Di-*t*-butyl(ferrocenylmethyl)phosphine: air-stability, structural characterization, coordination chemistry, and application to palladium-catalyzed cross-coupling reactions

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Abstract

Di-*t*-butyl(ferrocenylmethyl)phosphine (**1**) has been isolated and structurally characterized. This ligand was found to be reasonably air stable as a solid and it has been shown to possess electron donating ability similar to that of tri-*i*-propylphosphine. A palladium catalyst bearing this ligand performed room temperature Suzuki–Miyaura coupling reactions with aryl bromides. Modest Heck coupling reactivity with aryl bromides was also observed at 100 °C. Complexation of **1** with $Pd_2(dba)_3$ led to formation of $(\mathbf{1})_2Pd^0$. Addition of 4-bromoanisole to solutions containing both **1** and $Pd_2(dba)_3$ led to formation of an oxidative addition product when **1**:Pd ratios were $\leqslant 1$. With a 2:1 ratio of **1**:Pd, monophosphine complex formation and oxidative addition were significantly inhibited.
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1. Introduction

Ferrocene based phosphines have become increasingly popular for use as ligands in several catalytic processes. The electron-rich metallocene helps provide the electronic and steric characteristics that are often required to form a highly active catalyst. Palladium and nickel complexes with 1,1′-bis(diphenylphosphino)ferrocene (dppf) and similar bidentate ligands have shown high activity in several types of C–C bond forming cross-coupling reactions [1–11]. Examples of high activity in these processes using monophosphine derivatives have also been reported [8,12–16]. Substituents can be added to the cyclopentadienyl ring α to the phosphine-bearing carbon to form mono- and polydentate ligands which are suitable for use in asymmetric catalysis [17,18].

Phosphines have frequently been used over the past decade in the development of efficient catalysts for various cross-coupling reactions. Much of the research focus has been centered on the use of sterically demanding tertiary alkylphosphine ligands that enhance the rate determining oxidative addition step. Ligands such as *t*-Bu₃P [19–22], (*o*-biphenyl)PR₂ [23–25], BuP(1-adamantyl)₂ [26] and others [14,15,27] have been used to form catalysts that show high activities at moderate temperatures (20–100 °C), even with unactivated aryl chlorides. Many of these ligands oxidize rapidly in air, so they need to be handled in an inert atmosphere or converted to the corresponding phosphonium salt [28]. Ligands with similar bulk and electron donating ability that show resistance to oxidation would lead to simpler reaction preparations and longer catalyst lifetimes.

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Henderson [29,30] recently investigated the properties and coordination abilities of various primary phosphines and an arsine bearing ferrocene substituents. Despite the fact that these ligand types are commonly very air-sensitive, it was shown that primary phosphines with an alkyl linkage between the cyclopentadienyl ligand of the ferrocene and the phosphorus or arsenic atom were stable in air for over two years. In comparison, ferrocenylphosphine oxidizes in air after a few days. This air stability was an unexpected result since the aromatic effects of the cyclopentadienyl ring towards the central atom should be greatly diminished with the alkyl bridge present. A crystal structure of ferrocenylethylarsine shows that the ferrocene points away from the arsenic atom, which suggests that this air stability is not due to a weak intramolecular coordination or an indirect aromatic effect of the ferrocene to the phosphorus atom.

Recently, tertiary ferrocenylmethylphosphines were synthesized and used as ligands for Suzuki–Miyaura palladium catalysts [31]. However, these phosphines possessed an aryl substituent on the methyl bridge in order to maximize steric bulk. Catalytic activity of these complexes was high using many different aryl bromide reactants, but the *t*-butyl-substituted ligand was not air stable. It is unclear if this decrease in air stability was due to the introduction of the *t*-butyl substituents on phosphorous, the phenyl group on the methylene bridge, or a combination of the two. Di-*t*-butyl(ferrocenylmethyl)phosphine (**1**), which lacks the phenyl group on the methylene bridge, has been reported [32] but little is known about the properties of this ligand, including its reactivity towards oxygen. We have taken a closer look at **1**, examining its reactivity and its viability in various cross-coupling reactions.

2. Results and discussion

The synthesis of **1** was performed using a previously reported method, but the procedure needed to be extended since the authors did not fully isolate or characterize the ligand (Eq. (1)) [32]. Recrystallization of the crude product from methanol led to orange crystals with either a prismatic (**1a**, Fig. 1) or flattened rod shape (**1b**, Fig. 2). To investigate these differences, X-ray crystal structures of both crystal types were acquired. The crystallographic data is presented in Table 1. Selected bond lengths and angles for both crystals **1a** and **1b** are shown in Table 2. ORTEP drawings of the resultant spectra are presented in Figs. 1 and 2.
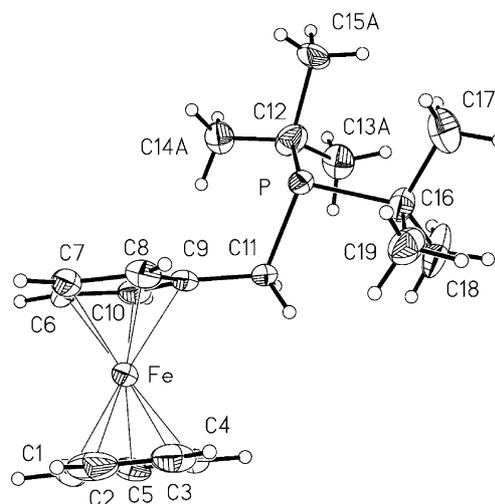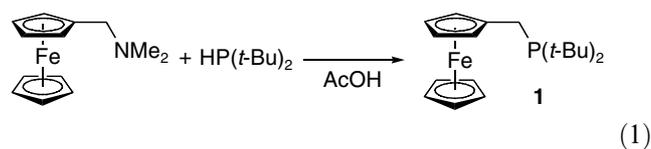

Fig. 1. ORTEP drawing of the prism-like crystal of di-*t*-butyl(ferrocenylmethyl)phosphine (**1a**), rotomer A. Ellipsoids are drawn at the 50% probability. Hydrogen atoms were placed in idealized positions.
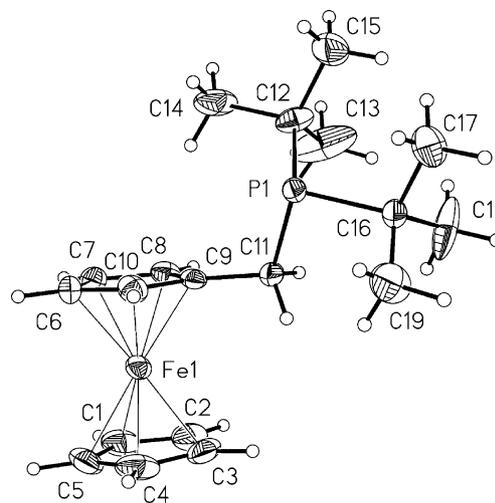

Fig. 2. ORTEP drawings of one of the two molecules of **1** in the asymmetric unit of the flattened rod shaped crystal of di-*t*-butyl(ferrocenylmethyl)phosphine (**1b**). The structure was inverted to have the same orientation as **1a**. Ellipsoids are drawn at the 50% probability. Hydrogen atoms were placed in idealized positions.

Crystal **1a** resolved into a structure containing only one phosphine in the asymmetric unit, although two different rotomers of one of the *t*-Bu groups were observed. Crystal **1b** had two molecules of **1** in the asymmetric unit, which had similar, although not identical, bond lengths and angles. Structures **1a** and **1b** were very similar with only small variations in the corresponding bond lengths and angles of these polymorphs. DSC studies of both crystal types showed a sharp melting point at 67.4 °C, so there appears to be little difference in the physical properties of the two polymorphs.

The Tolman electronic parameter, v, for this ligand was determined spectroscopically from (**1**)Ni(CO)$_3$, which was prepared in CH$_2$Cl$_2$ [33]. The symmetric

$$\text{(1)}$$

Table 1
X-ray crystallographic data

Compound	1a	1b(1,2)
Formula	$C_{19}H_{29}FeP$	$C_{19}H_{29}FeP$
Color, shape	Orange, prismatic	Orange, flattened rod
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$
Unit cell		
a (Å)	5.992(4)	28.310(7)
b (Å)	11.410(7)	11.188(3)
c (Å)	13.198(8)	11.591(3)
α (°)	90	90
β (°)	95.644(11)	101.729(4)
γ (°)	90	90
V (Å^3)	897.9(9)	3594.6(15)
Z	2	8
Density calcd. (g/cm^3)	1.273	1.272
Crystal size (mm)	$0.36 \times 0.24 \times 0.14$	$0.41 \times 0.22 \times 0.14$
λ (Mo Kα) (mm^{-1})	0.921	0.921
$F(0\,0\,0)$	368	1472
T (K)	173(2)	173(2)
$\theta_{min,\,max}$ (°)	1.55, 23.31	0.73, 23.30
Reflections collected	4097	15896
Independent reflections, R_{int}	2527, 0.0324	5138, 0.0202
Goodness-or-fit on F^{2a}	0.979	1.269
Final R indices [$I > 2\sigma(I)$], $R_1{}^b$, $w_2{}^c$	0.0357, 0.0832	0.0680, 0.1630
R indices (all data)	0.0405, 0.0846	0.0726, 0.1645
Absolute structure parameter	0.07(2)	na

[a] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of data and p is the number of parameters refined.
[b] $R = \sum\|F_o|-|F_c\|/\sum|F_o|$.
[c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(w(F_o^2)^2)]\}^{1/2}$. Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å).

Table 2
Selected bond lengths (Å) and angles (°)

	1a	1b[a]	1b′[a]
Bond lengths			
P–C$_{11}$	1.868(4)	1.883(7)	1.870(7)
C$_{11}$–C$_9$	1.492(6)	1.502(9)	1.512(9)
Fe–C$_9$	2.048(4)	2.056(6)	2.054(6)
P–C$_{12}$	1.876(4)	1.888(7)	1.899(7)
P–C$_{16}$	1.895(4)	1.892(7)	1.905(7)
Bond angles			
C$_9$–C$_{11}$–P	112.8(3)	112.4(5)	112.4(4)
C$_{11}$–C$_9$–Fe	126.5(3)	127.4(5)	127.6(4)
C$_{11}$–P–C$_{12}$	102.6(2)	102.8(3)	100.1(3)
C$_{11}$–P–C$_{16}$	100.6(2)	99.5(3)	102.3(3)
C$_{12}$–P–C$_{16}$	110.0(2)	110.6(3)	110.2(3)
C$_8$–C$_9$–C$_{11}$–P	65.4	65.5	66.8

[a] Second molecule of **1** in the asymmetric unit of **1b** (ORTEP not shown in Fig. 2).

carbonyl stretch was observed at 2059.1 cm^{-1}, which is close to the observed value for *i*-Pr$_3$P (2059.2 cm^{-1}). Ligand **1** is a weaker electron donor than *t*-Bu$_3$P (2056.1 cm^{-1}) [33], which suggests that Pd complexes of **1** might be expected to show lowered effectiveness in oxidative addition reactions with less reactive aryl halides. Spectroscopic cone angle determination through complexation with Ni(CO)$_4$ in toluene indicated that only one carbonyl could be exchanged with **1** after 63 h heating at 100 °C (2060, 1987 and 1976 cm^{-1} in toluene) [34]. A small amount of residual Ni(CO)$_4$ was also detected by FTIR spectroscopy (2046 cm^{-1}) which indicates a degree of substitution of 0.94 and an experimental ligand cone angle of approximately 186°. This effective steric bulk is slightly greater than that seen for *t*-Bu$_3$P, suggesting that the ferrocenylmethyl group has a significant steric effect.

Despite the presence of two tertiary butyl groups on the central phosphorus atom, **1** shows significant air stability. It was initially unknown if this characteristic, seen in analogous primary (ferrocenylalkyl)phosphines, would be retained due to the addition of two highly electron donating groups to the phosphorus atom [29,30]. After 54 days in the solid-state, ^{31}P NMR spectroscopy showed approximately 20% conversion of the ligand (34.1 ppm in THF) to a compound that appears to be di-*t*-butyl(ferrocenylmethyl)phosphine oxide (57.1 ppm in THF). The reasons for the low oxidation levels are still unclear since X-ray crystallography does not indicate any direct or indirect interaction between the ferrocene and the phosphorus atom. However, if a THF solution of the ligand is exposed to air, complete consumption of the ligand to primarily form the phosphine oxide occurs within 21 h. Thus, **1** can be manipulated as a solid in air for ease of use, but all solutions should be handled in an inert atmosphere.

2.1. Suzuki–Miyaura coupling

An *in situ* catalyst derived from **1** and $Pd_2(dba)_3$ gave good activity for Suzuki–Miyaura couplings of aryl bromides after conditions were optimized (Eq. (2)). Initial studies were performed using phenylboronic acid (**3a**) and either 4-bromotoluene or 4-bromoanisole as reactants in THF at room temperature (Table 3). Nearly complete reactions were normally detected in 2 h, but most reactions were allowed to progress for 20–24 h to maximize the conversion. Cs_2CO_3 proved to be a more effective base than KF for the initially tested aryl bromides, so it was used preferentially in subsequent reactions. Pd loadings could be lowered to 2 mol% without any detrimental effect. More electron deficient aryl bromides such as 4-bromobenzaldehyde (**2c**) and 4-bromoacetophenone (**2d**) coupled well using the optimal reaction conditions determined above. More sterically demanding aryl bromides such as 4-bromo-3-methylanisole (**2e**) led to a decrease in yield.
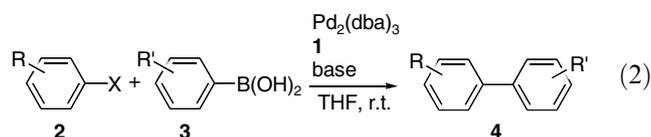
$$ (2) $$

Table 4 shows that the Suzuki coupling yields are affected by the steric and electronic properties of the arylboronic acid. Use of 4-fluorophenylboronic acid gave modest yields at room temperature and at 44 °C. Reactions with boronic acids bearing electron-donating groups showed high reactivity as expected. It does appear that steric effects can lower reaction yields, as evidenced when 2-methylboronic acid was used as a reactant. Low yields were seen by GC for the coupling of 4-chlorotoluene and phenylboronic acid at room temperature. A modest yield was obtained for this coupling at 64 °C, although the yield was significantly lower than that achieved with 4-bromotoluene at room temperature.

2.2. Heck coupling

As anticipated, Heck couplings with the **1**/$Pd_2(dba)_3$ catalyst system were not as facile as the Suzuki–Miyaura couplings. Styrene proved to be an ideal reactant as GC spectra of the reaction solutions showed

Table 3
Suzuki coupling of aryl bromides with **3a** using **1**/$Pd_2(dba)_3$

Aryl bromide	Mol% Pd[a]	Base	Yield (%)[b]
MeO–⬡–Br **2a**	4.0	KF	61
Me–⬡–Br **2b**	3.9	KF	100
2a	4.1[c]	KF	60
2a	3.9	Cs_2CO_3	100
2a	2.0	Cs_2CO_3	100(83)
2b	2.1	Cs_2CO_3	100(83)
2b	0.9	Cs_2CO_3	54
OHC–⬡–Br **2c**	2.0	Cs_2CO_3	100(86)
MeCO–⬡–Br **2d**	2.3	Cs_2CO_3	(72)
MeO–⬡(CH₃)–Br **2e**	1.8	Cs_2CO_3	(33)

[a] 1:1 **1**:Pd ratio.
[b] Yields determined by gas chromatography unless in parenthesis, which signifies isolated yield.
[c] $Pd(OAc)_2$ used as catalyst precursor.

Table 4
Suzuki coupling with **1**/$Pd_2(dba)_3$ under optimized conditions[a]

Aryl halide	Boronic acid	T (°C)	Time (h)	Yield (%)[b]
2a	F–⬡–B(OH)₂ **3b**	rt	24	66(52)
2a	**3b**	44	20	(30)
2a	Me–⬡–B(OH)₂ **3c**	rt	24	95(84)
2c	**3c**	rt	18	(54)
2a	⬡(CH₃)–B(OH)₂ **3d**	rt	24	70
2a	**3d**	44	20	(67)
2a	MeO–⬡–B(OH)₂ **3e**	rt	24	(46)
2b	**3e**	rt	24	(85)
2c	**3e**	rt	24	(90)
2d	**3e**	rt	24	(78)
Me–⬡–Cl **2f**	⬡–B(OH)₂ **3a**	rt	17	6[c]
2f	**3a**	64	21	22[d]

[a] $Pd_2(dba)_3$ (2 mol %), **1**, (2 mol %), and Cs_2CO_3 (3 equiv.) in THF.
[b] Yields determined by gas chromatography unless in parenthesis, which signifies isolated yield. Spectroscopic data for isolated compounds were consistent with literature data. Significant amounts of unreacted aryl bromide were present in low conversion results.
[c] 4 mol% of $Pd_2(dba)_3$ and 3 equiv. KF used.
[d] 4 mol% of $Pd_2(dba)_3$ used. 1,4-dioxane used as solvent.

Table 5
Heck couplings using **1**/Pd$_2$(dba)$_3$ at 80–85 °C[a]

| Base[b]	Mol% Pd	P:Pd ratio	Yield (%)[c]
Cs$_2$CO$_3$	2.8	1.04	0
Cy$_2$NMe[d]	3.7	0.58	22
Cy$_2$NMe	4.2	1.04	55
Cy$_2$NMe	3.6	1.49	4
NBu$_3$	4.0	0.71	40
Ph$_2$NEt	3.8	0.86	37

[a] **2b** (1 equiv), Styrene (2 equiv), Pd$_2$(dba)$_3$, **1**, 79–85 °C, 17–23 h, dioxane.
[b] 1.3–1.4 equiv relative to **2b**.
[c] Yields determined by gas chromatography.
[d] 2.4 equiv Cy$_2$NMe.

Table 6
Heck couplings using **1**/Pd$_2$(dba)$_3$ at 95–100 °C[a]

Aryl halide	Mol% Pd	P/Pd ratio	Yield (%)[b]
2g	5.6	0.72	100
2g	4.3	0.98	(47)
2h	5.3	0.76	57 (33)[c]
2b	5.1	0.78	86 (70)
2b	5.5	1.34	74
2b	2.9	0.90	75
2b	2.0	0.88	22
2a	5.2	0.78	(54)
2c	5.8	0.77	(77)
2d	5.7	0.73	(65)
2f	5.1	0.78	trace

[a] CyNMe$_2$ (1.3 equiv.), styrene (2 equiv.), Pd$_2$(dba)$_3$, **1**, 16.5–20.7 h, 95–99 °C, dioxane.
[b] Yields determined by gas chromatography unless in parenthesis, which signifies isolated yield. Spectroscopic data for isolated compounds was consistent with literature data.
[c] Isolated material contaminated with ≈10% (mol/mol) **2h**.

minimal side product concentrations (Eq. (3), Table 5). The application of Cs$_2$CO$_3$ led to no product formation, possibly due to the limited solubility of this base in 1,4-dioxane. Trialkylamines removed this complication and allowed coupling reactions to occur. Cy$_2$NMe gave higher yields than NBu$_3$ or Ph$_2$NEt and was used in subsequent studies. Initial catalyst optimizations were performed between 80 and 85 °C using 4-bromotoluene and styrene as reactants. It was found that reaction yields were significantly lowered if the catalyst loading was dropped below 4 mol% and if the ratio between Pd and **1** was not near 1. Table 6 shows that elevation of the reaction temperature to around 100 °C and an increase in catalyst loading to 5.0–5.5 mol% significantly increased product yields. Yield decreases similar to those observed in lower temperature studies were also seen with variations of catalyst loading and **1**:Pd ratios. Electron deficient aryl bromides led to similar isolated yields, indicating that catalyst efficiency has reached a plateau. Electron rich aryl bromide **2a** gave a lower yield of the coupled product compared to less electron rich aryl halides. As anticipated, reaction attempts with aryl chloride analogs led to virtually no product formation.

$$(3)$$
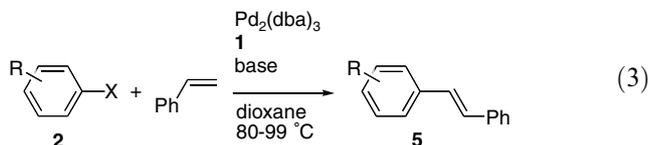
2.3. Complexation studies

To help understand the nature of the catalytic species in solution, THF and THF-d$_8$ solutions containing both Pd$_2$(dba)$_3$ and **1** at various concentration ratios were prepared and analyzed periodically by ^{1}H and ^{31}P NMR spectroscopy. In all cases, ^{31}P NMR spectra showed a strong signal at 59.5 ppm that appeared quickly and remained the most intense signal through three days of observations. ^{1}H NMR spectra acquired over the same time frame showed downfield shifts for the CH$_2$ bridge protons (0.15 ppm) and for the protons bound to the 2 and 5 positions of the substituted Cp group (0.54 ppm). A downfield shift of 0.164 ppm for the *t*-Bu group proton signal was also seen along with a change to an apparent triplet pattern ($^3J_{P-H}$ = 5.91 Hz). A triplet pattern is indicative of virtual coupling of two phosphorous nuclei coordinated to a metal center with a P–M–P bond angle of 180° [35]. Non-coordinated phosphine, with a ^{31}P NMR signal at 34.1 ppm, was only detected when the **1**:Pd ratio approached 2:1. The observed stoichiometry dependence along with the observed virtual coupling pattern are consistent with an (**1**)$_2$Pd^0 complex. The fact that the solution color remained dark purple, indicative of residual Pd$_2$(dba)$_3$, until a 2:1 ratio of **1**:Pd was reached also supports this conclusion.

As time progressed, a new set of resonances began to appear in NMR spectra for solutions with 0.48 and 1.06 ratios of **1**:Pd. For these solutions, both a broad ^{1}H NMR signal at 1.03 ppm and a ^{31}P NMR signal at 64.3 ppm began to appear in 30–60 min. These signals gradually grew in intensity over the next three days along with new weak resonances in the Cp region. In contrast, these signals did not appear in the 2.00 **1**:Pd ratio solution spectra even after three days. A ^{1}H NMR spectrum obtained at 268 K resolved the broad 1.03 ppm signal into two equal intensity doublets at 1.073 and 0.912 ppm, while the broad ferrocenyl resonance resolved to a single set of sharp peaks. Each doublet integrated for nine protons relative to the new set of ferrocene resonances, indicating that the *t*-butyl groups are diastereotopic in this complex. The observation of doublets for the *t*-butyl groups, rather than triplets shows that there is no P–P coupling in this complex.

Placing 5.6 equivalents of 4-bromoanisole into a 0.92 ratio of **1**:Pd solution in THF-d$_8$ initially resulted in a ^{31}P NMR spectrum that mirrored what was seen in experiments without aryl halide present. However, a new signal at 53.7 ppm along with a shoulder signal at 52.8 ppm became dominant in less than 2.5 h. All other ^{31}P NMR signals were no longer present after 8.25 h. The resultant product was isolated and washed with hexane to remove excess dibenzylidene acetone. Isolated yields were poor since the palladium product is also somewhat soluble in hexane.

The isolated oxidative addition product was fully characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum showed a 1:1 ratio for the integrated area of the anisole and ligand resonances. The *t*-butyl resonance of the oxidation addition product was a doublet in the ^{1}H NMR spectrum ([3]J_{P-H} = 13.56 Hz), which is inconsistent with the AXX′ pattern expected for a *trans*-(**1**)$_2$Pd(C$_6$H$_4$-*p*-OMe)Br structure. These results indicate that the product has a stoichiometry of (**1**)Pd(C$_6$H$_4$-*p*-OMe)Br. Based on other isolated aryl halide complexes of sterically demanding phosphines, a dimeric halide bridged structure, [(**1**)Pd(μ-Br)(C$_6$H$_4$-*p*-OMe)]$_2$ (**6**), could be proposed (Eq. (4)). These types of products have been observed upon oxidative addition to (*o*-tol$_3$P)$_2$Pd, for example [36]. Recently, Hartwig [37,38] reported the isolation of 3-coordinate, T-shaped LPd(Ar)X products from the oxidative addition of aryl halides to Pd[0] complexes of sterically demanding, electron rich alkylphosphines, such as *t*-Bu$_3$P. Given the similar steric and electronic properties of **1** and *t*-Bu$_3$P, formation of a three-coordinate product (**7**) is also possible. We cannot rule out either structure **6** or **7** based on our spectroscopic data. Unfortunately, attempts to grow crystals of the oxidative addition product (**6/7**) were unsuccessful.

$$1 + Pd_2(dba)_3 \xrightarrow[\text{THF}]{\text{2a}\atop\text{excess}} \mathbf{6} \text{ or } \mathbf{7} \qquad (4)$$

1:Pd = 1:1
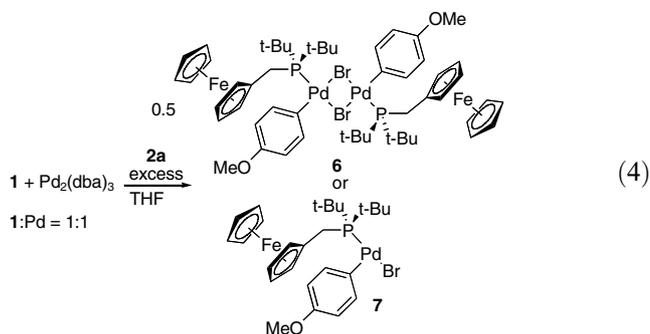
Replication of this experiment using a 1.9 ratio of **1**:Pd along with 3.0 equivalents of 4-bromoanisole in THF-d$_8$ showed only a small amount of oxidative addition product formation after 21 h stirring at room temperature. Since activity in full catalytic studies was significantly decreased under comparable **1**:Pd ratios, a decreased level of reactivity was anticipated. The slow oxidative addition of (**1**)$_2$Pd[0] is consistent with the slow rates of oxidative addition of phenyl iodide to (*t*-Bu$_3$P)$_2$Pd reported by Jutand [39] and Hartwig [38]. Fu [21] has shown that (*t*-Bu$_3$P)$_2$Pd[0] is not a competent Suzuki coupling catalyst unless an equivalent of is Pd$_2$(dba)$_3$ added to encourage monophosphine complex formation.

3. Conclusions

Di-*t*-butyl(ferrocenylmethyl)phosphine has been shown to possess several properties that will aid in cross-coupling efficiencies in large scale reaction procedures. The significant resistance towards oxidation in air as a solid has been retained from the primary phosphine analog. This air-stability allows for benchtop reaction mixture preparations in air. The strong electron donating ability and large effective cone angle lead to catalyst complexes which show good activity for room temperature Suzuki–Miyaura couplings with aryl bromides and moderate yields in Heck couplings at elevated temperatures.

Stoichiometric complexation studies show that **1** forms the expected (**1**)$_2$Pd[0] complex when mixed with Pd$_2$(dba)$_3$ independent of the **1**:Pd ratio in analogy to Fu's observations with (*t*-Bu$_3$)P [21]. With L:Pd ratios ⩽1, (**1**)$_2$Pd[0] is partially converted to a new species that is fluxional on the NMR time scale at room temperature. Key spectroscopic signatures of this new species include the inequivalence of the *t*-butyl groups and doublets rather than triplet patterns for the *t*-butyl resonances. This observed inequivalence indicates that there is an asymmetry in the coordination environment around the palladium center in this new complex that results in the *t*-butyl groups being diastereotopic. The doublet pattern for the *t*-butyl resonances indicates they are coupled to a single phosphorous nuclei, thus there is likely only one phosphine in the palladium coordination

environment [40]. Based on these observations, we have tentatively identified this new species as a monophosphine palladium(0)(dba) complex, (**1**)Pd(dba)$_n$ (**8**). Although we cannot confirm coordination of dba by spectroscopic means, the *trans*-dibenzylideneacetone ligand provides an asymmetric coordination environment that is typically fluxional at room temperature [41,42]. L$_2$Pd(dba) (L = tertiary phosphine) complexes have been previously reported [36,43–47], but LPd(dba)$_n$ complexes of monodentate phosphines have not previously been reported to our knowledge.

Observations of monophosphine Pd^0 complexes are uncommon unless other stabilizing ligands are present [48–50]. However, a number of authors have speculated that dissociation of a phosphine from a L$_2$Pd^0 resting state must occur to give a highly reactive monophosphine complex as the catalytically active species when bulky phosphines are used [21,36,49,51]. Involvement of a monophosphine-palladium(0) active species is consistent with our catalytic and stoichiometric results obtained with mixtures of **1**/Pd$_2$(dba)$_3$. Optimal catalytic activity is observed with **1**:Pd ratios near 1, while the activity significantly decreases at higher ratios. Similarly, oxidative addition occurs efficiently to give a palladium aryl halide complex (**6** or **7**) with a 1:1 ratio of **1**:Pd, but was significantly retarded at higher ratios. The apparent observation of monophoshine complex **8** at low **1**:Pd ratios suggests that **1** may be more readily dissociated than other sterically demanding alkylphosphines, such as (*t*-Bu)$_3$P.

Although ligand **1** appears to promote formation of monophosphine/Pd^0 species and undergoes oxidative addition with an electron rich aryl bromide at room temperature, it gives only moderately active catalysts when compared catalysts derived from *t*-Bu$_3$P [20,21] or other electron rich ferrocenyl ligands [10,13–15]. The modest activity of catalysts derived from **1** may indicate that while oxidative addition occurs efficiently, other steps in the catalytic cycle, such as transmetallation from boron or migratory insertion of alkenes, are inefficient. There are several approaches that can be taken to potentially enhance the ligand electronic and steric factors further in effort to improve catalytic activity. Introduction of more sterically demanding adamantyl substituents on the phosphorous might be expected to improve catalytic activity, particularly toward less reactive aryl chloride substrates. Functionalization of the ferrocene cyclopentadienyl rings with electron donating groups may also improve catalysts in this fashion as well, leading to more active catalysts.

While the catalytic utility of **1** may be limited, this ligand may prove useful in mechanistic studies of this important class of catalytic reactions. The unusual coordination chemistry at low L:Pd ratios warrants further exploration. Additional study of the coordination chemistry of **1** to more fully understand the coordination chemistry of this ligand may provide important insights for future ligand design.

4. Experimental

Standard Schlenk and drybox techniques were used for all reactions unless noted [52,53]. All solvents used were purified and dried before use following procedures found in Perrin and Armarego [54]. ^{1}H and ^{31}P NMR spectra were obtained on either a Bruker AX360 or a Bruker AX500 spectrometer. ^{1}H and ^{13}C NMR spectra are reported as positive parts per million (ppm) downfield from a tetramethylsilane (TMS) standard. ^{31}P NMR spectra are referenced from an external H$_3$PO$_4$ standard. Mass spectra were acquired on a VG Autospec high resolution mass spectrometer. A Varian CP-3800 gas chromatograph with a Varian CP-8410 autoinjector was used for all gas chromatography studies. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

X-ray crystallography data collection was performed using a Siemens SMART diffractometer with a CCD area detector, using graphite monochromated Mo Kγ radiation. The SHELXTL software, version 5, was used for solutions and refinement [55]. Absorption corrections were made with SADABS [56]. ORTEP drawings were made with SHELXTL [55] and ORTEP-3 [57,58].

In each structure, the atoms were readily located with high thermal motion observed for the alkyl substituents on the phosphorus atom. Once the gross structural features of each molecule were in place, it became apparent that these substituents were disordered in compound **1a**, and to a lesser extent in compound **1b**. The disorder appears to arise from two different rotamers of the *t*-butyl groups. In compound **1a,** *t*-butyl group C(12) was resolved into two rotamers, while *t*-butyl group C(16), although with high thermal motion, could not be resolved into two orientations. In compound **1b**, high thermal motion was observed in the methyl substituents, most notably C(13), but the disorder could not be satisfactorily resolved. The disordered atoms were refined in alternate least-squares cycles, each with 50% occupancy. Compound **1b** was a pseudo-enantiomer of **1a**. The structure was inverted so that **1a** and **1b** have the same orientation.

Complexations of Ni(CO)$_4$ with **1** were performed as directed by Tolman [33,34]. *N,N*-dimethylaminomethylferrocene, di-*t*-butylphosphine, nickel carbonyl and tris(dibenzylideneacetone)dipalladium were acquired from Strem Chemicals. All bases, boronic acids, aryl halides, olefins and solvents were purchased from either Aldrich Chemicals or Acros Organics.

4.1. Di-t-butyl(ferrocenylmethyl)phosphine (**1**)

The procedure reported by Dunina et al. [32] was adapted to form the crude product. Di-*t*-butylphosphine

(2.99 mL, 16.2 mmol) was mixed with *N,N*-dimethylaminomethylferrocene (1.409 mL, 7.117 mmol) in acetic acid (18.9 mL). The solution was heated at 95 °C for 90 h to ensure reaction completion. Acetic acid and excess di-*t*-butylphosphine were removed by vacuum evaporation. The product was extracted from the crude solid with hexane and was recrystallized in methanol (1.6567 g, 4.8121 mmol, 68% yield). ^{1}H NMR (d$_6$-benzene): δ 4.24 (m, 2H, subst. Cp), 4.03 (s, 5H, Cp), 3.93 (t, $^3J_{P-H} \cong ^3J_{H-H} = 1.85$ Hz, 2H, subst. Cp), 2.66 (d, $^2J_{P-H} = 1.85$ Hz, 2H, –CH$_2$–), 1.09 (d, $^3J_{P-H} = 10.48$ Hz, 18H, *t*-Bu). ^{13}C NMR (d$_6$-benzene): δ 70.4 (s), 69.5 (s), 67.8 (s), 31.8 (d, $J_{P-C} = 15.70$ Hz), 30.4 (s), 23.3 (d, $J_{P-C} = 25.70$ Hz). ^{31}P NMR (d$_6$-benzene): δ 33.3 (br). EI-MS: 344 *m/z* (M$^+$), 287 *m/z* (M$^+$-*t*-Bu), 231 *m/z* (M$^+$-2 *t*-Bu+H), 199 *m/z* (FcCH$_2$), 186 *m/z* (FcH), 121 *m/z* (CpFe). Anal. Calc. for C$_{19}$H$_{29}$FeP: C, 66.29; H, 8.49; Found: C, 66.24; H, 8.55%.

4.2. Palladium(di-t-butyl(ferrocenylmethyl)phosphine) (p-methoxyphenyl)bromide (6l7)

Pd$_2$(dba)$_3$ (24.4 mg, 26.6 µmol) and **1** (26.8 mg, 77.8 µmol) were dissolved in 2.5 mL THF. An excess of 4-bromoanisole (34.0 µL, 0.272 mmol) was added and the solution was stirred for two days in a sealed flask. The yellow solution was decanted from traces of palladium black and vacuum evaporated to yield an oil. The product was washed with four aliquots of hexanes to yield a small amount of yellow paste. ^{1}H NMR (CDCl$_3$): δ 7.27 (d, $J = 8.02$ Hz, 2H, Ph), 6.57 (d, $J = 8.63$ Hz, 2H, Ph), 4.72 (m, 2H, subst. Cp), 4.14 (m, 2H, subst. Cp), 4.02 (s, 5H, Cp), 3.65 (s, 3H, OMe), 3.08 (d, $^2J_{P-H} = 8.63$ Hz, 2H, –CH$_2$–), 1.26 (d, $^3J_{P-H} = 13.56$ Hz, 18H, *t*-Bu). ^{13}C NMR (CD$_2$Cl$_2$): δ 157.1 (s), 137.4 (s), 134.0 (s), 113.5 (s), 83.6 (s), 72.0 (s), 69.8 (s), 68.0 (s), 55.6 (s), 38.0 (s), 31.2 (s), 31.0 (s). ^{31}P NMR (CDCl$_3$): δ 53.4 (br).

4.3. Palladium(di-t-butyl(ferrocenylmethyl)phosphine) L$_n$ complex (8)

Pd$_2$(dba)$_3$ (12.3 mg, 13.4 µmol) and **1** (0.48–2.00 equiv.) were dissolved in 1.00 mL d$_8$-THF. Portions of each solution were placed in NMR tubes, which were sealed with septa and were examined by NMR spectroscopy over several days. ^{1}H NMR (d$_8$-THF, 268 K): δ 4.22 (br, 2H, subst. Cp), 3.93 (br, 5H, Cp), 3.80 (br, 2H, subst. Cp), 3.23 (br, 2H, –CH$_2$–), 1.07 (d, $^3J_{P-H} = 11.23$ Hz, 9H, *t*-Bu), 0.91 (d, $^3J_{P-H} = 12.82$ Hz, 9H, *t*-Bu). ^{31}P NMR (d$_8$-THF): δ 64.3 (br).

4.4. Suzuki–Miyuara coupling reactions

Solutions were prepared in nitrogen using either one dram vials capped with PTFE lined silicone septa or 50 mL round bottomed flasks. The appropriate aryl halide (1 equiv., usually 4×10^{-4} or 4×10^{-3} mol) was added via syringe to a mixture of base (3 equiv.), boronic acid (1.2–1.3 equiv.) and the catalyst components in solvent (1.0 or 10.0 mL depending on aryl halide amount). Usually a 1:1 phosphine to Pd ratio was employed with a catalyst loading of 0.9–4.1% in comparison with the aryl halide. The reaction mixtures were actively stirred at room temperature unless otherwise stated. Product yields were determined by gas chromatography analysis or by isolating the product through hexane extraction followed by column chromatography using silica gel and an appropriate solvent determined by thin layer chromatography.

4.5. Heck coupling reactions

Solutions were prepared in nitrogen-filled vials or flasks. Reactant concentrations are given in Tables 5 and 6. Small scale reactions were normally performed using 2×10^{-4} mol of aryl halide and 0.5 mL of solvent. Large scale reactions normally involved 2×10^{-3} mol of aryl halide in 5.0 mL of solvent. Product yields were determined by gas chromatography or by direct isolation of the resultant olefin through silica gel based column chromatography.

5. Supporting information available

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 252459 and 252460 for structures **1a** and **1b**. These data may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, Fax. +44 1223 336033.

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