Crystallographic Characterization of a Palladium(II) Metallamacrocycle Supported by an Amino-Functionalized Ferrocene and Its Use as an Efficient Suzuki-Coupling Catalyst

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Complexation of the bidentate ferrocenylamine $[\eta\text{-}C_5H_4(CH_2)_2N(CH_3)_2]_2Fe$ (**1**) with PdCl$_2$-(MeCN)$_2$ in MeOH at room temperature gives air-stable Pd$_2$Cl$_4\{Fe[\eta\text{-}C_5H_4(CH_2)_2N(CH_3)_2]\}_2$ (**2**; yield 71%) of limited solubility in common organic solvents. X-ray single-crystal diffraction analyses showed that **2** has self-assembled into a metallamacrocyclic structure comprising two trans palladium(II) atoms intercalated with two eclipsed bis[(2-(dimethylamino)ethyl)-cyclopentadienyl]ferrocene groups, thus forming a {Pd$_2$Fe$_2$} heterometallic molecular "rectangle". Chloride abstraction with NH$_4$PF$_6$ leads to decomplexation, giving $\{[\eta\text{-}C_5H_4(CH_2)_2N(CH_3)_2H]_2Fe\}\{PF_6\}_2$ (**3**), which is the protonated form of **1**. Complex **2** effectively catalyzes Suzuki cross-coupling reactions of aryl bromides with aryl boronic acids in MeOH at room temperature and 60 °C, giving generally high yields even under low catalytic loads. The reaction conditions are reported together with comparison with other common catalysts.

Introduction

Palladium-catalyzed Suzuki cross-coupling of halo-arenes with arylboronic acid is among the most powerful C–C bond-forming transformations available to synthetic organic chemists.[1] This methodology permits the use of organic solvents with inorganic bases, tolerates a wide range of functional groups with different levels of steric hindrance, and allows for scale-up production in industry.[2] Current technologies demand new catalysts that are inexpensive, accessible, moisture- and air-stable, nontoxic, and, perhaps most importantly, effective under mild experimental conditions toward inert aryl bromides and chlorides. Accordingly, the past decade has witnessed a flourish of activities in the development of such coupling reactions.[1b] In most cases, phosphine-stabilized catalysts are used, due to the superior donor capability of phosphines. However some of these ligands are relatively air- and moisture-sensitive and toxic and, therefore, difficult to handle. Recently, we and other teams have focused on phosphine-free catalysts.[3–13] A sample of the current literature has uncovered some elegant designs of N-heterocyclic carbene complexes,[5] imidazole,[6] palladium powder or on carbon,[7] acetate,[8a] and a metal-free system with microwave,[8b] as well as a group of emerging N-coordinated palladium systems, which include cyclometalated palladium complexes with imine,[9a] oxime,[9b–d] oxazoline,[9e] diazabutadiene,[10] tridentate bis(oxazolinyl)pyrrole,[11] and bis(pyrimidine),[12] and our recent 1,1′-N-substituted ferrocenediyl Pd(II) complex PdCl$_2$Fe[η-C$_5$H$_4$NC(H)Ph-N]$_2$ in aqueous media.[13] These developments, together with our longstanding interest in dppf (1,1′-bis(diphenylphosphino)ferrocene) chemistry,[14] provided us a platform to develop a new generation of ferrocene-based phosphine-free palladium catalysts of high efficiency.

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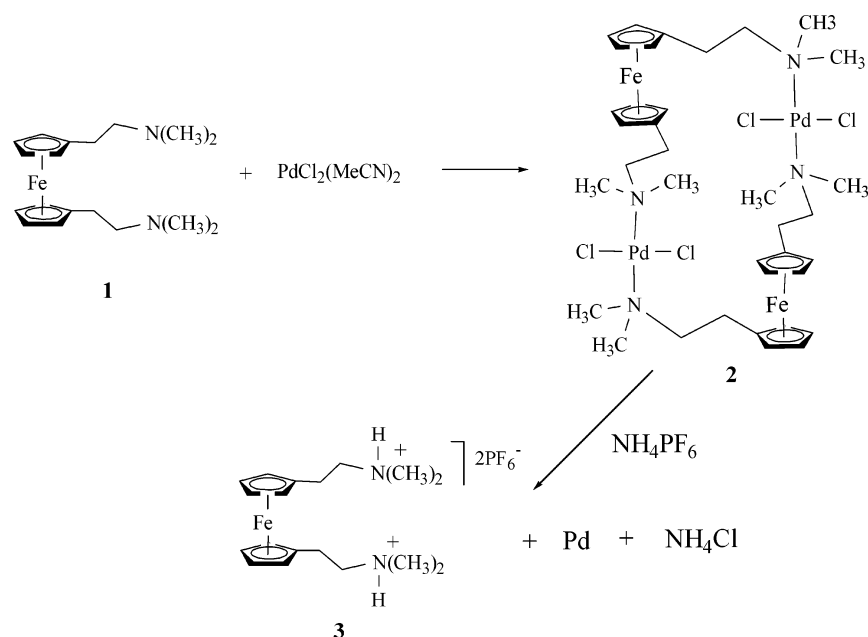‡ National University of Singapore.
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Scheme 1

We herein describe the synthesis and Suzuki activity of a small palladamacrocycle, which has two catalytic metal centers interlocked in close proximity.

Results and Discussion

Syntheses and Crystal Structures. The bidentate amine ligand bis[(2-(dimethylamino)ethyl)cyclopentadienyl]iron (**1**), recently reported in high yield by McGowan et al.,[15] met most of our requirements and prompted us to test its coordinative ability toward Pd-(II) and its catalytic efficiency. It reacts quantitatively and rapidly with $PdCl_2(MeCN)_2$ at ambient temperature, yielding the air- and moisture-stable metallamacrocyclic complex $Pd_2Cl_4\{Fe[\eta\text{-}C_5H_4(CH_2)_2N(CH_3)_2]\}_2$ (**2**) (Scheme 1). Mass spectrometric and microanalytical analyses supported the stoichiometric formula but gave little structural information. Its poor solubility in common organic solvents also precluded any reasonable NMR analyses (^1H and ^{13}C NMR). Similarly, attempts to obtain suitable diffraction-quality crystals of **2** were frustrated by the solubility problem. We then resorted to a one-step synthesis-cum-diffusion strategy at −30 °C such that suitable single crystals could be formed in the course of a slow reaction (see Experimental Section).

Single-crystal X-ray analysis proved that, in its solid state, **2** is dinuclear with two bidentate ferrocene-functionalized diamines bridging two Pd(II) centers (Figure 1; bond distances and angles are given in Table 1). This configuration allows the amine to traverse two palladium atoms instead of being confined at a metal center in a sterically more prohibitive chelating role. It also explains the preferential formation of a dinuclear
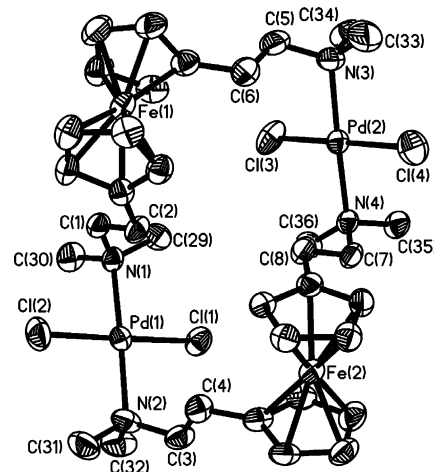
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Figure 1. Molecular structure of complex **2** (H atoms are omitted). Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Bond Lengths			
Pd(1)−N(1)	2.128(4)	Pd(1)−N(2)	2.128(5)
Pd(1)−Cl(1)	2.3049(16)	Pd(1)−Cl(2)	2.3061(16)
Pd(2)−N(3)	2.116(5)	Pd(2)−N(4)	2.118(4)
Pd(2)−Cl(3)	2.3057(17)	Pd(2)−Cl(4)	2.3071(19)
N(1)−C(30)	1.483(6)	N(1)−C(29)	1.487(7)
N(1)−C(1)	1.490(7)	Fe(1)−Cp(cent) (1)	1.648
Fe(1)−Cp(cent) (2)	1.649	Fe(2)−Cp(cent) (3)	1.644
Fe(2)−Cp(cent) (4)	1.650		

Bond Angles			
N(1)−Pd(1)−N(2)	177.08(17)	N(1)−Pd(1)−Cl(1)	91.43(12)
N(2)−Pd(1)−Cl(1)	89.11(15)	N(1)−Pd(1)−Cl(2)	87.57(12)
N(2)−Pd(1)−Cl(2)	91.91(15)	Cl(1)−Pd(1)−Cl(2)	178.90(7)
N(3)−Pd(2)−N(4)	177.59(18)	N(3)−Pd(2)−Cl(3)	89.59(18)
N(4)−Pd(2)−Cl(3)	91.03(13)	N(3)−Pd(2)−Cl(4)	91.65(18)
N(4)−Pd(2)−Cl(4)	87.64(13)	Cl(3)−Pd(2)−Cl(4)	177.63(8)

over a mononuclear complex. The trans disposition of the N-donor sites minimizes interligand and intermetal interactions. With two metallo ligands **1** bridging and locking two trans palladium atoms, it effectively results in a ((dimethylamino)ethyl)cyclopentadienyl-bridged
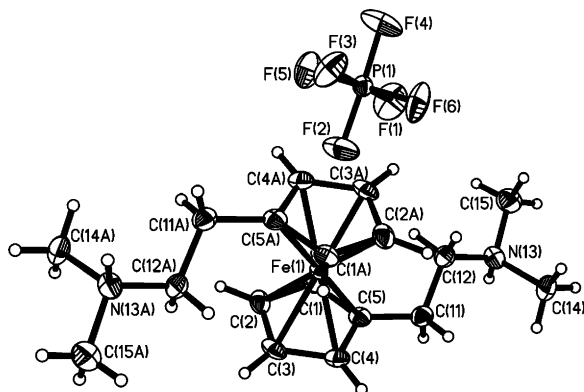
Figure 2. Molecular structure of complex **3** (one of the anions is omitted). Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Bond Lengths			
N(13)−C(12)	1.504(6)	N(13)−C(14)	1.497(8)
N(13)−C(15)	1.486(7)	C(11)−C(12)	1.505(7)
C(5)−C(11)	1.512(7)	Fe(1)−Cp(cent)	1.660

Bond Angles			
C(15)−N(13)−C(14)	110.6(5)	C(15)−N(13)−C(12)	111.1(4)
C(14)−N(13)−C(12)	113.1(5)	N(13)−C(12)−C(11)	112.6(4)
C(12)−C(11)−C(5)	113.6(4)		

$\{Pd_2Fe_2\}$ heterometallic "molecular rectangle". The two C_5 rings are approximately eclipsed and synclinal eclipsed ($\theta = 77.1°$), which serve to juxtapose the two square-planar trans Pd(II) atoms into proximity, thus forming a molecular "rectangle", without direct M−M interaction. The ferrocenyl entity is saturated, but the lability of two trans Cl−Pd−Cl functionalities provides in principle two noninterfering catalytic sites for Suzuki-type coupling, as described below. The metallamacrocyclic nature probably explains the poor solubility of this complex.

Each palladium is approximately square planar, with four similar Pd−N (average 2.123 Å) and Pd−Cl (average 2.306 Å) lengths; both of these are significantly longer than their counterparts in the cis-1,1′-N-substituted ferrocenediyl complex $PdCl_2Fe[\eta\text{-}C_5H_4NC(H)Ph\text{-}N]_2$, (2.056(10), 2.023(11) Å and 2.284(4), 2.291(3) Å, respectively).[13] The Pd−Cl bonds (in **2**), however, are still shorter than those in $PdCl_2(dppf)$ (2.333(4) and 2.350(9) Å).[16] An optimum strength of the Pd−Cl bond, which balances the complex stability and facility of Pd−Cl cleavage, is believed to be key to the coupling efficiency.

The frailty of the Pd−Cl bonds is demonstrated by the decomposition of **2** in the presence of a mild chloride extractor such as NH_4PF_6, even in a donor solvent such as CH_3CN and at room temperature. This readily resulted in decomplexation, releasing the ligand in its protonated form, viz. bis[(2-(dimethylamino)ethyl)cyclopentadienyl]iron dication (**3**), and black Pd powder (Scheme 1). The identity of **3** is verified by its crystal structure (Figure 2; bond distances and angles are given in Table 2), which depicts two antiperiplanar staggered C_5 rings bearing two (dimethylamino)ethyl substituents oriented at a torsional twist of $\theta = 180°$, with a molec-

ular center of inversion. This structure of **3** provides indirect structural evidence for **1**, whose X-ray structure has not been reported. Without the constraints imposed by the metal (as in **2**), the two ethylammonium tails in **3** have moved further away to an anti position. The iron−C_5 ring centroid distance (1.660 Å) is slightly longer than those found in **2** (average 1.648 Å). With both amines protonated, the dicationic complex has effectively lost its ligand behavior.

In sharp contrast to the rich coordination chemistry of its phosphorus analogue, dppf,[17] the ligand chemistry of this type of bis(alkylamine)-substituted ferrocene is surprisingly rare. A few notable examples are found in the dinuclear $(AlMe_3)_2\{Fe[\eta\text{-}C_5H_4(CH_2)_2N(CH_3)_2]\}_2$[18a] and the analogous 1,1′-bis((dimethylamino)methyl)ferrocene-bridged diplatinum complexes.[18b,c] In view of the rich heterometallic[19] and catalytic chemistry[20] developed for dppf and its phosphine-based relatives, there is clearly a rich scope for the amine-functionalized ferrocene to be explored.

Suzuki Cross-Coupling Reactions. Complex **2** is a highly active catalyst in the Suzuki cross-coupling of aryl bromides with arylboronic acids (Table 3). For example, in a suspension of **2** (0.5% mol) in MeOH containing K_2CO_3 (2.4 equiv), 4-bromoacetophenone couples with phenylboronic acid to give a near-quantitative yield of 4-acetylbiphenyl at ambient temperature after 1 h (entry 1). It is notable that the use of deactivated, electron-rich aryl bromides (e.g. entry 3) as well as activated, electron-poor ones (e.g. entry 1) also resulted in high yields. In general, this coupling can be satisfactorily carried out at room temperature. When there is a need to improve the yield, it can be carried out at elevated (60 °C) temperature or in the presence of water in the reaction system[21] (see entry 6). We also studied the coupling of some heterocycles and sterically bulky or highly substituted aryl bromides with boronic acid. The use of methoxyphenyl- or thienylboronic acids (entries 7 and 10) gave near-quantitative yields at 60 °C. Other substituted aryl bromides or arylboronic acids tend to give moderate yields. For example, the coupling of 5-bromo-1,2,4-trimethylbenzene with phenylboronic acid in the presence of 1 mol % of **2** at 60 °C for 2 h gives 2,4,5-trimethylbiphenyl in 54% yield (entry 12).

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Table 3. Suzuki Cross-Coupling of Aryl Bromides with Boronic Acids Catalyzed by 2
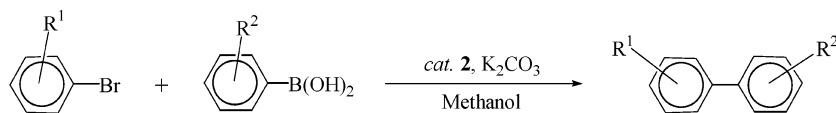
Entry	aryl bromides	boronic acid	product	conditions [a]	isolated yield (%)
1	H_3C-CO-C$_6$H$_4$-Br	C$_6$H$_5$-B(OH)$_2$	H_3C-CO-C$_6$H$_4$-C$_6$H$_5$	0.5 mol% R.T., 1 h	99
2	NC-C$_6$H$_4$-Br	C$_6$H$_5$-B(OH)$_2$	NC-C$_6$H$_4$-C$_6$H$_5$	0.5 mol% R.T., 1 h	96
3	CH_3O-C$_6$H$_4$-Br	C$_6$H$_5$-B(OH)$_2$	CH_3O-C$_6$H$_4$-C$_6$H$_5$	0.5 mol% R.T., 1 h	97
4	HOH_2C-C$_6$H$_4$-Br	C$_6$H$_5$-B(OH)$_2$	HOH_2C-C$_6$H$_4$-C$_6$H$_5$	0.5 mol% R.T., 1 h	95
5	HO-C$_6$H$_4$-Br	C$_6$H$_5$-B(OH)$_2$	HO-C$_6$H$_4$-C$_6$H$_5$	0.5 mol% R.T., 1 h	92 (100)[b]
6	O_2N-C$_6$H$_4$-Br	C$_6$H$_5$-B(OH)$_2$	O_2N-C$_6$H$_4$-C$_6$H$_5$	0.5 mol% R.T., 1 h	65 (97)[b] (90)[c]
7	H_3C-CO-C$_6$H$_4$-Br	CH_3O-C$_6$H$_4$-B(OH)$_2$	CH_3O-C$_6$H$_4$-C$_6$H$_4$-CO-CH_3	0.5 mol% 60 °C, 1 h	99
8	H_3C-CO-C$_6$H$_4$-Br	2,6-(CH_3)$_2$C$_6$H$_3$-B(OH)$_2$	2,6-(CH_3)$_2$C$_6$H$_3$-C$_6$H$_4$-CO-CH_3	0.5 mol% 60 °C, 1 h	66
9	H_3C-CO-C$_6$H$_4$-Br	F_3C-C$_6$H$_4$-B(OH)$_2$	F_3C-C$_6$H$_4$-C$_6$H$_4$-CO-CH_3	0.5 mol% 60 °C, 1 h	96
10	H_3C-CO-C$_6$H$_4$-Br	thiophene-B(OH)$_2$	thienyl-C$_6$H$_4$-CO-CH_3	1 mol% 60 °C, 1 h	100
11	3-CH_3O-C$_6$H$_4$-Br	C$_6$H$_5$-B(OH)$_2$	3-CH_3O-C$_6$H$_4$-C$_6$H$_5$	1 mol% 60 °C, 1 h	86
12	2,4-(CH_3)$_2$-C$_6$H$_3$-Br (with CH$_3$)	C$_6$H$_5$-B(OH)$_2$	trimethylbiphenyl	1 mol% 60 °C, 2 h	54
13	2-bromothiophene	C$_6$H$_5$-B(OH)$_2$	2-phenylthiophene	1 mol% 60 °C, 2 h	<5

[a] The catalytic loading of **2** is expressed on a "per-palladium center" basis. [b] At 60 °C, 1 h. [c] In H$_2$O/CH$_3$OH (v:v1:4), R.T. 1 h.

Unfortunately, 2-bromothiophene resists coupling with phenylboronic acid (entry 13).

The high efficiency of **2** at room temperature or 60 °C makes this a valuable catalyst for thermally sensitive substrates. To our knowledge, there have been only a few reports on efficient Suzuki cross-coupling reactions of aryl bromides at room temperature,[22-24] most of which are Pd/phosphine systems: e.g. use of the Pd-(OAc)$_2$/aminophosphine and Pd(OAc)$_2$/(*o*-biphenyl)P-(*t*-Bu)$_2$ by Buchwald et al.[22] and Pd$_2$(dba)$_3$/P(*t*-Bu)$_3$ by

Fu et al.[23] Success has also been experienced in other catalytic reagents such as Pd(PPh$_3$)$_4$ promoted by TlOH/TlOEt,[24a,b] (pentaphenylferrocenyl)di-*tert*-butylphosphine/Pd(dba)$_2$,[24c] PdCl$_2$(dppf) catalyzing alkylborane,[24d,e] an

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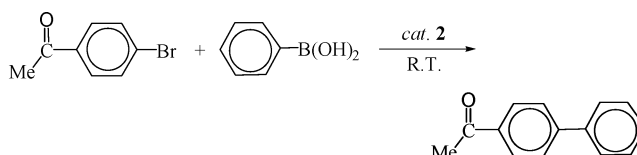**Table 4. Influence of Different Catalysts on the Coupling Reaction**[a]
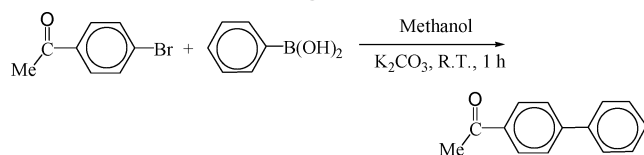
entry	catalyst	isolated yield (%)
1	**2**	99
2	$PdCl_2(MeCN)_2$/**1**	98
3	$PdCl_2(MeCN)_2$/**3**	88
4	$PdCl_2(MeCN)_2$/TMEDA[b]	<5[c]
5	$Pd(OAc)_2$/**1**	94
6	$Pd(OAc)_2$	67
7	**1**	<5
8	Pd/C	8

[a] Reaction duration generally not optimized. [b] TMEDA = tetramethylethylenediamine. [c] Time 16 h.

Table 5. Effect of the Solvent on the Coupling Reaction[a]

entry	solvent	time (h)	yield (%)
1	MeOH	1	99
2	THF	2	90
3	dioxane	2	54
4	CH_3CN	1.5	78
5	H_2O	1.5	64
6	DMF	1	100
7	toluene	3	29

[a] Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.67 mmol of phenylboronic acid, 1.2 mmol of K_2CO_3, 0.003 mmol of complex **2**, room temperature.

amphiphilic resin-supported palladium catalyzing aryl halides in H_2O,[24f] fiber-supported PPh_3-based palladium catalysts,[24g] ortho-palladated triaryl phosphate complexes,[24h] and sulfur-containing palladacycles,[24i] as well as some "ligand-free" examples such as $Pd(OAc)_2$ in aqueous $EtOH$[24j] or neat H_2O[24k] and $Pd(OAc)_2$/Bu_4N^+ in aqueous media catalyzing 5-arylfurfurals and arylthiophene-2-carboxaldehydes.[24l]

The activity of **2** is found to be superior to that in $PdCl_2(dppf)$, which catalyzes the reaction between 4-bromoacetophenone and phenylboronic acid in toluene at 70 °C in 94% yield.[25] In comparison with the other N-coordinated palladium catalysts, the catalytic activity of **2** is similar to those found in the $Pd(OAc)_2$/diazabutadiene system, whose reactions were carried out in dioxane at 80 °C,[10] and a tridentate bis(oxazolinyl)-pyrrole dimeric palladium complex at 70 °C in toluene.[11] A relatively modest yield (32%) was achieved by a polymer-supported bis(pyrimidine)-based palladium system in the coupling between 4-bromoanisole and phenylboronic acid.[12]

To demonstrate the catalytic value of the ligand **1** and the complex **2**, we carried out the coupling between 4-bromoacetophenone and phenylboronic acid in MeOH using different catalysts under very mild conditions, viz. room temperature for 1 h (Table 4). The best yields were obtained by using **2** as a catalyst or under conditions when **2** could be prepared in situ: viz., mixing of **1** and $PdCl_2(MeCN)_2$. Use of other palladium precursors such as $Pd(OAc)_2$ or the protonated form of **1**, viz. **3**, also gave satisfactory yields. Under similar conditions but for a prolonged period (16 h), very poor yields (<5%) were observed when $PdCl_2(MeCN)_2$ was supported by a common organic diamine, TMEDA, or when **1** was used without any source of palladium. In another "ligand-free" or, more appropriately, weakly ligated environment such as $Pd(OAc)_2$ without the support from **1**, we achieved a moderate yield (67%), which could be significantly improved to 94% when **1** was introduced (entry 5). These results suggest that **2**, or its precursor mixtures or their relatives, are most effective in promoting this type of C–C coupling under facile conditions. Although each catalytic run also generates some palladium metal due to catalyst decomposition, our experi-

mental data do not support the notion that nanoparticulate palladium could play a key role in the catalytic efficiency. The presence of **2** or its precursor **1** or its derivative **3** (entries 1, 2, 3, and 5) all perform significantly better than situations when the formation of such particulate Pd is favorable (entries 4 and 6). To further substantiate this, we tested the activity of commercial Pd/C reagent (10 wt %, from Aldrich) under similar catalytic conditions and found an unattractive yield of 8%.

Complex **2** can be conveniently prepared in good yield. Its high chemical stability and resistance to oxygen and water attack make it an attractive choice with practical significance.

To examine the solvent compatibility, the coupling between 4-bromoacetophenone and phenylboronic acid catalyzed by **2** was examined with a range of solvents (Table 5). Polar solvents such as DMF and MeOH were found to be the most productive. This could be attributed to the higher complex solubility and solvate donicity, the latter of which would help to stabilize the intermediate species. Accordingly, nonpolar solvents such as toluene generally give poorer yields.

An investigation of the influence of the base on the coupling between 4-bromoacetophenone and phenylboronic acid illustrates that common and less expensive inorganic bases, such as K_2CO_3, Na_2CO_3, NaOH, and KOH are the reagents of choice (Table 6). The organic base Et_3N is less effective. Interestingly, KF, although a common and effective base for $Pd_2(dba)_3$/phosphine Suzuki-type catalytic reactions,[23,26] proved to be less effective in the present system. The higher strength of the Pd–F bond may not support the ligand exchange process in the catalytic cycle.

It is important to achieve good yields using minimum amounts of catalysts, particularly so for the use of **2**, as opposed to commercially available reagents such as $Pd(OAc)_2$/PR_3. We therefore examined the effect of catalyst loading on a convenient coupling between 4-bromoacetophenone and phenylboronic acid (Table 7). High yields are maintained from normal catalyst loads down to a level of 0.015 mol %. A moderate yield (>47%) is achieved even at catalyst loadings as low as 0.0075 mol

(25) Colacot, T. J.; Qian, H.; Cea-Olivares, R.; Hernandez-Ortega. S. *J. Organomet. Chem.* **2001**, *637–639*, 691.

(26) Pramick, M. R.; Rosemeier, S. M.; Beranek, M. T.; Nickse, S. B.; Stone, J. J.; Stockland, R. A., Jr.; Baldwin, S. M.; Kastner, M. E. *Organometallics* **2003**, *22*, 523.

Table 6. Effect of the Base on the Coupling Reaction[a]
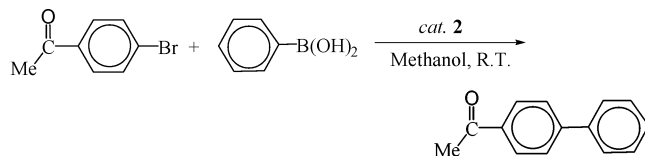
entry	base	time (h)	yield (%)
1	Cs_2CO_3	1	97
2	K_2CO_3	1	99
3	Na_2CO_3	1	89
4	NEt_3	2	69
5	KOH	1	97
6	NaOH	1	91
7	KF	2	76

[a] Reaction conditions: 0.5 mmol of 4-bromoacetophenone, 0.67 mmol of phenylboronic acid, 1.2 mmol of base, 0.003 mmol of complex **2**, 5 mL of methanol, room temperature.

Table 7. Influence of Low Catalyst Loading on the Coupling Reaction[a]
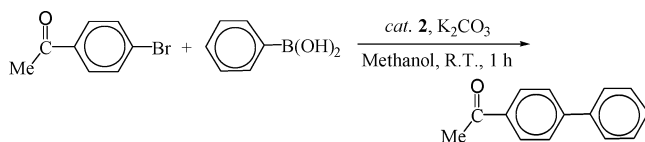
entry	amt of cat. **2** (mol %)	yield (%)	TON[a]
1	0.5	99	95
2	0.25	98	377
3	0.125	98	754
4	0.015	98	3042
5	0.0075	47	3220

[a] In units of (mol of product)/(mol of Pd).

% with a TON of 3220 (mol of product/mol of Pd). These are indications of an effective catalytic system that merits more downstream explorations.

As expected, aryl chlorides are more stubborn, and their coupling with phenylboronic acid under **2** only gave modest yields (Table 8). Use of an activated aryl chloride such as 4-chloroacetophenone in dioxane at 110 °C could give a good yield (78%), but other unactivated aryl chlorides such as 4-chloroanisole did not give attractive results. Other phosphine-stabilized[22,23] or N-heterocyclic carbene-based catalysts[5c] appear to be

more active toward the C−Cl bond. The higher chemical and thermal sensitivity of Pd−N bonds could be a source of the problem. The key Pd(0) intermediate is also better stabilized by phosphines rather than amines.

Conclusion

The use of metallamacrocycles in homogeneous catalysis is an attractive idea because of the high metal/molecule ratios that highlight the multisite-in-a-single-molecule advantage. The use of the present phosphine-free, amine-based palladamacrocycle **2** demonstrated that we can achieve very high yields under very mild conditions in Suzuki cross-coupling for both activated and unactivated aryl bromides. This could fuel further interest and development in the design of other macromolecular or supramolecular structures in similar catalysis. Although many N-coordinated trans-Pd(II) complexes are unstable and/or need special support, complex **2** is an exception, as it can be conveniently "self-assembled" in good yields, is easy to use, and is generally stable toward oxygen and water. Its macromolecular architecture could contribute significantly to these properties and activities. Its discovery has encouraged us to look at other similar high-metal-content single-source catalysts. It has also encouraged us to examine other catalytic systems beyond the Suzuki coupling.

Experimental Section

General Considerations. Conventional Schlenk techniques were used, unless otherwise indicated. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (¹H at 300.14 MHz, ¹³C at 75.43 MHz). Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in house. Compound **1**[15] and $PdCl_2(MeCN)_2$[27] were prepared according to literature procedures.

Synthesis of 2. To a red solution of **1** (285 mg, 0.87 mmol) in MeOH (8 mL) was added $PdCl_2(MeCN)_2$ (225 mg, 0.87 mmol), and the mixture was stirred at room temperature for 2 h. The resultant orange precipitate was isolated by filtration, washed with toluene and Et_2O, and dried in vacuo to afford an orange solid of **2** (312 mg, 0.31 mmol, 71% yield). Anal.

Table 8. Suzuki Cross-Coupling of Aryl Chlorides with Arylboronic Acids Catalyzed by 2[a]
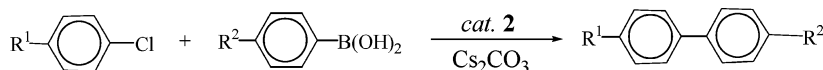
entry	aryl bromides	boronic acid	product	solvent	tem. (°C)	time	isolated yield (%)
1	$H_3C-C(O)-C_6H_4-Cl$	B(OH)₂	$H_3C-C(O)-$product	dioxane	110	17 h	78
2	NC−C₆H₄−Cl	B(OH)₂	NC−product	dioxane	110	2 h	34
3	$CH_3O-C_6H_4-Cl$	B(OH)₂	CH_3O-product	dioxane	110	2 h	11
4	$HC(O)-C_6H_4-Cl$	B(OH)₂	$HC(O)-$product	dioxane	110	2 h	22
5	$H_3C-C(O)-C_6H_4-Cl$	B(OH)₂	$H_3C-C(O)-$product	methanol	90	6 h	36

[a] Reaction duration generally not optimized.

Calcd for $C_{36}H_{56}N_4Cl_4Fe_2Pd_2$: C, 42.76; H, 5.58; N, 5.54. Found: C, 42.19; H, 5.51; N, 5.56. MS FAB$^+$ (*m/z*): 1011 [M]$^+$.

One-Pot, One-Step Procedure To Prepare and Grow Diffraction-Quality Crystals of 2. A methanol solution of $PdCl_2(MeCN)_2$ (3 mg, 0.012 mmol, 1 mL) was carefully introduced and laid above a toluene solution of **1** (8 mg, 0.024 mmol, 1 mL). The mixture was sealed and placed undisturbed in a freezer at -30 °C for about 1 week. During this period, diffusion slowly took place, which led to reaction and precipitation. The resultant mother liquor was removed and the deposit of orange needles of **2** (ca. 2 mg, 33% yield) collected. Microscopic examination of these crystals revealed that some are of X-ray diffraction quality.

Synthesis of 3. To a suspension of **2** (21 mg, 0.02 mmol) in CH_3CN (4 mL) was added NH_4PF_6 (7 mg, 0.04 mmol). The orange mixture was stirred at room temperature for 2 h. The resultant solution was filtered through a layer of Celite. The solvent was removed under vacuum to yield complex **3** as orange solids (11 mg, 0.02 mmol, 89% yield). ^{1}H NMR (CD$_3$-CN): δ 6.67 (2H, br, $C_5H_4(CH_2)_2$N*H*Me$_2$), 4.15 (8H, m, 2 × C_5H_4), 3.20 (4H, t, 2 × CH$_2$), 2.74 (4H, t, 2 × CH$_2$), 2.83 (12H, s, 4 × CH$_3$). ^{13}C NMR (CD$_3$CN): δ 83.4 ($C_5H_4(CH_2)_2$NHMe$_2$), 69.8 ($C_5H_4(CH_2)_2$NHMe$_2$), 59.3 (CH_2NHMe$_2$), 43.9 ($C_5H_4(CH_2)_2$-NH*Me*$_2$), 24.9 (CH_2CH$_2$NHMe$_2$). Anal. Calcd for $C_{18}H_{30}F_{12}N_2P_2$-Fe: C, 34.86; H, 4.88; N, 4.52. Found: C, 34.31; H, 4.87; N, 5.01. MS FAB$^+$ (*m/z*): 329 [M]$^+$ − H.

General Procedure for the Coupling Reactions of Aryl Bromides with Boronic Acids. General Procedure A. A typical procedure is given below on the reaction expressed in entry 1 of Table 3. Complex **2** (2.6 mg, 0.003 mmol), 4-bromoacetophenyl (100 mg, 0.5 mmol), and phenylboronic acid (82 mg, 0.67 mmol) were introduced to a flask under air. The flask was evacuated and refilled with N$_2$ gas. MeOH (5 mL) was added by syringe, followed by K$_2$CO$_3$ (166 mg, 1.2 mmol). The mixture was stirred at room temperature for 1 h, under ambient pressure of N$_2$. The solvent was then removed under reduced pressure. The resultant residual mixture was diluted with H$_2$O (10 mL) and Et$_2$O (10 mL), followed by extraction twice with Et$_2$O. The ethereal extract was collected and stripped of solvent under vacuum. The product was isolated by column chromatography on silica, with hexanes/ethyl acetate as eluent, to give 97 mg (99%) of 4-acetylbiphenyl as a solid and was analyzed by GC/MS.

General Procedure B. A typical procedure is given for the reaction represented by entry 7 in Table 3. Complex **2** (2.6 mg, 0.003 mmol), 4-bromoacetophenyl (100 mg, 0.5 mmol), and (4-methoxyphenyl)boronic acid (102 mg, 0.67 mmol) were introduced to a flask under air. The flask was evacuated and refilled with N$_2$ gas. MeOH (5 mL) was added by syringe, followed by K$_2$CO$_3$ (166 mg, 1.2 mmol). The mixture was stirred at 60 °C for 1 h, under ambient pressure of N$_2$. The solvent was then removed under reduced pressure. The resultant residual mixture was diluted with H$_2$O (10 mL) and Et$_2$O (10 mL), followed by extraction twice with Et$_2$O. The ethereal extract was collected and stripped of solvent under vacuum. The product was isolated by column chromatography on silica, with hexanes/ethyl acetate as eluent, to give 112 mg (99%) of 1-(4′-methoxybiphenyl-4-yl)ethanone as a solid and was analyzed by GC/MS.

Crystal Structure Analyses. Diffraction-quality single crystals were obtained at -30 °C as follows: **2** as orange needles, as described above; **3** as orange plates, obtained from a solution in CH$_3$CN layered with Et$_2$O after 4 days. The crystals were mounted on quartz fibers and X-ray data

(27) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60.

Table 9. Selected Crystal Data, Data Collection, and Refinement Parameters for Compounds 2 and 3

	2	3
formula	$C_{36}H_{56}Cl_4Fe_2N_4Pd_2$	$C_{18}H_{30}F_{12}FeN_2P_2$
formula wt	1011.15	620.23
color, habit	orange, needle	orange, plate
cryst size/mm	$0.30 \times 0.10 \times 0.09$	$0.26 \times 0.10 \times 0.03$
temp/K	223(2)	223(2)
cryst syst	$P\bar{1}$	$C2/c$
space group	triclinic	monoclinic
a/Å	11.3967(11)	29.228(5)
b/Å	11.8302(11)	6.0861(10)
c/Å	17.0171(16)	14.356(2)
α/deg	77.332(2)	90
β/deg	82.031(3)	112.638(4)
γ/deg	69.808(2)	90
V/Å^3	2095.9(3)	2356.8(7)
Z	2	4
D_c/g cm^{-3}	1.602	1.748
radiation used	Mo Kα	Mo Kα
μ/mm^{-1}	1.807	0.881
θ range/deg	1.23–27.50	1.51–27.50
no. of unique rflns measd	27 504	7851
max, min transmissn	0.8543, 0.6132	0.9740, 0.8032
final R indices ($I > 2\sigma(I)$)^{a,b}	R1 = 0.0578, wR2 = 0.1009	R1 = 0.0773, wR2 = 0.1966
R indices (all data)	R1 = 0.1146, wR2 = 0.1177	R1 = 0.1032, wR2 = 0.2117
goodness of fit on F^2 ^{c}	0.950	1.048
large diff peak and hole/e Å^{-3}	0.645 and -0.422	1.999 and -0.428

^{a} R1 = $(\sum|F_o| - |F_c|)/\sum|F_o|$. ^{b} wR2 = $[(\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} GOF = $[(\sum w|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The data were corrected for Lorentz and polarization effcts with the SMART suite of programs[28] and for absorption effects with SADABS.[29] Structure solution and refinement were carried out with the SHELXTL suite of programs.[30] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The data collection and processing parameters are given in Table 9.

Supporting Information Available: For the structures of **2** and **3**, complete listings of bond lengths and angles, ORTEP diagrams, and tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

(28) SMART version 5.1; Bruker Analytical X-ray Systems, Madison, WI, 2000.
(29) Sheldrick, G. M. SADABS, a Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 2000.
(30) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.