Steric and Electronic Effects of Benzoferrocenyl Phosphine Ligands on Palladium-Catalyzed Allylic Alkylation and Suzuki Coupling Reactions

Muralidhara Thimmaiah, Rudy L. Luck and Shiyue Fang*

Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, USA

Abstract: Five benzoferrocenyl phosphine ligands with the phosphorus atom attached to the 5-position of the benzoferrocene and some ligand-$Mo(CO)_5$ complexes were prepared and fully characterized; the structure of one ligand was confirmed by X-ray crystallography. These ligands were applied in palladium-catalyzed allylic alkylation and Suzuki coupling of chlorobenzene with phenylboronic acid. Results were compared with those reported previously using ligands having the phosphorus atom attached to the 4-position of benzoferrocene. This structural modification resulted in an increase of activity of the ligands in allylic alkylation reaction but a decrease of activity in Suzuki coupling reactions. The underlying reasons are analyzed with the help of X-ray single crystal determined structures and CO stretching frequencies in the IR spectra of complexes between the ligands and $Mo(CO)_5$.

Keywords: Benzoferrocene, Suzuki coupling, Allylic alkylation, Phosphine ligand, Catalysis.

INTRODUCTION

Transition metals such as palladium are widely used as catalysts in carbon-carbon and carbon-heteroatom bonds formation reactions and play a pivotal role in organic synthesis [1]. In homogeneous catalysis, the supporting ligand such as those based on tertiary phosphines has a critical influence on the activity of the catalyst; such an influence is generally analyzed as steric and electronic effects although the two

from this exploration would allow us to select the most active targets for enantioselective preparation. In addition, a number of publications implied potential chemical and configurational instability of benzoferrocenes [4], characterization of more examples of these ligands would further demonstrate their suitability for catalysis. To this end, five novel ligands (**2a**-**e**) were prepared and fully characterized; in addition, the X-ray determined single crystal structure of **2a** was obtained to confirm the proposed structure and for compari-

1a, R = Ph
1b, R = Et
1c, R = *i*-Pr
1d, R = Cy

2a, R = Ph
2b, R = Et
2c, R = *i*-Pr
2d, R = Cy
2e, R = C₅H₉

Cp* = C₅Me₅
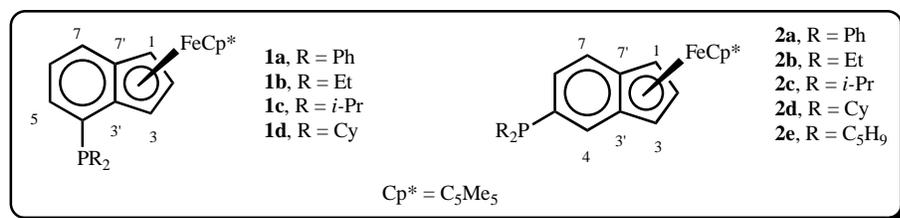
cannot be separated and they always affect each other [2]. Recently, we initiated a project to develop a new class of chiral benzoferrocenyl phosphine ligands and use them to solve some problems in enantioselective catalysis [3]. At the initial stage of the project, it was important to demonstrate the chemical and configurational stability of these ligands and their activity in transition metal-catalyzed reactions. Accordingly, we reported the synthesis and characterization of four such ligands (**1a-d**) and their applications in allylic alkylation and Suzuki coupling reactions [3]. We found that these ligands were indeed chemically and configurationally stable and some of them were highly active for these reactions. While making efforts to develop efficient methodologies for the preparation of these ligands in enantiopure form, we explored the steric and electronic effects of these ligands on their activity upon moving the phosphorus atom from the 4-position to the 5-position of benzoferrocene. The results

son with that of **1a** in analyzing the steric difference of the two sets of ligands (**1a-d** and **2a-e**); furthermore the IR spectra of several ligand-$Mo(CO)_5$ complexes were measured for analyzing electronic character of the ligands. The ligands (**2a-e**) were utilized in palladium-catalyzed allylic alkylations and Suzuki coupling reactions. We found that having the phosphorus atom attached to the 5-position as opposed to the 4-position of benzoferrocene changed the steric and electronic effects of the ligands and these changes increased the activity of the ligands in allylic alkylation but reduced their activity in Suzuki coupling. The underlying reasons are analyzed with the help of the X-ray determined crystal structures of **1a** and **2a**, and the CO stretching frequencies in the IR spectra of the complexes **1**-$Mo(CO)_5$ and **2**-$Mo(CO)_5$.

RESULTS AND DISCUSSION

The ligands **2a-e** were prepared from commercially available 6-bromo-1(*H*)-indene (**3**) in two steps (Scheme **1**). To prevent debromination, the solution of **3** in THF was cooled to -78 °C and then treated with *n*-BuLi followed by warming to rt slowly. This solution was then added dropwise

*Address correspondence to this author at the Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, USA; E-mail: shifang@mtu.edu
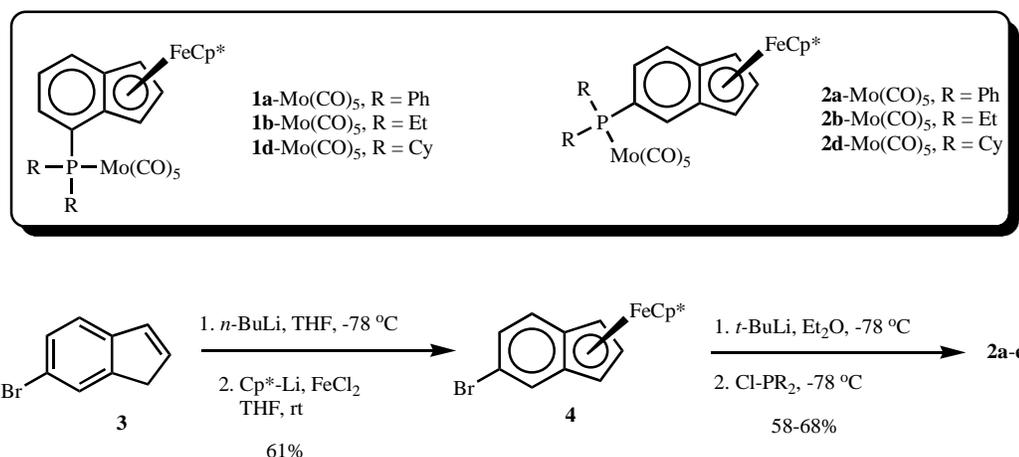
Scheme 1. Synthesis of benzoferrocenyl phosphine ligands **2a-e**.

to a solution of Cp*-Fe(II)-Cl in THF *via* cannula and the mixture stirred at rt for 3 h. Aqueous workup and recrystallization from cold hexanes gave **4** in 61% yield as a crystalline solid. Exchange of the bromine atom on **4** with *t*-BuLi followed by treatment with *P*-chlorodiphenylphosphine (**2a**) or *P*-chlorodialkylphosphine (**2b-e**) gave the desired phosphine ligands in 58-68% yields after aqueous workup and flash column chromatography purification. Similarly to the previously reported **1a-d** [3b], pure **2a-e** were stable in air at rt; but in solution, they were slowly oxidized to the corresponding phosphine oxides as indicated in their ^{31}P NMR spectra. All compounds (**4** and **2a-e**) were fully characterized with ^{1}H, ^{13}C and ^{31}P (**2a-e** only) NMR spectra and elemental analyses or high resolution MS. The structure of **2a** was confirmed with single crystal X-ray crystallography (Fig. **1**). Attempts to resolve the enantiomers of **2a-e** using chiral HPLC were unsuccessful under a variety of conditions including those that were used previously to resolve **1a,b** [3b].

To test the stability of these ligands, **2a,d** were dissolved in hexane, Et$_2$O and THF, respectively. The resulting solutions were stirred under nitrogen atmosphere at rt and at reflux, and were periodically analyzed with GC-MS; no decomposition was detected even after 48 h for both compounds. These ligands were stored in pure form under nitrogen at 0 °C for more than 6 months; no decomposition was detected by GC-MS and NMR.

Compound **2a** crystallized with two molecules in the asymmetric unit and both of these contained disorder in the position of the Cp* ring. The crystal structure of **2a** shows that the iron atom is coordinated to the 5-membered ring of indene in an η^5-fashion, and the distances between the iron and the five carbon atoms of the 5-membered ring are not identical as the ring is tilted upwards slightly and the iron atom is situated off center of the ring (Fig. **1**). The carbon and hydrogen atoms of the indenyl moiety are nearly planar and the plane is almost parallel to that of the Cp* (angle be-
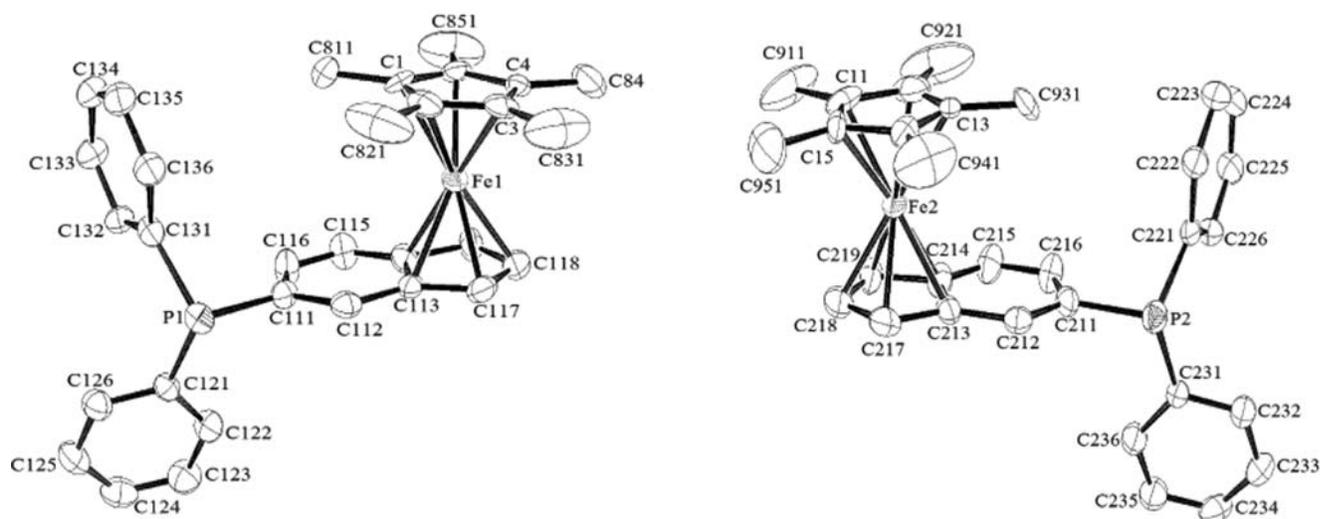
Fig. (1). ORTEP-3 drawing of the two major orientations of the molecules that constitute the asymmetric unit of **2a**. Thermal ellipsoids are drawn at the 20% probability level. Selected bond distances and angles: Fe1-C1, 2.039(12)Å; Fe1-C2, 2.029(10)Å; Fe1-C3, 2.036(12)Å; Fe1-C4, 2.048(8)Å; Fe1-C5,2.052(10)Å; Fe1-C113, 2.088(5)Å; Fe1-C114, 2.082(7)Å; Fe1-C117, 2.071(8) Å; Fe1-C118, 2.048(8)Å; Fe1-C119, 2.041(7)Å; P1-C131, 1.824(6) Å; P1-C111, 1.840(6)Å; P1-C121, 1.833(6)Å; C111-P1-C121, 101.4(3)°; C111-P1-C131, 100.0(3)°; C121-P1-C131, 103.5(3)°; Fe2-C11, 2.040(8)Å; Fe2-C12, 2.053(10)Å; Fe2-C13, 2.069(7)Å; Fe2-C14, 2.065(7)Å; Fe2-C15, 2.048(8)Å; Fe2-C213, 2.092(8)Å; Fe2-C214, 2.064(8)Å; Fe2-C217, 2.078(9)Å; Fe2-C218, 2.047(8)Å; Fe2-C219, 2.030(8)Å; P2-C211, 1.844(6)Å; P2-C221, 1.840(6)Å; P2-C231, 1.823(6)Å; C211-P2-C221, 99.8(3)°; C211-P2-C231, 102.2(3)°; C221-P2-C231, 102.3(3)°.
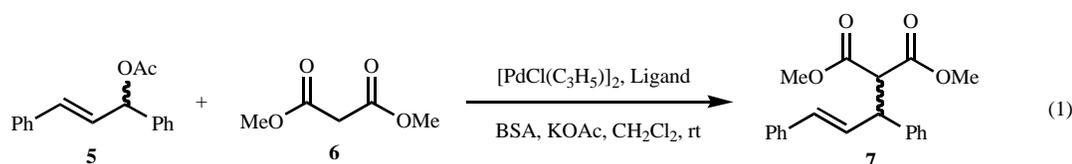
Equation 1.

tween planes is 5.36° and 4.80° for molecules Fe1 and Fe2, respectively, see Fig. **1**). In order to avoid the steric hindrance from the Cp* and the 5-membered ring of indene, one phenyl group attached to the phosphorus atom points towards the *exo* face of the indenyl ring and the other one adopts a position that is opposite to the 5-membered ring of the indenyl moiety. As a result of such an orientation of the two phenyl groups, the lone pair on the phosphorus atom is directed towards the *endo* face of the indenyl plane. These structural features were also observed for **1a** reported previously [3b]. The major structural difference between **2a** and **1a** is the steric hindrance around the phosphorus atom as indicated by their different ligand cone angles [5] roughly estimated here on the basis of the sum of the angles between the *ipso* carbon atoms bonded to phosphorus atom, which are 304.9° and 304.3° for the two molecules that represent **2a** and 306.8° for **1a**. More importantly, the bulky Cp* in **2a** is further away from the phosphorus atom than that in **1a**; and the lone pair of the phosphorus atom, to which the catalytic transition metal center is attached, in **1a** is almost covered by a methyl group of the Cp* [3b] while that in **2a** is further away from Cp* (Fig. **1**). Therefore, **2a** is a less hindered ligand than **1a**; and one could infer that **2b-d** are also less hindered ligands than the corresponding **1b-d**.

Phosphine-transition metal complexes containing carbonyls such as L-Mo(CO)$_5$ and L-Ni(CO)$_3$ have been used for determination of electron donor-acceptor properties of phosphine ligands [5a,6]; the frequency of A_1^2 band in the IR spectra of L-Mo(CO)$_5$ complexes correlates well with such properties [6b-d]. In order to analyze the electronic effects of the ligands on allylic alkylation and Suzuki coupling reactions, complexes **1a**-Mo(CO)$_5$, **1b**-Mo(CO)$_5$, **1d**-Mo(CO)$_5$, **2a**-Mo(CO)$_5$, **2b**-Mo(CO)$_5$, **2d**-Mo(CO)$_5$ and the known

Ph$_3$P-Mo(CO)$_5$ were prepared according to the procedure reported by Lammertsma and co-workers by oxidative removal of a CO from Mo(CO)$_6$ followed by in situ complexation with the phosphine ligands [7]. These complexes were also fully characterized with ^{1}H, ^{13}C and ^{31}P NMR and HRMS; their IR spectra were recorded and A_1^2 IR frequencies of them were identified. On the basis of the lower A_1^2 IR frequencies for all of the benzoferrocenyl phosphine ligands (including **1** and **2**) compared to that for PPh$_3$, we conclude that these ligands are stronger electron donors than PPh$_3$. From these data, we also conclude that **2a** has better electron donation ability than **1a**, and **2b,d** have similar electron donation capability as **1b,d**.

The new ligands (**2a-e**) were applied to the palladium-catalyzed allylic alkylation reaction between allyl acetate **5** and dimethyl malonate (**6**) (Eq. (**1**)). The catalysts were generated in situ by stirring [Pd(C$_3$H$_5$)Cl]$_2$ and a ligand in CH$_2$Cl$_2$ at rt for 1 h. Under previously established allylic alkylation reaction conditions using BSA [*N,O*-bis (trimethylsilyl)acetamine] and KOAc as base with an L/Pd ratio of 2.5/1.0 [3b], when ligands **2a,b** were used, quantitative conversions were achieved within 15 min to generate the sole product **7** as indicated by GC-MS (entries 1 and 2, Table **1**). Ligand **2c** was also highly active under these conditions for the reaction; quantitative conversion was achieved within 45 min (entry 3). The bulkier **2d,e** showed less activity, it took 44 h for the reaction to reach completion (entries 4 and 5).

In our previous report, when **1a-d** were applied to this reaction under similar conditions, **1a,b** showed high activity, and the bulkier **1c,d** showed significantly less activity [3b]. Comparing the two sets of ligands, **2a-d** are much more active than the corresponding **1a-d**. The biggest difference is between **2c,d** and **1c,d**, the latter gave much less conversions

Table 1. **Application of Ligands 2a-e and 1d in Allylic Alkylation Reactions**

Entry	Ligand	Substrate/Pd	Substrates	Conditions	Temperature	Time (h)	Conversion [a]
1	**2a**	100/4	**5, 6**	A	rt	0.25	100%
2	**2b**	100/4	**5, 6**	A	rt	0.25	100%
3	**2c**	100/4	**5, 6**	A	rt	0.75	100%
4	**2d**	100/4	**5, 6**	A	rt	44	100%
5	**2e**	100/4	**5, 6**	A	rt	44	100%
6	**2a**	1,000/1	**8, 6**	B	rt	6	96%
7	**2a**	10,000/1	**8, 6**	B	rt	72	85%
8	**1d**	100/4	**5, 6**	A	40 °C	4	100%

Conditions A: **5** 1 eq; **6** 3 eq; ligand 0.05 eq; [Pd(C$_3$H$_5$)Cl]$_2$ 0.02 eq; BSA 3 eq; KOAc 0.1 eq; CH$_2$Cl$_2$.
Conditions B: **8** 1 eq; **6** 2 eq; **2a**/[Pd(C$_3$H$_5$)Cl]$_2$ 2.5/1; NaH 2 eq; THF.
[a]Determined by GC. In all cases, only mono-allylated product (**7** or **9**) was detected by GC-MS.

(2)
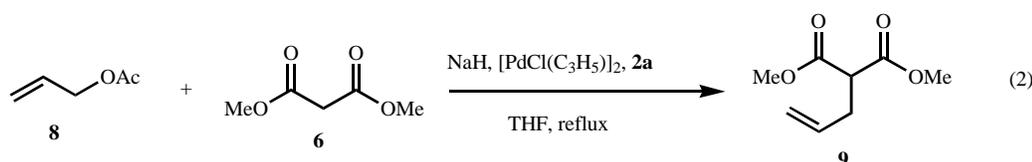
Equation 2.

than the former under similar conditions. Because **2a,b** are most active among **1a-d** and **2a-e**, and the phosphorus atom in **2a** is less sensitive to oxidation than that in **2b**, we chose **2a** to challenge the activity of ligands **2a-e** in allylic alkylation by lowering the catalyst loading to 0.1%. Under similar conditions (Conditions B, Table **1**), the reaction reached 96% conversion within 6 h (entry 6, Table **1**). When catalyst loading was further lowered to 0.01%, 72 h were needed to achieve 85% conversion (entry 7); but despite the long reaction time, the reaction was still very clean as indicated by GC-MS. In 2001, Santelli's group reported the catalytic activity of several common phosphine ligands including Ph₃P, 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb) and *cis,cis,cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane (tedicyp) in palladium-catalyzed allylic alkylation between allyl acetate and sodium dimethyl malonate [8]. They found that the monodentate Ph₃P was virtually inactive (1% conversion) when the catalyst loading was 0.01%; dppe and dppb showed higher activity at this catalyst loading, but the conversions were still low (50% and 49%, respectively). Our ligand **2a**, which is monodentate, showed higher activity than these ligands. However, compared with the tetradentate tedicyp, which showed 100% conversion in 3 h with 0.01% catalyst loading, **2a** is less active.

The activity of these ligands in the Suzuki coupling of chlorobenzene with phenylboronic acid was also assessed (Eq. (**2**)). Under conditions used previously with **1a-d** as ligands [3a], **2a-e** were found to be much less active. As shown in Table **2**, when the less bulky **2a,b** were used, there were no conversion in 24 h (entries 1 and 2); the bulkier **2c-e** showed some activity, but the conversions were low (entries 3-5). These results are in sharp contrast to those obtained using **1a-d** as ligands; among them, **1c,d** showed very high activity for this reaction under the same conditions [3a].

Locating the phosphorus atom on the 5-position as opposed to 4-position of benzoferrocenyl ligands significantly

improved their activity in allylic alkylation reaction. The higher activity of **2a-d** in allylic alkylation compared to that of the corresponding **1a-d** can be attributed to the reduced steric hindrance around the phosphorus atom, which allows substrates to access the catalytic center more easily; and this trend of activity was also observed within the two series of ligands. Because PPh₃ is less hindered than all these derived ligands, but much less active than **2a**, the electronic effect of the phosphines must also influence their activity. As shown in Table **3**, the lower A_1^2 IR frequencies of the complexes between the ligands and Mo(CO)₅ compared with that of Ph₃P-Mo(CO)₅ indicate that the benzoferrocenyl phosphines are better electron donor ligands than PPh₃. Under the present allylic alkylation reaction conditions, the ionization of allyl acetates should be the rate limiting step, and therefore **2a** is more active than PPh₃. Because **2a** is a better donor ligand than **1a** (Table **3**), this electronic effect may also contribute to the higher activity of **2a** compared with **1a** in addition to any steric effects. The electron donor abilities of **1b** and **2b**, and those of **1d** and **2d** are very close; therefore the difference between their activities can be attributed to the different steric environment around their phosphorus atoms.

Having the phosphorus atom on the 5-position as opposed to the 4-position on the benzoferrocenyl ligands significantly lowered their activity for the Suzuki coupling of aryl chlorides with boronic acids. In these reactions, the rate limiting step is the oxidative addition in which Pd(0) inserts into the C-Cl bond. Because of the relatively less reactive nature of C-Cl bonds, this step requires electron-rich and bulky phosphine ligands to form the mono-coordinated 12e LPd(0) complex [2]. The data in Table **3** show that **2a** is more electron rich than **1a**, and **2b,d** have similar electron donating capability as **1b,d**; therefore the reduced activity of **2a-e** compared with **1a-d** is caused by the reduced steric hindrance around the phosphorus atom, which reduces the likelihood of forming mono-coordinated LPd(0) complexes.

Table 2.   Application of Ligands 2a-e in Suzuki Coupling

$$Ph\text{-}Cl + Ph\text{-}B(OH)_2 \longrightarrow Ph\text{-}Ph$$

Entry	Ligand	Time (h)	Conversion [a]
1	**2a**	24	0%
2	**2b**	24	0%
3	**2c**	2	15%
4	**2d**	24	11%
5	**2e**	24	6%

Conditions: Ph-Cl 1 eq; Ph-B(OH)₂ 1eq; ligand 0.036 eq; Pd₂(dba)₃ 0.015 eq; Cs₂CO₃ 2 eq; 1,4-dioxane; reflux.
[a]Determined by GC.

Table 3. A_1^2 **IR Frequency Data for L-Mo(CO)$_5$ Complexes**

Complex	Frequency (cm^{-1})
Ph$_3$P-Mo(CO)$_5$	2073
1a-Mo(CO)$_5$	2071
1b-Mo(CO)$_5$	2070
1d-Mo(CO)$_5$	2066
2a-Mo(CO)$_5$	2067
2b-Mo(CO)$_5$	2069
2d-Mo(CO)$_5$	2067

In allylic alkylation reactions, the 14e L$_2$Pd(0) complex is believed to be responsible for the ionization of allyl acetates, which is the rate-limiting step of the reaction under the conditions we used [3a]; the rate of this ionization process decreases with increasing steric hindrance of the ligand. It is interesting to note that the seemingly more hindered L$_2$Pd of **1a**,**b** and **2a**,**b** could catalyze allylic alkylation reaction with high efficiency but the relatively less hindered LPd of **1c**,**d** and **2d** showed much lower efficiency for the same reaction, while the latter showed high efficiency for Suzuki coupling of aryl chlorides with arylboronic acids [3a]. One possible explanation is that mono-coordinated LPd does not exist or exist at very low concentration and L$_2$Pd predominates at rt even with the highly hindered ligands such as **1c**,**d** and **2d**; LPd can only exist with useful amount at elevated temperature when the ligand is bulky. As a result, ligands such as **1c**,**d** and **2d** showed low activity for allylic alkylation, which was performed at rt; but showed high activity in Suzuki coupling of aryl chlorides, which was performed at elevated temperature. If this is true, at elevated temperature, highly hindered ligands such as **1c**,**d** and **2d** should also show high activity for allylic alkylation. To test this hypothesis, **1d** was used as the ligand for allylic alkylation reaction under conditions A but at 40 °C (instead of rt), and indeed high activity was displayed; within 4 h quantitative conversion was observed (entry 8, Table **1**). This observation shows that L$_2$Pd complexes of **1c**,**d** and **2d** are not active for allylic alkylation but LPd complexes of the same ligands may be highly active for this reaction.

CONCLUSIONS

Five novel benzoferrocenyl phosphine ligands with the phosphorus atom attached to the 5-position (**2a-e**) were prepared and fully characterized. Like their analogs with the phosphorus atom attached to the 4-position (**1a-d**), these ligands are chemically stable and are suitable for applications in catalysis. IR analysis of the complexes of these ligands (**1** and **2**) with Mo(CO)$_5$ indicates that **2a** is a stronger electron donor than **1a**, and **2b**,**d** have similar electron donating capability as **1b**,**d**. With these electronic characteristics and the reduced steric hindrance around their phosphorus atom, **2a-d** have higher activity in allylic alkylation and lower activity in Suzuki coupling of aryl chlorides than the corresponding **1a-d**. Preparation of multidentate version of benzoferrocene ligands in enantiopure form and using them to solve problems in asymmetric catalysis are in

progress; results of these investigations will be reported in the near future.

EXPERIMENTAL SECTION

General Information

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Reagents and solvents available from commercial sources were used as received unless otherwise noted. THF, Et$_2$O and toluene were distilled from Na/benzophenone ketyl. CH$_2$Cl$_2$ and acetonitrile were distilled over CaH$_2$. Thin layer chromatography (TLC) was performed using Sigma-Aldrich TLC plates, silica gel 60F-254 over glass support, 0.25 μm thickness. Flash column chromatography was performed using Selecto Scientific silica gel, particle size 32-63 μm in diameter. ^{1}H, ^{13}C and ^{31}P NMR were measured on a Varian Unity spectrometer at 400 MHz; chemical shifts (δ) were reported to residue CHCl$_3$ (δ = 7.27 ppm for ^{1}H and 77.23 ppm for ^{13}C) and C$_6$D$_5$H (δ = 7.34 ppm for ^{1}H and 128.36 ppm for ^{13}C), and to the external standard H$_3$PO$_4$ (δ = 0 ppm for ^{31}P). GC-MS were measured on GCMS-QP5050A, Shimadzu; column, DB-5MS, 0.25 μm thickness, 0.25 mm diameter, 25 m length; MS, positive EI. Melting points were determined using a MEL-TEMP® melting point apparatus and are uncorrected. IR spectra were recorded in a solution of CHCl$_3$ on a PerkinElmer "Spectrum one FT-IR Spectrometer".

5-Bromoindenyl-pentamethylcyclopentadienyliron (4)

6-Bromo-1(*H*)-indene (**3**, 3.0 g, 15.4 mmol) in THF (150 mL) was cooled to -78 °C, *n*-BuLi (2.0 M in pentane, 7.7 mL, 15.4 mmol) was added *via* syringe along the wall of flask in a dropwise manner. After addition, the solution was warmed to rt slowly. Pentamethylcyclopentadiene (Cp*-H, 2.2 mL, 15.4 mmol) in THF (100 mL) in another round-bottomed flask was treated with *n*-BuLi (2.0 M in pentane, 7.7 mL, 15.4 mmol) at rt giving a white suspension. This white suspension was added *via* cannula to a suspension of anhydrous FeCl$_2$ (1.97 g, 15.4 mmol) in THF (100 mL) with vigorous stirring. After stirring at rt for 1 h, the solution of lithiated **3** was added dropwise *via* cannula, and the resulting deep red solution was stirred at rt. After 3 h, TLC (SiO$_2$, hexanes) indicated quantitative conversion. THF was removed under reduced pressure on a rotary evaporator. The deep red residue was partitioned between 10% K$_2$CO$_3$ (100 mL) and hexanes (200 mL), and the organic layer was further washed sequentially with 10% K$_2$CO$_3$ (25 mL) and water (25 mL). After drying over anhydrous Na$_2$SO$_4$, the deep red solution was concentrated to about 15 mL. Cooling the solution to -20 °C gave pure product **4** as deep red crystals (3.61 g, 61%): R_f = 0.75 (hexanes); mp 82-84 °C; ^{1}H NMR (C$_6$D$_6$) δ 7.10 (brs, 1H, H-4, H-6 or H-7), 6.93 (brs, 1H, H-4, H-6 or H-7), 6.89 (brs, 1H, H-4, H-6 or H-7), 4.02 (brs, 1H, H-1, H-2 or H-3), 3.99 (brs, 1H, H-1, H-2 or H-3), 3.52 (brs, 1H, H-1, H-2 or H-3), 1.46 (s, 15H, Cp*); ^{13}C NMR (C$_6$D$_6$) δ 130.1 (C-4, C-6 or C-7), 129.1 (C-4, C-6 or C-7), 126.0 (C-4, C-6 or C-7), 114.6 (C-5), 90.1 (C-3' or C-7'), 86.4 (C-3' or C-7'), 78.2 (C-1, C-2, C-3 or Cp*), 76.6 (C-1, C-2, C-3 or Cp*), 66.1 (C-1, C-2, C-3 or Cp*), 65.8 (C-1, C-2, C-3 or Cp*), 10.1 (Cp*-Me); EI-MS calcd. for C$_{19}$H$_{21}$BrFe (*m/z*) [M$^+$] 384, found 384; FAB-HRMS (NBA) calcd. for C$_{19}$H$_{21}$BrFe (*m/z*) [M$^+$] 384.0176; found 384.0177. Anal.

calcd. for $C_{19}H_{21}BrFe$ C 58.26, H 5.50; found C 59.05, H 5.38.

5-(Diphenylphosphino)indenyl-pentamethylcyclopentadienyliron (2a)

The deep red solution of **4** (1.0 g, 2.6 mmol) in Et_2O (50 mL) in a round-bottomed flask was cooled to -78 °C. To this solution was added *t*-BuLi (1.7 M in pentane, 3.3 mL, 5.7 mmol) slowly *via* syringe and the mixture was stirred at the same temperature for 30 min. *P*-Chlorodiphenylphosphine (1.1 mL, 5.7 mmol) was next added dropwise *via* syringe. After stirring at -78 °C for 2 h, the reaction was quenched with water, and the mixture partitioned between 10% K_2CO_3 (25 mL) and hexanes (50 mL). The isolated organic layer further washed sequentially with 10% K_2CO_3 (25 mL) and water (25 mL). After drying over anhydrous Na_2SO_4, the solution was concentrated to dryness. Flash column chromatography (SiO_2, pretreated with 5% Et_3N in hexanes; hexanes) gave product **2a** as deep purple crystals (0.87 g, 68%): R_f = 0.23 (hexanes); mp 126-128 °C; ^1H NMR (C_6D_6) δ 7.59-7.55 (m, 1H, Ph), 7.51-7.46 (m, 1H, Ph), 7.15-6.95 (m, 11H, Ph), 4.11 (dt, 1H, J = 2.4, 0.8 Hz, H-1 or H-3), 4.05 (dt, 1H, J = 2.4, 0.8 Hz, H-1, or H-3), 3.60 (t, 1H, J = 2.4 Hz, H-2), 1.47 (s, 15H, Cp*); ^{13}C NMR (C_6D_6) δ 138.8 (d, J_{CP} = 48.4 Hz, Ph), 136.8 (d, J_{CP} = 115.2 Hz, Ph), 134.4 (d, J_{CP} = 78.8 Hz, Ph), 133.7 (d, J_{CP} = 72.8 Hz, Ph), 130.6 (d, J_{CP} = 42.4 Hz, Ph), 128.6 (d, J_{CP} = 42.4 Hz, Ph), 128.4 (d, J_{CP} = 60.8 Hz, Ph), 126.7 (d, J_{CP} = 60.8 Hz, Ph), 88.36 (d, J_{CP} = 42.8 Hz, C-3'), 88.4 (C-7'), 78.1 (C-1 or C-3), 76.7 (C-1 or C-3), 66.4 (C-2 or Cp*), 66.3 (C-2 or Cp*), 10.2 (Cp*-Me); ^{31}P NMR (C_6D_6) δ -2.28; EI-MS calcd. for $C_{31}H_{31}FeP$ (*m/z*) [M$^+$] 490, found 490; FAB-HRMS (NBA) calcd. for $C_{31}H_{31}FeP$ (*m/z*) [M$^+$] 490.1513; found 490.1516.

5-(Diethylphosphino)indenyl-pentamethylcyclopentadienyliron (2b)

Following the procedure for the preparation of **2a**, compound **2b** was synthesized in 60% yield as a deep red sticky solid: R_f = 0.24 (hexanes); ^1H NMR (C_6D_6) δ 7.67 (d, 1H, J = 10 Hz, Ph), 7.16 (d, 1H, J = 8.8 Hz, Ph), 7.01 (dd, 1H, J = 8.4, 3.6 Hz, Ph), 4.15 (t, 2H, J = 2.4 Hz, H-1 and H-3), 3.61 (t, 1H, J = 2.4 Hz, H-2), 1.68-1.52 (m, 4H, PCH_2), 1.52 (s, 15H, Cp*-Me), 1.56-0.96 (m, 6H, Me); ^{13}C NMR (C_6D_6) δ 135.2 (d, J_{CP} = 127.6 Hz, Ph), 132.2 (d, J_{CP} = 66.8 Hz, C-5), 127.4 (d, J_{CP} = 18.0 Hz, Ph), 124.1 (d, J_{CP} = 42.4 Hz, Ph), 88.6 (C-7'), 88.5 (d, J_{CP} = 42.4 Hz, C-3'), 77.8 (C-2 or C-3), 76.4 (C-2 or C-3), 66.2 (C-2 or Cp*), 66.1 (C-2 or Cp*), 20.9 (d, J_{CP} = 79.2 Hz, PCH_2), 20.7 (d, J_{CP} = 78.8 Hz, PCH_2), 10.4 (d, J_{CP} = 42.4 Hz, Me × 2), 10.2 (Cp*-Me); ^{31}P NMR (C_6D_6) δ -13.59; EI-MS calcd. for $C_{23}H_{31}FeP$ (*m/z*) [M$^+$] 394, found 394; FAB-HRMS (NBA) calcd. for $C_{23}H_{31}FeP$ (*m/z*) [M$^+$] 394.1513; found 394.1513.

5-(Diisopropylphosphino)indenyl-pentamethylcyclopentadienyliron (2c)

Following the procedure for the preparation of **2a**, compound **2c** was synthesized in 65% yield as a deep red sticky solid: R_f = 0.17 (hexanes); ^1H NMR (C_6D_6) δ 7.68 (d, 1H, J = 11.2 Hz, Ph), 7.14 (d, 1H, J = 8.8 Hz, Ph), 6.98 (d, J = 8.4 Hz, Ph), 4.17 (s, 1H, H-1 or H-3), 4.15 (d, 1H, J = 2.4 Hz, H-1 or H-3), 3.58 (t, 1H, J = 2.4 Hz, H-2), 2.14-2.02 (m, 1H, PCH), 1.94-1.84 (m, 1H, PCH), 1.55 (s, 15H, Cp*-Me),

1.20-0.88 (m, 12H, Me); ^{13}C NMR (C_6D_6) δ 137.9 (d, J_{CP} = 145.6 Hz, Ph), 129.0 (d, J_{CP} = 79.2 Hz, C-5), 126.5 (Ph), 125.8 (Ph), 88.7 (C-3' and C-7'), 78.0 (C-1 or C-3), 76.4 (C-1 or C-3), 66.4 (C-2 or Cp*), 66.2 (C-2 or Cp*), 23.8 (d, J_{CP} = 54.4 Hz, PCH), 22.8 (d, J_{CP} = 48.4 Hz, PCH), 20.4 (d, J_{CP} = 72.8 Hz, Me), 20.1 (d, J_{CP} = 30.4 Hz, Me), 20.0 (Me), 18.8 (Me), 10.4 (Cp*-Me); ^{31}P NMR (C_6D_6) δ 14.2; EI-MS calcd. for $C_{25}H_{35}FeP$ (*m/z*) [M$^+$] 422, found 422; FAB-HRMS (NBA) calcd. for $C_{25}H_{35}FeP$ (*m/z*) [M$^+$] 422.1826; found 422.1829.

5-(Dicyclohexylphosphino)indenyl-pentamethylcyclopentadienyliron (2d)

Following the procedure for the preparation of **2a**, compound **2d** was synthesized in 62% yield as a deep red solid: R_f = 0.25 (hexanes); mp 116-118 °C; ^1H NMR ($CDCl_3$) δ 7.31 (dd, 1H, J = 11.6, 0.8Hz, Ph), 7.27 (d, 1H, J = 8.4 Hz, Ph), 7.04 (ddd, 1H, J = 8.80, 3.2, 1.2 Hz, Ph), 4.37 (d, 1H, J = 2.8 Hz, H-1 or H-3), 4.34 (d, 1H, J = 2.4 Hz, H-1 or H-3), 3.80 (t, 1H, J = 2.4 Hz, H-2), 2.05-1.58 [m, 10H, $PCH(CH_2)_2$], 1.68 (s, 15H, Cp*-Me), 1.39-0.98 [m, 12H, $(CH_2)_3$]; ^{13}C NMR ($CDCl_3$) δ 137.8 (d, J_{CP} = 146.0 Hz, Ph), 128.5 (d, J_{CP} = 60.4 Hz, C-5), 126.4 (d, J_{CP} = 42.4 Hz, Ph), 126.2 (Ph), 88.6 (d, J_{CP} = 54.4 Hz, C-3'), 88.6 (C-7'), 78.4 (C-1 or C-3), 76.4 (C-1 or C-3), 66.3 (C-2 or Cp*), 66.1 (C-2 or Cp*), 33.6 (d, J_{CP} = 48.8 Hz, PCH), 32.5 (d, J_{CP} = 42.4 Hz, PCH), 30.6 (d, J_{CP} = 66.4 Hz, CH_2), 30.2 (d, J_{CP} = 66.8 Hz, CH_2), 30.0 (d, J_{CP} = 42.4 Hz, CH_2), 29.1 (d, J_{CP} = 18.4 Hz, CH_2), 27.6 (d, J_{CP} = 54.8 Hz, CH_2), 27.5 (CH_2), 27.3 (CH_2), 27.3 (d, J_{CP} = 36.4 Hz, CH_2), 26.7 (CH_2), 26.6 (CH_2), 10.6 (Cp*-Me); ^{31}P NMR ($CDCl_3$) δ 7.13; EI-MS calcd. for $C_{31}H_{43}FeP$ (*m/z*) [M$^+$] 502, found 502; FAB-HRMS (NBA) calcd. for $C_{31}H_{43}FeP$ (*m/z*) [M$^+$] 502.2452; found 502.2449.

5-(Dicyclopentylphosphino)indenyl-pentamethylcyclopentadienyliron (2e)

Following the procedure for the preparation of **2a**, compound **2e** was synthesized in 58% yield as a deep red sticky solid: R_f = 0.21 (hexanes); ^1H NMR (C_6D_6) δ 7.72 (d, 1H, J = 11.2 Hz, Ph), 7.16 (d, 1H, J = 8.8 Hz, Ph), 7.05 (dd, 1H, J = 8.8, 3.2 Hz, Ph), 4.18 (d, 1H, J = 1.6 Hz, H-1 or H-3), 4.14 (d, 1H, J = 2.4 Hz, H-1 or H-3), 3.58 (t, 1H, J = 2.8 Hz, H-2), 2.26-2.16 (m, 1H, PCH), 2.04-1.94 (m, 1H, PCH), 1.91-1.22 (m, 16H, CH_2), 1.56 (s, 15H, Cp*-Me); ^{13}C NMR (C_6D_6) δ 136.8 (d, J_{CP} = 151.6 Hz, Ph), 132.5 (d, J_{CP} = 66.8 Hz, C-5), 126.8 (d, J_{CP} = 12.0 Hz, Ph), 125.2 (d, J_{CP} = 18.4 Hz, Ph), 88.6 (C-7'), 88.5 (d, J_{CP} = 48.8 Hz, C-3'), 77.9 (C-1 or C-3), 76.3 (C-1 or C-3), 66.4 (C-2 or Cp*), 66.1 (C-2 or Cp*), 38.2 (d, J_{CP} = 48.8 Hz, PCH), 36.7 (d, J_{CP} = 48.8 Hz, PCH), 31.7 (d, J_{CP} = 12.0 Hz, CH_2), 31.6 (d, J_{CP} = 48.8 Hz, CH_2), 31.4 (CH_2), 31.1 (d, J_{CP} = 48.8 Hz, CH_2), 27.0 (d, J_{CP} = 24.0 Hz, CH_2), 26.8 (d, J_{CP} = 30.4 Hz, CH_2), 26.3 (d, J_{CP} = 24.4 Hz, CH_2), 25.9 (d, J_{CP} = 24.4 Hz, CH_2), 10.5 (Cp*-Me); ^{31}P NMR (C_6D_6) δ 4.77; EI-MS calcd. for $C_{29}H_{39}FeP$ (*m/z*) [M$^+$] 474, found 474; FAB-HRMS (NBA) calcd. for $C_{29}H_{39}FeP$ (*m/z*) [M$^+$] 474.2139; found 474.2141.

[5-(Diphenylphosphino)indenyl-pentamethylcyclopentadienyliron]pentacarbonylmolybdenum [2a-Mo(CO)₅]

This complex was prepared following reported procedure [7]. $Mo(CO)_6$ (316.6 mg, 1.18 mmol) and $Me_3N=O$ (131.6 mg, 1.18 mmol) in an oven-dried 2-necked round-bottomed

flask were dried under vacuum, and the flask was back-filled with nitrogen. CH_2Cl_2 (3 mL) and MeCN (3 mL) were added *via* syringes. After stirring at rt for 90 min, the solution of **2a** (576.4 mg, 1.18 mmol) in dry toluene (4 mL) in a round-bottomed flask was added to the 2-necked flask *via* cannula. The resulting mixture was stirred at rt for 6 h, at which time TLC (SiO_2, hexanes/ether 1:1) indicated quantitative conversion. Solvents were removed under reduced pressure on a rotary evaporator and the residue was purified with flash column chromatography (SiO_2, pretreated with 5% Et_3N in hexanes; hexanes/ether 1:1). Product **2a**-$Mo(CO)_5$ was obtained as deep purple crystals (735.6 mg, 86%): $R_f = 0.70$ (hexanes/ether 1:1); mp 190-192 ˚C; ¹H NMR ($CDCl_3$) δ 7.75 (d, 1H, $J = 15.2$ Hz, Ph), 7.67-7.62 (m, 2H, Ph), 7.48-7.40 (m, 8H, Ph), 7.36 (dt, 1H, $J = 9.2, 0.4$ Hz, Ph), 7.05 (ddd, 1H, $J = 9.2, 8.0, 1.2$ Hz, Ph), 4.42 (d, 1H, $J = 2.8$ Hz, H-1 or H-3), 4.40 (d, 1H, $J = 2.4$ Hz, H-1 or H-3), 3.91 (t, 1H, $J = 2.8$ Hz, H-2), 1.57 (s, 15H, Cp*-Me); ¹³C NMR ($CDCl_3$) δ 210.7 (d, $J_{CP} = 84.8$ Hz, CO), 206.1 (d, $J_{CP} = 36.4$ Hz, CO × 4), 138.8 (d, $J_{CP} = 72.8$ Hz, Ph), 137.6 (d, $J_{CP} = 145.6$ Hz, Ph), 136.6 (d, $J_{CP} = 139.6$ Hz, Ph), 133.2 (d, $J_{CP} = 48.8$ Hz, Ph), 132.5 (d, $J_{CP} = 48.8$ Hz, Ph), 130.0 (d, $J_{CP} = 176$ Hz, Ph), 128.7 (Ph), 128.6 (Ph), 128.6 (d, $J_{CP} = 36.4$ Hz, Ph), 128.1 (d, $J_{CP} = 36.8$ Hz, Ph), 127.5 (d, $J_{CP} = 145.6$ Hz, Ph), 125.1 (d, $J_{CP} = 42.4$ Hz, Ph), 88.3 (C-7'), 87.3 (d, $J_{CP} = 54.8$ Hz, C-3'), 78.9 (C-1 or C-3), 77.8 (C-1 or C-3), 67.3 (C-2 or Cp*), 66.9 (C-2 or Cp*), 10.5 (Cp*-Me); ³¹P NMR ($CDCl_3$) δ 38.37; FAB-HRMS (NBA) calcd. for $C_{36}H_{31}FeMoO_5P$ (*m/z*) [M⁺] 728.0313; found 728.0318.

[5-(Diethylphosphino)indenyl-pentamethylcyclopentadienyl-iron]pentacarbonylmolybdenum [2b-Mo(CO)₅]

Following the procedure for the preparation of **2a**-$Mo(CO)_5$, compound **2b**-$Mo(CO)_5$ was synthesized in 50% yield as a deep purple sticky solid: $R_f = 0.52$ (hexanes/ether 100:1); ¹H NMR ($CDCl_3$) δ 7.68 (d, 1H, $J = 12.8$ Hz, Ph), 7.42 (d, 1H, $J = 8.4$ Hz, Ph), 7.04 (t, 1H, $J = 8.0$ Hz, Ph), 4.45 (s, 1H, H-1 or H-3), 4.40 (s, 1H, H-1 or H-3), 3.89 (s, 1H, H-2), 2.17-2.01 (m, 4H, PCH_2), 1.65 (s, 15H, Cp*-Me), 1.21-1.04 (m, 6H, Me); ¹³C NMR ($CDCl_3$) δ 210.3 (d, $J_{CP} = 84.8$ Hz, CO), 206.5 (d, $J_{CP} = 36.8$ Hz, CO × 4), 135.9 (d, $J_{CP} = 60.4$ Hz, Ph), 128.7 (d, $J_{CP} = 36.4$ Hz, Ph), 127.2 (d, $J_{CP} = 133.6$ Hz, C-5), 122.1 (d, $J_{CP} = 36.8$ Hz, Ph), 88.3 (C-7'), 87.8 (d, $J_{CP} = 54.4$ Hz, C-3'), 78.6 (C-1 and C-3), 67.1 (C-2 or Cp*), 66.7 (C-2 or Cp*), 24.6 (d, $J_{CP} = 91.2$ Hz, PCH_2), 23.9 (d, $J_{CP} = 91.2$ Hz, PCH_2), 10.6 (Cp*-Me), 8.8 (Me × 2); ³¹P NMR ($CDCl_3$) δ 26.66; FAB-HRMS (NBA) calcd. for $C_{28}H_{31}FeMoO_5P$ (*m/z*) [M⁺] 632.0313; found 632.0318.

[5-(Dicyclohexylphosphino)indenyl-pentamethylcyclopen-tadienyliron]pentacarbonylmolybdenum [2d-Mo(CO)₅]

Following the procedure for the preparation of **2a**-$Mo(CO)_5$, compound **2d**-$Mo(CO)_5$ was synthesized in 92% yield as a deep purple solid: $R_f = 0.50$ (hexanes); mp 152-154 ˚C; ¹H NMR ($CDCl_3$) δ 7.96 (d, 1H, $J = 10.4$ Hz, Ph), 7.49 (brs, 1H, Ph), 7.30 (brs, 1H, Ph), 4.62 (brs, 1H, H-1 or H-3), 4.53 (brs, 1H, H-1 or H-3), 4.01 (brs, 1H, H-2), 2.42-0.99 (m, 22H, Cy), 1.79 (s, 15H, Cp*-Me); ¹³C NMR ($CDCl_3$) δ 210.4 (d, $J_{CP} = 85.2$ Hz, CO), 207.4 (d, $J_{CP} = 30.4$ Hz, CO × 4), 139.0 (d, $J_{CP} = 60.8$ Hz, Ph), 127.1 (d, $J_{CP} = 30.4$ Hz, Ph), 125.5 (d, $J_{CP} = 30.4$ Hz, Ph), 123.6 (d, $J_{CP} = 109.2$ Hz, C-5),

88.7 (C-7'), 88.4 (d, $J_{CP} = 48.4$ Hz, C-3'), 78.8 (C-1 or C-3), 77.4 (C-1 or C-3), 67.0 (C-2 or Cp*), 66.3 (C-2 or Cp*), 36.8 (d, $J_{CP} = 72.8$ Hz, PCH), 35.6 (d, $J_{CP} = 72.8$ Hz, PCH), 28.6 (CH_2), 27.7 (CH_2 × 2), 27.4 (CH_2), 27.2 (CH_2), 27.1 (CH_2 × 2), 27.0 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 10.7 (Cp*-Me); ³¹P NMR ($CDCl_3$) δ 46.5; FAB-HRMS (NBA) calcd. for $C_{36}H_{43}FeMoO_5P$ (*m/z*) [M⁺] 740.1252; found 740.1259.

[4-(Diphenylphosphino)indenyl-pentamethylcyclopentadie-nyliron]pentacarbonylmolybdenum [1a-Mo(CO)₅]

Following the procedure for the preparation of **2a**-$Mo(CO)_5$, compound **1a**-$Mo(CO)_5$ was synthesized. The compound could not be purified by crystallization and column chromatography; HPLC analysis indicated 4 compounds (roughly in a ratio of 1:27:70:2) but on TLC only one spot could be seen. Because the three impurities were in smaller quantities, part of NMR data could be assigned: $R_f = 0.60$ (hexanes); ¹H NMR ($CDCl_3$) δ 7.90-7.12 (m, 13H, Ph), 4.26 (brs, 1H, H-1, H-2 or H-3), 3.72 (brs, 1H, H-1, H-2 or H-3), 3.66 (brs, 1H, H-1, H-2 or H-3), 1.49 (s, 15H, Cp*-Me); ¹³C NMR ($CDCl_3$) δ 211.2 (d, $J_{CP} = 97.2$ Hz, CO), 206.1 (d, $J_{CP} = 30.4$ Hz, CO × 4), 136.9-120.2 (Ph, could not be assigned), 92.9 (d, $J_{CP} = 12.0$ Hz, C-3' or C-7'), 88.1 (d, $J_{CP} = 12.0$ Hz, C-3' or C-7'), 78.3 (C-1 or C-3), 77.7 (C-1 or C-3), 66.3 (C-2 or Cp*), 66.1 (C-2 or Cp*), 10.3 (Cp*-Me); ³¹P NMR ($CDCl_3$) δ 41.2; FAB-HRMS (NBA) calcd. for $C_{36}H_{31}FeMoO_5P$ (*m/z*) [M⁺] 728.0313; found 728.0321.

[4-(Diethylphosphino)indenyl-pentamethylcyclopentadieny-liron]pentacarbonylmolybdenum [1b-Mo(CO)₅]

Following the procedure for the preparation of **2a**-$Mo(CO)_5$, compound **1b**-$Mo(CO)_5$ was synthesized in 83% yield as a deep purple solid: $R_f = 0.75$ (hexanes/ether 1:1); mp 110-112 ˚C; ¹H NMR ($CDCl_3$) δ 7.43 (d, 1H, $J = 7.2$ Hz, Ph), 7.23 (brs, 1H, Ph), 7.01 (brs, 1H, Ph), 4.55 (s, 1H, H-1 or H-3), 4.35 (s, 1H, H-1 or H-3), 3.86 (s, 1H, H-2), 2.78-2.52 (m, 2H, PCH_2), 2.46-2.20 (m, 2H, PCH_2), 1.64 (s, 15H, Cp*-Me), 1.42-1.10 (m, 6H, Me × 2); ¹³C NMR ($CDCl_3$) δ 210.6 (d, $J_{CP} = 78.8$ Hz, CO), 206.3 (d, $J_{CP} = 24.4$ Hz, CO × 4), 133.4 (d, $J_{CP} = 109.2$ Hz, C-5), 131.6 (Ph), 126.9 (d, $J_{CP} = 36.4$ Hz, Ph), 121.2 (d, $J_{CP} = 30.0$ Hz, Ph), 90.4 (d, $J_{CP} = 42.4$ Hz, C-3' or C-7'), 88.1 (C-3' or C-7'), 78.2 (d, $J = 12.0$ Hz, C-1), 77.3 (C-3), 67.3 (C-2 or Cp*), 65.8 (C-2 or Cp*), 21.6 (d, $J_{CP} = 90.8$ Hz, PCH_2), 20.1 (d, $J_{CP} = 85.2$ Hz, PCH_2), 10.7 (Cp*-Me), 9.3 (Me), 8.7 (Me); ³¹P NMR ($CDCl_3$) δ 28.45; FAB-HRMS (NBA) calcd. for $C_{28}H_{31}FeMoO_5P$ (*m/z*) [M⁺] 632.0313; found 632.0316.

[4-(Dicyclohexylphosphino)indenyl-pentamethylcyclopent-adienyliron]pentacarbonylmolybdenum [1d-Mo(CO)₅]

Following the procedure for the preparation of **2a**-$Mo(CO)_5$, compound **1d**-$Mo(CO)_5$ was synthesized in 87% yield as a deep purple solid: $R_f = 0.80$ (hexanes); mp 80-82 ˚C; ¹H NMR ($CDCl_3$) δ 7.67 (dd, 1H, $J_{HP,HH} = 16.8, 6.4$ Hz, Ph), 7.51 (dd, 1H, $J = 8.4, 2.4$ Hz, Ph), 7.07 (t, 1H, $J = 7.2$ Hz, Ph), 4.66 (d, 1H, $J = 2.4$ Hz, H-1 or H-3), 4.29 (d, 1H, $J = 2.4$ Hz, H-1 or H-3), 3.90 (t, 1H, $J = 2.4$ Hz, H-2), 3.06-2.94 (m, 1H, PCH), 2.85-2.75 (m, 1H, PCH), 2.47-0.84 (m, 20H, Cy), 1.59 (s, 15H, Cp*-Me); ¹³C NMR ($CDCl_3$) δ 210.6 (CO), 207.7 (CO × 4), 137.0 (Ph), 132.6 (Ph), 129.0 (Ph), 120.1 (Ph), 94.1 (C-3' or C-7'), 88.0 (C-3' or C-7'), 78.4 (C-1 and C-3), 66.2 (C-2 or Cp*), 65.1 (C-2 or Cp*), 40.1

(PCH), 33.7 (PCH), 29.4 (CH_2), 28.8 (CH_2), 28.2 (CH_2), 27.4 ($CH_2 \times 5$), 25.9 ($CH_2 \times 2$), 10.3 (Cp*-Me); ^{31}P NMR ($CDCl_3$) δ 63.16; FAB-HRMS (NBA) calcd. for $C_{36}H_{43}FeMoO_5P$ (*m/z*) [M$^+$] 740.1252; found 740.1258.

General Procedures for Palladium-Catalyzed Allylic Alkylation Reaction

Procedure A

The pre-catalyst [Pd(C_3H_5)Cl]$_2$ (0.02 eq) and a ligand (0.05 eq) were combined in a 2-necked round-bottomed flask and flushed with nitrogen. Freshly distilled CH_2Cl_2 was then added *via* syringe and the mixture was stirred at rt for 1 h. Allyl acetate **5** (1 eq) in CH_2Cl_2 was then added *via* cannula, dimethylmalonate (**6**, 3 eq) and BSA (3 eq) were added *via* syringes, and finally KOAc (0.1 eq) was added under positive nitrogen pressure. The reaction mixture was stirred at temperatures specified in Table **1** and monitored by GC-MS.

Procedure B

Ligand **2a** and the pre-catalyst [Pd(C_3H_5)Cl]$_2$ in a ratio of 2.5/1 (amounts were calculated according to substrate to palladium ratios in Table **1**) were combined in a 2-necked round-bottomed flask and flushed with nitrogen. Freshly distilled THF was added *via* syringe and the mixture was stirred at rt for 30 min, after which allyl acetate **8** (1 eq) was added *via* syringe. To another 2-necked round-bottomed flask, NaH (2 eq) was introduced under positive nitrogen pressure and THF was added *via* syringe. The mixture was cooled on an ice bath, and dimethylmalonate (**6**, 2 eq) was then added *via* syringe over 30 min. After stirring at 0 $^{\circ}$C for 15 min, the temperature was raised to 25 $^{\circ}$C and stirred for 30 min. This sodium malonate solution was transferred to the flask containing the catalyst and substrate **8** *via* cannula. The reaction mixture was stirred at rt and monitored by GC-MS.

General Procedure for Palladium-Catalyzed Suzuki Coupling of Chlorobenzene with Phenylboronic Acid

A 2-necked round-bottomed flask with a magnetic stirring bar and a reflux condenser were dried in an oven and cooled under nitrogen. Phenylboronic acid (1 eq), Pd$_2$(dba)$_3$ (0.015 eq; dba, dibenzylideneacetone) and Cs$_2$CO$_3$ (2 eq) were added under positive nitrogen pressure. The flask with the condenser was switched to vacuum for about 10 min and then turned back to nitrogen carefully. Chlorobenzene (1 eq) was then added *via* syringe. A ligand (**2a-e**, 0.036 eq) in a round-bottomed flask was dried under vacuum overnight and the flask was then switched to nitrogen atmosphere carefully. Freshly distilled 1,4-dioxane was added to both flasks *via* oven-dried syringes. Finally, the ligand solution was added to the 2-necked flask *via* cannula. The reaction mixture was then heated to reflux and monitored by GC-MS.

X-Ray Crystallography

A suitable crystal of compound **2a** (obtained by crystallization from hexanes at -20 $^{\circ}$C) was rolled in epoxy resin and mounted on a glass fiber. An Enraf Nonius CAD-4 X-Ray diffractometer was the instrument used for the determination. The windows program WinGX was used as the interface for the solution and refinement of the model [9]. The data were first reduced and corrected for absorption using psi-scans [10], and then solved using the program SIR97 [11]. Two molecules of **2a** constituted the asymmetric unit and both of

these contained rotational disorder in the Cp* rings (60/40 ratio for Fe1 and 70/30 for Fe2, Fig. **1**) which were accounted for using standard procedures available in the program SHELXL97 [12]. This sort of rotational disorder (29.3° and 38.6° clockwise for the Cp* ligands in Fe1 and Fe2 respectively, Fig. **1**) in the Cp* ligand has been previously observed and could be crystallographically imposed or non-random as is the case with **2a** [13]. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were refined at calculated positions with thermal parameters constrained to the carbon atom on which they were attached. Crystal data and final structural refinement parameters are listed in Table **4**.

Table 4.   Summary of Crystallographic Data for 2a

	2a
formula	$C_{31}H_{31}FeP$
fw, g·mol^{-1}	490.38
cryst syst	triclinic
space group	P -1
a (Å)	8.838(3)
b (Å)	11.952(4)
c (Å)	25.696(6)
α (deg)	100.70(2)
β (deg)	90.35(3)
γ (deg)	104.11(3)
V (Å^3)	2582.9(14)
Z	4
d_{calc} (g·cm^{-3})	1.261
μ (mm^{-1})	0.662
θ (deg)	1.62– 22.47
λ (Å)	0.71073
T (K)	293(2)
GOF	1.037
$R_1{}^a$, wR$_2$ *(I>2σ(I))*^{b}	0.061, 0.162^c

^{a}R$_1$=$\sum||F_o|$ - $|Fc||/\sum|F_o|$.
^{b}wR$_2$= $[\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.
^{c}w=1/[σ^2(Fo^2)+(0.0620P)^2 + 2.9602P] where P=(Fo^2+2(Fc)^2)/3.

Supplementary Materials

The images of ^{1}H, ^{13}C and ^{31}P NMR spectra for all new compounds can be found on pages 10-44 of this article. Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 672018 for compound **2a**; copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

ACKNOWLEDGEMENTS

REFERENCES

[1]   Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, California, **1994**.

[2]   (a) Littke, A. F.; Dai, C. Y.; Fu, G. C. *J. Am. Chem. Soc.,* **2000**, *122*, 4020-4028; (b) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.,* **2005**, *127*, 4685-4696; (c) Anderson, K. W.; Buchwald, S. L. *Angew. Chem. Int. Ed.,* **2005**, *44*, 6173-6177.

[3]   (a) Thimmaiah, M.; Fang, S. *Tetrahedron,* **2007**, *63*, 6879-6886; (b) Thimmaiah, M.; Luck, R. L.; Fang, S. *J. Organomet. Chem.,* **2007**, *692*, 1956-1962.

[4]   (a) Wechsler, D.; Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics,* **2007**, *26*, 6418-6427; (b) Curnow, O. J.; Fern, G. M.; Hamilton, M. L.; Zahl, A.; van Eldik, R.; *Organometallics,* **2004**, *23*, 906-912; (c) Curnow, O. J.; Fern, G. M. *Organometallics,* **2002**, *21*, 2827-2829; (d) Curnow, O. J.; Fern, G. M.; Hamilton, M. L.; Jenkins, E. M. *J. Organomet. Chem.,* **2004**, *689*, 1897-1910.

[5]   (a) Tolman, C. A. *Chem. Rev.,* **1977**, *77*, 313-348; (b) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.,* **2000**, *100*, 2741-2769.

[6]   (a) Tolman, C. A. *J. Am. Chem. Soc.,* **1970**, *92*, 2953-2956; (b) Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. H. *Inorg. Chem.,* **1981**, *20*, 578-583; (c) Davies, M. S.; Allen, G. W.; Aroney, M. J.; Hambley, T. W.; Pierens, R. K. *J. Mol. Struct.,* **1994**, *326*, 81-91;

[d] Palcic, J. D.; Baughman, R. G.; Golynskiy, M. V.; Frawley, S. B.; Peters, R. G. *J. Organomet. Chem.,* **2005**, *690*, 534-538.

[7]   van Assema, S. G. A.; de Kanter, F. J. J.; Schakel, M.; Lammertsma, K. *Organometallics,* **2006**, *25*, 5286-5291.

[8]   (a) Laurenti, D.; Feuerstein, L.; Pepe, G.; Doucet, H.; Santelli, M. *J. Org. Chem.,* **2001**, *66*, 1633-1637; (b) Doucet, H.; Santelli, M. *Synlett,* **2006**, 2001-2015.

[9]   Farrugia, L. J.; *J. Appl. Crystallogr.,* **1999**, *32*, 837-838.

[10]   North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. A,* **1968**, *24*, 351-359.

[11]   Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.,* **1999**, *32*, 115-119.

[12]   Sheldrick, G. M. SHELX-97, Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, **1998**.

[13]   (a) Weber, L.; Kleinebekel, S.; Lonnecke, P. *Z. Anorg. Allg. Chem.,* **2002**, *628*, 803-809; (b) Ohki, Y.; Takikawa, Y.; Hatanaka, T.; Tatsumi, K. *Organometallics,* **2006**, *25*, 3111-3113; (c) Scherer, O. J.; Meiers, J.; Regitz, M.; Hofmann, M. A.; Karaghiosoff, K.; Wolmershauser, G. *Z. Anorg. Allg. Chem.,* **2001**, *627*, 1532-1536; (d) Koch, B.; Scherer, O. J.; Wolmershauser, G. *Z. Anorg. Allg. Chem.,* **2000**, *626*, 1797-1802; (e) Triki, S.; Berezovsky, F.; Pala, J. S.; Garland, M. T. *Inorg. Chim. Acta,* **2000**, *308*, 31-36; (f) Chavez, I.; Alvarez-Carena, A.; Molins, E.; Roig, A.; Maniukiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manriquez, J. M. *J. Organomet. Chem.,* **2000**, *601*, 126-132; (g) Akita, M.; Sakurai, A.; Moro-Oka, Y. *Chem. Commun.,* **1999**, 101-102; (h) Weber, L.; Kaminski, O.; Quasdorff, B.; Stammler, H. G.; Neumann, B. *J. Organomet. Chem.,* **1997**, *529*, 329-341; (i) Driess, M.; Pritzkow, H.; Winkler, U. *J. Organomet. Chem.,* **1997**, *529*, 313-321; (j) Friedrich, G.; Scherer, O. J.; Wolmershauser, G. *Z. Anorg. Allg. Chem.,* **1996**, *622*, 1478-1486; (k) Akita, M.; Kato, S.; Terada, M.; Masaki, Y.; Tanaka, M.; Morooka, Y. *Organometallics,* **1997**, *16*, 2392-2412; (l) Jonas, K.; Klusmann, P.; Goddard, R. *Z. Naturforsch. B Chem. Sci.,* **1995**, *50*, 394-404; (m) Akita, M.; Terada, M.; Oyama, S.; Morooka, Y. *Organometallics,* **1990**, *9*, 816-825.