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

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ABSTRACT

Abstraction of chloride from $[Fe(CO)_4(PPh_2Cl)]$ (**1**) in the presence of PPh_3 leads to $[Fe(CO)_4(PPh_2(PPh_3))][AlCl_4]$ (**2**), an iron complex of a phosphine-coordinated phosphenium ion. The PPh_3 is readily displaced by ferrocene, leading to an electrophilic aromatic substitution reaction, and formation of $[Fe(CO)_4\{PPh_2Fc\}]$ (**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 $[Fe(CO)_4(PPhCl_2)]$ in the presence of ferrocene leads to a double substitution reaction, forming $[Fe(CO)_4\{PPhFc_2\}]$ (**13**).

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-phosphenium coordination [5], which quenches electrophilicity. These metal-coordinated phosphenium ions have been shown to undergo rapid reaction at room temperature with organic substrates, including arenes, 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 phosphine 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 electrophillicy toward P-C bond formation remains mostly unexplored for iron phosphenium 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

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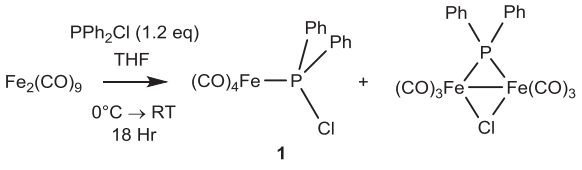
in iron-bound phosphenium ions [8b]. However, Friedel-Crafts like electrophilic aromatic substitution reactions have not been explored. For this study, we have chosen the $Fe(CO)_4$ fragment due to the simplicity of preparation of the precursor chlorophosphine complex, and because the π-acidity of the metal carbonyls lowers metal electron density, potentially enhancing electrophilicity at P.

2. Results and discussion

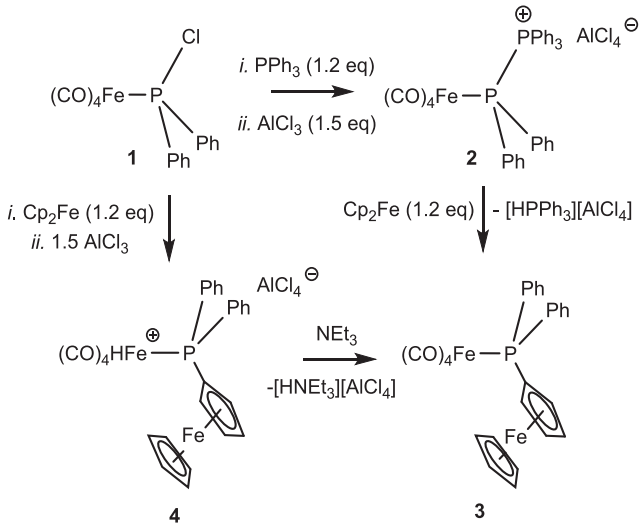
Coordination of chlorodiphenylphosphine to the $Fe(CO)_4$ fragment was carried out using a modification of a literature procedure, using the reactive iron carbonyl dimer $Fe_2(CO)_9$. Chlorodiphenylphosphine was added at 0 °C to an unstirred THF/$Fe_2(CO)_9$ mixture. The solution was then stirred slowly and allowed to warm to room temperature. Without cooling, or with stirring prior to phosphine addition, the nearly insoluble $Fe_2(CO)_9$ immediately forms deep green $Fe_3(CO)_{12}$, presumably from the reaction of 3 [$Fe(CO)_4$(THF)] fragments. After implementing this change, the desired phosphine complex was obtained in 69% yield (Scheme 1). The known bridging phosphido complex [$Fe_2(CO)_6$(μ-Cl)(μ-PPh_2)] [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 $^{31}P\{^1H\}$ 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 $AlCl_3$ leads to phosphenium ion complexes, while chloride abstraction with $AgOSO_2CF_3$ (AgOTf) leads to phosphine triflate complexes, which are effective surrogates for phosphenium ion complexes. Treatment of [$Fe(CO)_4(PPh_2Cl)$] (**1**) with $AlCl_3$ or $GaCl_3$ resulted in decomposition, at room temperature or at −30 °C, with notable gas evolution, most likely from carbonyl loss. This suggests that the iron phosphenium 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 phosphenium ion and phosphine triflate complexes were apparently unstable, attempts were made to trap transient phosphenium ions. Phosphine coordination has been shown to be an effective means of trapping free and metal-coordinated phosphenium ions [5,6g,10]. Chloride abstraction from **1** with $AlCl_3$ in the presence of PPh_3 resulted in the formation of [$Fe(CO)_4(PPh_2(PPh_3))$] [$AlCl_4$] (**2**), the PPh_3 adduct of the targeted phosphenium ion complex (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets at δ^P 93.0 and 8.5, with a $^1J_{PP}$ of 207 Hz (Fig. 1). The resonance at δ^P 8.5 is assigned to coordinated PPh_3, while the resonance at δ^P 93.0 is consistent with a base-coordinated phosphenium ion. The large *J* value also indicates formation of a direct P-P bond. For comparison, the analogous metal free $Ph_3P\rightarrow PPh_2^+$ cation has chemical shift values of δ^P 15 (PPh_3) and −10 (PPh_2), and a $^1J_{PP}$ of 340 Hz [5a]. The lower frequency of the PPh_3 resonance and smaller coupling constant in the $Fe(CO)_4$ complex may indicate a weaker P-P bond compared to the metal-free adduct, and suggest that the PPh_3 may be easily displaced. The ^{13}C NMR spectrum of **2** shows a doublet of doublets at δ^C 211.7 ($^2J_{CP}$ = 11 Hz, $^3J_{CP}$ = 2 Hz), confirming that the phosphine-coordinated phosphenium ion remains coordinated to the $Fe(CO)_4$ unit.



Scheme 1. Synthesis of [$Fe(CO)_4(PPh_2Cl)$] (**1**).



Scheme 2. Trapping reactions of an iron diphenylphosphenium complex.

Addition of ferrocene to a solution of **2** resulted in the formation of two major products with $^{31}P\{^1H\}$ NMR chemical shifts of δ^P 67.3 and 5.0 (Scheme 2). The resonance at δ^P 67.3 was assigned to [$Fe(CO)_4\{PPh_2(Fc)\}$] (**3**), the product of electrophilic aromatic substitution of the $Fe(CO)_4$ coordinated phosphenium ion onto ferrocene. This is a known compound and has previously been synthesized by reaction of the free ferrocenyldiphenylphosphine ligand with $Fe_3(CO)_{12}$ [11]. The resonance at δ^P 5.0 is consistent with a protonated phosphine, and the proton coupled ^{31}P NMR spectrum shows the resonance splitting into a doublet of $^1J_{PH}$ = 504 Hz, allowing us to assign this resonance to [$HPPh_3$][$AlCl_4$], which is generated from the acid by-product of electrophilic substitution. This reaction demonstrates that the triphenylphosphine is indeed readily displaced and that the $Fe(CO)_4$-bound phosphenium ion is capable of undergoing electrophilic substitution reactions as desired. Although this method produces the desired substitution product, the isolated yield of **3** is low (28%) and multiple side products with ^{31}P chemical shifts of δ^P 83-81, 12-5, −10 to −15 are observed. These compounds most likely arise from substitution reactions of PPh_3 onto the iron complex. These $^{31}P\{^1H\}$ NMR ranges correspond to disubstituted phosphine iron complexes [12], protonated free phosphines [13], and triaryl free phosphines, respectively.

We next examined the direct trapping of the phosphenium ion with the organic substrate by adding ferrocene to a solution of compound **1** prior to chloride abstraction with $AlCl_3$ (Scheme 2). The resulting solution contained the expected product **3** (20%) and an unknown product **4** with a ^{31}P chemical shift of δ^P 44 (80%). The ^1H NMR spectrum of **4** reveals the presence of a metal hydride, with the chemical shift of δ^H −7.73 and $^2J_{HP}$ = 41 Hz, allowing us to identify it as [$Fe(CO)_4H\{PPh_2(Fc)\}$][$AlCl_4$] (**4**), the protonated form of **3**. Addition of triethylamine to the solution, or column chromatography on alumina results in conversion of **4** to **3** and compound **3** can then be isolated in 73% yield. If the acid is not quenched, **4** decomposes in solution. Protonation of monosubstituted triaryl phosphine iron carbonyl complexes increases carbonyl lability and the protonated complexes decompose rapidly [14]. Compound **3** has been characterized by X-ray crystallography. An ORTEP diagram showing the molecular structure is given in Fig. 2. The structure

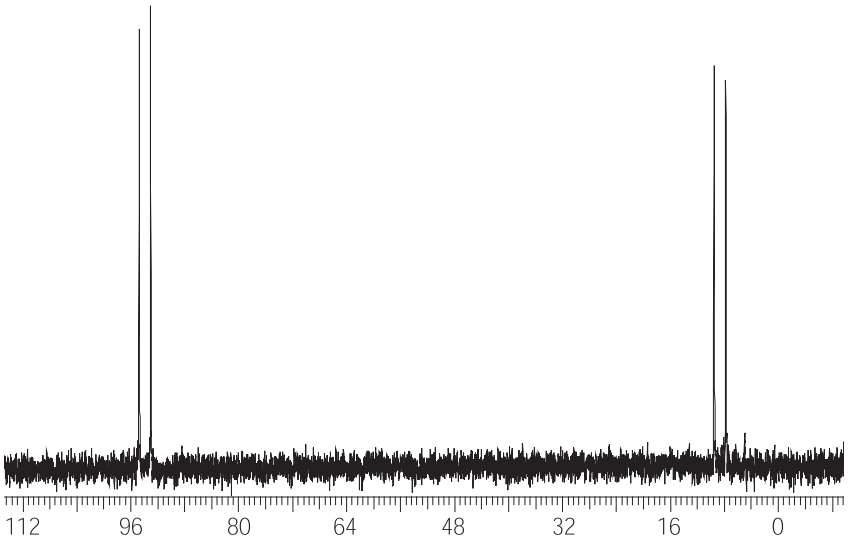


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of $[Fe(CO)_4(PPh_2(PPh_3))][AlCl_4]$ (**2**).

consists of a trigonal bipryamidal $Fe(CO)_4L$ 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 $AlCl_3$, leading to the formation of $[Fe(CO)_4\{PPh_2(C_6H_4NEt_2)\}]$ (**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 ^{31}P NMR chemical shift for **5** of δ^P 68.6 is consistent with those of other $Fe(CO)_4$-triarylphosphine complexes [15]. The ^{13}C NMR spectrum shows four resonances that can be assigned to the anilinyl ring and the ^{1}H 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 phosphenium ion. This contrasts with the chemistry of the tungsten system, where the lifetime of the phosphenium ion is long enough for multi-hour reactions [4b].

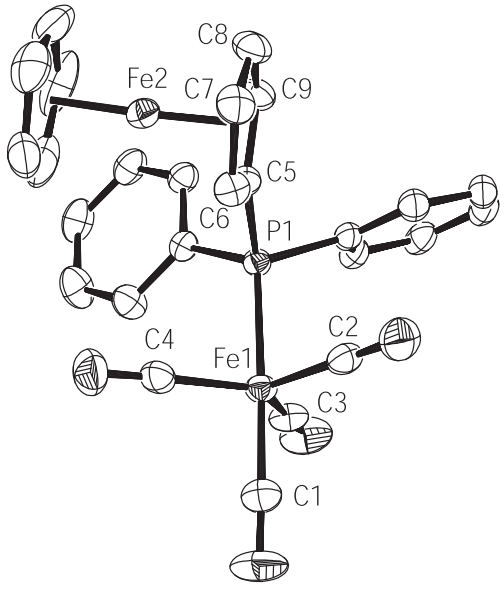
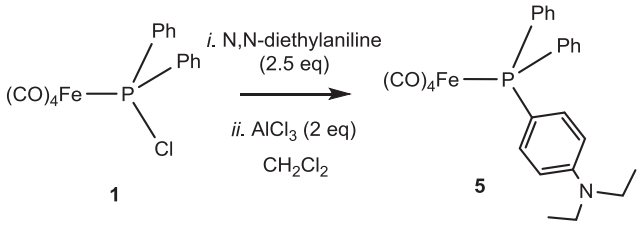


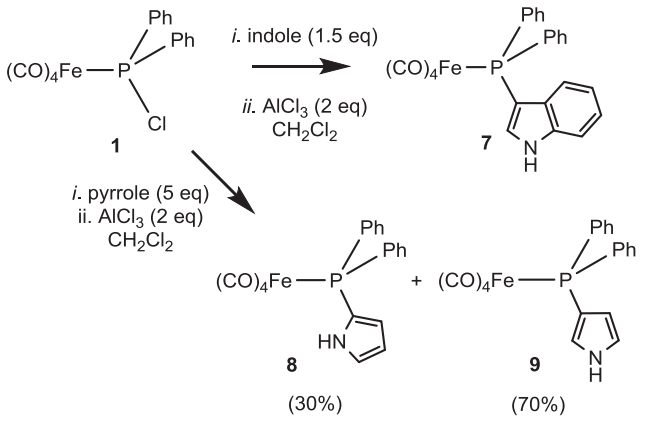
Fig. 2. ORTEP diagram showing the X-ray crystal structure of compound **3**. H atoms have been omitted, and thermal elliposoids are shown at the 50% level. Selected distances (Å) and angles (°): Fe1-P1 = 2.2452(5), P1-C5 = 1.807(2), Fe1-C1 = 1.788(2), Fe1-C2 = 1.793(2), Fe1-C3 = 1.792(2), Fe1-C4 = 1.788(2); Fe1-P1-C5 = 114.23(6), P1-Fe1-C1 = 175.59(7), P1-Fe1-C2 = 89.32(6), P1-Fe1-C3 = 87.02(6), P1-Fe1-C4 = 89.96(6), C2-Fe1-C3 = 117.0(1), C2-Fe1 C4 = 115.90(9), C3-Fe1-C4 = 127.0(1).

We next examined reactions of the iron phosphenium ion complex with heteroaromatics. Treatment of compound **1** with $AlCl_3$ and indole led to two products **6** and **7** in a 1:2 ratio, with ^{31}P chemical shifts of δ^P 27 and 51.9, respectively. Addition of a half equivalent of NEt_3 or filtration through alumina resulted in conversion of the minor product (δ^P 27) into the major product (δ^P 51.9), allowing us to identify these products as the protonated substitution product $[Fe(CO)_4H\{PPh_2(C_8H_5NH)\}][AlCl_4]$ (**6**) and neutral substitution product $[Fe(CO)_4\{PPh_2(C_8H_5NH)\}]$ (**7**), paralleling 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 C^3 as expected [16]. This substitution position is evident from the ^{13}C NMR spectrum, in which the C^3 carbons (δ^C 106.9) shows a $^{1}J_{CP}$ of 68 Hz, indicating a direct bond to P.

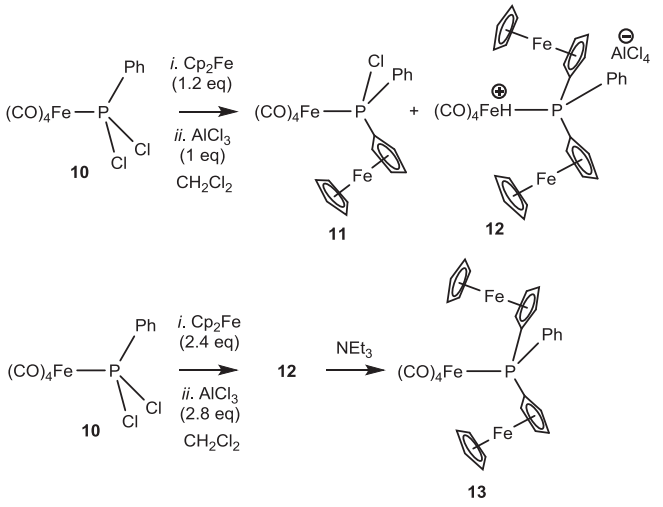
The reaction of the iron phosphenium ion complex with pyrrole led to two products **8** and **9**, with ^{31}P NMR resonances at δ^P 52.6 and



Scheme 3. Electrophilic aromatic substitution with N,N-diethylaniline.



Scheme 4. Electrophilic aromatic substitution of heteroaromatics.



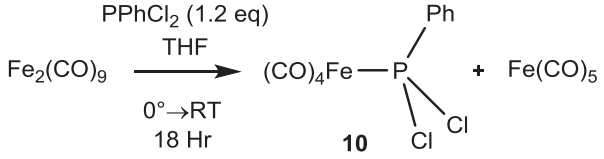
Scheme 6. Disubstitution at $Fe(CO)_4$ coordinated dichlorophenylphosphine.

51, in a 30:70 ratio (Scheme 4). These chemical shifts are consistent with substitution in the C^2 and C^3 positions of the pyrrole ring, as was previously observed in the tungsten system [4b]. In solution or during purification, compound **9** (δ^P 51) quickly decomposes, while compound **8** (δ^P 52.6) is significantly more stable. Characterization of the stable compound **8** reveals it to be the C^2 substituted isomer $[Fe(CO)_4\{PPh_2(2\text{-}C_4H_3NH)\}]$ (**8**). The key spectroscopic features that reveals the substitution position are the P-substituted pyrrole carbon, which appears at δ^C 121.0 ($^1J_{PC} = 65$ Hz), and the adjacent C^3 carbon, which appears at 120.7 ($^2J_{PC} = 10$ Hz). For C^3 substituted pyrryl phosphines, C^2 appears in the range of δ^C 125–130 and C^3 appears in the range of δ^C 115–120 [4b]. Although the only isolated product is C^2 substituted, the reaction unexpectedly favors C^3 substitution in a 70:30 ratio. Electrophilic substitution reactions of pyrrole normally favor C^2 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, benzophenone and acetanilide were attempted. However, with all of these substrates, the added $AlCl_3$ reacted preferentially with the organic substrate rather than with the iron chlorophosphine complex. Addition of excess $AlCl_3$ led to decomposition. This reactivity contrasts with the chemistry of the tungsten system, where thiophene, anisole, and diphenylamine can be successfully added to the metal coordinated phosphine [4b].

In order to pursue multiple P-C bond forming reactions at one P centre, the dichlorophosphine complex $[Fe(CO)_4(PPhCl_2)]$ (**10**) [17] was synthesized using the same method adapted for the synthesis of **1** (Scheme 5). As with the monochlorophosphine complex **1**, attempts to abstract chloride from **10** with $AlCl_3$ or AgOTf led to decomposition and we were unable to observe any experimental evidence for phosphenium ion or phosphine triflate complexes. This again contrasts with the chemistry of the tungsten system, where the chlorophenylphosphenium and chlorophenyl phosphine triflate complexes have significant lifetimes in solution [4a].

Generation of the iron phosphenium ion in situ with $AlCl_3$ in the presence of 1 equivalent ferrocene led to electrophilic aromatic substitution to form ferrocenyl phosphines. However, this reaction



Scheme 5. Synthesis of $[Fe(CO)_4(PPhCl_2)]$ (**10**).

was not selective, leading to a mixture of the monosubstituted product $[Fe(CO)_4(PPhClFc)]$ (**11**) and the protonated disubtituted complex $[Fe(CO)_4H(PPhFc_2)][AlCl_4]$ (**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 NEt_3, yielding the desired product $[Fe(CO)_4(PPhFc_2)]$ (**13**) (Scheme 6). The crystalline dark orange product was very stable and has a ^{31}P chemical shift at δ^P 58.0. Compound **13** was previously synthesized by reaction of $Fe_2(CO)_9$ with $PPh(C_{10}H_9Fe)_2$ [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 $AlCl_3$ all resulted in no change by $^{31}P\{^1H\}$ NMR, likely a result of preferential interaction between the substrate and $AlCl_3$, as previously discussed. Increasing the concentration of the Lewis acid did result in chemical shift changes to ranges indicative of monosubstitution (δ^P 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 phosphenium intermediate. The electron withdrawing chloro group destabilizes the cationic phosphenium ion complex, making chloride abstraction to form it less favorable. As a result, $AlCl_3$ reacts preferentially with most substrates rather than extracting chloride from the metal-coordinated phosphine. The greater difficulty of abstracting chloride from $[Fe(CO)_4(PPhCl_2)]$ (**10**) compared to the tungsten analog [4a] may indicate that the iron phosphenium ion complex is in fact more electrophilic than the tungsten phosphenium 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 phosphenium ion complexes stem not from the 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, labilizing the carbonyls [6d,6e].

3. Conclusions

We have demonstrated that $Fe(CO)_4$ bound phosphenium ions, generated in situ using chloride abstraction, are reactive toward

electrophilic aromatic substitution. However, when compared to the established tungsten system, the $Fe(CO)_4$ methodology is severely limited by the instability of the phosphenium ion complex. Generation of the phosphenium 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 phosphenium 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 phosphenium 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. CH_2Cl_2 and $CDCl_3$ were purified by trap-to-trap vacuum distillation from P_2O_5. 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 (^{1}H), 121.514 MHz (^{31}P), 75.488 MHz (^{13}C) or on a Varian Inova 500 spectrometer at 125.624 MHz (^{13}C) in $CDCl_3$ or CD_2Cl_2. The ^{31}P NMR chemical shifts were validated using an external standard of triphenyl phosphate (0.0485 M, $CHCl_3$, δ −17.3). IR spectra were recorded on a Digilab FTIR in CH_2Cl_2 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 Sciences Centre using a JEOL JMS-T100GCv AccuTOF-GCv4G Mass Spectrometer in field desorption ionization mode.

4.2. Synthesis of $[Fe(CO)_4(PPh_2Cl)]$ (**1**)

This procedure is a modified version of a published procedure [18], which was modified to reduce the formation of $Fe_3(CO)_{12}$. $Fe_2(CO)_9$ (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. PPh_2Cl (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 (νCO, CH_2Cl_2, cm^{-1}): 2059(m), 1989(w), 1953(s). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): 161.0 (t, $^3J_{PH}$ = 14 Hz). ^{1}H NMR (300 MHz, $CDCl_3$): 7.92–7.69 (m, 4H), 7.65–7.43 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 212.0 (d, $^2J_{CP}$ = 19 Hz, CO), 137.9 (d, $^2J_{CP}$ = 43 Hz, *ipso*-Ph), 132.3 (s, *p*-Ph), 131.7 (d, $^2J_{CP}$ = 15 Hz, *o*-Ph), 129.0 (d, $^3J_{CP}$ = 13 Hz, *m*-Ph). These values match previously published data [18].

4.3. Synthesis of $[Fe(CO)_4(PPh_2(PPh_3))][AlCl_4]$ (**2**)

A solution of $[Fe(CO)_4(PPh_2Cl)]$ (**1**) (150 mg, 0.386 mmol) and PPh_3 (121 mg, 0.461 mmol) in CH_2Cl_2 (3 mL) was added to $AlCl_3$ (77 mg, 0.58 mmol), resulting in an immediate colour change to red. The reaction was also carried out in $CDCl_3$ or CD_2Cl_2 to record NMR spectra. Attempts to isolate compound **2** as a solid resulted in decomposition to a mixture products. IR (νCO, CH_2Cl_2, cm^{-1}): 2057 (s), 1986(w), 1953(sh), 1942(s). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): 93.0 (d, $^1J_{PP}$ = 207 Hz), 8.5 (d, $^1J_{PP}$ = 207 Hz). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): 211.7 (dd, $^2J_{CP}$ = 11 Hz, $^3J_{CP}$ = 2 Hz, FeCO), 136.5 (d, $^4J_{CP}$ = 3 Hz, *p*-PPh_3), 136.4 (d, $^4J_{CP}$ = 3 Hz, *p*-PPh_2), 135.6 (d, $^1J_{CP}$ = 21 Hz, *ipso*-PPh_3), 135.1 (d, $^2J_{CP}$ = 9 Hz, *o*-PPh_3), 134.5 (dd, $^2J_{CP}$ = 12 Hz, $^3J_{CP}$ = 3 Hz, *o*-PPh_2), 134.3 (d, $^2J_{CP}$ = 12 Hz, *o*-PPh_2), 133.2 (dd, $^1J_{CP}$ = 53 Hz, $^2J_{CP}$ = 11 Hz, *ipso*-PPh_2), 131.1 (d, $^3J_{CP}$ = 14 Hz, *m*-PPh_2), 131.0 (d, $^3J_{CP}$ = 12 Hz, *m*-PPh_3), 130.3 (dd, $^3J_{CP}$ = 12 Hz, $^4J_{CP}$ = 2 Hz, *m*-PPh_2).

4.4. Reaction of $[Fe(CO)_4(PPh_2(PPh_3))][AlCl_4]$ (**2**) with ferrocene

A solution of **2** (0.21 mmol) was generated by dissolving **1** (80 mg, 0.21 mmol), PPh_3 (65 mg, 0.25 mmol) and $AlCl_3$ (36 mg, 0.27 mmol) in CH_2Cl_2 (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 $[Fe(CO)_4(PPh_2Fc)]$ (**3**). Yield: 31 mg, 28%. See section 4.5 for characterization of **3**.

4.5. Synthesis of $[Fe(CO)_4(PPh_2Fc)]$ (**3**)

A solution of $[Fe(CO)_4(PPh_2Cl)]$ (**1**) (150 mg, 0.386 mmol) and ferrocene (115 mg, 0.618 mmol) in CH_2Cl_2 (~3 mL) was added to $AlCl_3$ (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 (νCO, CH_2Cl_2, cm^{-1}): 2048(m), 1971(w), 1935(s). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): 67.3. ^{1}H NMR (300 MHz, $CDCl_3$): 7.62–7.43 (m, 10H, Ph), 4.55 (m, 4H, C_5H_4P), 3.81 (s, 5H, FeC_5H_5). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 213.6 (d $^2J_{CP}$ = 19 Hz, CO), 138.0 (d, $^1J_{CP}$ = 52 Hz, *ipso*-Ph), 132.8 (d, $^2J_{CP}$ = 10 Hz, *o*-Ph), 130.6 (d, $^4J_{CP}$ = 3 Hz, *p*-Ph), 128.4 (d, $^3J_{CP}$ = 11 Hz, *m*-Ph), 76.6 (d, $^1J_{CP}$ = 55 Hz, C_5H_4P), 75.1 (d, $^2J_{CP}$ = 12 Hz, C_5H_4P), 71.8 (d, $^3J_{CP}$ = 9 Hz, C_5H_4P), 70.1 (s, FeC_5H_5). Anal. Calcd. for $C_{26}H_{19}O_4Fe_2P$: C, 58.02%, H, 3.57%. Found: C%, 57.86 H%, 3.65. These values match previously published data [11].

4.6. Synthesis of $[Fe(CO)_4\{PPh_2(C_6H_4NEt_2)\}]$ (**5**)

$[Fe(CO)_4(PPh_2Cl)]$ (**1**) (150 mg, 0.386 mmol) was dissolved in CH_2Cl_2 (6 mL). N,N-diethylaniline (155 μL, 144 mg, 0.967 mmol) was added and the resulting solution was added to $AlCl_3$ (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 CH_2Cl_2/pentane solution at −30 °C. Yield: 95 mg, 49%. IR (νCO, CH_2Cl_2, cm^{-1}): 2046(m), 1969(w), 1935(s). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): 68.6. ^1H NMR (300 MHz, $CDCl_3$): 7.55–7.32 (m, 12H), 6.69 (d, 2H, $^3J_{HH} = 9.9$ Hz), 3.39 (q, 4H, $^3J_{HH} = 7.4$ Hz, CH_2), 1.19 (t, 6 H, $^3J_{HH} = 7.4$ Hz, -CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 214.1 (d, $^2J_{CP} = 19$ Hz, CO), 149.6 (d, $^4J_{CP} = 2$ Hz, C_6H_4), 136.0 (d, $^1J_{CP} = 50$ Hz, *ipso*-Ph), 135.4 (d, $^3J_{CP} = 12$ Hz, C_6H_4), 133.1 (d, $^2J_{CP} = 11$ Hz, *o*-Ph), 130.6 (d, $^4J_{CP} = 3$ Hz, *p*-Ph), 128.6 (d, $^3J_{CP} = 11$ Hz, *m*-Ph), 115.9 (d, $^1J_{CP} = 58$ Hz, C_6H_4), 111.1 (d, $^2J_{CP} = 12$ Hz, C_6H_4), 44.5 (s, CH_2), 12.7 (s, CH_3). Anal. Calcd. for $C_{26}H_{24}O_4NPFe$: C, 62.30%; H, 4.83%; N, 2.79%. Found: C, 62.27%; H, 4.83%; N, 2.78%.

4.7. Synthesis of [Fe(CO)$_4${PPh$_2$(C$_8$H$_5$NH)}] (**7**)

[$Fe(CO)_4(PPh_2Cl)$] (**1**) (128 mg, 0.329 mmol) and indole (96 mg, 0.83 mmol) were dissolved in CH_2Cl_2 (~2 mL), added to $AlCl_3$ (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 reduce pressure, and the residue was purified by column chromatography (alumina, 50:50 diethyl ether: petroleum ether ramped to 100:0). Evaporation of the solvent from the collected fractions yielded a beige powder, which was recrystallized from toluene at −30 °C, and washed with pentane. Yield: 48 mg, 31%. IR (*ν*CO, CH_2Cl_2, cm^{-1}): 2047(m), 1970(w), 1936(s). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): 51.9. ^1H NMR (300 MHz, $CDCl_3$): 8.65 (m, 1H, N*H*), 7.61 (m, 6H, Ph), 7.42 (m, 7H, Ph), 7.01 (m, 2H, Ph, indole H^2). ^{13}C NMR (75 MHz, $CDCl_3$): 214.1 (d, $^2J_{CP} = 20$ Hz, CO), 137.8 (d, $^4J_{CP} = 8$ Hz, C^{7a}), 136.1 (d, $^2J_{CP} = 26$ Hz, C^2), 135.3 (d, $^1J_{CP} = 51$ Hz, *ipso*-Ph), 132.6 (d, $^2J_{CP} = 11.6$ Hz, *o*-Ph), 130.8 (d, $^4J_{CP} = 2$ Hz, *p*-Ph), 128.8 (d, $^3J_{CP} = 11$ Hz, *m*-Ph), 128.2 (d, $^2J_{CP} = 4$ Hz, C^{3a}), 123.5 (s, C^5), 121.7 (s, C^6), 121.6 (s, C^4), 112.1 (s, C^7), 106.9 (d, $^1J_{CP} = 68$ Hz, C^3). High-res MS (FD ionization) calcd. for $C_{24}H_{16}O_4NPFe$: 467.0246 (6.3%), 469.01665 (100%), 470.02001 (26%), 471.02336 (3.2%) [M^+]. Found: 467.0208(6.5%), 469.0106(100%), 470.0192(28.8%), 471.0214(5.9%) [M^+].

4.8. Synthesis of [Fe(CO)$_4${PPh$_2$(2-C$_4$H$_3$NH)}] (**8**)

Pyrrole (89 μL, 86 mg, 1.3 mmol) was added to a solution of [$Fe(CO)_4(PPh_2Cl)$] (**1**) (100 mg, 0.257 mmol) in CH_2Cl_2 (3 mL). This solution was added to $AlCl_3$ (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). Yield: 28 mg, 26%. IR (*ν*CO, CH_2Cl_2, cm^{-1}): 2046(m), 1969(w), 1939(s). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): 52.6. ^1H NMR (300 Hz, $CDCl_3$): 8.63 (bs, 1H, N*H*), 7.56–7.39 (m, 10H, Ph), 7.14 (m, 1H, C_4H_3NH), 6.49 (m, 1H, C_4H_3NH), 6.38 (m, 1H, C_4H_3NH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 213.2 (d, $^2J_{CP} = 19$ Hz, CO), 135.0 (d, $^1J_{CP} = 54$ Hz, *ipso*-Ph), 132.6 (d, $^2J_{CP} = 11$ Hz, *o*-Ph), 131.1 (d, $^4J_{CP} = 3$ Hz, *p*-Ph), 128.9 (d, $^3J_{CP} = 11$ Hz, *m*-Ph), 124.7 (d, $^4J_{CP} = 7$ Hz, C_4H_3NH), 121.0 (d, $^1J_{CP} = 65$ Hz, *ipso*-C_4H_3NH), 120.7 (d, $^2J_{CP} = 10$ Hz, C_4H_3NH), 111.8 (d, $^2J_{CP} = 9$ Hz, C_4H_3NH). Anal. Calcd. for $C_{20}H_{24}O_4NPFe$: C, 57.31%; H, 3.37%; N, 3.34%. Found: C, 57.13%; H, 3.46%; N, 3.39%.

4.9. Synthesis of [Fe(CO)$_4$(PPhCl$_2$)] (**10**)

Fe_2CO_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. $PPhCl_2$ (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 evacuated to yield orange crystals. Yield: 0.678 g, 71%. IR (*ν*CO, CH_2Cl_2, cm^{-1}): 2070(m), 2005(w), 1977(s), 1966(s). ^{31}P NMR (121 Hz, $CDCl_3$): 207.9 (t, $^3J_{HP} = 18$ Hz). ^1H NMR (300 Hz, $CDCl_3$): 8.10 (m, 2H, Ph), 7.61 (m, 3H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 210.9 (d, $^2J_{CP} = 17$ Hz, CO), 141.8 (d, $^1J_{CP} = 39$ Hz, *ipso*-Ph), 133.7 (s, *p*-Ph), 130.1 (d, $^3J_{CP} = 17$ Hz, *m*-Ph), 129.2 (d, $^2J_{CP} = 14$ Hz, *o*-Ph). These values match previously published data [17c].

4.10. Synthesis of [Fe(CO)$_4$(PPhFc$_2$)] (**12**)

[$Fe(CO)_4(PPhCl_2)$] (**10**) (150 mg, 0.432 mmol) and ferrocene (193 mg, 1.04 mmol) were dissolved in CH_2Cl_2 (~2 mL). The orange solution was then added to $AlCl_3$ (161 mg, 1.21 mmol) and mixed for 5 min, resulting in a colour change to deep red. Triethylamine (120 μL, 0.864 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 CH_2Cl_2/pentane solution at −30 °C to produce of bright orange needle-like crystals. Yield: 196 mg, 70%. IR (*ν*CO, CH_2Cl_2, cm^{-1}): 2047(m), 1968(w), 1934(s). $^{31}P\{^1H\}$ NMR (121 Hz, $CDCl_3$): 58.0. ^1H NMR (300 Hz, $CDCl_3$): 8.01 (m, 3H, Ph), 7.45 (m, 2H, Ph), 4.60 (m, 2H, FeC_5H_4), 4.48 (m, 6H, FeC_5H_5), 3.99 (s, 10H, FeC_5H_5). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 214.4 (d, $^2J_{CP} = 18$ Hz, CO), 138.1 (d, $^1J_{CP} = 52$ Hz, *ipso*-Ph), 132.6 (d, $^2J_{CP} = 11$ Hz, *o*-Ph), 130.4 (d, $^4J_{CP} = 3$ Hz, *p*-Ph), 127.9 (d, $^3J_{CP} = 11$ Hz, *m*-Ph), 81.5 (d, $^1J_{CP} = 55$ Hz, C_5H_4Fe), 74.0 (d, $^2J_{CP} = 14$ Hz, C_5H_4Fe), 73.8 (d, $^3J_{CP} = 10$ Hz, C_5H_4Fe), 70.9 (d, $^3J_{CP} = 8$ Hz, C_5H_4Fe), 70.6 (d, $^2J_{CP} = 9$ Hz, C_5H_4Fe), 70.3 (s, FeC_5H_5). Anal. Calcd. for $C_{30}H_{23}Fe_3O_4P$: 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 crystalography

X-ray quality crystals of compound **3** were grown by slow diffusion of hexane into a saturated CH_2Cl_2 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 PLATFORM 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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.10.027.

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