Phosphorus-carbon bond forming reactions of iron tetracarbonyl-coordinated phosphenium ions

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ABSTRACT

Abstraction of chloride from [Fe(CO)₄(PPh₂Cl)] (1) in the presence of PPh₃ leads to [Fe(CO)₄(PPh₂(PPh₃))] [AlCl₄] (2), an iron complex of a phosphine-coordinated phosphenium ion. The PPh₃ is readily displaced by ferrocene, leading to an electrophilic aromatic substitution reaction, and formation of [Fe(CO)₄(PPh₂Fc)] (3) (Fc = ferrocenyl). Alternately, chloride abstraction from 1 in the presence of ferrocene leads directly to 3, via a transient phosphenium ion complex. The transient phosphenium ion complex also reacts with N,N-diethylaniline, indole, and pyrrole to form the respective p-anilinyl, 3-indolyl, and 2-pyrryl phosphine complexes via electrophilic aromatic substitution. Chloride abstraction from [Fe(CO)₄(PPhCl₂)] in the presence of ferrocene leads to a double substitution reaction, forming [Fe(CO)₄{PPhFc₂}] (13).

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1. Introduction

Given the importance of tertiary phosphine ligands in many areas of catalysis, the development of new methods for P-C bond formation continues to attract much interest [1]. Additionally, advances in computational design of catalysts [2] necessitate synthetic methods to realize those designs. Currently, the majority of P-C bond forming reactions involve addition of a strong carbon nucleophile, most typically a Grignard or organolithium reagent, to phosphorus electrophiles. An alternative method for P-C bond formation uses a Lewis acid to enhance P electrophilicity by abstracting chloride [3]. The resulting phosphenium ion undergoes electrophilic aromatic substitution with an aromatic substrate, in a reaction that is analogous to a Friedel-Crafts reaction. However, this method is not widely used, possibly due to high temperatures and slow reaction times. We have shown that electrophilic substitution reactions at phosphorus are much faster if the chlorophosphine precursor is coordinated to a tungsten pentacarbonyl fragment prior to chloride abstraction, and have demonstrated that this methodology is viable for the synthesis of a wide range of phosphines [4]. Coordination of the phosphenium ion to the electron-poor W(CO)₅ fragment enhances the electrophilicity of the phosphenium ion, and also protects the P lone pair, preventing phosphine-phosphorus coordination [5], which quenches electrophilicity. These metal-coordinated phosphenium ions have been shown to undergo rapid reaction at room temperature with organic substrates, including amines, heteroarenes, alkenes, and alkynes [4]. This method has advantages over the traditional methods using Grignard or organolithium reagents, particularly in selectivity and functional group tolerance. Functionalized phosphate products can be readily removed from the metal complex [4b]. One disadvantage of this methodology is that it is stoichiometric in tungsten, which means that it can become prohibitively expensive for large scale synthesis. This led us to consider alternate earth abundant transition metals for this methodology. In this paper, we will discuss our exploration of the P-C bond forming reactions of iron-coordinated phosphenium ions.

Iron-coordinated phosphenium ion complexes have been extensively studied [6]. The known examples of stable Fe-coordinated phosphenium ions contain strong π-donor ferrocenyl or amino groups on phosphorus, which stabilize the phosphenium ion, and the resulting metal complex. Despite these stabilizing groups, these complexes remain significantly electrophilic at P [6g]. However, application of this electrophilicity toward P-C bond formation remains mostly unexplored for iron phosphonium complexes. Alkyl migrations from the metal [7] and from coordinated stannyl ligands [8] have been demonstrated. Direct addition of organometallic nucleophiles has also been used to form P-C bonds
in iron-bound phosphonium ions [8b]. However, Friedel-Crafts like electrophilic aromatic substitution reactions have not been explored. For this study, we have chosen the Fe(CO)₄ fragment due to the simplicity of preparation of the precursor chlorophosphine complex, and because the π-acidity of the metal carboxyls lowers metal electron density, potentially enhancing electrophilicity at P.

2. Results and discussion

Coordination of chlorodiphenylphosphine to the Fe(CO)₄ fragment was carried out using a modification of a literature procedure, using the reactive iron carbonyl dimer Fe₂(CO)₉. Chlorodiphenylphosphine was added at 0 °C to an unsterilized THF/Fe₂(CO)₉ mixture. The solution was then stirred slowly and allowed to warm to room temperature. Without cooling, or with stirring prior to phosphine addition, the nearly insoluble Fe₃(CO)₁₂ immediately forms deep green Fe₃(CO)₁₂, presumably from the reaction of 3 [Fe(CO)₄(THF)] fragments. After implementing this change, the desired phosphonium complex was obtained in 69% yield (Scheme 1).

The known bridging phosphido complex [Fe₂(CO)₆(μ-Cl)(μ-PPh₂)] [9] is formed as a side product in this reaction. The proportion of this impurity can be reduced with slight excess of the phosphine. Once purified, compound 1 slowly decomposes in dichloromethane or pentane solution, showing ³¹P{¹H} resonances in the region expected for bridging phosphido complexes.

In the well-established tungsten pentacarbonyl chemistry, two chloride abstraction methods have proven successful. Chloride abstraction with AlCl₃ leads to phosphonium ion complexes, while chloride abstraction with Ag₂O₂CF₂ (AgOTf) leads to phosphine trflate complexes, which are effective surrogates for phosphonium ion complexes. Treatment of [Fe(CO)₄(PPh₂Cl)] (1) with AlCl₃ or GaCl₃ resulted in decomposition, at room temperature or at −30 °C, with notable gas evolution, most likely from carbonyl loss. This suggests that the iron phosphonium complexes are less stable than the corresponding tungsten complexes. Treatment of 1 with AgOTf resulted in the formation of multiple products, none of which showed reactivity towards an added nucleophile.

Since phosphonium ion and phosphine trflate complexes were apparently unstable, attempts were made to trap transient phosphonium ions. Phosphate coordination has been shown to be an effective means of trapping free and metal-coordinated phosphonium ions [5,6,9,10]. Chloride abstraction with AlCl₃ leads to phosphonium ion complexes, while chloride abstraction with Ag₂O₂CF₂ (AgOTf) leads to phosphine triflate complexes, which are effective surrogates for phosphonium ion complexes. Treatment of [Fe(CO)₄(PPh₂Cl)] (1) with AlCl₃ or GaCl₃ resulted in decomposition, at room temperature or at −30 °C, with notable gas evolution, most likely from carbonyl loss. This suggests that the iron phosphonium complexes are less stable than the corresponding tungsten complexes.

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consists of a trigonal bipyramidal Fe(CO)₄L unit, with the phosphine ligand occupying an axial position. The geometry at P is tetrahedral, and the substituents on P are staggered relative to the equatorial carbonyl ligands. The ferrocenyl unit is oriented such that the P- substituted Cp ring is nearly parallel with the P-Fe bond. All distances and angles are within the expected ranges.

Next, compound 1 was treated with N,N-diethylaniline and AlCl₃, leading to the formation of [Fe(CO)₄{PPh₂(C₆H₄NEt₂)}] (5), the expected para electrophilic aromatic substitution product (Scheme 3). In this case, additional of base was not required as the acid by-product is consumed by excess N,N-diethylaniline. The 31P NMR chemical shift for 5 of δP 68.6 is consistent with those of other Fe(CO)₄-triarylphosphine complexes [15]. The 13C NMR spectrum shows four resonances that can be assigned to the anilinyl ring and the 1H NMR spectrum shows the expected symmetrical pattern for para substitution, indicating the substitution has occurred in the para position as expected. Compound 5 is stable in solution, air and moisture and no signs of decomposition were observed after 3 h reflux in dichloroethane. Similar reactions with less activated aromatic substrates anisole, toluene, naphthalene, and anthracene resulted in decomposition. Reactions with these less activated substrates are presumably too slow given the short lifetime of the iron-bound phosphonium ion. This contrasts with the chemistry of the tungsten system, where the lifetime of the phosphonium ion is long enough for multi-hour reactions [4b].

We next examined reactions of the iron phosphonium ion complex with heteroaromatics. Treatment of compound 1 with AlCl₃ and indole led to two products 6 and 7 in a 1:2 ratio, with 31P chemical shifts of δP 27 and 51.9, respectively. Addition of a half equivalent of NEt₃ or filtration through alumina resulted in conversion of the minor product (δP 27) into the major product (δP 51.9), allowing us to identify these products as the protonated substitution product [Fe(CO)₄H{PPh₂(C₈H₅NH)}][AlCl₄] (6) and neutral substitution product [Fe(CO)₄{PPh₂(C₈H₅NH)}] (7), parallelizing the chemistry observed in the reaction with ferrocene (Scheme 4). Compound 7 was purified using column chromatography and isolated in 31% yield. However, it is unstable and decomposes in common organic solvents. This instability also accounts for the low isolated yield. Substitution onto the indole ring occurs at C₃ as expected [16]. This substitution position is evident from the 13C NMR spectrum, in which the C₃ carbons (δC 106.9) shows a JCP of 68 Hz, indicating a direct bond to P.

The reaction of the iron phosphonium ion complex with pyrrole led to two products 8 and 9, with 31P NMR resonances at δP 52.6 and
51, in a 30:70 ratio (Scheme 4). These chemical shifts are consistent with substitution in the C2 and C3 positions of the pyrrole ring, as was previously observed in the tungsten system [4b]. In solution or during purification, compound 9 ($^{31}$P 51) quickly decomposes, while compound 8 ($^{31}$P 52.6) is significantly more stable. Characterization of the stable compound 8 reveals it to be the C2 substituted isomer [Fe(CO)4(PPh2(2-C4H3NH))] (8). The key spectroscopic features that reveals the substitution position are the P-substituted pyrrole carbon, which appears at $^\delta$ 121.0 ($^J_{PC} = 65$ Hz), and the adjacent C3 carbon, which appears at 120.7 ($^J_{PC} = 10$ Hz). For C3 substituted pyrryl phosphines, C3 appears in the range of $^\delta$ 125–130 and C2 appears in the range of $^\delta$ 115–120 [4b]. Although the only isolated product is C2 substituted, the reaction unexpectedly favors C3 substitution in a 70:30 ratio. Electrophilic substitution reactions of pyrrole normally favor C2 substitution, unless the kinetics are very fast, in which case they show no regioselectivity [16].

To survey functional group tolerance, reactions with thiophene, anisole, diphenylamine and acetanilide were attempted. However, with all of these substrates, the added AlCl3 reacted preferentially with the organic substrate rather than with the iron chlorophosphine complex. Addition of excess AlCl3 led to decomposition. This reactivity offers no useful advantage. It is also possible that the iron phosphenium ion complex, however, its limited lifetime means that this instability of the Fe(CO)4-bound phosphenium ion complexes stem from their electrophilicity at P, but from carbonyl lability. As has been noted previously, phosphenium ions are strong π-acceptors and as a result will compete effectively with the carbonyls for metal electron density, stabilizing the carbonyls [6d,6e].

3. Conclusions

We have demonstrated that Fe(CO)₄ bound phosphonium ions, generated in situ using chloride abstraction, are reactive toward was not selective, leading to a mixture of the monosubstituted product [Fe(CO)₄{PPhClFc}] (11) and the protonated disubstituted complex [Fe(CO)₄H{PPhFc₂}][AlCl₄] (12) in a 4:1 ratio. Attempts to isolate 11 from this mixture failed, as it was extremely sensitive to hydrolysis. Chloride abstraction in the presence of excess ferrocene led to complete conversion to 12, which was deprotonated using 2 equivalents of NEt₃, yielding the desired product [Fe(CO)₄{PPhFc₂}] (13) (Scheme 6). The crystalline dark orange product was very stable and has a $^{31}$P chemical shift at $^\delta$ 58.0. Compound 13 was previously synthesized by reaction of Fe₂(CO)₉ with PPh(C₁₀H₈OFe)₂ [17c].

Chloride abstraction from 10 was also carried out in the presence of substrates N,N-diethylaniline, indole, and pyrrole. Using 1.2 equivalents of substrate and a single equivalent of AlCl₃ all resulted in no change by $^{31}$P{¹H} NMR, likely a result of preferential interaction between the substrate and AlCl₃, as previously discussed. Increasing the concentration of the Lewis acid did result in chemical shift changes to ranges indicative of monosubstitution ($^\delta$ 120 to 136); however, these compounds were present in minor quantities compared to the decomposition products, which also appeared during chloride abstraction without a nucleophile. The greater difficulty in extracting chloride from the dichlorophosphine complex reflects the lower stability of the chlorophenyl phosphonium intermediate. The electron withdrawing chlorophosphorus group destabilizes the cationic phosphonium ion complex, making chloride abstraction to form it less favorable. As a result, AlCl₃ reacts preferentially with most substrates rather than extracting chloride from the metal-coordinated phosphine. The greater difficulty of abstracting chloride from [Fe(CO)₄(PPhCl₂)] (10) compared to the tungsten analog [4a] may indicate that the iron phosphonium ion complex is in fact more electrophilic than the tungsten phosphonium ion complex, however, its limited lifetime means that this reactivity offers no useful advantage. It is also possible that the instability of the Fe(CO)₄-bound phosphonium ion complexes stem not from the electrophilicity at P, but from carbonyl lability. As has been noted previously, phosphonium ions are strong π-acceptors and as a result will compete effectively with the carbonyls for metal electron density, stabilizing the carbonyls [6d,6e].

Scheme 4. Electrophilic aromatic substitution of heteroaromatics.

Scheme 5. Synthesis of [Fe(CO)₄{PPhCl₂}] (10).

Scheme 6. Disubstitution at Fe(CO)₄ coordinated dichlorophenylphosphine.
electrophilic aromatic substitution. However, when compared to the established tungsten system, the Fe(CO)₄ methodology is severely limited by the instability of the phosphine ion complex. Generation of the phosphine ion in situ led to successful substitution reactions with the most nucleophilic organic substrates. However, for less activated substrates, the electrophilic substitution reaction is not competitive with decomposition of the phosphonium ion complex. This restricts potential substrates for the methodology. Another notable difference between the iron and tungsten systems is the tendency for the iron complexes to be protonated, a reaction that was never observed in the comparable tungsten chemistry. This reaction likely reflects the relative stability of the octahedral Fe(II) complexes that results from protonation, compared to the seven-coordinate W(II) complexes that would result from protonation of octahedral W(0) complexes. While the Fe(CO)₄ system has limitations, electrophilic addition reactions to Fe(CO)₄ coordinated phosphonium ions are a viable and less expensive alternative to the established W(CO)₅ methodology in reactions with strong nucleophiles.

4. Experimental section

4.1. General comments

All procedures except chromatography were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Pentane and diethyl ether were purified by trap-to-trap vacuum distillation from NaK/benzophenone. CH₂Cl₂ and CDCl₃ were purified by trap-to-trap vacuum distillation from P₂O₅. Solvents for chromatography were not purified. Aluminum chloride and ferrocene were purified by sublimation and stored under an inert atmosphere. Chlorodiphenylphosphine and dichlorophenylphosphine were used as received and stored under nitrogen. Note that any impurities resulting from hydrolysis or oxidation of these reagents are removed during column chromatographic purification of compounds 1 and 10 prior to the electrophilic substitution chemistry. The NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300.177 MHz (¹H), 121.514 MHz (³¹P), 75.488 MHz (¹³C) or on a Varian Inova 500 spectrometer at 125.624 MHz (¹³C) in CDCl₃ or CD₂Cl₂. The ³¹P NMR chemical shifts were validated using an external standard of triphenyl phosphate (0.0485 M, CHCl₃, δ = −17.3). IR spectra were recorded on a Digilab FTIR in CH₂Cl₂ solution. Elemental analyses were carried out by the Analytical and Instrumentation Laboratory in the Department of Chemistry at the University of Alberta. High-resolution mass spectra were carried out at the Saskatchewan Structural Centre using a JEOL JMS-T100GCV AccuTOF-GC/IV4G Mass Spectrometer in field desorption ionization mode.

4.2. Synthesis of [Fe(CO)₄(PPh₂Cl)] (1)

This procedure is a modified version of a published procedure [18], which was modified to reduce the formation of Fe₃(CO)₁₁, Fe₂(CO)₉ (1.00 g, 2.75 mmol) was added to a dry Schlenk flask and cooled to 0 °C. Freshly distilled THF (15 mL) was slowly added without stirring. PPh₃Cl (0.59 mL, 3.30 mmol) was then added. The solution was protected from light, allowed to warm to room temperature, and stirred for 16 h, resulting in a colour change to deep red. The solvent was removed under reduced pressure and the crude solid was extracted into diethyl ether/petroleum ether (10:90, 50 mL) and filtered to remove a cream coloured precipitate. The filtrate was evaporated under reduced pressure, and the residue was then purified using column chromatography (silica gel, 5:95 diethyl ether: petroleum ether). Evaporation of the solvent from the collected fractions yielded a yellow powder.

Yield = 0.740 g, 69%. IR (v(CO), CH₂Cl₂, cm⁻¹): 2059(m), 1989(w), 1953(s), ³¹P{¹H} NMR (121 MHz, CDCl₃): 1610 (δ, JCP = 14 Hz). ¹H NMR (300 MHz, CDCl₃): 7.92–7.69 (m, 4H), 7.65–7.43 (m, 6H). ¹³C (¹H) NMR (75 MHz, CDCl₃): 212.0 (δ, JCP = 19 Hz, CO), 137.9 (δ, JCP = 43 Hz, ipso-ph), 132.3 (s, p-Ph), 131.7 (δ, JCP = 15 Hz, o-Ph), 129.0 (δ, JCP = 13 Hz, m-Ph). These values match previously published data [18].

4.3. Synthesis of [Fe(CO)₄(PPh₂(PPh₃))][AlCl₄] (2) with ferrocene

A solution of [Fe(CO)₄(PPh₂Cl)] (1) (150 mg, 0.386 mmol) and PPh₃ (121 mg, 0.461 mmol) in CH₂Cl₂ (3 mL) was added to AlCl₃ (77 mg, 0.58 mmol), resulting in an immediate colour change to red. The reaction was also carried out in CDCl₃ or CD₂Cl₂ to record NMR spectra. Attempts to isolate compound 2 as a solid resulted in decomposition to a mixture products. IR (v(CO), CH₂Cl₂, cm⁻¹): 2057 (s), 1986(w), 1935(s). ³¹P{¹H} NMR (121 MHz, CDCl₃): 93.0 (δ, JPP = 207 Hz), 8.5 (δ, JPP = 207 Hz). ¹³C (¹H) NMR (125 MHz, CDCl₃): 211.7 (δ, JCP = 11 Hz, 3JCP = 2 Hz, FeCO), 136.5 (δ, JCP = 3 Hz, p-PPh₃), 136.4 (δ, JCP = 3 Hz, p-PPh₃), 135.6 (δ, JCP = 21 Hz, ipso-PPh₃), 135.1 (δ, JCP = 9 Hz, o-PPh₃), 134.5 (δ, JCP = 12 Hz, o-PPh₃), 133.2 (δ, JCP = 53 Hz, ipso-PPh₃), 131.1 (δ, JCP = 14 Hz, m-PPh₃), 131.0 (δ, JCP = 12 Hz, m-PPh₃), 130.3 (δ, JCP = 12 Hz, 3JCP = 2 Hz, m-PPh₃).

4.4. Reaction of [Fe(CO)₄(PPh₂(PPh₃))][AlCl₄] (2) with ferrocene

A solution of 2 (0.21 mmol) was generated by dissolving 1 (80 mg, 0.21 mmol), PPh₃ (65 mg, 0.25 mmol) and AlCl₃ (36 mg, 0.27 mmol) in CH₂Cl₂ (3 mL). This solution was added to ferrocene (50 mg, 0.25 mmol). After 10 min of stirring, the solvent was removed under reduced pressure, and the residue was purified using column chromatography (silica gel, 5:95 diethyl ether: petroleum ether). Evaporation of the solvent from the collected fraction resulted in a fine orange powder, which was recrystallized from pentane at ~30 °C, and shown to be [Fe(CO)₄(PPh₂Fc)] (3). Yield: 31 mg, 28%. See section 4.5 for characterization of 3.

4.5. Synthesis of [Fe(CO)₄(PPh₂Fc)] (3)

A solution of [Fe(CO)₄(PPh₂Cl)] (1) (150 mg, 0.386 mmol) and ferrocene (115 mg, 0.618 mmol) in CH₂Cl₂ (<3 mL) was added to AlCl₃ (82 mg, 0.62 mmol), resulting in an immediate colour change to red. After 10 min of stirring, the solvent was removed under reduced pressure, and the residue was purified using column chromatography (silica gel, 5:95 diethyl ether: petroleum ether). Evaporation of the solvent from the collected fraction resulted in a fine orange powder, which was recrystallized from pentane at ~30 °C. Yield: 150 mg, 73%. IR (v(CO), CH₂Cl₂, cm⁻¹): 2048(m), 1971(w), 1935(s). ³¹P{¹H} NMR (121 MHz, CDCl₃): 673. ¹H NMR (300 MHz, CDCl₃): 7.62–7.43 (m, 10H, Ph), 4.55 (m, 4H, C₅H₄P), 3.81 (s, 5H, FeC₅H₅), ²¹C (¹H) NMR (75 MHz, CDCl₃): 213.6 (δ, JCP = 19 Hz, CO), 138.0 (δ, JCP = 52 Hz, ipso-ph), 132.8 (δ, JCP = 10 Hz, o-Ph), 130.6 (δ, JCP = 3 Hz, p-Ph), 128.4 (δ, JCP = 11 Hz, m-Ph), 76.6 (δ, JCP = 55 Hz, C₅H₅P), 75.1 (δ, JCP = 12 Hz, C₅H₅P), 71.8 (δ, JCP = 9 Hz, C₅H₅P), 70.1 (s, FeC₅H₅). Anal. Calc'd. for C₅₅H₄₃O₃Fe₃P: C, 58.02%, H, 3.57%. Found: C, 57.86 H, 3.65. These values match previously published data [11].

4.6. Synthesis of [Fe(CO)₄(PPh₂(C₄H₉NEt₂))] (5)

[Fe(CO)₄(PPh₂Cl)] (1) (150 mg, 0.386 mmol) was dissolved in CH₂Cl₂ (6 mL), N,N-diethylamine (155 µL, 1.44 mmol) was added and the resulting solution was added to AlCl₃ (103 mg,
0.772 mmol), resulting in an immediate colour change to green, followed by a slow colour change to brown. The solvent was removed under reduced pressure and the residue was purified using column chromatography (alumina, 5:95 diethyl ether: petroleum ether). Evaporation of the solvent from the collected fractions produced a bright yellow powder, which was recrystallized from a saturated CH2Cl2/petroleum ether at −30 °C. Yield: 95 mg, 49%. IR (v(CO), CH2Cl2, cm−1): 2046(m), 1969(w), 1939(s). 31P{1H} NMR (121 MHz, CDCl3): 68.6. 1H NMR (300 MHz, CDCl3): 7.55–7.32 (m, 12H), 6.69 (d, 2H, 3JHH = 9.9 Hz), 3.39 (q, 4H, 3JHH = 7.4 Hz, CH2), 1.19 (t, 6H, 4JHH = 7.4 Hz, -CH3). 13C{1H} NMR (75 MHz, CDCl3): 136.0 (d, 3JCP = 50 Hz, FeC5H5), 135.4 (d, 3JCP = 12 Hz, C4H4), 131.1 (d, 3JCP = 11 Hz, C4H4), 130.6 (d, 3JCP = 3 Hz, C5H4), 128.6 (d, 3JCP = 11 Hz, m-Ph), 115.9 (d, 3JCP = 58 Hz, C4H4), 111.1 (d, 3JCP = 12 Hz, C4H4), 44.5 (s, CH2), 12.7 (s, CH3). Anal. Calcd. for C26H24O4NPFe: C, 62.30%; H, 4.83%; N, 2.79%. Found: C, 62.27%; H, 4.36%; N, 3.39%.

4.7. Synthesis of [Fe(CO)4(PPh2(C8H5NH))] (7)

[Fe(CO)4(PPh2(C8H5NH))] (1) (128 mg, 0.329 mmol) and indole (96 mg, 0.83 mmol) were dissolved in CH2Cl2 (~2 mL), added to AlCl3 (131 mg, 1.97 mmol), and mixed, resulting in a colour change to red. The resulting solution was filtered through a short alumina plug to yield a light orange solution. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (alumina, 50:50 diethyl ether: petroleum ether) to yield an immediate orange, solid. The solution was evaporated to yield orange crystals. Yield: 0.678 g, 71%. IR (v(CO), CH2Cl2, cm−1): 2070(m), 2005(w), 1977(s). 31P NMR (121 Hz, CDCl3): 207.9 (t, 3JPP = 18 Hz). 1H NMR (300 MHz, CDCl3): 8.10 (m, 2H, Ph), 7.61 (m, 3H, Ph), 131.9 (d, 3JCP = 17 Hz, Ph), 130.1 (3JCP = 14 Hz, m-Ph), 129.2 (d, 3JCP = 14 Hz, o-Ph). These values match those previously published [17c].

4.8. Synthesis of [Fe(CO)4(PPh2(2-C4H3NH))] (8)

Pyrrole (89 μL, 86 mg, 1.3 mmol) was added to a solution of [Fe(CO)4(PPh2Cl)] (1) (100 mg, 0.257 mmol) in CH2Cl2 (3 mL). This solution was added to AlCl3 (68 mg, 0.51 mmol), resulting in a colour change to brown/red. The solution was filtered through a short alumina plug to yield a light orange solution. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, 30:70 diethyl ether: petroleum ether) to yield a light orange solution. The solvent was removed under reduced pressure and the crude product was extracted into diethyl ether/petroleum ether (10:90, 50 mL), and filtered to remove a cream coloured precipitate. The filtrate was evaporated under reduced pressure then purified using column chromatography (alumina, 15:85 diethyl ether: petroleum ether). The filtrate was evaporated to yield orange crystals. Yield: 0.678 g, 71%. IR (v(CO), CH2Cl2, cm−1): 2070(m), 2005(w), 1977(s). 31P{1H} NMR (121 Hz, CDCl3): 207.9 (t, 3JPP = 18 Hz). 1H NMR (300 MHz, CDCl3): 8.10 (m, 2H, Ph), 7.61 (m, 3H, Ph), 131.9 (d, 3JCP = 17 Hz, Ph), 130.1 (3JCP = 14 Hz, m-Ph), 129.2 (d, 3JCP = 14 Hz, o-Ph). These values match those previously published [17c].

4.9. Synthesis of [Fe(CO)4(PPh2Cl2)] (10)

FeC8O3 (1.00 g, 2.75 mmol) was added to a dry Schlenk flask and cooled to 0 °C. Freshly distilled THF (15 mL) was slowly added without stirring. PPh2Cl2 (0.485 mL, 639 mg, 3.57 mmol) was then added. The flask was protected from light and the solution was stirred, allowed to warm to room temperature, and then stirred for 16 h, resulting in a colour change to deep red. The solvent was removed under reduced pressure and the crude solid was extracted into diethyl ether/petroleum ether (10:90, 50 mL), and filtered to remove a cream coloured precipitate. The filtrate was evaporated under reduced pressure then purified using column chromatography (alumina, 15:85 diethyl ether: petroleum ether). The filtrate was evaporated to yield orange crystals. Yield: 0.678 g, 71%. IR (v(CO), CH2Cl2, cm−1): 2070(m), 2005(w), 1977(s). 31P{1H} NMR (121 Hz, CDCl3): 207.9 (t, 3JPP = 18 Hz). 1H NMR (300 MHz, CDCl3): 8.10 (m, 2H, Ph), 7.61 (m, 3H, Ph), 131.9 (d, 3JCP = 17 Hz, Ph), 130.1 (3JCP = 14 Hz, m-Ph), 129.2 (d, 3JCP = 14 Hz, o-Ph). These values match those previously published [17c].

4.10. Synthesis of [Fe(CO)4(PPh2Cl2)] (12)

[Fe(CO)4(PPh2Cl2)] (10) (150 mg, 0.432 mmol) and ferrocene (193 mg, 1.04 mmol) were dissolved in CH2Cl2 (~2 mL). The orange solution was then added to AlCl3 (161 mg, 1.21 mmol) and mixed for 5 min, resulting in a colour change to deep red. Triethylamine (120 μL, 0.684 mmol) was then added to the solution, the solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (silica gel, 10:90 diethyl ether: petroleum ether). Evaporation of the solvent from the collected fractions resulted in orange crystals, which were recrystallized from a saturated CH2Cl2/petroleum ether at −30 °C to produce of bright orange needle-like crystals. Yield: 196 mg, 70%. IR (v(CO), CH2Cl2, cm−1): 2047(m), 1968(w), 1934(s). 31P{1H} NMR (121 Hz, CDCl3): 58.0. 1H NMR (300 MHz, CDCl3): 8.01 (m, 3H, Ph), 7.45 (m, 2H, Ph), 4.60 (m, 2H, FeC5H5), 4.48 (m, 6H, FeC5H5), 3.99 (s, 10H, FeC5H5). 13C{1H} NMR (75 MHz, CDCl3): 214.4 (d, 3JCP = 18 Hz, CO), 138.1 (d, 3JCP = 52 Hz, ipso-Ph), 132.6 (d, 3JCP = 11 Hz, o-Ph), 130.4 (d, 3JCP = 3 Hz, p-Ph), 127.9 (d, 3JCP = 11 Hz, m-Ph), 81.5 (d, 3JCP = 55 Hz, C4H4), 73.7 (d, 3JCP = 14 Hz, C4H4), 73.3 (d, 3JCP = 10 Hz, C4H4), 70.9 (d, 3JCP = 8 Hz, C4H4), 70.6 (d, 3JCP = 9 Hz, C4H4), 70.3 (s, FeC5H5). Anal. Calcd. for C30H32Fe3O4P: C, 55.77%; H, 3.60%. Found: C, 55.81%; H, 3.59%. These values agree with previously published data [11].

4.11. X-ray crystallography

X-ray quality crystals of compound 3 were grown by slow diffusion of hexane into a saturated CH2Cl2 solution. Programs for diffractometer operation, data collection, cell indexing, data reduction and absorption correction were those supplied by Bruker AXS Inc., Madison, WI. Diffraction measurements were made on a PLATiFORM diffractometer/SMART 1000 CCD using graphite-monochromated Mo-Kα radiation at −80 °C. Unit cells were determined from randomly selected reflections obtained using the SMART CCD automatic search, centre, index and least-squares routines. Integration was carried out using the program SAINT and an absorption correction was performed using SADABS. Structure solution was carried out using the SHELX [19] suite of programs and the Olex2 graphical interface [20]. The initial solution was obtained using intrinsic phasing and refined by successive least-squares cycles. All non-hydrogen atoms were refined anisotropically.
Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

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References