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Iron Phosphine Catalyzed Cross-Coupling of Tetraorganoborates and Related Group 13 Nucleophiles with Alkyl Halides

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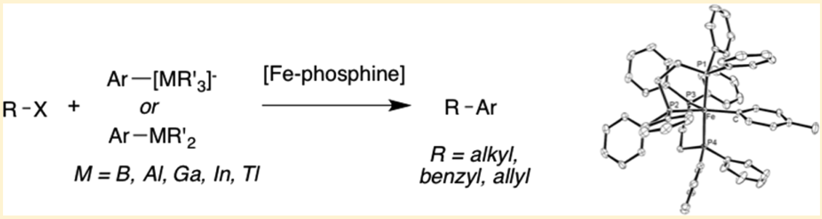
Ⓢ *Supporting Information*



ABSTRACT: Iron phosphine complexes prove to be good precatalysts for the cross-coupling of alkyl, benzyl, and allyl halides with not only aryl triorganoborate salts but also related aluminum-, gallium-, indium-, and thallium-based nucleophiles. Mechanistic studies revealed that while Fe(I) can be accessed on catalytically relevant time scales, lower average oxidation states are not formed fast enough to be relevant to catalysis. EPR spectroscopic studies reveal the presence of bis(diphosphine)iron(I) complexes in representative catalytic reactions and related processes with a range of group 13 nucleophiles. Isolated examples were studied by Mössbauer spectroscopy and single-crystal X-ray structural analysis, while the electronic structure was probed by dispersion-corrected B3LYP DFT calculations. An EPR study on an iron system with a bulky diphosphine ligand revealed the presence of an $S = {}^1/_2$ species consistent with the formation of a mono(diphosphine)iron(I) species with inequivalent phosphine donor environments. DFT analysis of model complexes allowed us to rule out a T-shaped Fe(I) structure, as this is predicted to be high spin.

■ INTRODUCTION

Palladium-catalyzed cross-coupling reactions are ubiquitous in organic synthesis, but there is a growing need to replace expensive, toxic, environmentally deleterious metals with more benign, sustainable metals in a range of catalytic processes. With its high natural abundance and low cost and toxicity, iron makes an ideal potential substitute for palladium.

While iron-catalyzed cross-coupling (Scheme 1) can be traced back 70 years, with intermittent reports in the intervening decades,[1,2] it is only comparatively recently that the field has attracted serious and sustained attention,[3] triggered in particular by groundbreaking reports in 2002–2004 from the groups of Fürstner,[4] Nakamura,[5] and Hayashi.[6] In the past decade there has been a significant number of papers published on the cross-coupling of alkyl, aryl, and vinyl halides and related substrates.[7–9]

Scheme 1. Iron-Catalyzed Cross-Coupling

$$R^1\text{-}X + R^2\text{-}M \xrightarrow[\text{- MX}]{\text{[Fe-cat]}} R^1\text{-}R^2$$

The majority of the reports published to date focus on the use of Grignard reagents in iron-catalyzed cross-coupling, but following on from our reported use of iron phosphine catalysts in Grignard cross-coupling,[10] such complexes have been found to be applicable not only with Grignards[11] but also with a range of softer nucleophiles, including diorganozincs,[12] tetraorganoborates,[12c.13] diorgano(pinacolato)borates,[14] tetraorganoaluminates,[12c.15] and tetraorganoindates.[12c]

We now report the optimization and use of iron-phosphine catalysts for the cross-coupling of alkyl halides and related substrates with a range of tetraorganoborate substrates, including for the first time those based on 9-BBN, as well as related organo-group 13 nucleophiles.

■ RESULTS AND DISCUSSION

Iron Phosphine Complexes for the Coupling of BR_4^- Nucleophiles. We previously found that the preformed

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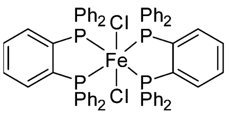
iron(II) and iron(I) complexes **1**−**3** can be used as effective precatalysts in the coupling of benzyl or 2-heteroaryl halides with tetraarylborate salts.[12c,13a] We were interested to see whether appropriate modifications in the structure of the phosphine ligands would lead to enhanced catalyst performance. Accordingly, we prepared the ligands **4**−**7**.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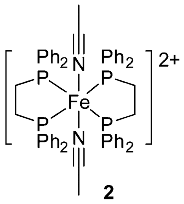
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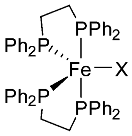
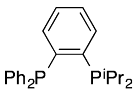

3a: X =Cl
b: X = Br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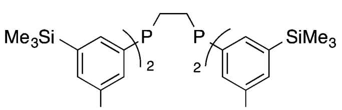
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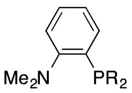
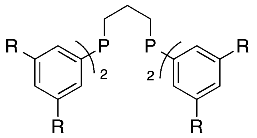

5a: R = Ph
b: R = Cy


7a: R = Me
b: R = SiMe₃

The crystal structures of four of the ligands are shown in Figure 1, while the performance of iron catalysts based on these ligands and the commercially available ligands dpbz, dppe, dmpe, depe, and dppp[16] in the representative cross-coupling reaction of the benzyl bromide **8a** with sodium tetraphenylborate are summarized in Table 1.

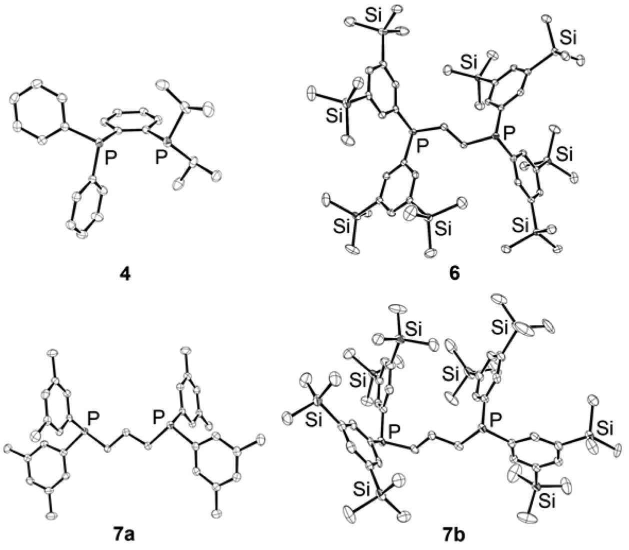
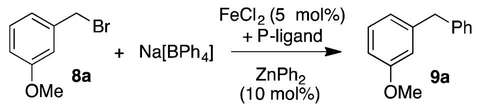


Figure 1. Single-crystal X-ray structures of ligands **4**, **6**, and **7a**,**b**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at the 50% probability level.

The mixed alkyl/aryl bis(phosphine) ligand **4** showed a slightly poorer performance in comparison with dpbz, while the mixed amino-phosphine analogues **5a**,**b** performed significantly worse. The commercially available ligands dppe, dppp, dmpe, and depe also gave disappointing results under the conditions employed here; indeed, the alkyl-substituted ligands dmpe and depe showed activity comparable to or worse than that of iron chloride in the absence of phosphine. In contrast, the sterically encumbered analogues of dppe and dppp, ligands **6** and **7**, performed reasonably well. The good results obtained with dpbz, coupled with its commercial availability, led us to focus on this ligand for the remainder of the studies.

Table 1. Ligand Influence in a Representative Suzuki Reaction[a]



entry	ligand	ligand:Fe	yield of **9a**, %[b]
1	dpbz	1:2[c]	99
2	dpbz	1:1	96
3	**4**	1:2	93
4	**4**	1:1	92
5	**5a**	1:2	45
6	**5b**	1:2	46
7	dppe	1:2	54
8	dppe	1:1	50
9	dppe	1:1[d]	55
10	**6**	1:2	90
11	**6**	1:1	91
12	dmpe	1:2[e]	25
13	depe	1:2	35
14	dppp	1:2	48
15	dppp	1:1	40
16	**7a**	1:2	88[f,g]
17	**7b**	1:2	83[f,h]
18	none		31

[a] All reactions run at 85 °C for 4 h. [b] Spectroscopic yield based on ^{1}H NMR (1,3,5-$(MeO)_3C_6H_3$ internal standard). [c] Complex **1** used as precatalyst. [d] $[FeCl_2(dppe]$ used as precatalyst. [e] $[FeCl_2(dmpe)_2]$ used as precatalyst. [f] $Zn(4\text{-tolyl})_2$ used as additive. [g] Combined yield of **9a** (82%) and 4-tolyl analogue **9b** (6%). [h] Combined yield of **9a** (75%) and 4-tolyl analogue **9b** (8%).

The outcome of the reactions summarized in Scheme 2 shows that essentially only one of the aryl groups is transferred from the tetraphenylborate ion during the reaction with **8a** catalyzed by complex **1**. This of course wastes three aryl residues. A second issue is the scarcity of commercially available tetraarylborate salts. While we previously found that aryltrialkylborate salts can be exploited in place of tetraarylborates,[13a] they tended to give poorer yields. Therefore, we decided to reinvestigate the use of mixed aryltrialkylborate and diaryldialkylborate salts. These are easily accessed from commercially available precursors and the appropriate aryllithium or Grignard reagents.

Scheme 2. Extent of Aryl Transfer

$$\mathbf{8a} + n\,\mathrm{Na[BPh_4]} \xrightarrow[\substack{\mathrm{ZnPh_2} \\ (10\ \mathrm{mol\%})}]{\mathbf{1}\ (5\ \mathrm{mol\%})} \mathbf{9a} \qquad \begin{array}{r} n = 0.25\text{: } 30\% \\ 0.50\text{: } 45\% \\ 1.00\text{: } 94\% \end{array}$$

While in most cases the borate salts were produced as required and used without characterization, their formation was confirmed by ^{11}B NMR spectroscopy. Thus, the spectra of the product mixtures formed in the representative reactions of

$B(^sBu)_3$, 9-BBN-^{i}Pr, or 9-BBN-Ph with 4-tolylmagnesium chloride (Scheme 3) showed sharp singlets at δ −12.5, −16.0, and −15.1 ppm corresponding to the borates **10a−c**, respectively.[17]

Scheme 3. Formation of Di- and Trialkylborates

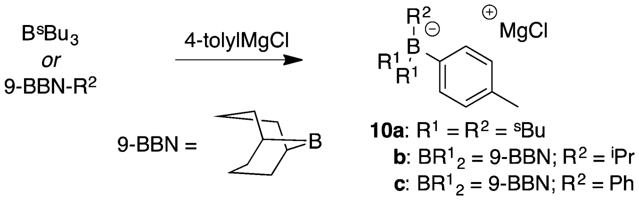
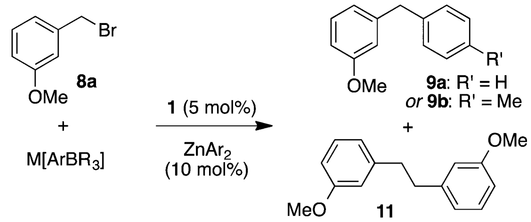


Table 2 summarizes the results of the coupling of the arylborates with the representative benzyl bromide **8a** catalyzed by complex **1**. The survey of borates formed from commercially available trialkylboranes (entries 1−9) revealed that an increase in the steric bulk of the alkyl group resulted in more selective cross-coupling. As observed before with tetraarylborate salts,[12c,13a] the reaction requires substoichiometric quantities of either an organozinc reagent or zinc chloride (compare entries 6−8 and 15−17); in the absence of zinc additives, homocoupling of the electrophile predominated. With 9-BBN-based nucleophiles, the best activity was seen with the diarylborate salts; however, an acceptable yield was obtained with MgCl[9-BBN(^{i}Pr)4-tolyl], provided it was used in slight excess (entry 15).

Table 2. Survey of Aryl Triorganoborates as Nucleophiles[a]



entry	M[R_3BAr]	yield, %[b]	
		9a or 9b	11
1	Li[Et_3BPh]	5	34
2	Li[Bu_3BPh]	54	15
3	Li[*s*-Bu_3BPh]	15	51
4	MgCl[Et_3B(4-tolyl)]	32	23
5	MgCl[Bu_3B(4-tolyl)]	52	16
6	MgCl[$^sBu_3B$(4-tolyl)]	73	13
7	as above no Zn salt	18	65
8	as above with $ZnCl_2$[c]	78	21
9	MgCl[$^sBu_3BPh$]	56	24
10	MgBr[9-BBN(Me)Ph][d]	51	49
11	Li[9-BBN(Bu)Ph][d]	58	32
12	MgBr[9-BBN(^{s}Bu)Ph][d]	25	46
13	MgBr[9-BBN$(Ph)_2$][d]	93	7
14	MgCl[9-BBN(^{i}Pr)4-tolyl][e]	71	20
15	MgCl[9-BBN(^{i}Pr)4-tolyl][e,f]	85	15
16	as above no Zn salt	30	50
17	as above with $ZnCl_2$[c]	77	18

[a] All reactions run at 85 °C for 4 h. [b] Spectroscopic yield based on ^{1}H NMR 1,3,5-$(MeO)_3C_6H_3$ internal standard). [c] 20 mol %. [d] Formed in situ from Ph-9-BBN and appropriate RMgX or RLi (1:1). [e] Formed in situ from ^{i}Pr-9-BBN and appropriate 4-tolylMgCl. [f] 1.2 equiv of borate used.

Table 3 summarizes the coupling of a range of alkyl halides with MgX[9-BBN(^{i}Pr)Ar] or MgX[$^sBu_3BPh$]. As can be seen, the reactions progressed reasonably well with benzyl and secondary alkyl halide substrates, but lower activity was observed with a representative primary alkyl halide (entry 20).

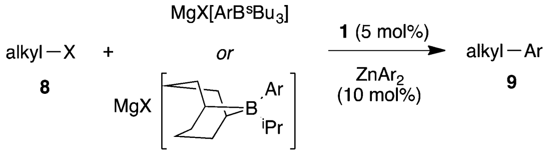
Disappointingly low activity was seen with allyl bromide substrates (entries 24 and 25), irrespective of which boron-containing nucleophile was used. In contrast, we have recently shown that iron catalysis can give good results in the coupling of allyl halides when arylboron pinacol esters, activated with alkyllithium reagents, are used as the nucleophile.[14c] Substrates with sensitive functional groups (ester, cyano) were tolerated, as were aryl bromide residues on benzyl halide substrates, confirming the preference for benzyl halides over aryl halides observed previously.[12a,c,13a] In contrast, no product was obtained in the coupling of a nitro-substituted benzyl bromide (entry 16). Typically the 9-BBN-derived reagents show marginally enhanced performance, but the requirement for an extra step in the synthesis of these borates from commercially available MeO-9-BBN detracts slightly from their appeal in comparison with the reagents prepared in one step from tri-*sec*-butylborane.

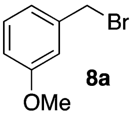
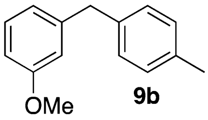
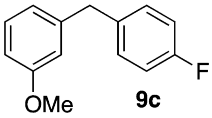
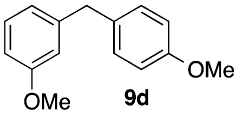
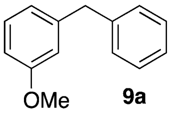
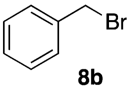
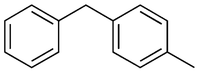
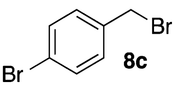
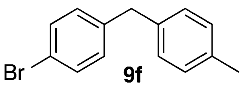
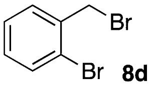
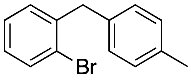
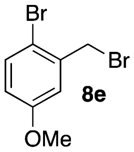
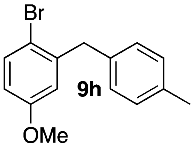
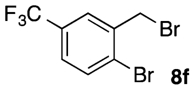
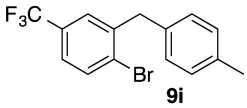
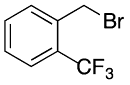
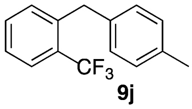
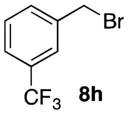
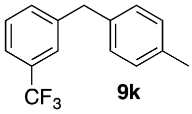
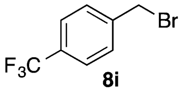
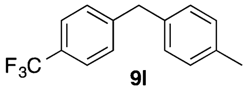
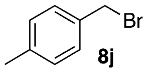
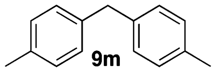
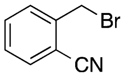
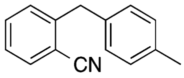
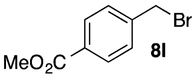
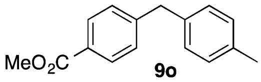
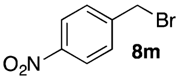
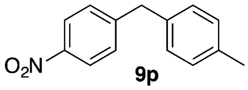
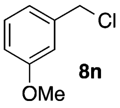
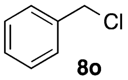
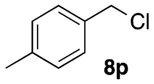
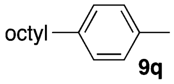
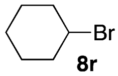
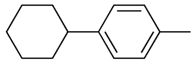
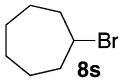
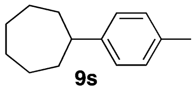
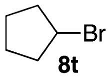
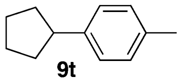
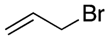
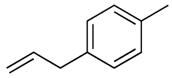
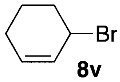
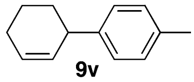
Cross-Coupling of Heavier Group 13 Nucleophiles. Nakamura and co-workers demonstrated that complex **1** is an effective precatalyst for the coupling of tetraarylaluminates with representative primary and secondary alkyl halides,[15] while we found that the dppe-containing complexes **2** and **3a** can also be exploited.[12c] These latter complexes also show activity in the representative coupling of a tetraarylindate with a benzyl bromide.[12c] We therefore decided to compare relative activities of group 13 aryl nucleophiles in the representative cross-coupling reactions with **8a**, catalyzed by complex **1**, and these results are summarized in Table 4. In all cases, except with thallium, we used the appropriate tetraarylmetalate, prepared immediately prior to use. To the best of our knowledge, the equivalent tetraarylthallates are not known beyond systems with perhalogenated aryls and these show a far lower propensity to undergo transmetalation.[18] Accordingly, we used triphenylthallium instead and for comparison we also examined the use of the neutral nucleophiles M(4-tolyl)$_3$ (M = Al, In).

All of the group 13 nucleophiles tested showed activity. With aluminum and indium there was no need to add cocatalytic zinc for good performance when 1−1.2 equiv of the nucleophile was used. With boron-, gallium-, and thallium-based nucleophiles poorer activity was seen in the absence of zinc. On comparison of entries 2 and 3, it is apparent that more than one aryl group can be transferred from the aluminum center. This hypothesis is further supported by the observation that a neutral triarylaluminum is also a competent nucleophilic coupling partner (entry 4). Similar results were observed for indium, although in this case a zinc additive proved beneficial when less than 1 equiv of the tetraarylindate was used (entry 10).

Table 5 summarizes the results of the coupling of a representative range of electrophiles with MgCl[M(4-tolyl)$_4$] (M = Al, In). As can be seen, in most cases good to excellent conversions to the desired cross-coupled products were observed. In the majority of cases, the indate performed as well or better than the aluminate. A range of benzyl bromides and chlorides were successfully coupled, including those with sensitive functional groups such as cyano and ester residues as

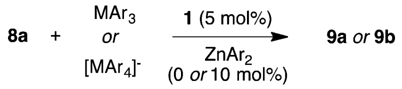
Table 3. Coupling of Aryltrialkylborates[a]



Entry	Alkyl halide	Product	Yield with: (a) R = ^{s}Bu, (b) BR$_3$ = ^{i}PrBBN, %[b]
1	 **8a**	 **9b**	(a) 73 (b) 85
2		 **9c**	(a) 68 (b) 77
3		 **9d**	(a) 77 (b) 73
4		 **9a**	(a) 56
5	 **8b**	 **9e**	(a) 62 (50)
6	 **8c**	 **9f**	(a) 72 (b) 83
7	 **8d**	 **9g**	(a) 58 (52)
8	 **8e**	 **9h**	(a) 73 (b) 75
9	 **8f**	 **9i**	(a) 58 (54)
10	 **8g**	 **9j**	(a) 70 (46)
11	 **8h**	 **9k**	(a) 70 (48)
12	 **8i**	 **9l**	(a) 60 (55)
13	 **8j**	 **9m**	(a) 62 (b) 86
14	 **8k**	 **9n**	(a) 50
15	 **8l**	 **9o**	(a) 67 (b) 71
16	 **8m**	 **9p**	(a) 0
17	 **8n**	**9b**	(a) 84 (78) (b) 86[c]
18	 **8o**	**9e**	(a) 71
19	 **8p**	**9m**	(a) 69 (58)
20	octyl—Br **8q**	 **9q**	(a) 45 (b) 44
21	 **8r**	 **9r**	(a) 30 (b) 50
22	 **8s**	 **9s**	(a) 64 (b) 90
23	 **8t**	 **9t**	(a) 41 (b) 65
24	 **8u**	 **9u**	(a) 26 (b) 54
25	 **8v**	 **9v**	(a) 22 (b) 10

[a] All reactions run at 85 °C for 4 h. [b] Spectroscopic yield based on ^{1}H NMR (1,3,5-(MeO)$_3$C$_6$H$_3$ internal standard), isolated yield in parentheses. [c] [FeCl$_2$(dppp)] + 1 equiv of dppp used in place of **1**.

Table 4. Coupling of Group 13 MR_3 and $[MR_4]^-$ Nucleophiles[a]

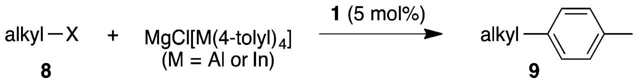


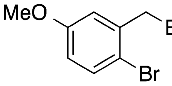
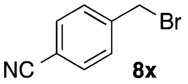
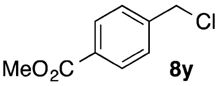
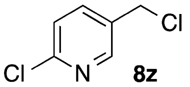
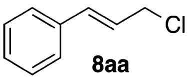
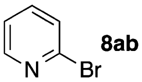
$$\mathbf{8a} + \begin{matrix}MAr_3\\ or\\ [MAr_4]^-\end{matrix} \xrightarrow[\text{ZnAr}_2\ (0\ or\ 10\ \text{mol\%})]{\mathbf{1}\ (5\ \text{mol\%})} \mathbf{9a}\ or\ \mathbf{9b}$$

entry	nucleophile	Nu:8a	additive	yield, %[b]
1	Na[BPh_4]	1.2	$ZnPh_2$	99
2	MgCl[Al(4-tolyl)$_4$]	1.2		99
3	MgCl[Al(4-tolyl)$_4$]	0.6		86
4	Al(4-tolyl)$_3$	1.2		69
5	MgCl[Ga(4-tolyl)$_4$]	1.2		58
6	MgCl[Ga(4-tolyl)$_4$]	0.5		39
7	MgCl[Ga(4-tolyl)$_4$]	0.5	Zn(4-tolyl)$_2$	54
8	MgCl[$GaPh_4$]	1.2	$ZnPh_2$	94
9	MgCl[In(4-tolyl)$_4$]	1.0		91
10	MgCl[In(4-tolyl)$_4$]	0.5	Zn(4-tolyl)$_2$	86
11	In(4-tolyl)$_3$	1.0		69
12	$TlPh_3$	1.2		50
13	$TlPh_3$	1.2	$ZnPh_2$	90

[a] All reactions run at 85 °C for 4 h. [b] Spectroscopic yield based on ^1H NMR (1,3,5-$(MeO)_3C_6H_3$ internal standard).

Table 5. Coupling of a Representative Range of Electrophiles with MgCl[M(4-tolyl)$_4$] (M = Al, In)[a]



Entry	Electrophile	Yield of 9 with M = Al, %[b]	Yield of 9 with M = In, %[b]
1	**8a**	99 (98)	91
2	**8c**	66	95
3	**8f**	83	85 (82)
4	 **8w**	80 (49)	88
5	**8g**	69	87 (84)
6	**8h**	95	93 (66)
7	**8l**	82	92 (90)
8		70	89 (75)
9	**8n**	99	91
10	**8o**	95	94
11	**8p**	89	92
12		72	93
13		n.d.	80 (58)
14	**8q**	n.d.	78 (51)
15	**8r**	n.d.	65 (49)
16	**8s**	n.d.	79 (67)
17	**8t**	n.d.	75 (40)
18	**8u**	70	75 (21)
19	**8v**	54	64 (26)
20		72 (55)	48
21		41 (32)	33

[a] All reactions run at 85 °C for 4 h. [b] Spectroscopic yield based on ^1H NMR (1,3,5-$(MeO)_3C_6H_3$ internal standard), isolated yield in parentheses.

well as aromatic bromides and chlorides. Primary and secondary alkyl bromides could also be coupled with the indate to give reasonable yields of the desired products. The indate and aluminate nucleophiles gave better yields in the couplings with allyl halides (entries 18−20) in comparison with the equivalent borates (Table 3, entries 24 and 25).[19] 2-Bromopyridine could also be coupled; however, the yield was low (entry 21). This result is in contrast with that for substrate **8z**, where no substitution of the pyridyl chloride residue was observed (entry 13), and presumably reflects the greater reactivity of the pyridyl bromide.[20]

Mechanistic Considerations. There is some debate in the literature as to what the lowest oxidation state is for the iron center in the catalytic cycle when using arylmetal nucleophiles as coupling partners, with suggestions ranging from Fe(−II) through to Fe(II). An Fe(−II)/Fe(0) manifold has been proposed,[7y] on the basis of comparative stoichiometric studies of isolated organoiron species in a variety of oxidation states and their performance as (pre)catalysts. However, as we have previously suggested,[21] the differences in activity can be better explained by the presence or absence of Cp/Cp* ligands in the complexes, rather than their oxidation state.[22] No compelling evidence currently exists that oxidation states as low as Fe(−II) are relevant in the catalytic cycle with aryl nucleophiles, although it is apparent that Fe(−II) complexes with labile ligands are excellent precatalysts. Similarly it has been shown that an Fe(−I) species with labile anthracene ligands can serve as a competent precatalyst.[7am]

The formation of catalytically active zerovalent iron nanoparticles in certain Grignard cross-coupling reactions[7n] demonstrates that oxidation states lower than Fe(II) can be accessed under catalytically relevant conditions. However, these nanoparticles may be a resting state for higher-valent active intermediates, since they react with excess alkyl halides in the absence of nucleophilic coupling partners to give homogeneous solutions.[14c] There has also been a claim that a homoleptic Fe(0) "ate" complex can be isolated under appropriate conditions;[7y] however, this was based on repeating a crystal structure analysis originally undertaken by Shilov,[23] which had previously been shown to have been solved in the incorrect space group and the compound was more likely an Fe(II) hydride.[24] Interestingly, EPR spectra of freshly formed suspensions of iron nanoparticles produced from ArMgX show the presence of a soluble $S = {}^1/_2$ species consistent with the formation of a low-spin Fe(I), suggesting that homogeneous species below the Fe(II) oxidation state can indeed be accessed.[14c] Such Fe(I) species have been proposed as possible catalytic intermediates in the coupling of aryl Grignards and related nucleophiles by Kochi,[2b,25] Norrby,[26] us,[27,12c,14c] and others.[28,7y]

With regard to the Fe(II) oxidation state, iron(II) mesityl complexes have been isolated with both chelating diamine[29,30] and diphosphine ligands,[7bj] and it has been proposed that such complexes represent the lowest oxidation state species in the catalytic cycle.[29] It is important to recognize, though, that the use of such sterically encumbered nucleophiles may represent a special rather than a general case in iron-catalyzed cross-coupling, since bulky aryl ligands on the metal may severely inhibit reduction below Fe(II).[31]

It is crucially important to distinguish between thermodynamically accessible and *kinetically* relevant oxidation states. For a proposed intermediate to be kinetically viable, it must be produced on reaction with the nucleophile on a time scale commensurate with the rate of catalytic turnover and similarly must react with the electrophile at an appropriate rate. Here we focus our attention on the former consideration.[32]

The formation of **9b** from **8a** and MgCl[M(4-tolyl)$_4$] (M = Al, In), with complex **1** acting as precatalyst, is shown in Figure 2. The reactions both reach 50% completion, corresponding to 10 turnovers of the cycle, within 30 s.

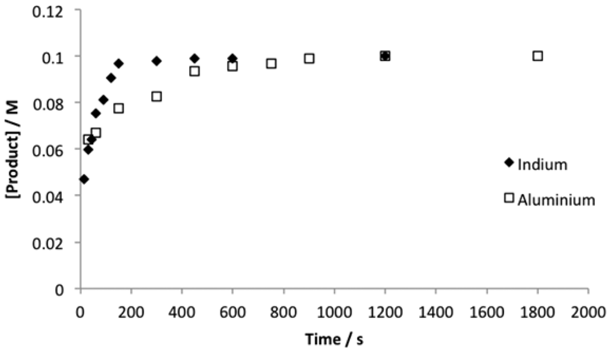


Figure 2. Reaction progress for the formation of **9b** in the coupling of **8a** with either MgCl[In(4-tolyl)$_4$] or MgCl[Al(4-tolyl)$_4$] at 85 °C, catalyzed by **1**.

Reduction of the precatalyst by the arylmetal nucleophile is accompanied by the formation of 4,4′-bitolyl (Scheme 4); thus, the amount of bitolyl formed acts as a proxy for the average oxidation state of the bulk of the iron. Monitoring the rate at which the biaryl is produced provides an indication of whether a given oxidation state is accessed fast enough to be viable in catalysis.

Scheme 4. Correlation of Average Oxidation State with Biaryl Formation

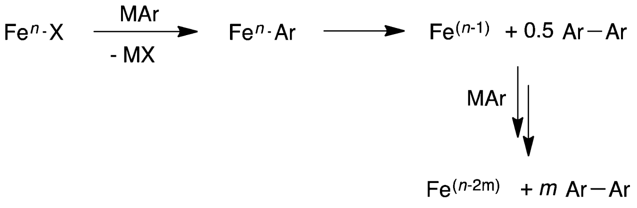


Figure 3 shows the production of 4,4′-bitolyl in the reactions of complex **1** under the same conditions as the catalytic reactions, but without the electrophile **8a**. With both Al- and In-based nucleophiles, the amount of bitolyl produced at the first sampling point (30 s) was consistent with the reduction of the bulk of the iron to Fe(I). While it is apparent that the amount of bitolyl increases beyond these points, suggesting that lower oxidation state iron species are thermodynamically accessible with both nucleophiles, the rate at which these reductions occur in comparison with the rate of catalysis indicates that oxidation states below Fe(I) are unlikely to be kinetically relevant to cross-coupling.

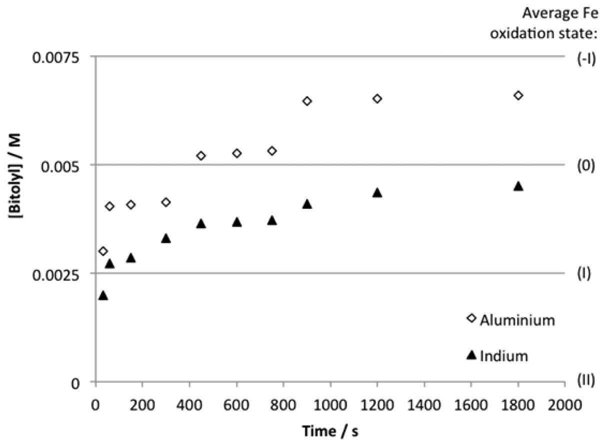
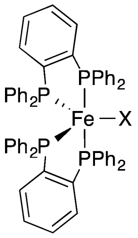
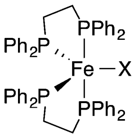


Figure 3. Reduction of **1** in the presence of 20 equiv of MgCl[M(4-tolyl)$_4$] (M = Al, In) at 85 °C.

We previously obtained similar results in iron-catalyzed Negishi reactions, with evidence pointing toward Fe(I) being the lowest kinetically relevant oxidation state when complex **1** was used as the precatalyst. Furthermore, we isolated the Fe(I) complexes **12a–c** from the reactions of **1** with either Ar$_2$Zn or Grignard reagents. While **12a,c** both proved to be catalytically competent, the rate of catalysis with **12a** is too slow for it to be an on-cycle intermediate, while **12c** shows a performance very similar to that of the precatalyst **1**, consistent with it being on-cycle or in equilibrium with an on-cycle intermediate. Similarly, we showed that [FeCl$_2$(dppe)] reacts with benzyl Grignards or the boronate Li[PhB(pinacolato)(^{t}Bu)] to give the Fe(I) complexes **3a,b**.[12c,14c] Kinetic and spectroscopic data for a Suzuki reaction catalyzed by [FeCl$_2$(dppe)] was found to be consistent with the intermediacy of an iron(I) species with a single chelating phosphine ligand, with the five-coordinate iron(I) species **3b** acting as an off-cycle resting state.[14c]



12a: X = 4-tolyl
b: X = Cl
c: X = Br



3c: X = 4-tolyl
d: X = Ph

We have not previously structurally characterized Fe(I) complexes with both dppe and an aryl ligand. Accordingly, the complex **3c** was prepared by the reaction of the 4-tolyl Grignard with the isolated iron(I) halide complex **3a**. The previously reported complex **12a** could also be conveniently prepared from **12b** by this method. The single-crystal X-ray structures of **3c** and the related phenyl complex are shown in Figures 4 and 5, respectively, while the EPR spectrum of **3c** and its simulated spectrum are shown in Figure 6.[33]

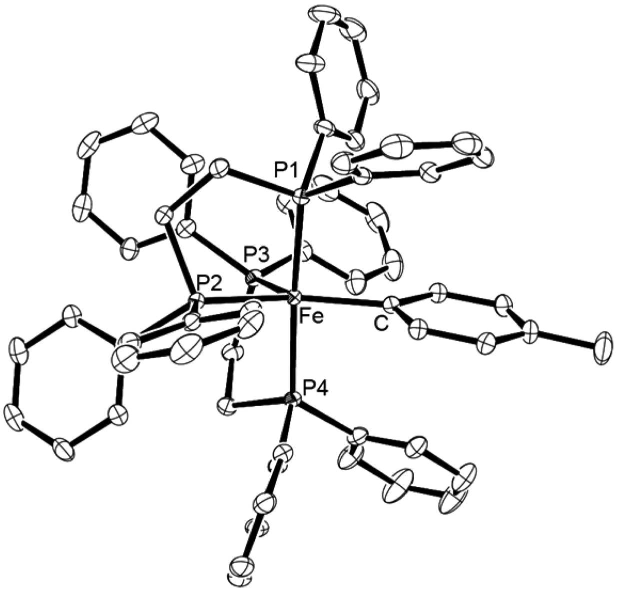


Figure 4. Single-crystal X-ray structure of **3c**. Hydrogen atoms and solvate are omitted for clarity, and thermal ellipsoids are set at the 50% probability level.

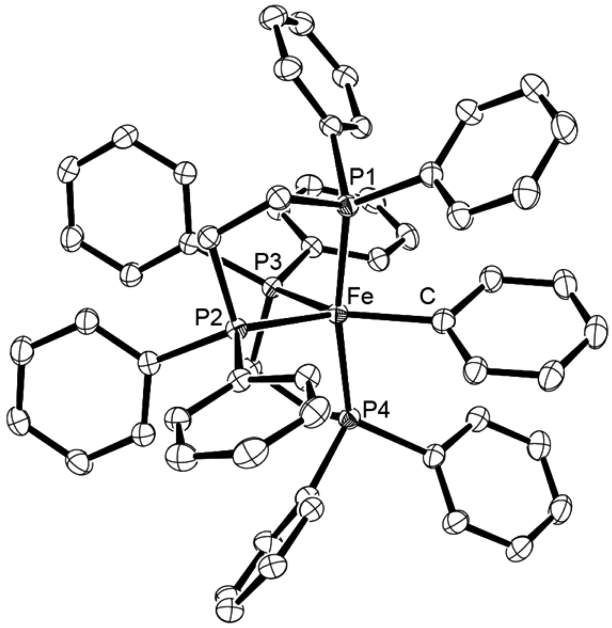


Figure 5. Single-crystal X-ray structure of **3d**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at the 50% probability level.

The solid-state structure of **3c** shows a distortion from trigonal bipyramidal toward square-based pyramidal more pronounced than that observed in complex **12a**,[27] while the geometry about the iron in **3d** is closer to trigonal bipyramidal. This suggests that any subtle differences in electronically preferred geometry are overridden by packing effects in the crystal.

The spin Hamiltonian parameters used in the simulation of the EPR spectrum (Table S1 in the Supporting Information) fit well with the quantum chemical calculations based on a low-spin ($S = {}^{1}/_{2}$) Fe(I) center.[34] Similarly, a density functional theory (standard B3LYP functional, with -D2 dispersion correction, see the Supporting Information for full details) analysis of the ground-state structure of **3c** gave a geometry and electronic structure consistent with low-spin Fe(I) character (Figure 7), with the low-spin state preferred by 14.2 kcal/mol.[34] The Mulliken spin density corresponding to the unpaired electron is located primarily on the Fe atom (87.2%), with only very small contributions from the ligating P and C atoms and the other ligand atoms.

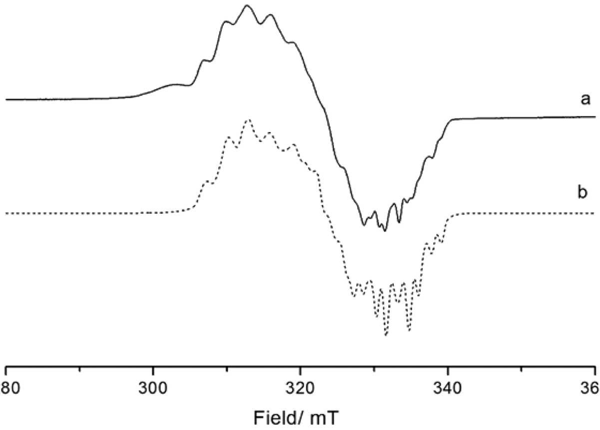


Figure 6. EPR spectrum of complex **3c** (140 K): (a) experimental; (b) simulated. The spectrum also shows the presence of a small amount of residual **3a**, as evidenced by the weak resonance at ~305 mT.

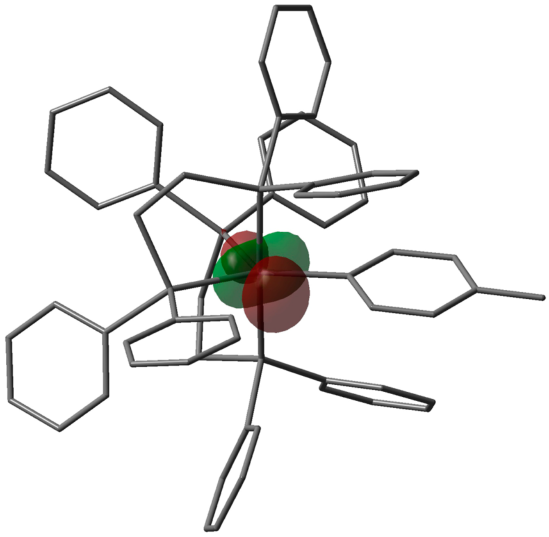


Figure 7. Calculated SOMO (isovalue ±0.05 (electron/bohr^{3})$^{1/2}$) of low-spin complex **3c**, with the ligand residues shown in wireframe.[34]

In order to further characterize isolated Fe(I) complexes, ^{57}Fe Mössbauer spectra of the iron(I) bis(phosphine) complexes **3a–c** and **12b,c** were recorded at 80 K. Figure 8 shows the spectra for the dppe-containing series. The spectra of the halide complexes **3a,b** fit well to single iron species with Mössbauer parameters of δ = 0.42 mm/s, ΔE_Q = 0.51 mm/s and δ = 0.42 mm/s, ΔE_Q = 0.50 mm/s, respectively.

The analogous dpbz-containing complexes **12b,c** (Figure S5, Supporting Information) display similar isomer shifts (δ = 0.43 and 0.44 mm/s, respectively) and slightly larger quarupole splittings (ΔE_Q = 0.61 and 0.65 mm/s, respectively). The asymmetry in the quadrupole split transitions observed in the halide complexes with both dppe and dpbz ligation persists at 5

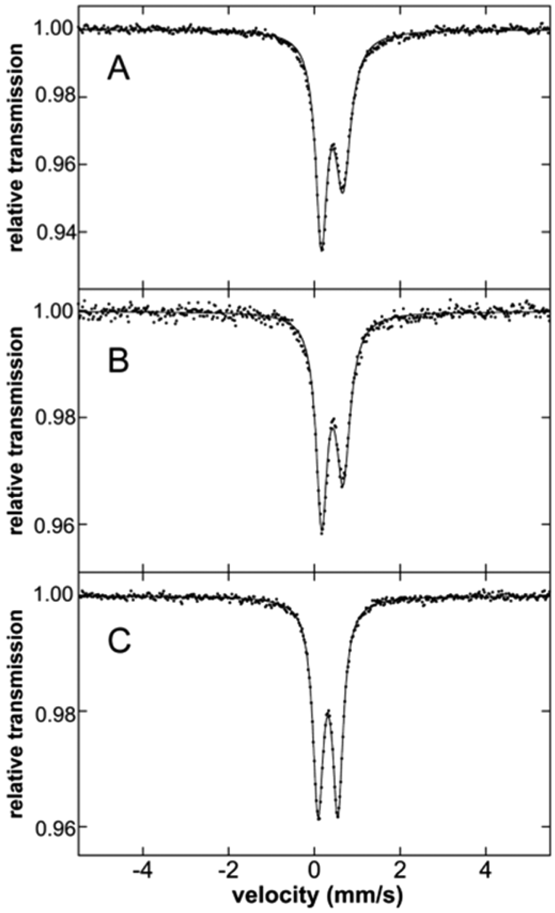


Figure 8. ^{57}Fe Mössbauer spectra (80 K) of (A) complex **3a**, (B) complex **3b**, and (C) complex **3c**. For each spectrum the data (dots) and best fits (solid lines) are shown.

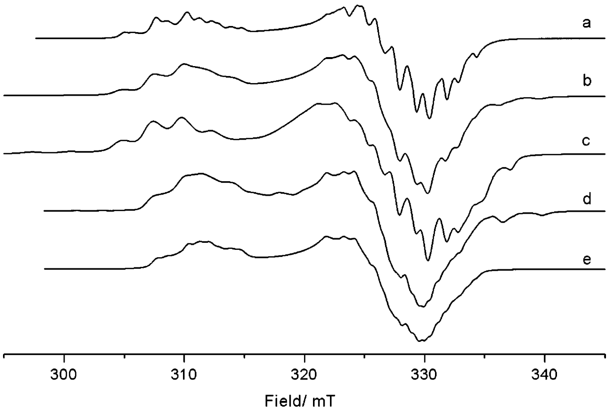


Figure 9. EPR spectra (140 K) of (a) complex **12a** (for comparison), (b) a sample removed from the coupling of **8n** with MgCl[PhB^{s}Bu$_3$] catalyzed by **1** in the presence of 10 mol % of ZnPh$_2$, (c) reaction of **1** with 20 mol % of MgCl[PhB^{s}Bu$_3$], (d) reaction of **1** with 20 mol % of MgCl[9-BBN(^{i}Pr)4-tolyl], and (e) complex **12b** (for comparison).

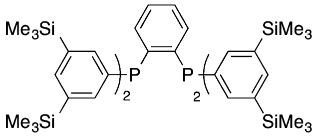
K (and at 250 K for complex **12b**; see the Supporting Information, Figures S5 and S6) and is likely to be due to relaxation and/or texture effects.[35] The spectrum of **3c** is well-fit to a single iron species with parameters of δ = 0.32 mm/s and ΔE_Q = 0.46 mm/s, where the decrease in isomer shift observed upon 4-tolyl coordination is consistent with the stronger electron-donating properties of this ligand in comparison with the halide ligands.

In order to determine whether any of the isolated Fe(I) complexes may be relevant in the coupling reactions of tetraorganoborate nucleophiles, we recorded an EPR spectrum of a sample removed from the catalytic reaction of **8n** with MgCl[PhB^{s}Bu$_3$] catalyzed by **1** in the presence of substoichiometric amounts of diphenylzinc. The spectrum (Figure 9, spectrum b) shows two S = $^1/_2$ complexes, **12b** (minor component) and a species assigned as [FePh(dpbz)$_2$] (**12d**), on the basis of the close similarity of its spectrum to that of complex **12a** (spectrum a).

A zinc additive is essential for optimum catalytic activity with tetraorganoborate nucleophiles (see Table 2, entry 16), and one possible role it may play is to provide an aryl zinc reagent in situ that undergoes more effective transmetalation to the iron center. Indeed, examining the reaction of the borate **10a** with 0.2 equiv of ZnCl$_2$ by ^{11}B NMR spectroscopy[36] showed a diminution of the peak corresponding to the borate anion and an increase in the amount of residual B^{s}Bu$_3$, which is suggestive of the concomitant formation of an arylzinc species. However, an EPR spectrum of the reaction mixture of complex **1** with 20 equiv of MgCl[PhB^{s}Bu$_3$] in the *absence* of a zinc additive (Figure 9, spectrum c) shows that **12b,d** are both formed. Similarly the equivalent reaction with MgCl[9-BBN(^{i}Pr)4-tolyl] yields Fe(I) species, although in this case the chloride complex **12b** predominates (Figure 9, spectrum d).

With regard to other group 13 nucleophiles, the spectrum[36] of a sample removed from the coupling of **8n** with MgCl[Al(4-tolyl)$_4$] catalyzed by **1** shows the presence of the halide complex **12b**, as do spectra recorded for the reactions of **1** with excess MgCl[M(4-tolyl)$_4$] (M = Al, In).[36] In these cases there was evidence to indicate the formation of some of the aryl complex **12a** as a minor component. The EPR spectrum of the equivalent reaction mixture with MgCl[Ga(4-tolyl)$_4$] showed the solution to contain predominantly **12a**;[36] however, the reaction was accompanied by significant precipitation and therefore the spectrum may not accurately represent the product distribution.

It is apparent that dpbz and dppe complexes of iron readily form low-spin (S = $^1/_2$) five-coordinate complexes of the form P$_4$FeX in the presence of a range of nucleophilic substrates. Indeed, the dppe analogues form even when the ratio of dppe to iron is 1:1, implying rapid ligand redistribution.[14c] In contrast, we recently showed that a bulky analogue of dpbz, ligand **13**, which has been exploited in a range of iron-catalyzed cross-coupling reactions,[14a,b] does not give a P$_4$FeX species. Instead, the EPR spectroscopic data are consistent with the formation of an S = $^1/_2$ complex of the form FeX(**13**) with inequivalent P-donor environments.[14c]



13

We were interested to see whether a bulky analogue of dppe, ligand **6**, would behave in the same way as dppe and dpbz or whether its bulk would prevent the formation of a five-coordinate P$_4$Fe(I) intermediate. Figure 10 shows the EPR spectrum recorded after the reaction of FeCl$_2$ with **6a** and 20 equiv of MgCl[4-tolylB^{s}Bu$_3$]. It is apparent that the solution contains an S = $^1/_2$ complex with a single ligand of **6** with nonequivalent P-donor environments. The signals are very

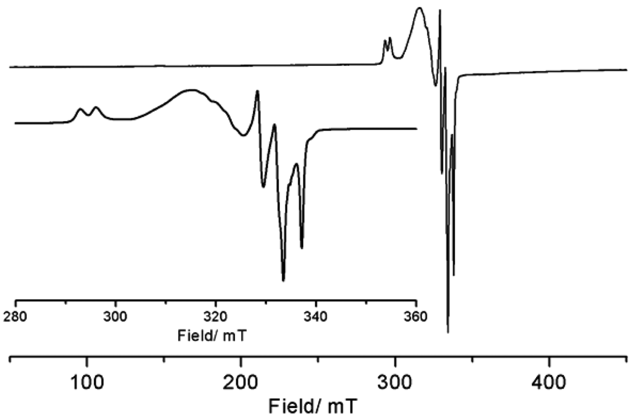
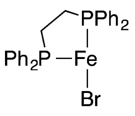


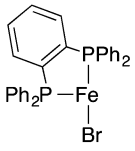
Figure 10. EPR spectrum (140 K) of mixture obtained on reacting $FeCl_2$ with 2 equiv of **6** and 20 equiv of MgCl[(4-tolyl)B^{s}Bu$_3$] in THF at room temperature.

similar to those observed previously for FeX(**13**) and are consistent with a low-spin Fe(I) complex of the form FeX(**6**) (X = halide, 4-tolyl).

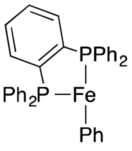
With regard to the nonequivalency of the P-donor environments, it may seem reasonable to assume that these iron(I) complexes of ligands **6** and **13** are three-coordinate T-shaped species, analogous with d^8 Pt(II) T-shaped complexes[37] but with a singly occupied d$_{z^2}$ orbital. To probe this, we used DFT to examine the ground-state structures of truncated complexes using the model compounds **14a′−c′**.



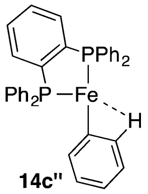
14a'



14b'



14c'



14c''

The bromide-containing models **14a′**,**b′** display a pronounced preference for high-spin (S = $^3/_2$) ground states, with calculated quartet−doublet gaps of 17.8 and 18.4 kcal/mol, respectively. Similarly, a high-spin ground state is preferred for **14c′** by 14.3 kcal/mol, although in this case the calculated HS−LS gap is reduced to 11.3 kcal/mol on the inclusion of an agostic interaction in the model (**14c″**). While the low-spin models do show a pronounced tendency toward a T-shaped geometry, the energetically more favorable high-spin systems tend toward a Y-shaped geometry (Table 6).

The calculated preference for high-spin ground states for models **14a′−c′** means that is highly unlikely that the S = $^1/_2$ species observed in solution are three-coordinate. It is far more probable that the observed nonequivalence of the phosphine donors results from the iron centers adopting a higher coordination number, most likely by a secondary interaction with a π system on one of the ligands.[38]

Table 6. Selected Bond Angles for Low-Spin and High-Spin Models 14

	P$_a$−Fe−X	P$_b$−Fe−X	P$_a$−Fe−P$_b$
LS-**14a′**	128.9	139.2	85.7
LS-**14b′**	121.6	153.9	83.5
LS-**14c′**	104.6	169.9	84.2
LS-**14c″**	106.6	167.5	85.8
HS-**14a′**	130.7	134.2	84.9
HS-**14b′**	131.6	141.0	83.7
HS-**14c′**	134.0	134.0	82.3

■ CONCLUSIONS

We have demonstrated that a range of chelating diphosphine complexes of iron(II) can be used as precatalysts in the Suzuki coupling of tetraarylborates with benzyl halides. The judicious choice of appropriate BR_3 precursors allows the use of easily prepared [ArBR$_3$]$^-$ reagents, in place of tetraarylborates, in the coupling with a range of electrophilic partners. Furthermore, these coupling reactions can be extended to [MAr$_4$]$^-$ or MAr$_3$ nucleophiles (M = Al, Ga, In, Tl).

From a mechanistic perspective, we have presented evidence that suggests that while lower average oxidation states can be accessed upon reacting a representative precatalyst with [M(4-tolyl)$_4$]$^-$ (M = Al, In), only reduction to Fe(I) is fast enough to be relevant in the catalytic cycle. EPR spectroscopic data show that well-defined iron(I) complexes of the type P$_4$FeX readily form with smaller chelating diphosphine ligands under catalytic conditions with [ArMR$_3$]$^-$ (M = B, Al, In), in addition to our previous observations that they can be produced in the presence of arylzinc, aryl- and benzylmagnesium, and Li[PhB(pinacolato)(^{t}Bu)] reagents.[27,12c,14c,21] With very bulky chelating diphosphines, EPR data suggest that P$_4$FeX complexes do not form; instead, low-spin Fe(I) species of the type P$_2$FeX are produced.

It should be noted that, while the data are consistent with the formation of Fe(I) complexes under catalytic conditions, this does not necessarily indicate that these species lie on the catalytic cycle. In order to address this, we are currently undertaking detailed kinetic experiments, the results of which will be reported in due course.

■ EXPERIMENTAL SECTION

General Procedures. All air-sensitive manipulations were carried out using standard Schlenk-line and glovebox techniques. Solvents were dried and purified using Anhydrous Engineering double-alumina and alumina−copper catalyst dry columns. Commercial grade solvents were used for chromatography and extraction. [FeCl$_2$(dpbz)$_2$],[39] [FeCl$_2$(dppe)],[40] [FeCl$_2$(dppp)],[41] [FeCl$_2$(dmpe)$_2$],[42] Ph-9-BBN and ^{i}Pr-9-BBN,[43] and bromodiphenylthallium[44] were synthesized according to literature procedures. All other reagents were purchased from commercial suppliers and used without further purification. X-band EPR spectra of frozen solutions in THF (140 K) were recorded on a Bruker EMX spectrometer operating at 100 kHz field modulation and 10 mW microwave power and equipped with a high-sensitivity Bruker cavity (ER 4119HS). Spectral simulations were performed using the Sim32[45] and EasySpin[46] software packages. All solid samples for ^{57}Fe Mössbauer spectroscopy were run on nonenriched samples of the as-isolated complexes. All samples were prepared in an inert-atmosphere glovebox equipped with a liquid nitrogen fill port to enable sample freezing to 77 K within the glovebox. Each sample was loaded into a Delrin Mössbauer sample cup for measurements and loaded under liquid nitrogen. Low-temperature ^{57}Fe Mössbauer measurements were performed using a SeeCo MS4Mössbauer spectrometer integrated with a Janis SVT-400T He/N$_2$ cryostat for measurements at 5 and 80 K with a 0.07 T applied magnetic field. Isomer shifts were determined relative to α-Fe at 298 K. All Mössbauer spectra were fit using the program WMoss (SeeCo).

Preparation of 1-(Diphenylphosphino)-2-(diisopropylphosphino)benzene (4). (2-Bromophenyl)diphenylphosphine (0.3 mmol, 0.103 g) was dissolved in Et$_2$O and the solution stirred. n-Butyllithium (2.5 M in hexanes, 0.3 mmol, 0.120 mL) was added dropwise, and the reaction mixture was stirred for 30 min. Chlorodiisopropylphosphine (0.3 mmol, 0.046 g) was added, and the reaction mixture was stirred for a further 30 min. A saturated aqueous solution of NH_4Cl (5 mL) was added, and the aqueous layer was washed with CH_2Cl_2 (3 × 5 mL). The combined organic fractions were dried with $MgSO_4$ and evaporated to dryness. The product was recrystallized from methanol (96%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.2−7.1 (4H, m, Ar*H*), 6.9−6.8 (10H, m, Ar*H*), 1.9 (2H, hept, *J* = 6.9 Hz, C*H*), 1.07 (3H, d, *J* = 7.1 Hz, CH_3), 1.02 (d, *J* = 7.1 Hz, CH_3), 0.76 (3H, d, *J* = 6.9 Hz, CH_3), 0.72 (3H, d, *J* = 6.9 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 146.3 (dd, *J* = 31.7 Hz, *J* = 9.8 Hz), 142.3 (dd, *J* = 30.0 Hz, *J* = 16.7 Hz), 138.0 (dd, *J* = 13.3 Hz, *J* = 6.3 Hz), 134.2 (d, *J* = 19.6 Hz), 133.8 (d, *J* = 8.1 Hz), 132.5, 129.0, 128.6, 128.3, 128.2, 24.7 (d, *J* = 13.9 Hz), 20.1 (d, *J* = 17.3 Hz), 19.5 (d, *J* = 10.3 Hz). ^{31}P NMR (160 MHz, THF, 25 °C): δ −2.7 (d, *J* = 154 Hz), −10.0 (d, *J* = 154 Hz). MS (EI) *m*/*z* (%): 378.2 (13) $[M]^+$, 335.1 (100), 301.1 (4), 292.1 (18), 183.0 (54). Anal. Calcd for $C_{24}H_{28}P_2$: C, 76.17; H, 7.46. Found: C, 76.26; H, 7.48.

Preparation of 2-(Diphenylphosphino)-*N*,*N*-dimethylaniline (5a). *N*,*N*-Dimethylaniline (120 mmol, 14.53 g) was dissolved in hexane (40 mL). Over a period of 1 h, *n*-butyllithium (2.5 M in hexanes, 100 mmol, 16.5 mL) was added. The solution was heated to reflux and stirred for 5 h before being cooled to room temperature. The solution was cooled to −78 °C, and chlorodiphenylphosphine (100 mmol, 22.12 g) was added. The reaction mixture was stirred for 1 h before being warmed to reflux and stirred for a further 5 h. Once the mixture was cooled, degassed water (30 mL) was added and the mixture was stirred vigorously for 10 min. The organic layer was then removed, and the aqueous layer was washed with Et_2O (2 × 30 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was recrystallized from CH_2Cl_2/EtOH (42%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.37−7.20 (12H, m, Ar*H*), 7.01 (1H, td, *J* = 7.7 Hz, *J* = 1.28 Hz, Ar*H*), 6.81 (1H, dd, *J* = 7.7 Hz, J = 1.28 Hz, Ar*H*), 2.61 (6H, s, NCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 158.1 (d, *J* = 20.0 Hz), 138.2 (d, *J* = 12.3 Hz), 134.5, (d, *J* = 8.4 Hz), 134.3, 133.7 (d, *J* = 20.0 Hz), 129.8, 128.3, 128.2, 124.4, 120.6 (d, *J* = 2.3 Hz), 45.5. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ −13.87. MS (EI) *m*/*z* (%): 306.4 (100) $[M + H]^+$, 228.3 (28), 214.3 (34), 185.2 (15). Anal. Calcd for $C_{20}H_{20}NP$: C, 78.67; H, 6.60; N, 4.59. Found: C, 78.36; H, 6.80; N, 4.50.

Preparation of 2-(Dicyclohexylphosphino)-*N*,*N*-dimethylaniline (5b). 2-Bromo-*N*,*N*-dimethylaniline was dissolved in Et_2O and the solution cooled to −40 °C. Over a period of 1 h, *n*-butyllithium (1.6 M in hexanes) was added and the resulting suspension was warmed to room temperature. The solvent was removed by filter cannula and the precipitate washed with cold hexanes and redissolved in Et_2O. Chlorodicyclohexylphosphine was added dropwise, and the mixture was stirred for 48 h, following which all volatiles were removed in vacuo. The residue was dissolved in CH_2Cl_2 and washed with $NaHCO_3$ and water, following which the organic layer was collected, dried over $MgSO_4$, and filtered and the volatiles were removed in vacuo. The residue was dissolved in pentane and passed through a plug of silica; removal of the solvent yielded the product as a white solid (30%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.39−7.32 (1H, dt, *J* = 7.5, 2.0 Hz), 7.28 (1H, m), 7.13 (1H, m), 7.08−7.00 (1H, td, *J* = 7.3, 1.3 Hz), 2.72 (6H, s), 1.93−1.50 (12H, m), 1.38−0.92 (10H, m). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ 160.5, 133.4 (d, *J* = 3.2 Hz), 131.6, 129.4, 123.2, 119.8 (d, *J* = 3.4 Hz), 46.0 (d, *J* = 5.2 Hz), 33.9 (d, *J* = 14.4 Hz), 29.1 (d, *J* = 8.9 Hz), 27.5 (d, *J* = 11.7 Hz), 27.3 (d, *J* = 7.7 Hz), 26.6. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ −12.68.

Preparation of 1,2-{Bis[3,5-bis(trimethylsilyl)phenyl]-phosphino}ethane (6). 1,2-Bis(dichlorophosphino)ethane (1.0 mmol) was dissolved in THF (5 mL) and the solution cooled to −78 °C. To this solution was added [3,5-bis(trimethylsilyl)phenyl]-magnesium bromide (4.5 mmol, 0.42 M in THF) dropwise, and the mixture was warmed to room temperature and stirred for 16 h. A saturated aqueous solution of NH_4Cl (5 mL) was added, and the aqueous layer was washed with CH_2Cl_2 (3 × 5 mL). The combined organic fractions were dried with $MgSO_4$ and evaporated to dryness. The crude residue was triturated with methanol (2 × 10 mL) and the product obtained as a white solid (68%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.59 (4H, app s, Ar*H*), 7.57−7.53 (8H, m, Ar*H*), 2.22−2.18 (4H, m, PCH_2), 0.22−0.18 (72H, m, SiCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 139.5 (d, *J* = 2.77 Hz), 138.5 (2C), 138.2 (d, *J* = 9.73 Hz, (2C)), 135.9, 24.79, −0.95. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C).: δ −12.53. HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{50}H_{88}P_2Si_8$ 975.4515; found 975.4588. Anal. Calcd for $C_{50}H_{88}P_2Si_8$: C, 61.54; H, 9.09. Found: C, 61.29; H, 8.91.

Preparation of 1,3-[Bis(3,5-dimethylphenyl)phosphino]-propane (7a). 1,3-Bis(dichlorophosphino)propane (1.0 mmol) was dissolved in THF (5 mL) and the solution cooled to −78 °C. (3,5-Dimethylphenyl)magnesium bromide (4.4 mmol, 1.5 M in THF) was added, and the reaction mixture was stirred for 30 min before it was warmed to room temperature. A degassed saturated solution of aqueous NH_4Cl was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$, filtered, and evaporated to dryness. The crude residue was triturated with ethanol (2 × 3 mL) and the product obtained as a white crystalline solid (48%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.92 (4H, s, Ar*H*), 6.90 (4H, s, Ar*H*), 6.84 (4H, s, Ar*H*), 2.18 (24H, s), 2.07 (4H, t, *J* = 8.07 Hz), 1.51 (2H, tt, *J* = 9.54 Hz, *J* = 2.93 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 137.5, 137.3, 136.6, 136.5, 129.4, 129.2, 28.6, 21.7, 20.3. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ −17.63. HRMS (ESI) *m*/*z*: [M + H]+ calcd for $C_{35}H_{42}P_2$ 525.28; found 525.284.

Preparation of 1,3-{Bis[3,5-bis(trimethylsilyl)phenyl]-phosphino}propane (7b). 1,3-Bis(dichlorophosphino)propane (1.18 mmol, 0.290 g) was dissolved in THF and cooled to −78 °C. [3,5-Bis(trimethylsilyl)phenyl]magnesium bromide (5.0 mmol, 0.18 M in THF) was added dropwise, and the reaction mixture was stirred for 30 min before it was warmed to room temperature. A degassed saturated solution of aqueous NH_4Cl was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic fractions were dried with $MgSO_4$, filtered, and evaporated to dryness. The product was recrystallized from degassed ethanol (48%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.60 (4H, app q, *J* = 1.1 Hz, Ar*H*), 7.53 (8H, app dd, *J* = 7.3 Hz, *J* = 1.1 Hz, Ar*H*), 2.25 (4H, t, *J* = 7.7 Hz, PCH_2), 1.77 (m, CH_2C$H_2$$CH_2$), 0.22 (72H, s, SiC$H_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 139.4 (d, *J* = 5.2 Hz), 138.3, 138.1 (d, *J* = 18.4 Hz), 136.3 (d, *J* = 14.5 Hz), 30.0 (t, *J* = 12.0 Hz), 23.3 (t, *J* = 16.4 Hz), −1.1. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ −17.53 (s). HRMS (CI) *m*/*z*: $[M + H]^+$ calcd for $C_{51}H_{91}P_2Si_8$ 989.4754; found 989.4744. Anal. Calcd for $C_{51}H_{91}P_2Si_8$: C, 61.88; H, 9.16; found: C, 61.06; H, 8.77.

General Procedure for Iron-Catalyzed Suzuki Coupling with Na[BPh$_4$] (GP1) (Table 1). The Fe salt or complex (0.025 mmol), Na[BPh$_4$] (0.214 g, 0.625 mmol), and ligand (0, 0.025, or 0.05 mmol as appropriate) were dissolved in toluene (5 mL), and the mixture was stirred at room temperature for 10 min. $ZnPh_2$ (1.0 mL, 0.05 M, 0.05 mmol) was added, and the reaction mixture was stirred for a further 10 min. **8a** (70 μL, 0.5 mmol) was then added and the reaction mixture heated to 85 °C for 4 h. The mixture was cooled and quenched with water (5 mL), and 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) was added as an internal standard. The organic fractions were extracted into CH_2Cl_2 (3 × 10 mL), and the extracts were combined and filtered through a plug of $MgSO_4$. The solvent was removed in vacuo and the residue redissolved in $CDCl_3$ for ^1H NMR analysis.

General Procedure for Iron-Catalyzed Suzuki Coupling with MgCl[(^{s}Bu)$_3$B(4-tolyl)] (10a) (GP2) (Table 2). Tri-*sec*-butylborane (0.6 mmol, 1 M in THF) was placed in a Schlenk tube and cooled to −78 °C. To this solution was added 4-tolylmagnesium chloride (0.6 mmol, 2 M in THF), and the mixture was warmed to room temperature and stirred for a further 30 min. **1** (25 mg, 0.025 mmol) and Zn(4-tolyl)$_2$ (0.05 mmol, 0.05 M in THF) were added, resulting in a red solution. Toluene (3 mL) and the appropriate alkyl halide (0.5 mmol) were then added, and the reaction mixture was heated to 85 °C for 4 h. The reaction mixture was quenched and product distribution determined as described in GP1. Alternatively, the product was isolated using flash-column chromatography.

General Procedure for Iron-Catalyzed Suzuki Coupling with Borates Generated from Ph-9-BBN (GP3) (Table 2). Ph-9-BBN (0.105 mL, 0.5 mmol) was dissolved in THF and the solution cooled to −78 °C. To this solution was added the appropriate organometallic reagent (0.5 mmol), and the mixture was warmed to room temperature and stirred for a further 30 min. **1** (25 mg, 0.025 mmol) and $ZnPh_2$ (0.05 mmol, 0.05 M in THF) were added, resulting in a red solution. Toluene (3 mL) and **8a** (0.5 mmol) were then added, and the reaction mixture was heated to 85 °C for 4 h. The reaction mixture was quenched and product distribution determined as described in GP1.

General Procedure for Iron-Catalyzed Suzuki Coupling with MgCl[9-BBN(^{i}Pr)(4-tolyl)] (10b) (GP4) (Table 2). ^{i}Pr-9-BBN (0.119 mL, 0.6 mmol) was dissolved in THF and the solution cooled to −78 °C. To this solution was added 4-tolylmagnesium chloride (0.6 mmol, 2 M in THF), and the mixture was warmed to room temperature and stirred for a further 30 min. **1** (25 mg, 0.025 mmol) and Zn(4-tolyl)$_2$ (0.05 mmol, 0.05 M in THF) were added, resulting in a red solution. Toluene (3 mL) and the appropriate alkyl halide (0.5 mmol) were then added, and the reaction mixture was heated to 85 °C for 4 h. The reaction mixture was quenched and product distribution determined as described in GP1.

General Procedure for Iron-Catalyzed Coupling of Aryl Aluminum Reagents with Benzyl Halides (GP5) (Table 4). $AlCl_3$ (0.3 or 0.6 mmol as appropriate) was dissolved in THF (1 mL) and cooled to 0 °C. To this solution was added 4-tolylmagnesium chloride (3 or 4 equiv as appropriate), and the mixture was warmed to room temperature and stirred for a further 30 min. **1** (25 mg, 0.025 mmol), toluene (3 mL), and the appropriate benzyl halide (0.5 mmol) were added, and the mixture was heated to 85 °C for 4 h. The reaction mixture was quenched and product distribution determined as described in GP1. Alternatively, the product was isolated using flash-column chromatography.

General Procedure for Iron-Catalyzed Coupling of Aryl Gallium Reagents with 3-Methoxybenzyl Bromide (8a) (GP6) (Table 4). $GaCl_3$ (0.25 or 0.6 mmol, 0.5 M in pentane) was placed in a Schlenk tube, and the solvent was removed in vacuo. The residue was redissolved in Et_2O (2 mL) and cooled to 0 °C, the appropriate aryl Grignard reagent (4 equiv) was added, and the resulting suspension was warmed to room temperature. **1** (25 mg, 0.025 mmol) and $ZnAr_2$ (0.05 mmol where appropriate) were added, resulting in a red solution. Toluene (3 mL) was added, the mixture was heated to 85 °C, **8a** (70 μL, 0.5 mmol) was added, and the reaction mixture was stirred at the same temperature for 4 h. The reaction mixture was quenched and product distribution determined as described in GP1.

General Procedure for Iron-Catalyzed Coupling of Aryl Indium Reagents with Alkyl Halides (GP7) (Table 4). $InCl_3$ (0.25 or 0.5 mmol as appropriate) was dissolved in THF (2 mL) and cooled to 0 °C. To this solution was added 4-tolylmagnesium chloride (3 or 4 equiv as appropriate), and the mixture was warmed to room temperature and stirred for a further 30 min. **1** (25 mg, 0.025 mmol), Zn(4-tolyl)$_2$ (0.05 mmol where appropriate), toluene (3 mL), and the appropriate alkyl halide (0.5 mmol) were added, and the mixture was heated to 85 °C for 4 h. The reaction mixture was quenched and product distribution determined as described in GP1. Alternatively, the product was isolated using flash-column chromatography.

Iron-Catalyzed Coupling of Triphenylthallium with 3-Methoxybenzyl Bromide (Table 4). Ph_2TlBr (0.22 g, 0.5 mmol) was dissolved in THF (2 mL) and cooled to −78 °C. To this solution was added phenyllithium (0.27 mL, 1.8 M in THF), and the mixture was warmed to room temperature and stirred for a further 30 min. **1** (25 mg, 0.025 mmol), $ZnPh_2$ (0.05 mmol where appropriate), toluene (3 mL), and **8a** (70 μL, 0.5 mmol) were added, and the mixture was heated to 85 °C for 4 h. The reaction mixture was quenched and product distribution determined as described in GP1.

Reaction Profiles for Iron-Catalyzed Coupling of 3-Methoxybenzyl Bromide (8a) with [In(4-tolyl)$_4$]MgCl or [Al(4-tolyl)$_4$]MgCl (Figure 2). The appropriate nucleophile (1.0 mmol) was generated according to GP5 or GP7. **1** (50 mg, 0.05 mmol), 1,3,5-trimethoxybenzene (84 mg, 0.5 mmol), and toluene (5 mL) were then added, and the mixture was heated to 85 °C. **8a** (140 μL, 1.0 mmol) was dissolved in toluene (sufficient to give a total reaction volume of 10 mL) in a separate Schlenk and heated to 85 °C, and this was then added to the reaction mixture. Samples (0.1 mL) were taken and quenched in 1/1 EtOAc/H_2O at appropriate time points. For each sample, the organic layer was removed and filtered and the solvent removed in vacuo. The residue was redissolved in $CDCl_3$ for ^{1}H NMR analysis.

Reduction Profiles for [FeCl$_2$(dpbz)$_2$] (1) with [In(4-tolyl)$_4$]MgCl or [Al(4-tolyl)$_4$]MgCl (Figure 3). The appropriate nucleophile (1.0 mmol) was generated according to GP5 or GP7, toluene (5 mL) was added, the mixture was heated to 85 °C, and a sample (0.1 mL) was taken and quenched to determine the initial concentration of 4,4′-bitolyl. In a separate Schlenk tube, **1** (50 mg, 0.05 mmol) and 1,3,5-trimethoxybenzene (84 mg, 0.5 mmol) were suspended in toluene (to give a total volume of 10 mL) and heated to 85 °C. The nucleophile solution was added, and samples (0.1 mL) were taken and quenched in 1/1 EtOAc/H_2O at the appropriate time points. For each sample, the organic layer was removed and filtered and the solvent removed in vacuo. The residue was redissolved in $CDCl_3$ for ^{1}H NMR analysis.

Synthesis of [Fe(4-tolyl)(dppe)$_2$] (3c). 4-Tolylmagnesium chloride (10 mmol, 2 M in THF) was added to a deep red solution of [FeCl(dppe)$_2$] (200 mg, 225 μmol) in THF (10 mL). Dioxane (1 mL) was added to the reaction mixture, the colorless precipitates that formed within 1 h were filtered off, and the solvent was removed from the solution in vacuo. The crude product was dissolved in Et_2O (5 mL), layered with hexanes (2 mL), and stored at −35 °C overnight. The product was isolated by filtration as a deep red-brown amorphous solid (51 mg, 24%) and characterized by EPR and Mössbauer spectroscopy and single-crystal X-ray analysis (see main text). Magnetic moment: 1.78 μ_B (Evans method). Anal. Calcd for $C_{59}H_{55}FeP_4$: C, 75.08; H, 5.87. Found: C, 74.30; H, 5.91.

Synthesis of [Fe(phenyl)(dppe)$_2$] (3d). To a solution of [FeCl$_2$(dppe)] (1.90 mmol) in THF/dioxane (6/1, 20 mL) at −30 °C was slowly added phenylmagnesium bromide (1.0 M in THF, 4.18 mmol). After the mixture was stirred at −30 °C for 1 h, salts were removed by filtration at −30 °C. The volume was reduced to ~5 mL, and 20 mL of hexane was added at −30 °C, leading to the isolation of crystalline **3d** (~220 mg) as a purple-red solid which was characterized by EPR spectroscopy and single-crystal X-ray analysis (see main text). We were unable to obtain a satisfactory elemental analysis for **3d**, despite repeated attempts, presumably due to its sensitivity.

EPR Spectroscopic Study of Iron-Catalyzed Coupling of 3-Methoxybenzyl Chloride and MgCl[(^{s}Bu)$_3$BPh] (Figure 9b). Phenylmagnesium chloride (2.0 mmol, 2 M in THF) was added to tri-*sec*-butylborane (2.0 mmol, 1 M in THF) at −78 °C. The mixture was warmed to room temperature, and $ZnPh_2$ (0.2 mmol) and **1** (0.102 g, 0.1 mmol) were added followed by THF (1 mL), yielding a deep red solution. **8n** (0.291 mL, 2.0 mmol) was added, and an aliquot (120 μL) was removed after 2 min and analyzed by EPR spectroscopy, showing the formation of two $S = {}^1/_2$ species consistent with a mixture of **12a** (major) and **12b** (minor).

In Situ Generation of Fe(I) by Reduction of [FeCl$_2$(dpbz)$_2$] (1) with MgCl[(^{s}Bu)$_3$BPh] (Figure 9c). Phenylmagnesium chloride (2.0 mmol, 2 M in THF) was added to tri-*sec*-butylborane (2.0 mmol, 1 M in THF) at −78 °C. The mixture was warmed to room temperature, and **1** (0.102 g, 0.1 mmol) was added followed by THF (1 mL), yielding a deep red solution. An aliquot (120 μL) was removed and analyzed by EPR spectroscopy, showing the formation of two $S = {}^1/_2$ species consistent with a mixture of **12a** (major) and **12b** (minor).

In Situ Generation of [FeCl(dpbz)$_2$] (12b) by Reduction of [FeCl$_2$(dpbz)$_2$] (1) with MgCl[9-BBN(^{i}Pr)(4-tolyl)] (10b) (Figure 9d). 4-Tolylmagnesium chloride (2.0 mmol, 2 M in THF) was added to a solution of ^{i}Pr-9-BBN (2.0 mmol, 1 M in THF) at −78 °C. The mixture was warmed to room temperature, and **1** (0.102 g, 0.1 mmol) was added followed by THF (1 mL), yielding a deep red solution. An aliquot (120 μL) was removed and analyzed by EPR spectroscopy, showing the formation of **12b**.

EPR Spectroscopic Study of Iron-Catalyzed Coupling of 3-Methoxybenzyl Chloride (8n) and MgCl[Al(4-tolyl)$_4$] or MgCl[In(4-tolyl)$_4$] (Figure S3, Supporting Information). 4-Tolylmagnesium chloride (8.0 mmol, 2 M in THF) was added to a solution of either $InCl_3$ (2.0 mmol, 1 M in THF) or $AlCl_3$ (2.0 mmol, 0.5 M in

THF) at 0 °C. The mixture was warmed to room temperature, and **1** (0.102 g, 0.1 mmol) was added, resulting in a deep red solution. **8n** (0.291 mL, 2.0 mmol) was added, and an aliquot (120 μL) was removed after 2 min and analyzed by EPR spectroscopy.

In Situ Generation of [FeCl(dpbz)$_2$] (12b) by Reduction of [FeCl$_2$(dpbz)$_2$] (1) with MgCl[Al(4-tolyl)$_4$] and MgCl[In(4-tolyl)$_4$] (Figure S3, Supporting Information). 4-Tolylmagnesium chloride (8.0 mmol, 2 M in THF) was added to a solution of either $InCl_3$ (2.0 mmol, 1 M in THF) or $AlCl_3$ (2.0 mmol, 0.5 M in THF) at 0 °C. The mixture was warmed to room temperature, and **1** (0.102 g, 0.1 mmol) was added, resulting in a deep red solution. An aliquot (120 μL) was removed and analyzed by EPR spectroscopy, showing the formation of **12b**.

In Situ Generation of [Fe(4-tolyl)(dpbz)$_2$] (12a) by Reduction of [FeCl$_2$(dpbz)$_2$] (1) with MgCl[Ga(4-tolyl)$_4$] (Figure S3, Supporting Information). $GaCl_3$ (2.0 mmol, 0.5 M in pentane) was added to a Schlenk tube and the solvent removed in vacuo. The vessel was cooled to −78 °C ,and THF (1 mL) was added, followed by 4-tolylmagnesium chloride (8.0 mmol, 2 M in THF). The mixture was warmed to room temperature, and **1** (0.102 g, 0.1 mmol) was added, resulting in a deep red solution. An aliquot (120 μL) was removed and analyzed by EPR spectroscopy, showing the formation of **12a**.

In situ Reduction of [FeBr$_2$(6)] (Figure 10). $FeBr_2$ (22 mg, 0.1 mmol) and **6** (196 mg, 0.2 mmol) were dissolved in THF (3 mL) and stirred for 5 min at room temperature. To this solution was added MgCl[(^{s}Bu)$_3$BPh] (2.0 mmol, 2 M in THF) and the resulting solution stirred for 10 min at room temperature. An aliquot (120 μL) was removed and analyzed by EPR spectroscopy, showing the formation of an $S = {}^1/_2$ species.

Reaction of MgCl[(^{s}Bu)$_3$B(4-tolyl)] (10a) with ZnCl$_2$ (Figure S2, Supporting Information). A solution of **10a** was prepared according to GP2. $ZnCl_2$ (7 mg, 0.05 mmol) was palced in a Schlenk tube, and this was treated with tolyl tri-*sec*-butylborate (0.25 mmol). The reaction was monitored by ^{11}B NMR spectroscopy, and the change in intensity of the peaks was followed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF and xyz files giving spectroscopic data for the isolated organic products, EPR spectra, ^{57}Fe Mössbauer spectra, experimental details for the DFT calculations, and crystallographic data for **3c**,**d**, **4**, **6**, and **7a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) Abbreviations: dpbz, 1,2-bis(diphenylphosphino)benzene; dppe, 1,2-bis(diphenylphosphino)ethane; dmpe, 1,2-bis(dimethylphosphino)ethane; depe, 1,2-bis(diethylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane.

(17) The shifts are similar to those of mixed aryl−alkyl tetraorganoborate salts. See for instance: Bedford, R. B.; Gower, N. J.; Haddow, M. F.; Harvey, J. N.; Nunn, J.; Okopie, R. A.; Sankey, R. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 5435. In all three cases the tetraorganoborates were the major species observed. See the Supporting Information for spectra..

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(31) It should be noted that Nakajima and Ozawa showed that an Fe(II) PNP-pincer complex can be reduced to a (PNP)Fe^{I}(mes) species on reaction with mesitylmagnesium reagents with the concomitant formation of $^{1}/_{2}$ equiv of bimesitylene. See: Nakajima, Y.; Ozawa, F. *Organometallics* **2012**, *31*, 2009.

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