Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Iron catalysed Negishi cross-coupling using simple ethyl-monophosphines

Caleb A. Brown,[a] Terence A. Nile,[b] Mary F. Mahon[a] and Ruth L. Webster[a*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

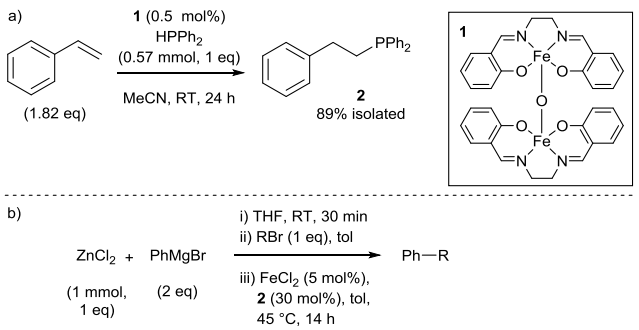
DOI: 10.1039/b000000x

Monophosphines prepared by iron catalysed hydrophosphination have been used as pro-ligands in iron catalysed Negishi cross-coupling of alkyl bromides and diphenyl zinc reagents. The cross-coupling has been investigated with monophosphines with varying electronic properties and we find the simplest, unsubstituted phosphine to offer the optimum reaction conditions (both in terms of yield of diarylmethane product and cost-effectiveness of the phosphine). *In situ* catalyst generation from monophosphine and $FeCl_2$ was used in catalysis; however, preparation of a discrete homonuclear iron complex was also achieved and this four-coordinate iron-phosphine complex was isolated and used in catalysis.

Introduction

Catalysis with first row transition metals (FRTMs) is currently undergoing a period of intense activity, with many elegant transformations being directed towards the synthesis of small organic molecules.[1] Justifiably the reasons for this attention rest with the acute need to harness these inexpensive, environmentally benign and non-toxic metals with a growing global focus on sustainable green synthetic protocols. Catalytic C–C bond forming reactions with the FRTMs is crucial, for example, the desire to generate high value products by replacing transformations traditionally carried out by the Platinum Group Metals (PGMs) is a key target, however, tuning a FRTM catalyst to undertake a two-electron process rather than the more favourable one-electron transformation is a challenge. Traditional PGM cross-couplings are used on an industrial scale and as a result, their mechanistic details are generally well-understood, in contrast mechanistic understanding of FRTM catalysis is exacting, not least because reactions with metals such as iron invariably proceed with paramagnetic pre-catalysts or paramagnetic reactive intermediates. However, the FRTMs often undertake catalysis complimentary to that of the PGMs. A classic example is iron catalysed cross-coupling of organometallic reagents and alkyl halides:[2] alkyl halides containing halogen-substituted aromatic rings are also tolerated by iron catalysts whereas the palladium catalysed reaction is likely to lead to competitive aryl-aryl bond forming reactions.[3]

We have recently demonstrated the synthetic utility of an Fe(III) salen complex (**1**) in the hydrophosphination (HP) of styrenes (Scheme 1a).[4] During these studies we proved that the ethyl-monophosphine product (**2**) is a useful pro-ligand for iron-catalysed Negishi cross-coupling (Scheme 1b). To our surprise, although the synthesis of ethyl-monophosphines is routinely used as a synthetic benchmark in TM catalysed HP chemistry,[5] to the best of our knowledge, we are the first to develop a synthetic application for these phosphines. On top of this, the iron catalysed Negishi cross-coupling of aryl zinc reagents and benzyl bromides often relies on the use of diphosphines:[2i] although these are commercially available, many such as dpbz are prohibitively expensive and have limitations in terms of steric and electronic variability. Elegant advances have been made with more simple diphosphines,[2r,6] but reports of iron catalysed Negishi cross-coupling with monophosphines is limited and, given the principal rationale for developing iron catalysis is often based on cost effectiveness, we envisaged that use of an inexpensive phosphine ligand would enhance the field. We herein report the extended scope of this synthetic methodology using simple monophosphines.



Scheme 1. a) We have previously demonstrated that a simple, air-stable Fe (III) complex (**1**) can catalyse the hydrophosphination of styrenes; b) preliminary results showing phosphine **2** can be employed as a ligand for Fe-catalysed Negishi cross-coupling.

Results and discussion

Tertiary phosphine **2** was prepared on a large scale using the HP techniques developed in our laboratory. In our hands, we find this to be the most convenient, reproducible and cleanest route to this class of phosphine. Attempted S_N2 reaction of $HPPh_2$ with (2-bromoethyl)benzene in the absence and presence of base[7] often led

to low yield of product and/or complex mixtures. Using controlled drop-wise addition, varying the order of addition, using low temperatures and/or reducing reactions times did not reduce the complexity of the product mixture. Use of a stoichiometric amount of LiHMDS, $HPPh_2$ and (2-bromoethyl)benzene was effective giving 72% of **2** after 4 h at RT, however, the need for a stoichiometric organometallic reagent, which results in a stoichiometric amount of waste by-product, is somewhat less attractive. Our HP route led to high isolated yield of product on a large scale (90%; 4.8 mmol diphenylphosphine and 6.7 mmol styrene) and the catalyst loading could be further lowered from 0.5 mol% to 0.2 mol% with the reaction still being carried out at RT. Increasing the scale of the reaction is also beneficial in removing a minor impurity observed to co-elute with **2**.[8]

Following the optimised synthesis of **2**, we decided to explore the potential of other phosphines to facilitate this transformation. Three additional phosphines (**3** to **5**) with variable electronic properties were prepared using the Fe-catalysed HP methodology with little deviation in yield (Figure 1).

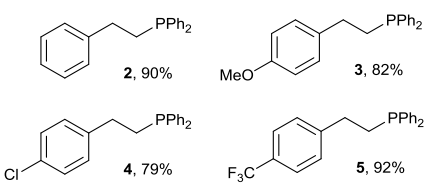
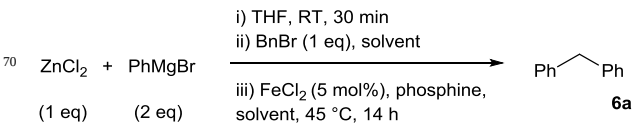


Fig. 1. Phosphines prepared using HP catalysed by **1** for use in Fe-catalysed Negishi cross-coupling. HP carried out on a 4.8 mmol $HPPh_2$ scale.

Using the coupling of diphenyl zinc (prepared by the transmetallation of phenylmagnesium bromide with zinc chloride) and benzyl bromide as our standard Negishi reaction we first investigated the effect of solvent. *In situ* catalyst preparation was also used in the first instance. Similar to other reports in the literature, use of THF as the principal solvent is deleterious to reactivity,[2d] giving only 18% diphenylmethane product (**6a**, Table 1, Entry 1). Pre-reduction, whereby $FeCl_2$ and the phosphine are first added to the $ZnCl_2$ solution followed by PhMgBr, with benzyl bromide added last, further lowers the yield of **6a** to 8% (Entry 2). In our preliminary report,[5] toluene was used as the solvent of choice and an unoptimised loading of 30 mol% **2**, it is clear that toluene is best suited for this reaction based on these results and other reports in the area.[2d,i,q] The use of 30 mol% phosphine also proves to be fundamental to the formation of **6a**: the spectroscopic yield of **6a** drops to 49% when the ligand loading is halved to 15 mol% (compare Entries 3 and 5). A mercury drop test demonstrates that the reaction mixture is not heterogenous in nature, with only a minor reduction in yield being observed (Entry 4).[9] With optimised solvent conditions in hand we note that the electronic properties of the phosphine also have an effect on catalysis: use of an electron rich phosphine (**3**) leads to a reduction in spectroscopic yield of **6a** to 37% (Entry 6). A moderately electron poor phosphine (**4**, Entry 7) provides a modest yield of **6a**, but is still lower than that observed with **2**. Introduction of a strongly electron withdrawing *p*-CF_3 group increases the yield of **6a** further (Entry 8), but does not offer any substantial benefits over unsubstituted variant **2**. Due to the minor difference in yield when comparing phosphines **2** and **5**, along with the inexpensive nature of the unsubstituted styrene used to make **2**, we proceeded to optimise the reaction conditions using **2**. Although the predominant aim of this research is to develop an application for a commonly synthesised yet largely ignored phosphorus motif, we proceeded to test common phosphines in order to illustrate wider options in this area of Negishi cross-coupling. PCy_3 is a poor ligand in the standard reaction (Entry 10), whilst PPh_3 is comparable to **2** (Entry 11). This is in stark contrast to results obtained with $PPh_3/Fe(acac)_3$.[2i]

Table 1: Optimisation of iron-catalysed Negishi cross-coupling



Entry	Phosphine	Solvent	Spec. Yield (%)[a]
1	0.3 mmol **2**	THF	18
2	0.3 mmol **2**	THF with pre-reduction	8
3	0.3 mmol **2**	toluene	74
4[b]	0.3 mmol **2**	toluene, Hg	71
5	0.15 mmol **2**	toluene	49
6	0.3 mmol **3**	toluene	37
7	0.3 mmol **4**	toluene	51
8	0.3 mmol **5**	toluene	76
9	ligand-free	toluene	16
10	0.3 mmol PCy_3	toluene	29
11	0.3 mmol PPh_3	toluene	71

General reaction conditions: PhMgBr (670 µL, 2 mmol, 2 eq; 3 M in Et_2O), $ZnCl_2$ (136 mg, 1 mmol) in THF (0.5 mL) then solvent (4 mL) and benzyl bromide (1 mmol, 1 eq). $FeCl_2$ (6 mg, 5 mol%) and phosphine in solvent (3 mL). [a]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an analytical standard (see experimental section for methodology). [b]Three drops of Hg added to the reaction mixture (~1.5 mmol).

We questioned whether a discrete, mononuclear iron complex could be synthesised using phosphine **2**. Reaction of two equivalents of **2** with $FeCl_2{\cdot}THF_{1.5}$ in dry, degassed acetone leads to the formation of a white powder which is confirmed to have the structure **7** by X-ray crystallography (Figure 2) and elemental analysis. The single crystal X-ray structure of **7** shows an approximate C_{2V} arrangement of two phosphine and two chloride ligands around the metal centre. It is a highly air-sensitive solid which can only be prepared in acetone, where attempted synthesis in THF or CH_2Cl_2 simply leads to precipitation of nanoparticulate iron. Interestingly, once synthesised and isolated, complex **7** is stable in CH_2Cl_2 and X-ray quality crystals can be grown by slow evaporation of this solvent. Bond angles around the metal centre are 129.51(3)° for Cl1–Fe1–Cl2 and 116.50(2)° for P1–Fe1–P2. There is an unsymmetrical bonding angle observed at the phosphines where P1–Fe1–Cl1 is 96.48(2)° and P2–Fe1–Cl1 is substantially wider at 103.04(2)°. In contrast the bond angles at Cl2 are far more symmetrical (P1–Fe1–Cl2 is 106.90(3)° and P2–Fe1–Cl2 is 105.16(2))°. There is also a slight lengthening of the Fe1–Cl2 bond (2.2513(6) Å versus 2.2340(7) Å for Fe1–Cl1). The Fe–Cl and Fe–P bond lengths are consistent with those observed for similar four-coordinate Fe (II) complexes reported in the literature.

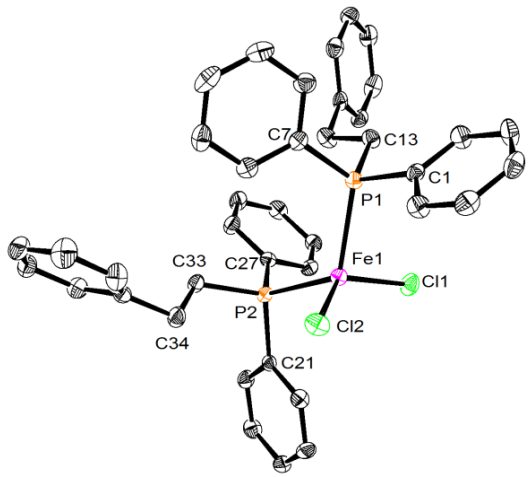
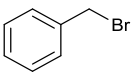
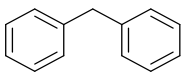
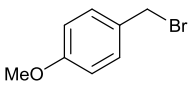
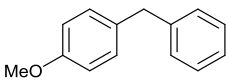
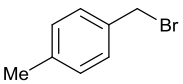
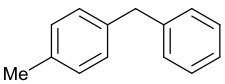
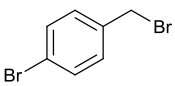
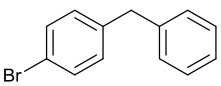
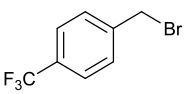
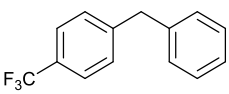
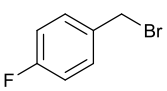
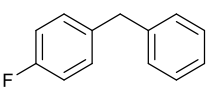
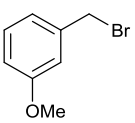
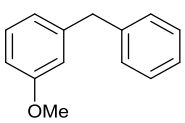
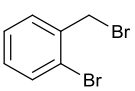
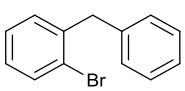
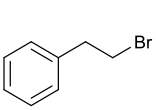
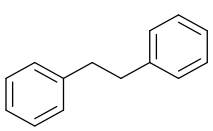
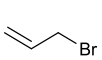
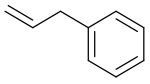
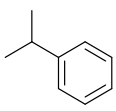


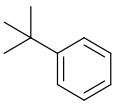
Fig. 2. X-ray crystal structure of complex **7** (thermal ellipsoids set at 50%). Selected bond lengths (Å) Fe1–Cl1 2.2340(7); Fe1–Cl2 2.2513(6); Fe1–P1 2.4415(7); Fe1–P2 2.4656(8); P1–C1 1.828(2); P1–C7 1.829(2); P1–C13 1.832(2); P2–C21 1.831(2); P2–C27 1.824(2); P2–C33 1.833(2); C13–C14 1.534(4); C33–C34 1.534(3). Selected bond angles (°): Cl2–Fe1–Cl1 129.51(3); Cl2–Fe1–P1 106.90(3); Cl1–Fe1–P2 103.04(2); Cl2–Fe1–P2 105.16(2); Cl1–Fe1–P1 96.48(2); P2–Fe1–P1 116.50(2).

Given the optimum ligand stoichiometry necessary for the Negishi cross-coupling (six equivalents per iron centre, Table 1, Entry 3), we attempted to prepare the octahedral complex (**8**) where four equivalents of phosphine are used per equivalent of $FeCl_2 \cdot THF_{1.5}$. This would allow us to evaluate the effectiveness of in situ catalyst preparation *versus* the use of a pre-synthesised complex. Formation of the octahedral complex is not conclusive: a complex forms within minutes in dry, degassed acetone and is recrystallized to give an off-white powder, with micro-analytical data of the bulk sample consistent with formation of the desired octahedral complex, however, after several single crystal X-ray analyses the structure is consistently revealed to be identical to that of **7**. This result is perhaps unsurprising as, to the best of our knowledge, no examples of octahedral Fe(II) complexes exist which are ligated by four PR_3 ligands and two chlorides.[11] Investigation of the efficiency with which complex **7** carries out the cross-coupling of benzyl bromide and diphenyl zinc reinforces that the quantity of phosphine in the catalytic mixture is important even with a discrete mononuclear complex: only 32% **6a** forms with 5 mol% complex **7**.

We next proceeded to explore the substrate scope using **2** as the pro-ligand. We also continued to use *in situ* catalyst generation (Table 1, Entry 3) due to ease of handling and inability to conclusively form complex **8**. A range of benzyl bromides are tolerated in the reaction including electron donating (Table 2, Entries 2 and 6) and electron withdrawing substrates (Table 2, Entry 5). The power of the iron catalysed Negishi cross-coupling is demonstrated by halogen-substituted benzyl bromides (Entries 4 and 7), where under palladium catalysed cross-coupling we would anticipate transfer of the aryl group from the diaryl zinc to the aromatic fragment of the benzyl bromide, thus forming a biaryl motif. With iron catalysis we observe complementary reactivity, where there is no evidence for biaryl formation and no indication that dehalogenation is taking place. The elegant nature of iron catalysis is further demonstrated by substrates containing β-protons; allyl and isopropyl bromides couple to benzyl bromide in good yield (Entries 8 to 10) without undergoing β-hydride elimination (a major deactivation pathway observed during palladium catalysis). Unfortunately, steric bulk proves to be limiting when *tert*-butyl bromide is used in catalysis, with no product being formed.

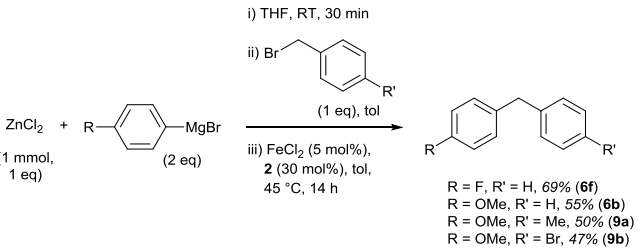
Table 2: Alkyl bromide substrate scope in the iron-catalysed Negishi cross-coupling

Entry	Bromide	Product		Spec. Yield (%)[a]
1			**6a**	74
2			**6b**	51
3			**6c**	60
4			**6d**	67
5			**6e**	51
6			**6f**	72
7			**6g**	85
8			**6h**	43
9			**6i**	47
10			**6j**	44
11			**6k**	60

12			**6l**	0

General reaction conditions: PhMgBr (670 µl, 3 M solution in Et_2O), $ZnCl_2$ (136 mg, 1 mmol) in THF (0.5 mL) then toluene (4 mL) and alkyl bromide (1 mmol). $FeCl_2$ (6 mg, 5 mol%) and **2** (87 mg, 30 mol%) in toluene (3 mL), 45 °C, 14 h. [a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an analytical standard, see experimental section for methodology and isolated yield.

Varying the electronic properties was also investigated (Scheme 2). It is interesting to note that when synthesising **6b** and **6f**, irrespective of whether the methoxy or fluoride group originates from the benzyl bromide or diaryl zinc reagent, the spectroscopic yields are very similar (compare Table 2, Entries 2 and 6 to Scheme 2). Moderate yields of di-functionalised diarylmethane motif are obtained when using a 4-methoxy diaryl zinc reagent (Scheme 2, **9a** and **9b**). It should also be noted that when alkyl zinc reagents were used, for example diethyl zinc and allyl zinc, no coupling to benzyl bromide occurs (only unreacted benzyl bromide is observed by ^{1}H NMR spectroscopy). In these cases, the zinc reagent was added to the iron solution at low temperature (addition at both −78 °C and 0 °C was attempted), along with RT and 45 °C (closed system) reactions for 14 h.



Scheme 2: Negishi cross-coupling varying the diaryl zinc reagent (spectroscopic yield, see experimental section for isolated yield).

Conclusions

We have prepared simple monophosphines using HP methodology developed in our own laboratory. These phosphines, in the presence of $FeCl_2$, competently catalyse the Negishi cross-coupling of alkyl bromides and diaryl zinc reagents. This is a rare example of a monophosphine being used to carry out such a transformation and indeed we have demonstrated that PPh_3 in the presence of $FeCl_2$ is similarly proficient. *In situ* catalyst preparation proves to be the easiest method to facilitate the transformation, however, the air-sensitive four-coordinate complex **7** was also isolated and characterised by X-ray crystallography.

Experimental

General considerations

Reagents were purchased from Sigma Aldrich and used without further purification. Solvents were dried over CaH_2 or Na (reflux), distilled and then degassed using three freeze-pump-thaw cycles. NMR data was collected at 250, 300, 400 or 500 MHz on Bruker instruments in $CDCl_3$ at 293 K and referenced to residual protic solvent or TMS. Spectroscopic yields were calculated from the distinctive methylene peak of the products (~ 4 ppm) using 0.1 mmol of 1,3,5-trimethoxybenzene as the analytical standard. UV-vis spectrum was collected using a 10 µM solution of **7** in CH_2Cl_2.

General method for the synthesis of 1.

Following the literature method,[4] $Fe(OAc)_2$ (109 mg, 0.6 mmol, 1 eq) was weighed into a flask and dissolved in ethanol (5 mL). A solution of *N*,*N*'-bis(salicylidene)ethylenediamine (200 mg, 0.7 mmol, 1.2 eq) in ethanol (10 mL) was then added forming a red solution. The mixture was then stirred at 80 °C for 2 h. The flask was allowed to cool to RT before filtering the solid and subsequent washing with ethanol. The dark red solid was dried under vacuum for 2 hours.

General method for the synthesis of phosphines 2 to 5.

1 (8 mg, 0.2 mol%) was weighed into a Schlenk tube under an inert atmosphere. CH_3CN (5 mL) was added followed by styrene (0.86 mL, 7.5 mmol, 1 eq) and diphenylphosphine (1.04 mL, 6 mmol, 0.8 eq). After stirring at RT for 48 h, the Schlenk tube was placed under vacuum to remove the excess styrene and solvent. The product was isolated by column chromatography (2% EtOAc/pentane). The phosphines have been isolated and analysed previously.[5]

General method for Negishi reaction to form cross-coupled products 6a to 6k.

PhMgBr (670 µL, 2 mmol, 3 M solution in Et_2O) was added to a solution of $ZnCl_2$ (136 mg, 1 mmol) in THF (0.5 mL) and stirred under N_2 for 30 min. Toluene (4 mL) was added, followed by the appropriate benzyl bromide (1 mmol). The mixture was transferred by cannula to a stirred solution of $FeCl_2$ (6 mg, 5 mol%) and phosphine (0.3 mmol) in toluene (1 mL), washing the $ZnPh_2$ solution through with toluene (2 mL). The reaction was stirred at 45 °C for 14 h, quenched with H_2O, extracted into EtOAc and dried over $MgSO_4$. 1,3,5-Trimethoxybenzene (0.1 mmol, 10 mol%) was added to the dried, filtered EtOAc solution, this was then concentrated and an NMR sample prepared by diluting the whole sample with 1 mL $CDCl_3$, an aliquot was removed and further diluted with $CDCl_3$ prior to analysis by ^{1}H NMR. Compounds were isolated by column chromatography (100% pentane to 5% EtOAc/pentane).

General method for the synthesis of 7 and 8.

$FeCl_2{\cdot}THF_{1.5}$ (17 mg, 0.064 mmol) and **2** (0.128 mmol or 0.257 mmol) were mixed in a vial in an argon filled glovebox. Dry, degassed acetone (1 mL) was added and the reaction mixture stirred for 4 h. During this time the solution turned yellow followed by precipitation of an off-white solid. The solution was cooled to −30 °C for 15 minutes then the supernatant was removed, the precipitate was washed with a further 2 × 1 mL cold acetone then dissolved in CH_2Cl_2, filtered through a pipette plugged with glass paper and crystals grown by slow evaporation of the solvent. NMR data are consistent with the formation of paramagnetic complexes.

Analysis data for products

Compound **6a**, Table 2, Entry 1

Colourless oil, 102 mg (61%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.30-7.14 (m, 10H), 3.97 (s, 2H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 141.2, 128.9, 128.5, 126.1, 41.9; IR (neat) ν 3060, 3032, 2929, 1595, 1476 cm^{-1}. Data matches that of a commercial sample (CAS: 101-81-5).

Compound **6b**, Table 2, Entry 2
Colourless oil, 98 mg (49%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.28-7.22 (m, 3H), 7.16 (d, *J* 8.4 Hz, 2H), 6.87 (d, *J* 8.4 Hz, 2H), 3.94 (s, 2H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 157.9, 141.6, 133.3, 129.9, 128.8, 128.4, 126.0, 113.9, 55.3, 41.0; IR (neat) ν 3025, 2860, 1594, 1494, 1437 cm^{-1}. Data matches literature reports.[12]

Compound **6c**, Table 2, Entry 3
Colourless oil, 88 mg (49%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.42-7.32 (m, 2H), 7.32-7.22 (m, 3H), 7.22-7.12 (m, 4H), 4.03 (s, 2H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 141.5, 138.1, 135.6, 129.2, 128.9, 128.9, 128.5, 126.1, 41.6, 21.1; IR (neat) ν 3022, 2850, 1595, 1491 cm^{-1}. Data matches literature reports.[2i,8]

Compound **6d**, Table 2, Entry 4
White solid, 85 mg (34%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.48-7.16 (m, 9H), 3.94 (s, 2H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 140.4, 139.9, 131.5, 130.6, 128.9, 128.5, 126.3, 119.8, 41.6; IR (neat) ν 3025, 2920, 1598, 1484 cm^{-1}. Data matches literature reports.[2i,8]

Compound **6e**, Table 2, Entry 5
Colourless oil, 112 mg (47%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.58 (d, *J* 8.0 Hz, 2H), 7.38-7.20 (m, 7H), 4.06 (s, 2H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 145.3, 140.0, 129.2, 128.9, 128.7, 128.2 (q, *J* 33 Hz), 126.5, 125.4 (q, *J* 4 Hz), 124.4 (q, *J* 270 Hz), 41.7; IR (neat) ν 3031, 2931, 1595, 1481 cm^{-1}. Data matches literature reports.[2i,8]

Compound **6f**, Table 2, Entry 6
Colourless oil, 127 mg (69%). ^{1}H NMR (500 MHz; 298 K; $CDCl_3$) δ 7.28 (t, *J* 7.3 Hz, 2H), 7.21-7.18 (m, 5H), 6.96 (t, *J* 8.8 Hz, 2H), 3.93 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz; 298 K; $CDCl_3$) δ 161.3 (d, *J* 244.2 Hz), 140.7, 136.5 (d, *J* 2.9 Hz), 130.0 (d, *J* 7.6 Hz), 128.8, 128.5, 126.2, 115.4 (d, *J* 21.0 Hz), 41.0; IR (neat) ν 3035, 2944, 1589, 1489 cm^{-1}. Data matches literature report.[13]

Compound **6g**, Table 2, Entry 7
Colourless oil, 155 mg (78%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.30-7.12 (m, 6H), 6.79-6.70 (m, 3H), 3.91 (s, 2H), 3.71 (s, 3H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 159.9, 142.9, 139.9, 129.5, 128.9, 128.5, 126.2, 121.4, 114.9, 111.4, 55.1, 42.1; IR (neat) ν 3030, 2973, 1595, 1496 cm^{-1}. Data matches literature reports.[14]

Compound **6h**, Table 2, Entry 8
Colourless oil, 98 mg (40%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.57 (d, *J* 9.0 Hz, 1H), 7.37-7.01 (m, 8H), 4.12 (s, 2H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 140.4, 139.6, 132.8, 131.1, 128.9, 128.5, 127.9, 127.6, 126.2, 124.9, 41.7; IR (neat) ν 3018, 2920, 1591, 1513, 1447 cm^{-1}. Data matches literature reports.[15]

Compound **6i**, Table 2, Entry 9
Colourless oil, 84 mg (45%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.38-7.02 (m, 10H), 2.92 (s, 2H); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 141.8, 128.4, 128.3, 125.9, 37.0; IR (neat) ν 3029, 2930, 1595, 1481 cm^{-1}. Data matches that of a commercial sample (CAS: 103-29-7).

Compound **6j**, Table 2, Entry 10
Colourless oil, 48 mg (40%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.33-7.18 (m, 5H), 6.06-5.93 (m, 1H), 5.13-5.05 (m, 2H), 3.40 (d, 2H, *J* 6.5 Hz); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 148.8, 128.3, 126.4, 125.8, 34.1, 24.0; IR (neat) ν 3028, 2902, 1639, 1494 cm^{-1}. Data matches that of a commercial sample (CAS: 300-57-2).

Compound **6k**, Table 2, Entry 11
Colourless oil, 68 mg (57%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.45-7.30 (m, 5H), 3.03 (septet, 1H, *J* 6.9 Hz), 1.40 (d, 6H, *J* 6.9 Hz); $^{13}C\{^1H\}$ NMR (63 MHz; 298 K; $CDCl_3$) δ 140.0, 137.4, 128.6, 128.4, 126.0, 115.7, 40.1; IR (neat) ν 3028, 2960, 1494, 1464 cm^{-1}. Data matches that of a commercial sample (CAS: 98-82-8).

Complex **7**
Isolated as a white powder (35 mg, 77%). ^{1}H NMR (500 MHz; 298 K; CD_2Cl_2) δ 13.42 (br), 7.55 (br), 7.14 (br), 0.85 (br), 0.12 (br), -0.92 (br); $^{13}C\{^1H\}$ NMR (125 MHz; 298 K; CD_2Cl_2) δ 173.4, 148.7, 135.1, 128.5, 128.3, 126.4, 31.6, 31.0, -0.5; elemental analysis: C 67.9, H 5.4 (calcd); C 68.1, H 5.0 (obs.); m.p. 164 °C (decomp.); IR (solid) ν 3054 (w), 3023 (w), 1602 (w), 1583 (w), 1484 (s), 1433 (s), 1238 (br), 1097 (s), 748 (s), 738 (s), 732 (s), 723 (s).

Crystal Data for $C_{40}H_{38}Cl_2FeP_2$ (**7**).
M = 707.39, λ = 0.71073 Å, triclinic, space group P-1, a = 9.4059(4), b = 10.4593(5), c = 19.1213(8)Å, α = 89.049(4), β = 84.880(4), γ = 68.014 °, U = 1737.08(13) Å^3, Z = 2, D_c = 1.352 g cm^{-3}, μ = 0.708 mm^{-1}, F(000) = 736. Crystal size = 0.3550 × 0.2201 × 0.1414 mm, unique reflections = 7961 [$R_{(int)}$ = 0.0294], observed reflections [I>2σ(I)] = 6167, data/restraints/parameters = 7961/0/406. Observed data; R1 = 0.0432, wR2 = 0.0814. All data; R1 = 0.0638, wR2 = 0.0886. Max peak/hole = 0.443 and −0.341 eÅ^{-3}, respectively. CCDC 1035920.

Compound **6b**, Scheme 2
Colourless oil, 99 mg (50%). Data matches literature reports.[11]

Compound **6f**, Scheme 2
Colourless oil, 117 mg (63%). Data matches literature reports.[12]

Compound **9a**, Scheme 2
Colourless oil, 102 mg (48%). ^{1}H NMR (500 MHz; 298 K; $CDCl_3$) δ 7.14-7.08 (m, 6H), 6.86-6.84 (m, 2H), 3.90 (s, 2H), 3.79 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz; 298 K; $CDCl_3$) δ 157.7, 138.6, 135.1, 133.6, 129.7, 129.2, 128.8, 113.7, 55.0, 40.4, 20.8. Data matches literature reports.[11c]

Compound **9b**, Scheme 2

White solid, 113 mg (41%). ^{1}H NMR (500 MHz; 298 K; $CDCl_3$) δ 7.50 (d, *J* 8.3 Hz, 2H), 7.08-7.01 (m, 4H), 6.85 (d, *J* 8.3 Hz, 2H), 3.84 (s, 2H), 3.78 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz; 298 K; $CDCl_3$) δ 158.4, 140.3, 132.6, 131.0, 130.1, 129.4, 119.4, 113.8, 54.8, 40.2; m.p. 88 °C. Data matches literature reports.[16]

Notes and references

[a] *Department of Chemistry, University of Bath, Claverton Down, Bath, UK, BA2 7AY.Tel:+44(0)1225 386103 E-mail: r.l.webster@bath.ac.uk*

[b] *Department of Chemistry and Biochemistry, University of North Carolina Greensboro, Greensboro, North Carolina, 27405, USA.*

The participation of Caleb Brown (Home institution: Guilford College, Greensboro, North Carolina, USA) was made possible by the support of the National Science Foundation (Grant number 1262847) through its Research Experiences for Undergraduates program, which is gratefully acknowledged. The University of Bath is also thanked for additional funding.

† Electronic Supplementary Information (ESI) available: cif file or complex **7**. See DOI: 10.1039/b000000x/

1 a) C. Bolm, J. Legros, J. Le Paih and L. Zani, *Chem. Rev.* **2004**, *104*, 6217-6254; b) A. Correa, O. G. Mancheno and C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108-1117; c) S. Enthaler, K. Junge and M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317-3321; d) B. D. Sherry and A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500-1511; e) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293-1314.

2 a) A. Furstner and A. Leitner, *Angew. Chem. Int. Ed.* **2002**, *41*, 609-612; b) A. Furstner, A. Leitner, M. Mendez and H. Krause, *J. Am. Chem. Soc.* **2002**, *124*, 13856-13863; c) R. Martin and A. Furstner, *Angew. Chem. Int. Ed.* **2004**, *43*, 3955-3957; d) T. Nagano and T. Hayashi, *Org. Lett.* **2004**, *6*, 1297-1299; e) M. Nakamura, K. Matsuo, S. Ito and B. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 3686-3687; f) M. Nakamura, S. Ito, K. Matsuo and E. Nakamura, *Synlett* **2005**, 1794-1798; g) G. Cahiez, V. Habiak, C. Duplais and A. Moyeux, *Angew. Chem. Int. Ed.* **2007**, *46*, 4364-4366; h) G. Cahiez, C. Duplais and A. Moyeux, *Org. Lett.* **2007**, *9*, 3253-3254; i) R. B. Bedford, M. Huwe and M. C. Wilkinson, *Chem. Commun.***2009**, 600-602; j) S. Ito, Y. Fujiwara, E. Nakamura and M. Nakamura, *Org. Lett.* **2009**, *11*, 4306-4309; k) T. Hatakeyama, N. Nakagawa and M. Nakamura, *Org. Lett.* **2009**, *11*, 4496-4499; l) T. Hatakeyama, S. Hashimoto, K. Ishizuka and M. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 11949-11963; m) T. Hatakeyama, Y. Fujiwara, Y. Okada, T. Itoh, T. Hashimoto, S. Kawamura, K. Ogata, H. Takaya and M. Nakamura, *Chem. Lett.* **2011**, *40*, 1030-1032; n) X. Qian, L. N. Dawe and C. M. Kozak, *Dalton Trans.* **2011**, *40*, 933-943; o) O. M. Kuzmina, A. K. Steib, D. Flubacher and P. Knochel, *Org. Lett.* **2012**, *14*, 4818-4821; p) B. A. F. Le Bailly, M. D. Greenhalgh and S. P. Thomas, *Chem. Commun.***2012**, *48*, 1580-1582; q) X. W. Lin, F. Zheng and F. L. Qing, *Organometallics* **2012**, *31*, 1578-1582; r) E. F. Chard, L. N. Dawe and C. M. Kozak, *J. Organomet. Chem.***2013**, *737*, 32-39; s) D. J. Frank, L. Guiet, A. Kaslin, E. Murphy and S. P. Thomas, *RSC Adv.* **2013**, *3*, 25698-25701; t) S. Kawamura and M. Nakamura, *Chem. Lett.* **2013**, *42*, 183-185; u) J. R. Schmink and M. T. Tudge, *Tetrahedron Lett.* **2013**, *54*, 15-20.

3 a) J. K. Stille, *Angew. Chem. Int. Ed. in English* **1986**, *25*, 508-523; b) N. Miyaura and A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457-2483; c) I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009-3066; d) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359-1469; e) A. F. Littke and G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176-4211.

4 K. J. Gallagher and R. L. Webster, *Chem. Commun.***2014**, *50*, 12109-12111.

5 a) L. Rosenberg, *ACS Catal.* **2013**, 2845-2855; b) V. Koshti, S. Gaikwad and S. H. Chikkali, *Coord. Chem. Rev.* **2014**, *265*, 52-73.

6 R. B. Bedford, E. Carter, P. M. Cogswell, N. J. Gower, M. F. Haddow, J. N. Harvey, D. M. Murphy, E. C. Neeve and J. Nunn, *Angew. Chem. Int. Ed.* **2013**, *52*, 1285-1288.

7 M. T. Honaker, B. J. Sandefur, J. L. Hargett, A. L. McDaniel and R. N. Salvatore, *Tetrahedron Lett.* **2003**, *44*, 8373-8377.

8 M. F. Cain, R. P. Hughes, D. S. Glueck, J. A. Golen, C. E. Moore and A. L. Rheingold, *Inorg. Chem.* **2010**, *49*, 7650-7662.

9 a) R. B. Bedford, M. Betham, D. W. Bruce, S. A. Davis, R. M. Frost and M. Hird, *Chem. Commun.***2006**, 1398-1400; b) G. M. Whitesides, M. Hackett, R. L. Brainard, J. P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown and E. M. Staudt, *Organometallics* **1985**, *4*, 1819-1830.

10 a) O. Seewald, U. Florke and G. Henkel, *Acta Crystallographica Section E* **2005**, *61*, m1829-m1830; b) K. L. Fillman, J. A. Przyojski, M. H. Al-Afyouni, Z. J. Tonzetich and M. L. Neidig, *Chem. Sci.* **2015**.

11 For early examples with bisphosphines see: a) M. V. Baker, L. D. Field and T. W. Hambley, *Inorg. Chem.* **1988**, *27*, 2872-2876; b) F. Cecconi, M. Di Vaira, S. Midollini, A. Orlandini and L. Sacconi, *Inorg. Chem.* **1981**, *20*, 3423-3430.

12 a) G. A. Molander and M. D. Elia, *J. Org. Chem.* **2006**, *71*, 9198-9202; b) M. Amatore and C. Gosmini, *Chem. Commun.***2008**, 5019-5021; c) R. B. Bedford, M. A. Hall, G. R. Hodges, M. Huwe and M. C. Wilkinson, *Chem. Commun.***2009**, 6430-6432.

13 M. J. Burns, I. J. S. Fairlamb, A. R. Kapdi, P. Sehnal and R. J. K. Taylor, *Org. Lett.* **2007**, *9*, 5397-5400.

14 E. Alacid and C. Nájera, *Org. Lett.* **2008**, *10*, 5011-5014.

15 H.-B. Sun, B. Li, S. Chen, J. Li and R. Hua, *Tetrahedron* **2007**, *63*, 10185-10188.

16 M.-B. Li, X.-L. Tang and S.-K. Tian, *Advanced Synthesis & Catalysis* **2011**, *353*, 1980-1984.

