Photoexcitation of iron–allyl complexes $(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)Fe(CO)(\eta^1\text{-}CH_2CR{=}CH_2)$ $(R = H, CH_3)$ which contains a tethered phosphine ligand

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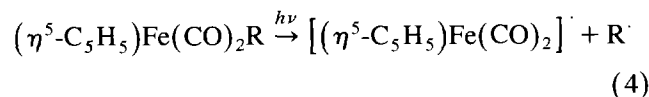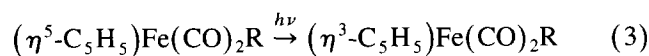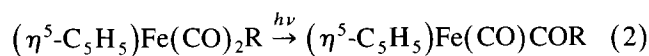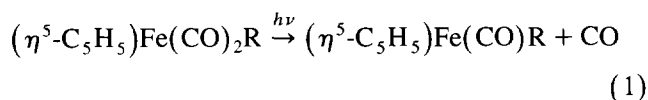Received 4 February 1997; received in revised form 9 April 1997

Abstract

Photoexcitation of the phosphino ligand chelated iron–allyl complexes $(\eta^5:\eta'\text{-}C_5H_4CH_2CH_2PPh_2)Fe(CO)(\eta'\text{-}CH_2CR{=}CH_2)$ (**1a**: R = H; **1b**: R = CH_3) gives a mixture of Fe–CO bond cleavaged compound $(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)Fe(\eta^3\text{-}CH_2CRCH_2)$ (**2**) and Fe–allyl bond homolysis compounds $[\eta^4:\eta^1\text{-}(1\text{-}CH_2CR{=}CH_2)C_5H_4CH_2CH_2PPh_2]Fe(CO)_2$ (**3**) and $[\eta^4:\eta^1\text{-}(3\text{-}CH_2CR{=}CH_2)C_5H_4CH_2CH_2PPh_2]Fe(CO)_2$ (**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 $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ 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 $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ gave exclusive loss of triphenylphosphine either photochemically [3] or thermally [4]. For instance, photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_3$ in the presence of tri-p-tolylphosphine gave exclusive phosphine exchange product $(\eta^5\text{-}C_5H_5)Fe(CO)(P(p\text{-}Tol)_3)CH_3$ [3]. The allyl complex $(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(\eta^1\text{-}allyl)$ lost triphenylphosphine ligand to form $(\eta^5\text{-}$

$C_5H_5)Fe(CO)(\eta^3\text{-}allyl)$ when it was heated above 40°C [4].

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2R \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)R + CO \quad (1)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2R \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Fe(CO)COR \quad (2)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2R \xrightarrow{h\nu} (\eta^3\text{-}C_5H_5)Fe(CO)_2R \quad (3)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2R \xrightarrow{h\nu} [(\eta^5\text{-}C_5H_5)Fe(CO)_2]^{\cdot} + R^{\cdot} \quad (4)$$

We have been interesting in the chemistry of chelate iron phosphine complexes of the type $(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)Fe(CO)R$ [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 $(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)Fe(CO)(\eta^1\text{-}CH_2CR{=}CH_2)$ (**1a**:

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R = H; **1b**: R = CH$_3$) which behave differently from that of the related, non-chelate complex (η^5-C$_5$H$_5$)Fe(PPh$_3$)(CO)(η^1-allyl) [4].

2. Results and discussion

2.1. Preparation of (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)-Fe(CO)(η^1-CH$_2$CR=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 (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)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 ^{1}H NMR spectrum, the diastereotopic methylene protons of the methallyl 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 ($^2J_{HH}$) and the couplings between the methylene protons and the ^{31}P
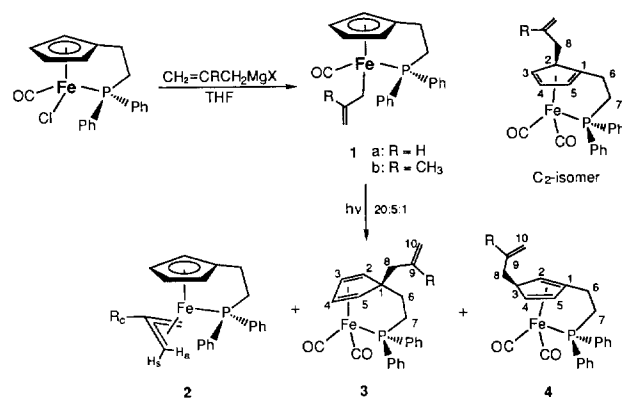
Scheme 1.

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

2.2. Photoexitation of 1a and 1b

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 ^{31}P NMR spectrum im-
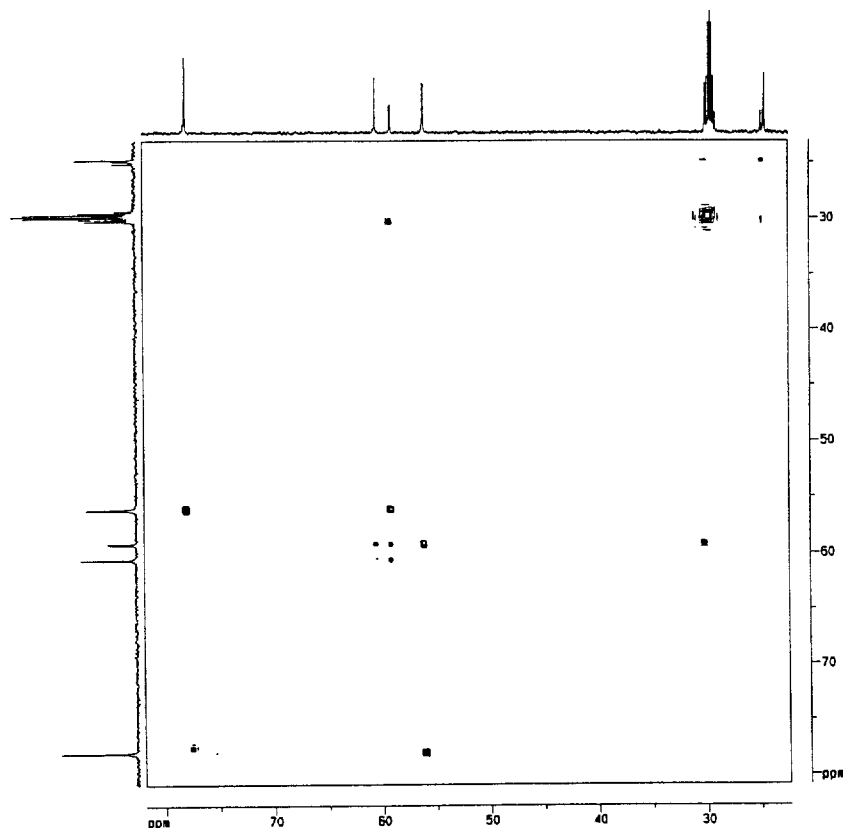

Fig. 1. The significant part of the INADEQUATE spectrum of **3b**.

mediately after irradiation 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 ^{1}H 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 ^{1}H 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 ^{1}H and ^{31}P 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 ^{31}P NMR spectra, compared to δ −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 ^{1}H and ^{13}C NMR spectra, therefore it was assigned as C$_1$-isomer. Assignment of the complex **4** as C$_3$-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 ^{13}C NMR spectrum of **4b**, resonance at δ 47.2 (CH) was assigned to the sp^3 carbon, C$_3$. The resonance at δ 116.8 was assigned to the olefinic C$_1$. The other three olefinic CH carbons consists of one down-field resonance at δ 82.6 (C$_5$) 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 C$_2$-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, $^3J_{CP}$ = 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)$(\eta^1$-CH$_2$CR=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 C$_1$ position or on the C$_3$ position to provide C$_1$-isomer **3** or C$_3$-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, CH$_3$) 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 1 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$_5$H$_5)$Fe(CO)(PPh$_3$)CH$_3$ and the thermolysis of $(\eta^5$-C$_5$H$_5)$Fe(PPh$_3$)(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 $(\eta^5:\eta^1$-C$_5$H$_4$CH$_2$CH$_2$PPh$_2)$Fe(CO)(CH$_3$) 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 CaF$_2$ 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. ^{1}H NMR (300 MHz), ^{13}C NMR (75

MHz) and ^{31}P(^{1}H) NMR (121 MHz) were obtained with a Bruker AC-300 FT spectrometer. On the assignment of ^{1}H and ^{13}C 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 $(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)$-$Fe(CO)(\eta^1-CH_2CH=CH_2)$ (1a)

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 methallyl-magnesium chloride (13 ml × 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 CH_2Cl_2 (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 (CH_2Cl_2): 1899 cm^{-1}. UV (acetone): $\lambda_{max} = 392$ nm ($\epsilon = 212$), 482 (84). ^{31}P{^{1}H} NMR (CD_3COCD_3): δ 92.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 94.4. ^{1}H NMR (CD_3COCD_3): 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). ^{1}H NMR ($CDCl_3$): 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, ^{56}Fe): 417 (12, $M^+ + 1$), 361 (78, $M^+-C_4H_7$), 333 (100, $M^+-C_4H_7-CO$). Anal. Found: C, 69.36; H, 5.98. $C_{24}H_{25}OPFe$ Calc.: C, 69.25; H, 6.05%.

4.3. Photoexcitation 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)

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 ^{31}P and ^{1}H NMR spectra were deduced from the spectra of the reaction mixture.

$(\eta^5:\eta^1-C_5H_4C_2)$ (**2a**): ^{31}P{^{1}H} NMR (CD_3COCD_3): δ 90.5. ^{1}H NMR (CD_3COCD_3): 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, $J = 1.8$ Hz, 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). ^{13}C NMR (CD_3COCD_3): 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 (CH_2, $J_{cp} = 28$ Hz, C_1), 33.7 (CH_2 × 2, $J_{cp} = 6.7$ Hz, allyl), 23.1 (CH_2, $J_{cp} = 9$ Hz, C_2).

$(\eta^5:\eta^1-C_5H_4CH_2CH_2PPh_2)Fe[\eta^3-CH_2C(CH_3)CH_2]$ (**2b**): ^{31}P{^{1}H} NMR (CD_3COCD_3): δ 90.1. ^{1}H NMR (CD_3COCD_3): 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, CH_3), -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 = CH_3) and $[\eta^4:\eta^1-(3-CH_2CR=CH_2)C_5H_4CH_2CH_2PPh_2]Fe(CO)_2$ (4a: R = H; 4b: R = CH_3)

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**.

[η^4:η^1-(1-CH_2CH=CH_2)$C_5H_4CH_2CH_2PPh_2$]-Fe(CO)$_2$ (**3a**): yellow liquid, 14% yield. R_f = 0.33 (5% EtOAc in hexane). IR (CH_2Cl_2): 1971s, 1906s cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.3. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 58.4. ^1H NMR ($CDCl_3$): δ 7.67–7.60 (4H, m, Ph), 7.41–7.37 (6H, m, Ph), 5.63–5.48 (1H, m, H_9), 5.30–5.28 (2H, m, H_3 and H_4), 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, H_7), 2.00–1.98 (2H, m, H_2 and H_5), 1.78 (2H, dt, J = 20.1, 6.9 Hz, H_6), 1.69 (2H, d, J = 7.4 Hz, H_8). Anal. Found: C, 66.85; H, 5.45. $C_{24}H_{23}O_2PFe$ Calc.: C, 67.00; H, 5.39%.

[H^4:η^1-(3-CH_2CH=CH_2)$C_5H_4CH_2CH_2PPh_2$]Fe-(CO)$_2$ (**4a**): yellow liquid, 3% yield. R_f = 0.27 (5% EtOAc in hexane). IR (CH_2Cl_2): 1964s, 1904s cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 74.5. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 71.8. ^1H NMR ($CDCl_3$): 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. $C_{24}H_{23}O_2PFe$ Calc.: C, 67.00; H, 5.39%.

[η^4:η^1-(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}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 861.9. $^{31}P\{^1H\}$ 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, H_3 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, H_7), 2.00 (2H, br. s, H_2 and H_5), 1.83 (2H, dt, J = 20.2, 6.9 Hz, H_6), 1.69 (2H, s, H_8), 1.63 (3H, s, CH_3). ^1H NMR (CD_3COCD_3): δ 7.75–7.68 (4H, m, Ph), 7.46–7.40 (6H, m, Ph), 5.37–5.35 (2H, m, H_3 and H_4), 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, H_6), 1.70 (2H, s, H_8), 1.63 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 215.9 (CO × 2, J_{cp} = 6.8 Hz), 143.6 (C, C_9), 140.0 (C × 2, J_{cp} = 39.9 Hz, Ph–$C_{1'}$), 132.4 (CH × 4, J_{cp} = 10.7 Hz, Ph–$C_{2'}$), 130.0 (CH × 2, Ph–$C_{4'}$), 129.1 (CH × 4, J_{cp} = 9.2 Hz, Ph–$C_{3'}$), 113.6 (CH_2, C_{10}), 78.0 (CH × 2, C_3 and C_4), 60.5 (CH_2, C_8), 59.1 (C, J_{cp} = 15.4 Hz, C_1), 56.1 (CH × 2, J_{cp} = 5.5 Hz, C_2 and C_5), 30.2 (CH_2, J_{cp} = 3.6 Hz, C_6), 25.0 (CH_2, J_{cp} = 30.6 Hz, C_7), 24.8 (CH_3). MS (FAB, ^{56}Fe): 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. $C_{24}H_{25}O_2PFe$ Calc.: C, 67.58; H, 5.67%.

[η^4:η^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}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 74.5. $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 71.8. ^1H NMR ($CDCl_3$): 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, H_2 or H_4), 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, H_8). ^1H NMR (CD_3COCD_3): 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, H_5), 4.61 (1H, H_{10a}), 4.51 (1 H, H_{10b}), 3.11 (1 H, H_2 or H_4), 3.09–2.97 (1H, 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, H_8). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 222.9 (CO), 217.1 (CO, J_{cp} = 20.2 Hz), 143.3 (C, C_9), 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 × 2, J_{cp} = 11.0 Hz, Ph), 129.8 (CH, Ph), 129.3 (CH, Ph), 128.4 (CH × 2, J_{cp} = 5.5 Hz, Ph), 128.3 (CH × 2, J_{cp} = 5.5 Hz, Ph), 115.0 (C, J_{cp} = 7.6 Hz, C_1), 110.4 (CH_2, C_{10}), 82.0 (CH, C_5), 59.6 (CH, C_2 or C_4), 54.5 (CH, C_3), 52.1 (CH_2, J_{cp} = 5.6 Hz, C_8), 47.0 (CH, J_{cp} = 7.6 Hz, C_4 or C_2), 41.7 (CH_2, J_{cp} = 24.4 Hz, C_7), 24.9 (CH_2, J_{cp} = 9.9 Hz, C_6), 22.9 (CH_3). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): 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 × 2, J_{cp} = 8.8 Hz, Ph), 129.1 (CH × 2, J_{cp} = 8.5 Hz, Ph), 116.8 (C, J_{cp} = 7.6 Hz, C_1), 111.0 (CH_2, C_{10}), 82.6 (CH, C_5), 60.7 (CH, J_{cp} = 3.2 Hz, C_2 or C_4), 55.6 (OH, C_3), 52.7 (CH_2, 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, ^{56}Fe): 443 (5, M$^+$-1), 389 (100, M$^+$–C_4H_7), 333 (57, M$^+$–2CO–C_4H_7). Anal. Found: C, 67.74; H, 5.55. $C_{24}H_{25}O_2PFe$ Calc.: C, 67.58; H, 5.67%.

Acknowledgements

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