80--3.78 (1H, m, Cp), 3.58 (1H, dddd, J = 13.3, 11.4, 7.4, 5.9 Hz, H_{1a}), 3.19 (1H, dddd, J = 13.3, 12.3, 5.8, 3.5 Hz, H_{1b}), 2.49 (1H, dddd, J = 39.3, 13.6, 7.4, 3.5 Hz, H_{2a}), 1.89 (1H, dtd, J =13.6, 11.4, 5.8 Hz, H_{2b}), 1.82 (1H, t, J = 7.4 Hz, CH_2R), 1.64 (3H, s, CH_3), 0.47 (1H, t, J = 7.4 Hz, CH_2R). ¹H NMR (CDCl₃): δ 7.81–7.74 (2H, m, phenyl), 7.42-7.39 (3H, m, phenyl), 7.32-7.29 (3H, m, phenyl), 7.24-7.18 (2H, m, phenyl), 4.82-4.80 (1H, m, Cp), 4.37 (1H, s, Cp), 4.25 (2H, s, vinyl), 3.97 (1H, s, Cp), 3.88 (1H, s, Cp), 3.37 (1H, dddd, J = 13.2, 11.9,7.3, 6.0 Hz, H_{1a}), 3.08 (1H, dddd, J = 13.2, 12.0, 5.9,

3.7 Hz, H_{1b}), 2.44 (1H, dddd, J = 38.0, 13.6, 7.3, 3.7 Hz, H_{2a}), 1.90 (1H, dtd, J = 13.6, 11.9, 5.9 Hz, H_{2b}), 1.80 (1H, t, J = 7.4 Hz, CH_2R), 1.71 (3H, s, CH_3), 0.56 (1H, t, J = 7.4 Hz, CH_2R). MS (FAB, ⁵⁶Fe): 417 (12, M⁺+1), 361 (78, M⁺-C₄H₇), 333 (100, M⁺-C₄H₇-CO). Anal. Found: C, 59.36; H, 5.98. C₂₄H₂₅OPFe Calc.: C, 69.25; H, 6.05%.

4.3. Photoexcitation of
$$(\eta^5: \eta^1 - C_5 H_4 C H_2 C H_2 P P h_2) - Fe(CO)(\eta^1 - C H_2 C R = C H_2)$$
 (1a: $R = H$; 1b: $R = C H_3$)

To two 5 mm NMR tubes were charged with 1a (10 mg) and 1b (10 mg), respectively. Both tubes were evacuated and flushed with argon. To each tubes were added acetone- d_6 (0.5 ml). The orange-red solutions were then immersed in a cold bath (0°C) and irradiated for 30 min with a Hanovia 450 W medium pressure Hg lamp from a distance of about 5 cm using a running water cooling. The resulting yellow-orange solutions were recorded, respectively, with a NMR spectrophotometer. The sample from the irradiation of 1a gave three resonances at δ 90.5, 58.4 and 71.8 in a ratio of 20:5:1 and the sample from the irradiation of 1b gave three resonances at δ 90.1, 59.3 and 71.8 in a ratio of 20:5:1 in the 31p NMR spectra. The major products were assigned as 2a and 2b, respectively. Their ³¹P and ¹H NMR spectra were deduced from the spectra of the reaction mixture.

 $(\eta^{5}:\eta^{1}-C_{5}H_{4}C_{2})$ (2a): ³¹P{¹H} NMR (CD₃COCD₃): δ 90.5. ¹H NMR (CD₃COCD₃): δ 7.52–7.32 (10H, m, phenyl), 4.55 (2H, t, J = 1.8 Hz, Cp), 4.40–4.28 (1H, m, H_c), 3.45 (2H, q, J = 7.2 Hz), 3.35 (2H, t, J = 1.8Hz, Cp), 2.63 (2H, dq, J = 6.6, 0.8 Hz, H_s), 2.24 (2H, dt, J = 24.2, 7.2 Hz), -0.73 (2H, ddt, J = 16.1, 10.4, 0.8 Hz, Ha). ¹³C NMR (CD₃COCD₃): δ 138–128 (Ph's), 108.0 (C, Cp), 76.0 (CH × 2, Cp), 71.4 (CH × 2, Cp), 55.5 (CH, ally), 47.2 (CH₂, $J_{cp} = 28$ Hz, C₁), 33.7 (CH₂ × 2, $J_{cp} = 6.7$ Hz, allyl), 23.1 (CH₂, $J_{cp} = 9$ Hz, C₂).

 $(\eta^{5}: \eta^{1}-C_{5}H_{4}CH_{2}CH_{2}PPh_{2})Fe[\eta^{3}-CH_{2}C(CH_{3})CH_{2}]$ (2b): ³¹P{¹H} NMR (CD₃COCD₃): δ 90.1. ¹H NMR (CD₃COCD₃): δ 7.54–7.32 (10H, m, phenyl), 4.60 (2H, br. s, Cp), 3.42 (2H, q, J = 7.2 Hz), 3.22 (2H, br. s, Cp), 2.44 (2H, s, H_s), 2.13 (2H, dt, J = 24.5, 7.2 Hz), 1.94 (3H, s, CH₃), -0.79 (2H, d, J = 17.4 Hz, H_a).

4.4. General procedure for the preparation of $[\eta^4:\eta^1-(1-CH_2CR=CH_2)C_5H_4CH_2CH_2PPh_2]Fe(CO)_2$ (3a: R = H; 3b: R = CH₃) and $[\eta^4:\eta^1-(3-CH_2CR=CH_2)C_5H_4CH_2CH_2PPh_2]Fe(CO)_2$ (4a: R = H; 4b: R = CH₃)

In a pyrex test tube was charged with 1 (200 mg) and THF (50 ml). The orange-red solution was bubbled with argon for at least 10 min, followed by irradiation (Hanovia 450 W medium pressure Hg lamp) at 0°C for 30 min. Because 2 is very sensitive to air, it could not be isolated in pure form. When 3 and 4 were requested for isolation, the yellow-orange solution was concentrated and flashed through a short SiO_2 column with 20% EtOAc in hexane to remove the decomposition materials. The yellow liquid after removing solvents was then chromatographed on silica gel (Licroprep Si60, Merck), using 2% EtOAc in hexane as eluent, to give 3 and 4.

[η⁴:η¹-(1-CH₂CH=CH₂)C₅H₄CH₂CH₂PPh₂]-Fe(CO)₂ (3a): yellow liquid, 14% yield. $R_f = 0.33$ (5% EtOAc in hexane). IR (CH₂Cl₂): 1971s, 1906s cm⁻¹. ³¹P{¹H} NMR (CDCl₃): δ 61.3. ³¹P{¹H} NMR (CD₃COCD₃): δ 58.4. ¹H NMR (CDCl₃): δ 7.67-7.60 (4H, m, Ph), 7.41-7.37 (6H, m, Ph), 5.63-5.48 (1H, m, H₉), 5.30-5.28 (2H, m, H₃ and H₄), 4.90 (1H, d, J = 10.2 Hz, H_{10a}), 4.84 (1H, d, J = 17.0 Hz, H_{10b}), 2.34 (2H, q, J = 6.9 Hz, H₇), 2.00-1.98 (2H, m, H₂ and H₅), 1.78 (2H, dt, J = 20.1, 6.9 Hz, H₆), 1.69 (2H, d, J = 7.4 Hz, H₈). Anal. Found: C, 66.85; H, 5.45. C₂₄H₂₃O₂PFe Calc.: C, 67.00; H, 5.39%.

[H^4 : η^1 -(3-CH₂CH=CH₂)C₅H₄CH₂CH₂PPh₂]Fε-(CO)₂ (**4a**): yellow liquid, 3% yield. $R_f = 0.27$ (5% EtOAc in hexane). IR (CH₂Cl₂): 1964s, 1904s cm⁻¹. ³¹P{¹H} NMR (CDCl₃): δ 74.5. ³¹P{¹H} NMR (CD₃COCD₃): δ 71.8. ¹H NMR (CDCl₃): δ 7.60–7.54 (2H, m), 7.40–7.30 (8H, m), 5.61–5.49 (2H, m), 4.89– 4.79 (2H, m), 2.98–2.90 (2H, m), 2.69–2.50 (5H, m), 1.51–1.47 (2H, m). Anal. Found: C, 66.68; H, 5.50. C₂₄H₂₃O₂PFe Calc.: C, 67.00; H, 5.39%.

 $[\eta^4:\eta^1\cdot(1-CH_2C(CH_3)=CH_2)C_5H_4CH_2CH_2PPh_2] Fe(CO)_2$ (3b): yellow liquid, 15% yield. $R_f = 0.33$ (5%) EtOAc in hexane). IR (CH_2Cl_2): 1971s, 1906s cm⁻¹. $^{31}P{^{1}H}$ NMR (CDCl₃): 861.9. $^{31}P{^{1}H}$ NMR (CD_3COCD_3) ; δ 59.3. ¹H NMR $(CDCl_3)$: δ 7.68–7.71 (4H, m, Ph), 7.42–7.33 (6H, m, Ph), 5.30 (2H, br. s, H₃ and H_4), 4.66 (1H, br. s, H_{10a}), 4.46 (1H, br. s, H_{10b}), 2.35 (2H, dt, J = 9.4, 6.9 Hz, H₇), 2.00 (2H, br. s, H₂ and H_5), 1.83 (2H, dt, J = 20.2, 6.9 Hz, H_6), 1.69 (2H, s, H₈), 1.63 (3H, s, CH₃). ¹H NMR (CD₃COCD₃): δ 7.75-7.68 (4H, m, Ph), 7.46-7.40 (6H, m, Ph), 5.37-5.35 (2H, m, H₃ and H₄), 4.66–4.44 (1H, m, H_{10a}), 4.49–4.48 (1H, m, H_{10b}), 2.50 (2H, dt, J = 9.4, 6.9 Hz, H_7), 2.11–2.08 (2H, m, H_2 and H_5), 1.85 (2H, dt, J = 20.4, 6.9 Hz, H₆), 1.70 (2H, s, H₈), 1.63 (3H, s, CH₃). ¹³C{¹H} NMR (CD₃COCD₃): δ 215.9 (CO × 2, $J_{cp} = 6.8$ Hz), 143.6 (C, C₉), 140.0 (C × 2, $J_{cp} = 39.9$ Hz, Ph-C₁'), 132.4 (CH × 4, $J_{cp} = 10.7$ Hz, Ph-C₂'), 130.0 (CH × 2, Ph-C₄'), 129.1 (CH × 4, $J_{cp} = 9.2$ Hz, Ph- $C_{3'}$), 113.6 (CH₂, C_{10}), 78.0 (CH × 2, C_3 and C_4), 60.5 (CH₂, C₈), 59.1 (C, $J_{cp} = 15.4$ Hz, C₁), 56.1 (CH × 2, $J_{cp} = 5.5$ Hz, C_2 and C_5), 30.2 (CH₂, $J_{cp} = 3.6$ Hz, C_6), 25.0 (CH₂, $J_{cp} = 30.6$ Hz, C_7), 24.8 (CH₃). MS (FAB, ⁵⁶Fe): 443 (4, M⁺-1), 389 (70, $M^+-C_4H_7$; 333 (100, $M^+-2CO-C_4H_7$). Anal. Found:

C, 67.85; H, 5.60. C₂₄H₂₅O₂PFe Calc.: C, 67.58; H, 5.67%.

 $[\eta^4:\eta^1-(3-CH_2C(CH_3)-CH_2)C_5H_4CH_2CH_2PPh_2] Fe(CO)_2$ (4b): yellow liquid, 3% yield. $R_f = 0.27$ (5%) EtOAc in hexane). IR (CH_2Cl_2): 1963s, 1904s cm⁻¹. ³¹P{¹H} NMR ($CDCl_3$): δ 74.5. ³¹P{¹H} NMR (CD₃COCD₃): δ 71.8. ¹H NMR (CDCl₃): δ 7.61–7.54 (2H, m, Ph), 7.42–7.38 (3H, m, Ph), 7.32–7.29 (5H, m, Ph), 5.52 (1H, H_5), 4.62–4.61 (1H, m, H_{10a}), 4.50 (1H, H_{10b}), 3.02–3.00 (1H, m, H₂ or H₄), 2.96–2.91 (1H, m), 2.79-2.74 (1H, m), 2.67-2.46 (4H, m), 1.60 (3H, s), 1.48–1.44 (2H, m, H₈). ¹H NMR (CD₃COCD₃): δ 7.67-7.60 (2H, m, Ph), •7.47-7.43 (3H, m, Ph), 7.41-7.34 (5H, m, Ph), 5.68 (1 H, H₅), 4.61 (1H, H_{10a}), 4.51 $(1 \text{ H}, \text{H}_{10b}), 3.11 (1 \text{ H}, \text{H}_2 \text{ or } \text{H}_4), 3.09-2.97 (1\text{H}, \text{m}),$ 2.89–2.64 (3H, m), 2.57 (1H, H_4 or H_2), 2.60–2.46 (1H, m), 1.59 (3H, s), 1.47 (2H, d, J = 6.6 Hz, H₈). ¹³C{¹H} NMR (CDCl₃): δ 222.9 (CO), 217.1 (CO, $J_{cn} = 20.2$ Hz), 143.3 (C, C₉), 137.4 (C, $J_{cp} = 35.2$ Hz, Ph), 136.2 (C, $J_{cp} = 35.0$ Hz Ph), 132.1 (CH × 2, $J_{cp} =$ 11.1 Hz, Ph), 130.9 (CH \times 2, $J_{cp} = 11.0$ Hz, Ph), 129.8 (CH, Ph), 129.3 (CH, Ph), 128.4 (CH \times 2, $J_{cp} = 5.5$ Hz, Ph), 128.3 (CH \times 2, $J_{cp} = 5.5$ Hz, Ph), 115.0 (C, $J_{cp} = 5.5$ Hz, Ph), 128.3 (CH \times 2, $J_{cp} = 5.5$ Hz, Ph), 115.0 (C, $J_{cp} = 5.5$ Hz, Ph) Fin), 128.5 (CH × 2, $J_{cp} = 5.5$ Hz, Fin), 115.0 (C, $J_{cp} = 7.6$ Hz, C₁), 110.4 (CH₂, C₁₀), 82.0 (CH, C₅), 59.6 (CH, C₂ or C₄), 54.5 (CH, C₃), 52.1 (CH₂, $J_{cp} = 5.6$ Hz, C₈), 47.0 (CH, $J_{cp} = 7.6$ Hz, C₄ or C₂), 41.7 (CH₂, $J_{cp} = 24.4$ Hz, C₇), 24.9 (CH₂, $J_{cp} = 9.9$ Hz, C₆), 22.9 (CH₃). ¹³C{¹H} NMR (CD₃COCD₃): 8224.1 (CO), 218.2 (CO, $J_{cp} = 19.9$ Hz), 143.8 (C, C_9), 138.3 (C, $J_{cp} = 35.2$ Hz, Ph), 137.1 (C, $J_{cp} = 35.2$ Hz Ph), 132.9 (CH × 2, $J_{cp} = 11.0$ Hz, Ph), 131.8 (CH × 2, $J_{cp} = 10.9$ Hz, Ph), 130.7 (CH, Ph), 130.2 (CH, Ph), 129.3 (CH \times 2, J_{cp} = 8.8 Hz, Ph), 129.1 (CH \times 2, J_{cp} = 8.5 Hz, Ph), 116.8 (C, $J_{cp} = 7.6$ Hz, C₁), 111.0 (CH_2, C_{10}) , 82.6 (CH, C₅), 60.7 (CH, $J_{cp} = 3.2$ Hz, C₂ or \tilde{C}_4), 55.6 (OH, C_3), 52.7 (CH₂, \tilde{C}_8), 47.2 (CH, $J_{cp} = 7.6$ Hz, C_4 or C_2), 42.1 (CH_2 , $J_{cp} = 25.3$ Hz, C_7), 25.1 (CH_2 , $J_{cp} = 9.6$ Hz, C_6), 23.1 (CH_3). MS (FAB, ⁵⁶Fe): 443 (5, M⁺-1), 389 (100, M⁺-C_4H_7), 333 (57, M⁺-2CO-C₄H₇). Anal. Found: C, 67.74; H, 5.55. C₂₄H₂₅O₂PFe Calc.: C, 67.58; H, 5.67%.

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