Metal Unsaturation and Ligand Hemilability in Suzuki Coupling

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$$R^1 \text{—} \bigcirc \text{—} X \ + \ R^2 \text{—} \bigcirc \text{—} B(OH)_2 \ \xrightarrow{\text{catalyst}} \ R^1 \text{—} \bigcirc \text{—} \bigcirc \text{—} R^2 \quad (1)$$

ABSTRACT

The combinative and complementary use of a hemilabile difunctional ligand on a metal, notably palladium, that is coordinatively and electronically unsaturated has led to the isolation of a string of unexpected low-valent complexes that are structurally intriguing. The ligands of interest are primarily ferrocenes functionalized by [P,N] and [P,O] donors. The characterization of these active Suzuki catalysts, which support sp^2–sp^2 couplings, give valuable insights into the key Suzuki intermediates such as those arising from the reductive elimination, transmetallation, and oxidative addition steps. In this Account, we shall review and discuss our recent results in relation to selected developments in other laboratories.
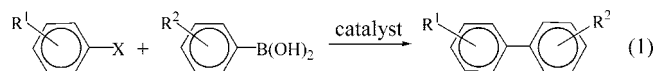
1. Introduction

Transition metal-catalyzed C–C and C–X (X = heteroatom) bond formation is a powerful synthetic methodology in organic syntheses.[1,2] A typical example is found in palladium-catalyzed (Miyaura) Suzuki cross-coupling[3] (eq 1) of haloarenes with aryl boronic acids. Recent catalyst developments have expanded the application scope to natural product syntheses, materials design, and large-scale pharmaceutical production etc.[4] The attractive features of this coupling include the flexible use of organic solvents with common inorganic bases, readily available substrates, air and moisture stability, functional group tolerance, coupling of sterically demanding groups, low toxicity of boronic acids, and facile removal of the boron-containing byproducts.
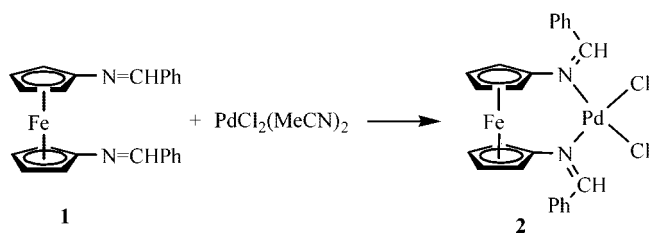
The common Suzuki catalysts are phosphine complexes such as $Pd(PPh_3)_4$ with strong P-donors. The coupling pathway requires a sequential oxidative addition at an active Pd(0) by aryl halide, activation followed by transmetallation [this is not a typical transmetallation because boron is strictly not a metal; however, the idea of organo–ligand crossover between an organometalloid and an organopalladium to prepare the latter for reductive elimination is consistent with the concept of transmetallation; details of this step are described in the literature (e.g., Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651–2710)] with the organoboronate substrate, and reductive elimination to yield the desirable product. A precatalyst such as $Pd(PPh_3)_4$ would need to enter the catalytic cycle through two successive ligand dissociations to give the 14-electron active catalytic complex $Pd^0(PPh_3)_2$. As such low-coordinate and low-valent palladium complexes are notoriously unstable, their formation is energetically unfavorable. Facile decomposition of such active catalysts also contributes to poor turnover. It is therefore desirable if one could design a "smart catalyst" that enters the catalytic cycle without going through a high energetic barrier and yet is both chemically stable and catalytically active. A strategy that we have developed recently is the complementary use of electronically and coordinatively tunable hemilabile ligands[5] and reactive low-coordinate metals.[6] These ligands are sensitive to the dynamic needs of the metal at different stages of the catalytic cycle. Ideally, such a ligand not only can protect the catalytic intermediates but also can activate all the key steps.
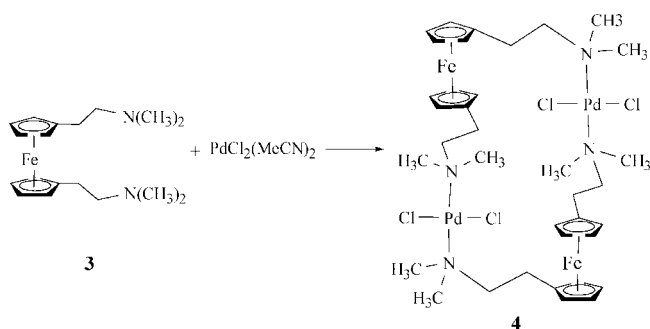
Accordingly, as an extension of our ongoing work in 1,1′-bis(diphenylphosphino)ferrocene (dppf) chemistry,[7] we designed a series of ferrocene-based hemilabile ligands with hybrid and contrasting donors. The ferrocenyl core plays the important role of a spectator in giving the difunctional donors the desirable coordinative mobility and serving as an electronic reservoir needed for pendant/donating switches. The redox-active Fe(II) provides an additional electronic buffer that allows the catalytic metal to remain active in different redox stages. Such a smart catalyst helps in tackling challenging problems such as C–Cl and C–F bond activation, sp^3–sp^3 coupling, and sterically hindered, room temperature, and aqueous reactions. Some of these challenges in Suzuki coupling can be achieved through the use of ferrocene-based [P,N], [P,O], [P,CN σ], [P,CN π], and [N,N] ligands in conjunction with active Pd compounds. Some unusual and highly active catalytic species that are both electronically and coordinatively unsaturated complexes have been isolated and crystallographically characterized. We shall summarize and review these from the perspective of other selected developments in this field.

Zhiqiang Weng (born in 1971 in China) came to Singapore to join the graduate program of the National University of Singapore (NUS) after he graduated from Fuzhou University with B.Sc. (1994) and M.Sc. (1997) degrees. Upon graduation with a Ph.D. (2003) degree in the area of organochromium chemistry, he joined the Institute of Chemical and Engineering Sciences (ICES) of Singapore in 2003 as a Research Fellow, starting work in homogeneous catalysis. In October 2005, he returned to NUS as a Research Fellow to start his independent research, specializing in the synthesis of new and sensitive organotransition metal complexes and their catalytic applications in organic synthesis and olefin oligomerization.

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Scheme 1

Scheme 2

Chart 1. P,O Ligands for Suzuki Coupling


activated, electron-poor substrates under ambient conditions, giving generally high yields even under low catalytic loads. There is no evidence of any Fe → Pd dative bonding stabilization in **4** or its catalytic intermediates. Active and unsaturated catalysts that are supported by only weak N donors are generally too reactive to be isolated.

2. Suzuki Coupling with Phosphine-Free Catalysts

Our earlier use of phosphine-free catalysts such as [N,N]-functionalized ferrocene-based ligands is targeted to provide a nontoxic system that is moisture- and air-stable. Other related approaches are found in N-heterocyclic carbene complexes,[8] imidazole,[9] palladium powder,[10] acetate,[11a] metal-free[11b] and ligand-free[11c] systems, and N-coordinated palladium systems, which include cyclometallated palladium complexes with imine,[12] oxime,[13a] oxazoline,[13b] diazabutadiene,[14a] Dabco,[14b] bis(oxazolinyl)pyrrole,[15] and aminopyridyl.[16] In sharp contrast to the rich coordination chemistry of its phosphorus analogue viz. dppf, the ligand chemistry of [N,N] ferrocene-based ligands is ill-developed.

The diimine functionalized ferrocenyl ligand Fe(η-C_5H_4N=CHPh)$_2$ (**1**) coordinates easily at room temperature with PdCl$_2$(MeCN)$_2$ to give a stable chelate complex PdCl$_2$Fe(η-C_5H_4N=CHPh)$_2$ (**2**) (Scheme 1).[17] Similar reaction using a bidentate diamine with a larger bite angle, Fe[η-$C_5H_4C_2H_4N(CH_3)_2$]$_2$ (**3**), leads to the isolation of a stable metallamacrocyclic complex Pd$_2$Cl$_4${Fe[η-$C_5H_4(CH_2)_2N(CH_3)_2$]}$_2$ (**4**) (Scheme 2).[18]

Complex **2** is highly active toward Suzuki cross-coupling of aryl iodides and bromides with aryl boronic acids as a suspension in aqueous media. The products can be conveniently isolated, whereas the recovered catalyst remains active for up to five runs.

Complex **4** can be viewed as a dimeric version of **2**. Two Pd(II) centers are doubly bridged by two metalloligands to give effectively a {Pd$_2$Fe$_2$} heterometallic "molecular rectangle". Use of soluble metal polygons as catalysts is rare but could offer advantages such as chemical stability, bimetallic cooperation, and single catalysts with multiple sites. Complex **4**, which is air- and moisture-stable, promotes cross-coupling of aryl boronic acids with deactivated, electron-rich aryl bromides and

3. Suzuki Coupling with Catalysts Containing Hemilabile Ligands

Currently, the most common ligands used for Suzuki coupling reaction are electron-rich and sterically hindered monophosphine.[19] The use of N-heterocyclic carbenes as phosphine alternatives is emerging.[20] These ligands have good donating properties, giving stable catalysts, but are handicapped by the lack of coordinative flexibility. Therefore, designing a new class of ligands that have hybrid and difunctional properties to support different catalytic intermediates formed within a single system is appealing.

The P,O and P,N ligands reported by Buchwald et al. exemplify the value of hybrid ligands. The palladium complexes of a new ligand, 2-(2′,6′-dimethoxybiphenyl)-dicyclohexylphosphine (SPhos, **5**) (Chart 1), efficiently catalyze highly hindered aryl boronic acid and aryl halides.[21] Milstein et al. prepared an electron-rich, bulky methoxy-benzyl phosphine (dmobp, **6**) to stabilize unsaturated Pd(0), Pd(I), and Pd(II). Coordination of the methoxy group in the proximity highlights the hemilabile effect.[22]

Other P,O ligands used in Suzuki coupling include amide phosphine (**7**),[23a,b] acetal phosphines (**8**),[23c] ferrocenyl-supported alkoxy phosphines (**9**),[23d] and **10**.[23e] Other donor combinations such as P,N and P,S ligands (Chart 2) have also been used. Examples include 2-(dicyclohexylphosphino)-2′-(N,N-dimethylamino)biphenyl (**11**),[24a] 2-(dimethylamino)-2′-diphenylphosphino-1,1′-binaphthyl (MAP) through P,C$_\sigma$ coordination (**12**),[24b] phosphino-substituted N-aryl pyrroles (PAP, **13**),[24c] N-(2-diphenylphosphino)phenyl-2,6-diisopropylanilide (**14**),[24d] axially dissymmetric P,S-heterodonor ligands (**15**),[25a] (1-phenylphosphino)-1′-(methylthio)-ferrocene (**16**),[25b] iminophosphine,[25c] aminephosphine,[25d] 1-phosphabarrelene phosphine sulfide-substituted ligands,[25e] and the P,S-chelating thioether aminophosphonites.[25f]

Chart 2. P,N and P,S Ligands for Suzuki Coupling

11 **12** **13**

14 **15** **16**
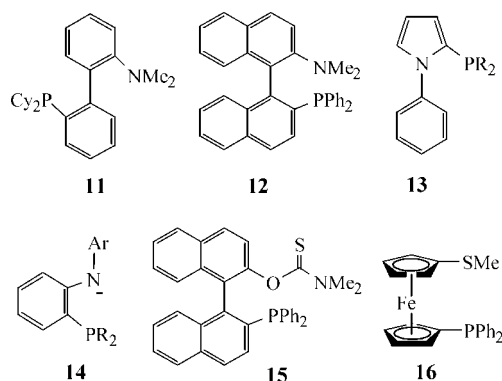
Chart 3. Ferrocene-Based P,N and P,O Ligands for Suzuki Coupling

17 **18a–c**

R = H, Ph
R′ = *t*-Bu, Cy
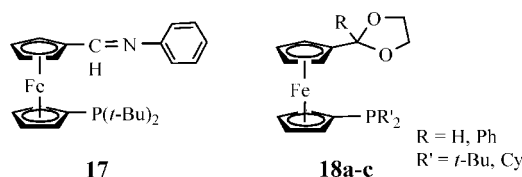
To fully exploit the hemilabile function, the desirable ligand should have the following features. (1) It must be a difunctional ligand with at least two basic sites that have significantly different donating abilities. (2) The electronic character of each donor atom can be tuned by chemical alteration of its attached or nearby substituents. (3) The two donating sites are separated by a metallocenyl moiety that is stereogeometrically flexible and redox active. (4) Its potential as a unidentate, chelating, and bridging ligand must be demonstrated. (5) It can support unsaturated metal through its electronic and spatial effects. On the basis of these considerations, the ferrocene-based [P,N] (**17**) and [P,O] ligands (**18**) were prepared (Chart 3).

A mixture of $Pd_2(dba)_3$ and $[\eta\text{-}C_5H_4CH=N(C_6H_5)]Fe[\eta\text{-}C_5H_4P(t\text{-Bu})_2]$ (**17**) (dba = dibenzylideneacetone) efficiently catalyzes the Suzuki cross-couplings of a range of aryl boronic acids and aryl chlorides, affording the desired biaryl products in high isolated yields.[26] For example, 4-chlorobenzonitrile couples with phenyl boronic acid at a low catalyst load (0.01 mol % Pd) to give 4-biphenylcarbonitrile in a good TON of 10 000. Other catalysts that give exceedingly high TONs have been identified.[27]

The advantage of using hybrid P,O ligands such as **18a–c** over monodentate monophosphine (**19**) or bidentate diphosphine (**20**) ligand is evident in the coupling between 4-chlorobenzonitrile and phenyl boronic acid (Table 1). Under similar catalytic conditions, the isolated yield of 4-acetylbiphenyl is quantitative for **18**, whereas the controls (**19** and **20**) gave insignificant products.[28] The co-presence of a strong coordinating group (phosphorus) and a much weaker and restrictive donor (oxygen) gives the ligands (**18**) the needed flexibility to produce high activities that are comparable to the activities of some other P,O ferrocenyl systems, such as aryl-MOPFs (**9**).[23d]

Table 1. Effect of Ligand on the Suzuki Cross-Coupling[a]

Ligand =

18a **18b** **18c** **19** **20**

| entry	ligand	isolated yield (%)
1	**18a**	84
2	**18b**	100
3	**18c**	100
4	**19**	trace
5	**20**	26

[a] With a 0.2 mol % Pd load.

Scheme 3

21 **22**
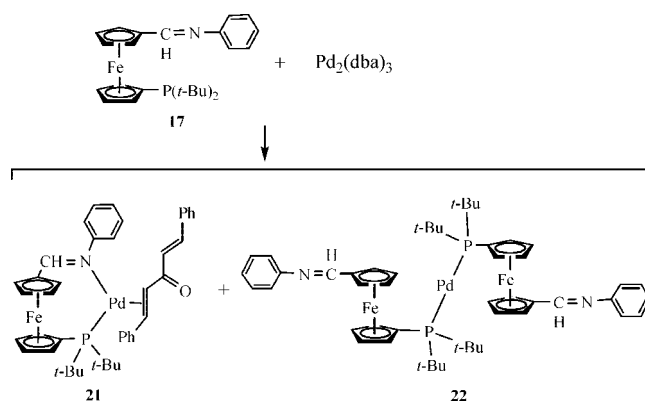
The hemilability function meets the needs of the metal, which sequentially switches between saturated and unsaturated states. Use of these hybrid ligands helped us trap a number of saturated and unsaturated species under both stoichiometric and catalytic conditions. Reaction of $Pd_2(dba)_3$ with **17** (1:1 L:Pd ratio) in a NMR tube gives two main products, $[\eta\text{-}C_5H_4CH=N(C_6H_5)]Fe[\eta\text{-}C_5H_4P(t\text{-Bu})_2]Pd(dba)$ (**21**) and $Pd\{[\eta\text{-}C_5H_4CH=N(C_6H_5)]Fe[\eta\text{-}C_5H_4P(t\text{-Bu})_2]\}_2$ (**22**), formed in a ratio of ∼4:1 (Scheme 3). When the concentration of **17** is doubled, **22** becomes the sole species. The latter can be synthesized (94%) independently from a reaction of **17** with $(C_5H_5)Pd(C_3H_5)$ (2:1).[29]

Complex **21** is a 16-electron Pd(0) with a heterodifunctional chelate. It provides a crystallographic proof that an imine nitrogen, albeit weakly basic, can coordinate when the metal is unsaturated. The exposed metal is further stabilized by olefinic coordination from the adventitious dibenzylideneacetone (dba). dba-coordinated Pd(0) complexes have been identified in the literature,[30] including those in P,C (**23–25**),[31,32] P,O (**26**),[23c] P,N (**27**),[33] and P,P (**28**) complexes[34] (Chart 4). Although the role of dba in many catalytic cycles has been largely ignored, it could play a stabilizing function to keep the active Pd(0) in solution and suppress decomposition to Pd metal. The use of dba or hemilabile ligands to support molecular Pd(0) could be one of our best strategies for developing ligandless catalysts in truly homogeneous systems, as

opposed to those ligandless catalysts that are based on Pd/C.[10] The benefits of coordinatively deficient [PdL] catalysts in Suzuki and other couplings have been described.[35]
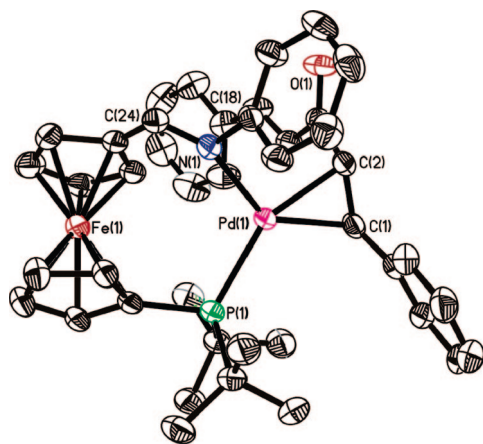
(21)

Some pertinent bond parameters of **21** are compared with those of other LPd[0](η^2-dba) complexes (Table 2). Their Pd–C$_{olefin}$ bond distances are comparable and similar to that of (η^2-dppf)Pt(η^2-dba).[36] The Pd–P bond length [2.3385(10) Å] of **21** is notably longer and its chelate P–Pd–N angle [110.94(8)°] larger than the others. These indicate the steric and spatial demand of ligand **17**, which also helps to protect Pd(0) from overexposure. The weakness of the Pd–P bond in **21** may suggest a weak chelate. Indeed, in **22**, the ligand opens up to give a unidentate metalloligand with a dangling imine. This is an unusual complex not only because it is a 14-electron linear Pd(0), some of which[29] are given in Chart 5, but also because it is also rare to witness two potentially bidentate ligands on the same metal, each of which is unidentate thus resulting in a highly unsaturated metal. The ferrocenyl moiety stabilizes the active metal through a spatial shield.
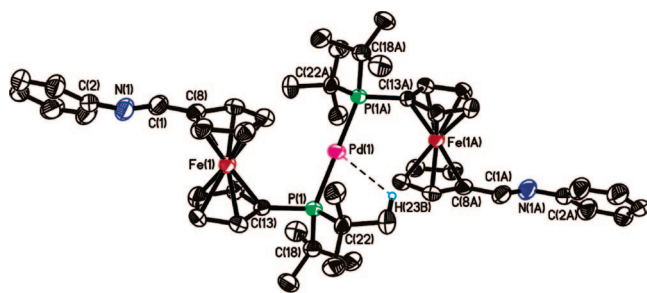

[Pd(1)···H(23B) 2.931 Å]

(22)

A list of the Pd–P lengths and P–Pd–P angles for **22** and other Pd[0](PR$_3$)$_2$ complexes is given in Table 3. Not all two-coordinated Pd(0) complexes are linear. The strict linearity is observed in **22** and **30–32**. Complexes **29** and **36** are slightly distorted, whereas **33–35** prefer a bent geometry. A supplementary intramolecular Pd–arene interaction in **33** could explain its angular distortion. In **22**, the closest Pd–X nonbonding contacts are found in Pd···H(23B)

Chart 4. A Sample of dba-Coordinated Complexes of Pd(0)
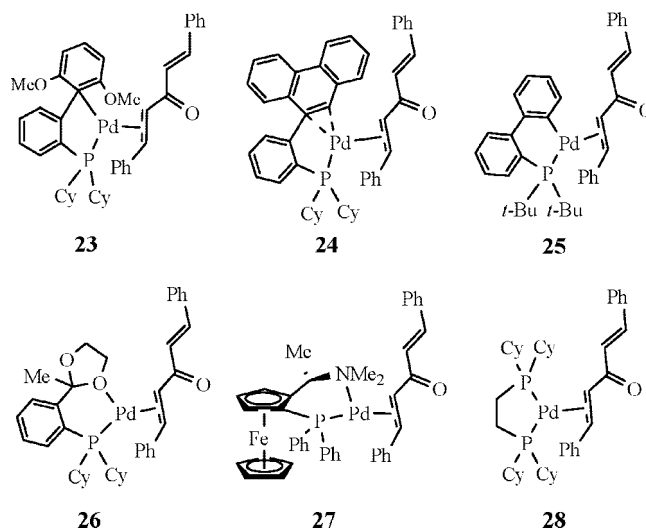
(2.931 Å), which is significantly longer than those in **29** and **31** (2.73 and 2.508 Å, respectively).[29] This rules out the possibility of agostic interaction and supports it being an authentic two-coordinate Pd(0).

The dynamic properties of **17** help to stabilize **21** and **22** under different stoichiometric conditions with or without supplementary support from the adventitious dba. These highly active complexes catalyze the formation of 4-biphenylcarbonitrile in near-quantitative yields at 90 °C under 0.25 mol % Pd (Table 4). At a lower catalyst load of 0.01 mol % (Pd), the activity of **22** is superior to that of **21** (100 and 52%, respectively).

An advantage of an unsaturated low-valent metal is that it could undergo oxidative addition with an aryl halide directly, without going through the barrier of reduction or ligand dissociation. In fact, this step could be the r.d.s. of palladium-catalyzed cross-coupling reactions.[37] Isolation of a catalytic active species like **21** or **22** enabled us to carry out the oxidative addition stoichiometrically. A mixture of **17** and Pd$_2$(dba)$_3$ (giving mainly **21** in situ) or a solution of **22** with C$_6$F$_5$I in THF at room temperature gives [η-C$_5$H$_4$CH=N(C$_6$H$_5$)]Fe[η-C$_5$H$_4$P(t-Bu)$_2$]Pd(I)(C$_6$F$_5$) (**37**) (41 or 31% yield, respectively) as the only identifiable product (Scheme 4).

Similar oxidative addition has been reported by Milstein et al. in the reaction between Pd(0) complex **34** (Scheme 5) and haloarenes which gives **38** with a P,O chelating Pd(II).[22]

Complex **37** is a Pd(II) oxidative addition product with the expected P,N chelate and the more *trans*-labilizing aryl ligand opposite the weaker Pd–N bond. Preliminary experiments revealed that **37** reacts with phenylboronic acid in the presence of KF/Cs$_2$CO$_3$ in dioxane to give the hetero-coupling product 2,3,4,5,6-pentafluorobiphenyl in ca. 75% yield. This is consistent with **37** being a key intermediate in Suzuki coupling.

It is commonly assumed that metal-containing intermediates in Suzuki and related couplings are mononuclear complexes, such as that found in **37**. This is not necessarily correct especially in cases when phosphine is deficient

Table 2. Comparison of Selected Bond Parameters of [Pd⁰L(η²-dba)]

complex	Pd–P bond length (Å)	Pd–C_{olefin} bond length (Å) (mean)	P–Pd–E angle (E = N, O, or C) (deg)
21	2.3385(10)	2.129(3)	110.94(8)
23	2.2850(8)	2.133(3)	83.01(7)
24	2.3001(17)	2.143(6)	–
25	2.3269(18)	2.145(6)	96.25(18)
26	2.2924(7)	2.102(2)	87.38(5)
27	2.2655(12)	2.110(4)	97.96(6)
28	2.296(1)	2.150(4)	88.26(5)

Chart 5. Complexes of [Pd⁰(PR₃)₂]
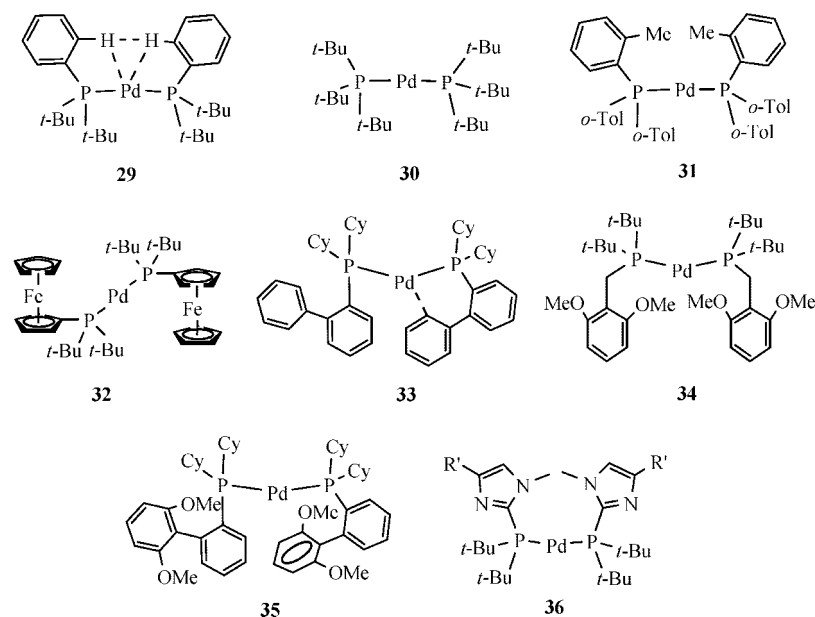
Table 3. Comparison of Selected Bond Parameters of [Pd⁰(PR₃)₂]

complex	Pd–P bond length (Å) (mean)	P–Pd–P angle (deg)
22	2.2828(16)	180.0
29	2.278(4)	176.8(1)
30	2.285(3)	180.0
31	2.276(1)	180.0
32	2.2764(7)	180.0
33	2.2761(11)	154.82(4)
34	2.2913(19)	166.86(7)
35	2.2685(8)	164.48(3)
36	2.2861(4)	173.964(14)

Table 4. Catalytic Yield Comparison of 21 and 22

| catalyst	**21**	**22**
0.25 mol % (Pd)	98%	100% yield
0.01 mol % (Pd)	52%	100% yield

or when the hemilabile ligand carries a donor that is poorly basic. This is evident when the P,O ligand **18** is mixed with Pd₂(dba)₃ and C₆F₅I stiochiometrically. Several oxidative addition products (**39–42**) have been identified (Scheme 6); among them, **39** and **42** have been crystallographically established. Complex **39a** is a dinuclear Pd(II) with doubly bridging iodide and the ligand **18a** being a P-only donor with dangling cyclic acetal. It suggests that facile dimerization could provide a stabilizing mechanism for active oxidative addition intermediates. Although such dinuclear structure is saturated, it could return to its active form through bridge cleavage in a

coordinating solvent or through re-chelation of a hemilabile ligand. The latter is spectroscopically observed in **40**.

When the L:M ratio is ≥2:1, the mononuclear form regenerates with an active trans–cis isomerization between **41** and **42**. The latter formation allows productive transmetallation to take place followed by cis coupling of the aryl residues. Isolation of these complexes pointed to two alternative catalytic pathways via the dinuclear (route A) or geometric isomeric (route B) forms, both of which can be supported by a hemilabile ligand (Scheme 7).

Guram et al. isolated two similar oxidative addition products from the reaction of phenyl backbone-derived P,O ligands with Pd(dba)₂ and excess 4-*tert*-Bu-C₆H₄Br, viz., (P,O)₂Pd(4-*t*-Bu-C₆H₄)Br (**43**) and (P,O)Pd(4-*t*-Bu-C₆H₄)Br (**44**) (Scheme 8).[38] It is notable that introducing a methyl group into the dioxolane can influence the catalytic intermediates by favoring the monophosphine over the *trans*-bisphosphine species.

Grotjahn et al. also reported a new type of hemilabile imidazol-2-ylphosphine ligand system, which allows steric adjustment at the P-donor and basic imidazole N-3 (Scheme 9).[29e] The two types of oxidative addition products are represented by the expected *trans*-bis(phosphine)Pd(R)(X) **45** and the mononuclear P,N chelating **46**. The nature of haloarenes and R on the phosphine also influence the product preference. Complexes **44** and **46** are analogous to **37**, whereas **43** and **45** are related to **42**.
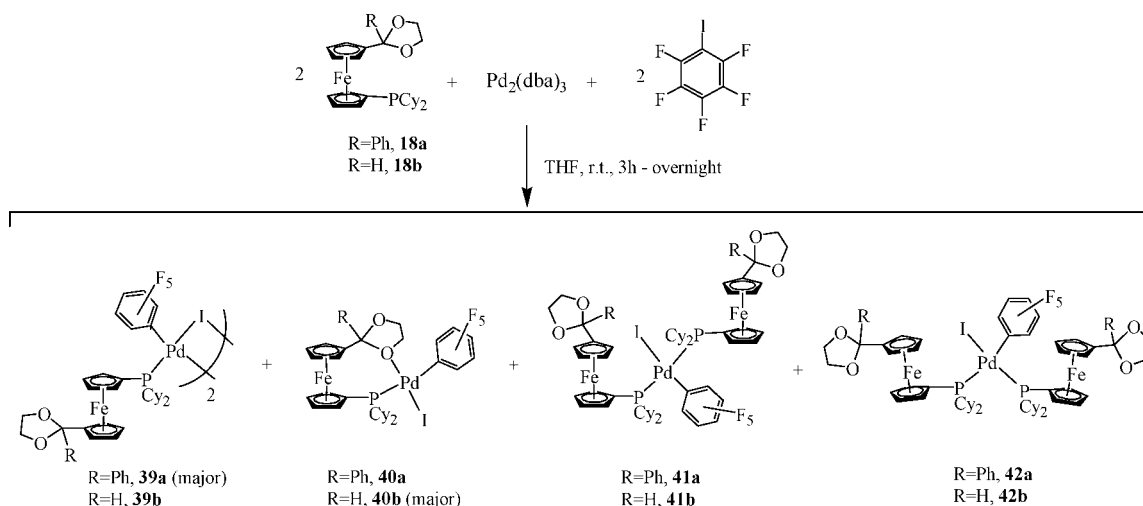
Scheme 4
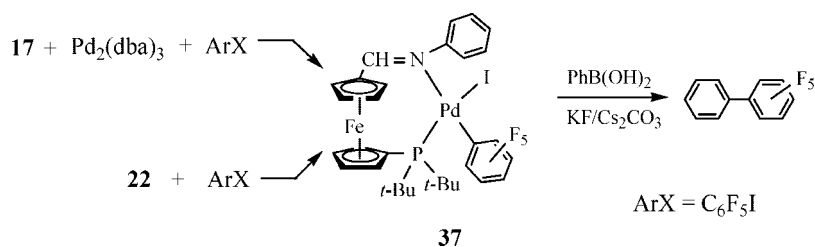
Scheme 5
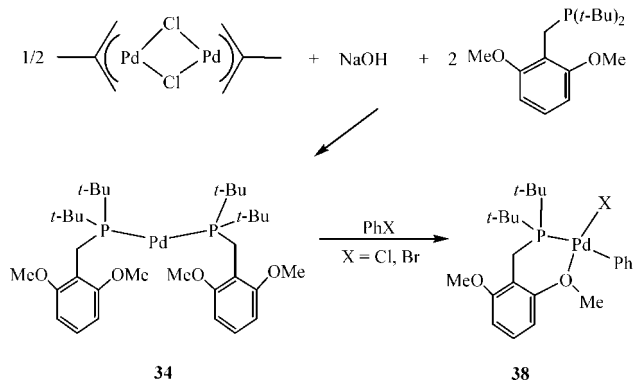
Since the M:L ratios are different in the two routes, one could in principle push the catalytic path toward route B from route A by increasing the ligand dosage. A slight increase in TON (from ~1000 to 2000) is observed for **18a**, while there is an ~20-fold TON increase [from ~2000 (max) to ~44600] for most of the electron-rich substrates when the ligand dosage of **18b** to Pd is doubled. There is little effect on the ortho-substituted electron-neutral substrates, which support the possibility that different types of substrates would favor different mechanistic pathways. It is likely that both pathways are operative whereby the dominance of either is influenced by the choice of ligands, substrates, and steric factors.[28]
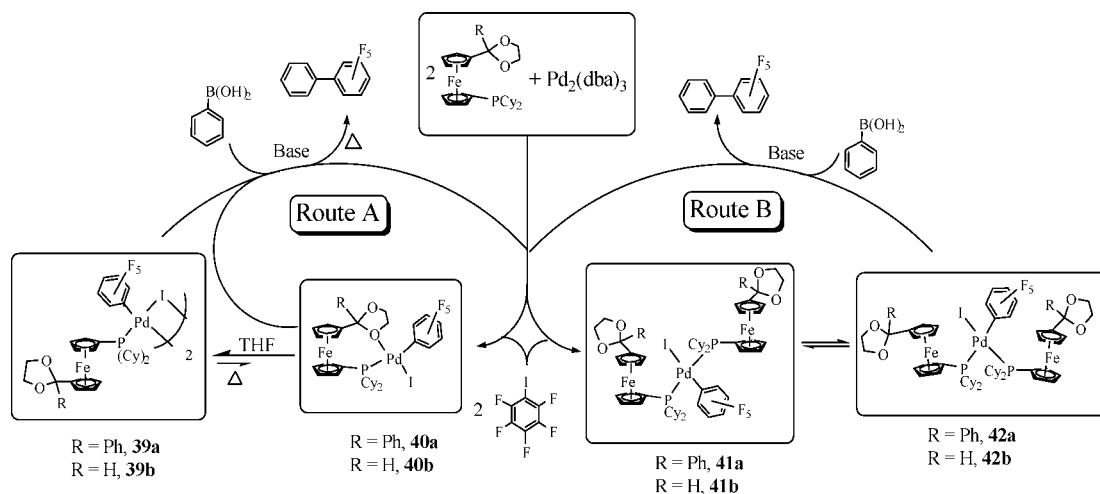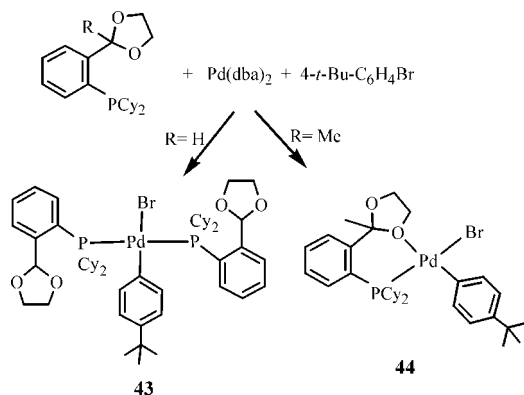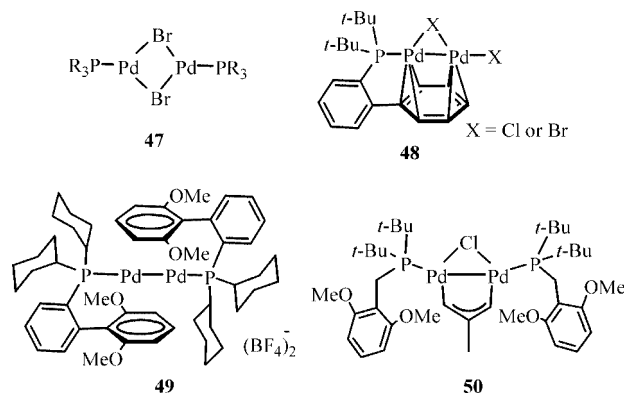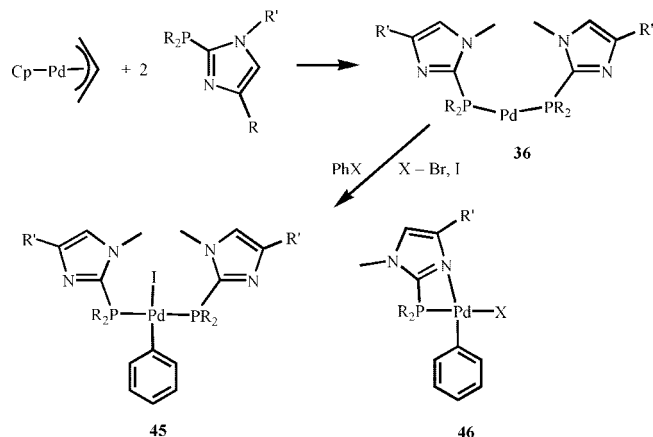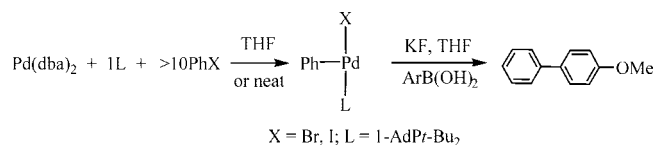
A promising future of hemilabile ligand research is to design intelligent ligands that have the dynamic qualities to cater to different types of substrates by promoting and supporting different catalytic pathways as a means of

achieving maximum yields. This is possible only if the hemilabile ligands can stabilize and activate different forms of reaction intermediates. A related prospect is to take advantage of the switchable coordination modes of the hybrid ligand to trigger a sequential activation and stabilization mechanism. This would provide a lead in designing stable catalysts without compromising their activities. Another approach can be demonstrated by Hartwig's recent work with a new class of structurally unique three-coordinated arylpalladium halide complexes with a hindered phosphine ligand (Scheme 10).[39] Instead of using an unsaturated Pd(0) to promote the oxidative addition, one could promote the subsequent transmetallation and reductive elimination through the generation of an unsaturated oxidative addition complex intermediate. It remains to be seen whether coordinatively unsaturated Pd(II) or Pd(I) intermediate could be stabilized by hemilabile ligands.

4. Suzuki Coupling by a Pd(I) Catalyst

In most Pd-mediated cross-coupling reactions, Pd(II) or Pd(0) sources such as $Pd(OAc)_2$ or $Pd_2(dba)_3$ with phosphine ligands are used by default. Recently, a rare use of Pd(I) has been reported (Chart 6).[40] Hartwig et al. and Prashad et al. have reported high activity of a Pd(I) dimer, $[Pd_2(\mu\text{-}Br)_2(P\text{-}t\text{-}Bu_3)_2]$ (**47**), in cross-coupling reactions.[40a,b] Vilar et al. used the new Pd(I) dimer **48** as a precatalyst for amination of aryl chloride.[40c] Barder used the isolated phosphine arene-ligated Pd(I) dimer **49** as a precatalyst to promote Suzuki reaction.[40d] Milstein et al. reported that partial reduction of

Scheme 6

Scheme 7

R = Ph, **39a**
R = H, **39b**

R = Ph, **40a**
R = H, **40b**

R = Ph, **41a**
R = H, **41b**

R = Ph, **42a**
R = H, **42b**

Scheme 8

43

44

Chart 6. Pd(I) Dimer for Cross-Coupling Reactions

X = Cl or Br

47

48

49

50

Scheme 9

36

45

46

Scheme 10

X = Br, I; L = 1-AdP*t*-Bu$_2$

[Pd(2-methylallyl)Cl]$_2$ in the presence of the ligand **6** gives a Pd(I) dimer **50**, which promotes Suzuki coupling by providing an active 12-electron Pd(0).[22] Our preliminary results[41] showed that the known "solvent-saturated" Pd(I)–Pd(I) complex [Pd$_2$(CH$_3$CN)$_6$][SbF$_6$]$_2$ (**51**) is active in promot-

ing Suzuki cross-coupling reactions of aryl bromides with various aryl boronic acids at room temperature in a CH$_3$CN/H$_2$O mixture giving good to excellent yields. The use of Cs$_2$CO$_3$ as a base with the CH$_3$CN/H$_2$O solvent mixture gives the best yields. The anion also has an effect on the catalyst activity with the less basic and much bigger SbF$_6^-$ performing better than BF$_4^-$. X-ray single-crystal crystallographic analysis revealed a "naked" Pd–Pd bonded dimer stabilized only by the solvent ligand CH$_3$CN. This appears to be the ideal source for unsaturated Pd(I) and other exquisite forms of Pd materials.[42] These results have posed a range of unanswered questions. (1) Is it prerequisite for Pd(I) to reduce to Pd(0) before it can enter the catalytic cycle? (2) Could a radical pathway be proposed for Suzuki or other related cross-coupling reactions? (3) Can Suzuki coupling proceed through a Pd(I)/Pd(III) instead of Pd(0)/Pd(II) cycle? (4) Instead of oxidative addition and then reductive elimination at the metal center, can we benefit from oxidative addition across a Pd–Pd bond and reductive elimination to regenerate the Pd–Pd bond? Such knowledge could help in the design of the next generation of active catalysts.

5. Summary

Ferrocene-based hemilabile ligands functionalized with P,N and P,O donors are highly efficient and effective

in promoting Suzuki couplings. Their remarkable ability to stabilize low-valent and unsaturated metals has enabled us to isolate and study the structural features of species that are mechanistically significant. These ligands are electronically, sterically, and stereogeometrically tunable. Such tuning provides a fine balance between (thermodynamic) stability and (catalytic) activity, thereby allowing the syntheses of complexes that model catalytic intermediates. As we begin to understand better the synergic and complementary effect of hemilabile ligand and unsaturated metal, we can expect a larger variety of ligand designs, an example of which is given in our recent use of N,S-heterocyclic carbenes with functionalized side arms.[43] The use of imidazolylphosphines with supporting H-bonding is another example.[29e] The benefits of hemilability in other catalytic systems are also beginning to emerge.[44]

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