Reactivity-Tunable Palladium Precatalysts with Favorable Catalytic Properties in Suzuki–Miyaura Cross-Coupling Reactions

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Abstract

In this study, two $(\text{HO})\text{R}_2\text{P}\rightarrow\text{Pd}(\text{II})\text{Cl}_2\leftarrow\text{NHC}$ precatalysts (**1s**) were designed and synthesized. Using these precatalysts, yields of unreactive aryl chloride, benzyl chloride, and benzoyl chloride were obtained in three to tens of minutes. Upon deprotonation, density-functional theory calculations and electrospray ionization mass spectrometry revealed that NHC was dissociated from the deprotonated precatalysts. Subsequently, the anionic $(\text{O}^-)\text{R}_2\text{P}\rightarrow\text{Pd}(\text{II})\text{Cl}_2$ species could be reduced using ethoxide to form $\text{Pd}(0)$ catalytic species. The cation and anion functions of salt additives were elucidated. The cation size could be used to modulate the catalytic properties of **1s** through outer-sphere electrostatic interactions between the coordinated $\text{R}_2\text{P}(\text{O}^-)$ and alkali metal ions. Through this study, we newly designed $\text{Pd}(\text{II})$ precatalysts with superb catalytic properties that are stable and highly efficient.

Introduction

Palladium complexes, such as the $\text{Pd}(\text{I})\text{--Pd}(\text{I})$ dimer of Mingos,¹ Hartwig,² and Schoenebeck³ and the mononuclear $\text{Pd}(\text{II})$ complexes of Buchwald,^{4,5} Nolan,^{6,7} and Organ,⁸ have been developed as highly active and well-defined precatalysts for cross-coupling reactions.^{9,10,11,12} In 2006, Organ *et al.* reported $\text{Pd}\text{--PEPPSI}\text{--NHC}$ precatalysts with a general structure of $\text{NHC}\rightarrow\text{Pd}(\text{II})\text{Cl}_2\leftarrow 3\text{-chloropyridine}$.⁸ These precatalysts could be activated by organometallic reagents,⁸ aliphatic amines bases,^{13,14} or alkoxides to form $\text{NHC}\text{--Pd}(0)$ active species. Subsequently, the trans throw-away 3-chloropyridine could dissociate to produce monodentate $\text{NHC}\text{--Pd}(0)$ active species.^{8,15} Therefore, $\text{Pd}\text{--PEPPSI}\text{--NHCs}$ have been successfully added to several unactivated organic electrophiles, indicating applicability and universality in this type of precatalyst.^{16,17,18,19,20,21,22,23,24} However, few studies have reported new $\text{Pd}(\text{II})$ precatalysts since the development of $\text{Pd}\text{--PEPPSI}\text{--NHC}$.

Salt additives are indispensable in transition metal (TM)-catalyzed cross-coupling reactions.^{25,26} Bases, which can be dissociated from salt, facilitate transmetalation during Suzuki–Miyaura reactions (SMRs).^{27,28,29} However, although cation size influences chemical selectivity, the role of cations in SMRs has been infrequently studied.^{30,31} Phipps *et al.* reported a site-selective oxidative addition of C–Cl bonds for SMRs,^{32,33} Sonogashira reactions,³² Buchwald–Hartwig reactions,^{32,33} and concerted metalation–deprotonation (CMD)-type C–H activation³⁴ achieved through substitution of the anionic sulfonate groups of Buchwald-type ligands (Figure 1a). This site selectivity occurs because of three-membered electrostatic interactions between the anionic sulfonated phosphine, deprotonated substrate, and alkali metal ions of the salt additive.³³

Walsh *et al.* reported room-temperature deprotonative cross-coupling of aryl chloride³⁵ that could be catalyzed by a $\text{Pd}(0)$ complex bearing a deprotonatable H–NiXantphos ligand (Figure 1b); they suggested that the ionic $\text{M}^+\cdots(\text{NiXantphos})\text{Pd}(0)$ was an active species (M^+ : Li^+ , Na^+ , or K^+ dissociated from salt; NiXantphos : the deprotonated form of H–NiXantphos). The catalytic yields were proportional to the size

of M^+ ($Li^+ < Na^+ \sim K^+$), and the neutral (N–Bn–NiXantphos)Pd(0) and (Xantphos)Pd(0) were off-state species, indicating that cation size controlled chemical reactivity. This strategy has been applied in Buchwald–Hartwig coupling (TM = Pd),³⁷ arylation of diarylmethanes (TM = Ni),³⁸ and benzylic arylation of toluenes (TM = Ni).^{39, 40}

Phosphinous acid (PA: R_2P-OH) is the unstable tautomer of secondary phosphine oxide (SPO: $R_2P(=O)H$)⁴¹ and can serve as a tautomerized form of SPO in the absence⁴² or presence of TMs.⁴³ The thermodynamically more stable SPO acts as a preligand,⁴⁴ with PA assuming the role of a genuine ligand. Notably, PA is a deprotonatable weak acid, and deprotonated PA^- (R_2P-O^-) acts as a strong, electron-donating ligand. This renders PA an actor ligand with numerous functionalities.^{45, 46, 47, 48} Breuil *et al.* demonstrated that a reactivity shift in PA^- -coordinated Ni^{2+} catalysts through outer-sphere (Lewis base) $\rightarrow$ (Lewis acid) interactions with the inner-sphere coordinated and deprotonated PA^- and external $B(C_6F_5)_3$ (Figure 1c).³⁶

Herein, we re-examine PA ligands and present two novel examples of the superb catalytic properties of heteroleptic precatalysts (**1s**) that can be activated by bases through outer-sphere deprotonation of the coordinated PA ligand at 35°C (Figure 2). Rather than Pd–PEPPSI–NHC, NHC was proposed as the throw-away ligand for the deprotonated **1s** based on the results of electrospray ionization mass spectrometry and density-functional theory (DFT) calculations, which indicated that the out-sphere noncovalent electrostatic interaction between $PR_2(O^-)$ and alkali metal ions (M^+) could be exploited to modulate the catalytic properties of **1s** (Figure 2c).

Results And Discussion

The two precatalysts were obtained through a reaction between $[(NHC)PdCl_2]_2$ ($NHC = NHC_{IPr}$ or NHC_{IMes}) and two folds of bis(*p*-tolyl)phosphine oxide (SPO_{tolyl}) at room temperature over 3 hours (Figure 2a). Column chromatography yielded 85% and 80% isolation for **1a** and **1b**, respectively. The crystal structures revealed that the NHC_{IPr} and bis(*p*-tolyl)phosphinous acid (PA_{tolyl} : $(tolyl)_2P-OH$) were trans to one another in **1a** and in the cis position in **1b** (Figure 2b). A weak intramolecular hydrogen bond was noted between $P-OH \cdots Cl^-$ (2.218 Å) in **1a**. No such interactions were observed in **1b** because of steric repulsion between the PA_{tolyl} and NHC_{IMes} aryl groups. The cis relationship between NHC_{IMes} and PA_{tolyl} in **1b** likely occurred because of the packing force of the solid state. DFT calculations indicated that the trans **1a** was approximately 9.4 kcal/mol more stable in free energy than the cis isomer was (Figure S1[a]). Similarly, the trans isomer of **1b** was 9.5 kcal/mol more energetically favorable than its cis counterpart was (Figure S1[b]). The C–Pd and Pd–P bond distances were 2.046(3) and 2.2783(8) in **1a** and were 2.002(5) and 2.2251(13) Å in **1b**.

The chemical shift of P–OH protons for both **1a** and **1b** occurred at 6.7 ppm, indicating existence of an intramolecular hydrogen bond between $P-OH \cdots Cl$ ligands. Moreover, two peaks appeared at 85.3 (trans)

and 86.5 ppm (cis) in the phosphorus-31 NMR (^{31}P NMR) spectrum for **1a** and at 84.3 (trans) and 85.4 ppm (cis) for **1b**. The cis and trans isomers were in an equilibrium ratio of approximately 1/8.7 in both **1a** and **1b** at 20°C (Figure S2 and S3). In the variable-temperature ^{31}P NMR spectra of **1a** and **1b**, no clear variation in the cis/trans equilibrium ratio was observed within a temperature range of -80 to 80°C.

The results indicated that **1a** and **1b** are highly effective precatalysts for SMRs. When 0.5 mmol phenyl chloride and 1.06 eq. phenylboronic acid were reacted at 35°C for 4 hours, an optimal combination of base and solvent was achieved in 1.0 mol% **1a**-catalyzed SMR, with KO^tBu (1.5 eq.) and EtOH (1 mL; Table S1). We then optimized the reaction time for the KO^tBu and EtOH set in the **1a**-catalyzed SMR (Table S2). The **1a**-catalyzed SMR was completed in 3 minutes (99% yield), indicating that **1a** could be efficiently converted to Pd(0) active species in EtOH. Alcohol reportedly plays a key role in reducing Pd(II) in $\text{NHC-Pd(II)Cl}_2\text{-P(OR)}_3$ precatalysts.⁴⁹ Use of a weaker base K_3PO_4 in EtOH was also efficient, given that SMRs were performed with 1.3 eq. phenylboronic acid for 8 minutes (99% yield; Table S2). The microliter syringe, glass vial, and EtOH were preheated at 35°C for this SMR.

Under the aforementioned optimized conditions, in situ generation of **1a** using $[(\text{NHC}_{\text{IPr}})\text{PdCl}_2]_2$ (0.5 mol%) and 2 eq. of $\text{SPO}_{\text{tolyl}}$ (1 mol%) was tested. However, the SMR yield drastically decreased to 15% after 3 minutes. When 0.5 mol% $[(\text{NHC}_{\text{IPr}})\text{PdCl}_2]_2$ and $[(\text{NHC}_{\text{IMes}})\text{PdCl}_2]_2$ were used as precatalysts with the same reaction conditions and times, the biphenyl yields were 31% and 29%, respectively. In addition, the isolated yields catalyzed by the commercially available $\text{Pd(P}^t\text{Bu}_3)_2$ and $(\text{dppf})\text{PdCl}_2$ were 2% and 1% over 5 minutes, respectively (Table S3). Furthermore, when 1 mol% highly efficient Pd-PEPPSI- NHC_{IPr} was used as the precatalyst, the isolated biphenyl yield was 45%.

As illustrated in Figure 3a, we independently optimized the SMR times. The results revealed that **1a** was a more effective precatalyst than **1b** was, although **1b** had demonstrated its effectiveness in most cases. Arylboronic acids with electron-donating (EDGs) or electron-withdrawing groups (EWGs) were tolerated in the **1a**-catalyzed SMRs (products **a-c**). The EWGs of arylboronic acids generally hinder transmetalation and vice versa; therefore, formation of product **c** from **1a** required 30 minutes. Sterically hindered ortho-methylated phenyl chloride and phenylboronic acid influenced the yields of the desired products (**d-f**). Although high yields were obtained with 2,6-dimethylphenyl chloride (**g, i**), 90 minutes were required to obtain moderate yields when (2,6-dimethylphenyl)boronic acid was used as the reagent (**h**). The yields of **g, h**, and **i** demonstrated that transmetalation could be the rate-determining step in **1a**- and **1b**-catalyzed SMRs. Furthermore, the yields of **j** and **k** revealed the same reactivity toward steric hindrance in aryl chloride and arylboronic acid. High yields were obtainable through use of a heteroatomic aromatic reagent of 2-chloropyridine (**l**). The functional group tolerance in **1**-catalyzed SMRs is inferable from the satisfactory yields of **m, n**, and **o**. In some cases, **1a** was a more effective precatalyst than **1b** was (Figure 3).

Benzyl chlorides with C(sp³)–Cl bonds reacted at 35°C were also employed as electrophiles (Figure 3b). Excellent yields were observed when a strong KO^tBu base was used. ParaEDG- or EWG-substituted benzyl chlorides performed well, with the **1a**-catalyzed SMR of steric-hindered 2-(chloromethyl)-1,3-dimethylbenzene being completed in 15 and 25 minutes for **1a** (ad: 94%) and **1b** (ad: 91%), respectively. Finally, the **1s** were used to the acylative SMR to broaden the applicability to include challenging electrophiles (Figure 3c). Because benzoyl chloride is susceptible to nucleophilic attacks, toluene and K₃PO₄ were employed. The reaction proceeded efficiently under mild reaction conditions (35°C for 1 hour).

Buono *et al.* conducted a DFT study, involving a thorough assessment of electron-donating properties using Tolman's electronic parameter (TEP) of PA, deprotonated PA[−], and PA[−]⋯alkali metal (R₂P–O[−]⋯M⁺¹) species.⁵⁰ The theoretical TEPs indicated electron-donating properties in the deprotonated phosphinito ligand R₂P–O[−] that could be remotely tuned through cations of different sizes, such as Li⁺, Na⁺, and K⁺. The authors proposed that their design was “a promising basis for the rational design of SPO-metal complexes with unprecedented catalytic properties in the future.” We hypothesized that the electron-donating properties of the deprotonated PA ligand would be tunable by controlling the electrostatic interaction between the negatively charged oxygen atom in R₂P–O[−] and alkali metal cations to, in turn, manipulate the electron density delocalization from the negatively charged oxygen atom to the coordinated phosphorus site. To our knowledge, **1a** and **1b** are the first highly effective precatalysts obtained by modulating the outer-sphere electrostatic interaction.

The manner in which the **1a**-catalyzed SMR yields were influenced by the size of the alkali metal ions (Figure 4a, Table S4) and the basicity of the bases (Figure 4b, Table S5) are illustrated in Figure 4. All SMRs were performed at 35°C. Four series of bases—MF, M₂CO₃, MOH, and MO^tBu—were employed (M: alkali metal ion). Notably, the yields were proportional to the size of the alkali metal ions in all series of salt additives (Figure 4a). The addition of lithium salts resulted in negligible yields, even when a strong base, such as O^tBu[−], was the counterion. The sodium ion was only effective when O^tBu[−] was the anionic base (77% yield). Notably, moderate to high yields were obtained when a fourth-period sodium salt was added to the reaction mixture (66–99%). This indicates that large alkali metal ions facilitate SMR through weak electrostatic interactions between alkali metal ions and the negatively charged oxygen in R₂P–O[−].

Longer reaction times were required when weak bases were present in the salt additives (Figure 4a). For example, to achieve moderate conversions, a reaction time of 60 minutes was required for the KF (66%) and K₂CO₃ (68%) salt additives. However, high catalytic yields were obtained in 5 and 3 minutes for KOH (82%) and KO^tBu (99%), respectively, indicating a strong base promotes the deprotonation of R₂P–OH. As illustrated in Figure 4b, the basicity of the base drastically affected the SMR conversion yields when the reactions were conducted at 35°C for 10 minutes. These findings indicate that the basicity of the base was proportional to the yields in the **1a**-catalyzed SMRs. Notably, to achieve more favorable yields, larger

alkali metal ions, such as Rb⁺ (67%) and Cs⁺ (78%), can be employed in conjunction with a weak base, such as F⁻, for a longer reaction time (Figure 4a).

To eliminate the influence of salt solubility on SMR yields, the **1a**-catalyzed SMRs were conducted at 35°C in 0.5 mL of H₂O and 0.5 mL of EtOH (Table S6). The results indicated that the influences of the cation size and the basicity of the bases did not change. For M₂CO₃ reacted for 15 minutes, the GC conversions were 78% (Li⁺), 80% (Na⁺), 90% (K⁺, Rb⁺), and 91% (Cs⁺). For the weaker MF base, a clear trend was observed; when they were reacted for 60 minutes, the GC conversions were 4% (Li⁺), 44% (Na⁺), 59% (K⁺), 64% (Rb⁺), and 69% (Cs⁺). When 1 mL of H₂O was used as a solvent, the GC conversions were 58% for Li₂CO₃ and 8% for LiF (Table S7).

Subsequent DFT calculations were performed to evaluate the gas-phase (in EtOH) bond dissociation free energies (BDFEs) for the dissociation of NHC and PA_{toly} from the **1a** precatalyst. In **1a**, the BDFE of PA_{toly} was 8.0 (8.1) kcal/mol smaller than that of NHC_{IPr} (Figure 5a). Upon deprotonation of PA_{toly}, the BDFE of PA_{toly}⁻ ((toly)₂P-O⁻) (38.6 [28.2] kcal/mol) was unexpectedly discovered to be substantially larger than that of NHC_{IPr} (15.5 [13.8] kcal/mol; Figure 5b). The same trends were observed for the BDFEs of NHC_{IMes} and PA_{toly} in **1b** (Figure S4). These DFT calculations indicate that the formation of anionic (O⁻) (toly)₂P→Pd(II)Cl₂ species is plausible under **1**-catalyzed SMR conditions.

Experimental observations of the mass spectrum supported the hypothesis drawn from the DFT calculations (Figure 6). Electrospray ionization (ESI) was performed in negative ion mode, which not only ionized the precatalyst **1a** (MW 796.16) but also simulated the deprotonation process in SMRs (Figure 6a). The mass spectrum revealed deprotonation of the **1a** ion at *m/z* 795.25, indicating a parent ion for **1a** (Figure 6d). Although the anionic (O⁻)(toly)₂P→Pd(II)Cl₂ (*m/z* 407.08) appeared in the spectrum (Figure 6c), the ligand PA_{toly}⁻ (*m/z* 229.23) demonstrated a negligible ion abundance nearing background levels (Figure 6b). A similar phenomenon was demonstrated by **1b** (Figure S5). These results revealed the prevalence of NHC_{IPr} and NHC_{IMes} in the dissociations from **1a** and **1b**, indicating NHCs may be a throw-away ligand because of the smaller BDFE of its system.

Because the parent and fragment ions of the precatalysts were both observed in the mass spectrum (Figure 6a), the fragment yield (FY) can be estimated using the following equation:

$$FY (\%) = \frac{I(f^-)}{[I(f^-) + I(p^-)]},$$

where $I(p^-)$ is the intensity of the parent ion signal and $I(f^-)$ is the intensity of the total fragment ion signals of the anionic (O⁻)(toly)₂P→Pd(II)Cl₂. This fraction indicates the number of molecules capable of obtaining sufficient internal energy to overcome the BDFE before detection. Because the internal energy of the ions produced by the ESI source have been approximated to have a thermal-like Boltzmann distribution,^{51, 52} the relative BDFE grades in the distinct throw-away ligands were compared through

determination of the FYs in the mass spectrum. The inlet capillary temperature of the ESI source was varied between 380 and 315°C to adjust the internal energy of the produced ions, and the FY of deprotonated **1a** and **1b** were estimated using series spectra (Figures S6 and S7). The FY significantly increased with the temperature, indicating a higher probability of NHC–PdCl₂ bond dissociation (Figure S8). The series spectrum illustrated that **1a** had a lower temperature threshold for full dissociation and a higher FY than **1b** at the same inlet temperature, suggesting a lower BDFE in deprotonated **1a**. The experimental results demonstrated that **1a** was more suitable for forming anionic (O[−])(tolyl)₂P→Pd(II)Cl₂ than **1b** was, despite BDFEs between deprotonated **1a** (15.5 [13.8 in EtOH] kcal/mol) and **1b** (14.0 [13.9] kcal/mol) being similar in DFT calculations. The precatalyst **1a** preemptively dissociates and subsequently reduces to Pd(0) active species and is, therefore, a more efficient precatalyst than **1b** (Figure 3).

The **1a**-catalyzed SMRs proceeded smoothly in EtOH under optimized reaction conditions (Figure 3a and 3b). Thus, EtOH likely contributes to the base-promoted reduction of (O[−])(tolyl)₂P→Pd(II)Cl₂ to Pd(0) active species.^{53, 54} This may be because the presence of O^tBu[−] in EtOH can generate ethoxide ligand (OEt[−]) for the subsequent formation of Pd(0) catalysts and aldehydes. To investigate the reduction pathway, diphenylmethanol (0.1 mmol) was reacted with **1** (0.1 mmol) and KO^tBu (0.2 mmol) in 0.5 mL of toluene (Table S8 and Scheme S1) at 35°C for 30 minutes. Benzophenone yields of were isolated to be 66% in the **1a** reaction and 38% in the **1b**, with this formation suggesting existence of reduced (O[−])(tolyl)₂P→Pd(0) species.

Following the use of Multiwfn to analyze the wavefunctions of the optimized structures,⁵⁵ the minimum value ($V_{\min}$) of the molecular electrostatic potential in the lone pair region can be used to quantify the electron-donating properties of a ligand.^{56, 57} The $V_{\min}$ for the (tolyl)₂P–OH and (tolyl)₂P–O[−]⋯M⁺ (M⁺ = Li⁺, Na⁺, K⁺) obtained through the DFT calculations are presented in Figure 5c. The $V_{\min}$ of the P atom in the deprotonated PA (tolyl)₂P–O[−]) was extremely large (−152.9 kcal/mol) despite not occurring under genuine SMR conditions, in which salt was generally required to promote the reaction. To qualitatively determine a realistic reaction environment for our model, alkali metals were positioned near the negatively charged oxygen atom to achieve geometric optimization. Using wavefunctions of the optimized structures, we analyzed the $V_{\min}$ for (tolyl)₂P–O[−]⋯M⁺. The calculated $V_{\min}$ values were −42.0 (Li⁺), −48.3 (Na⁺), and −81.8 (K⁺) kcal/mol, which indicate that large alkali metal ions electrostatically interacted less with the (tolyl)₂P–O[−]. Therefore, the electron density could be more smoothly delocalized from the negatively charged oxygen onto the P donor of the (tolyl)₂P–O[−]⋯M⁺.

The optimized structures for the plausible (O[−])(tolyl)₂P→Pd(0) and (M⁺⋯O[−])(tolyl)₂P→Pd(0) active species are displayed in Figure 5d. A Hirshfeld charge analysis on the Pd(0) atom was then performed, revealing that the Pd(0) in (K⁺⋯O[−])(tolyl)₂P→Pd(0) had a higher electron density (−0.11 au) than its Li⁺

(−0.09 au) and Na^+ (−0.05 au) counterparts. The experimental yields (Figure 4a) could be explained by the DFT results. Notably, the formation of undesired black palladium precipitants was observed immediately after SMR completion. With Li^+ salts, the stronger outer-sphere electrostatic interaction rendered the $\text{Pd}(0)$ less electron-rich and postponed the formation of black palladium precipitants. Our experimental observations suggest that small alkali metal ions can be employed when highly unreactive substrates are used or high temperatures are required.

Conclusion

In this study, PA and NHC-ligated heteroleptic $(\text{HO})\text{R}_2\text{P} \rightarrow \text{Pd}(\text{II})\text{Cl}_2 \leftarrow \text{NHC}$ were successfully synthesized as novel, highly efficient precatalysts for SMRs. We demonstrated that the basicity of an anionic base associates with the deprotonation of $\text{R}_2\text{P}-\text{OH}$. Our newly designed $\text{Pd}(\text{II})$ precatalysts with superb catalytic properties can be controlled by modifying the size of alkali metal ions. This study may facilitate future development of PA-coordinated heteroleptic $\text{Pd}(\text{II})$ precatalysts.

Declarations

Declarations

Competing interests

The authors declare no competing interests.

Author contributions

S.-W. L. conducted the experiments. Y. G. performed the DFT calculations. W.-C. L., P.-R. Z. and I.-C. L. performed the mass spectrometry experiments and analyzed the data. T.-H. L performed the $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ and $(\text{dppf})\text{PdCl}_2$ -catalyzed SMRs and data analysis. I.-C. L. wrote the paragraphs regarding the analysis of mass spectrometry experiments. Y.-C. C. directed the project and wrote the manuscript.

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Declarations

Data availability

The data supporting the findings of this study are available within the article and its Supplementary Information. CCDC 2088530 and 2088531 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif

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Author contributions

S.-W. L. conducted the experiments. Y. G. performed the DFT calculations. W.-C. L., P.-R. Z. and I.-C. L. performed the mass spectrometry experiments and analyzed the data. T.-H. L performed the $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ and $(\text{dppf})\text{PdCl}_2$ -catalyzed SMRs and data analysis. I.-C. L. wrote the paragraphs regarding the analysis of mass spectrometry experiments. Y.-C. C. directed the project and wrote the manuscript.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Ligand-enabled (a) site selectivity,^{32, 33, 34} (b) catalytic reactivity,³⁵ and (c) change of chemical reactivity due to outer-sphere electrostatic or Lewis base–acid interactions³⁶

(a)

(b)

(c) ESI⁺ mass + DFT study

Figure 2

(a) Synthesis and (b) X-ray structures for **1a** and **1b** and (c) plausible active species (HO) $(\text{tolyl})_2\text{P}^+\text{Pd}(\text{II})\text{Cl}_2\text{-NHC}_{\text{IPr}}$ of **1a**

Figure 3

(a) Aryl chlorides (1 mmol), (b) benzyl chlorides (1 mmol), or (c) benzoyl chlorides (1 mmol) reacted with various arylboronic acids in **1**-catalyzed SMRs

Figure 4

(a) Size effect of alkali metal ions on biphenyl yield (Table S4): MO^tBu (3 mins), MOH (5 mins), M₂CO₃ (60 mins), and MF (60 mins), and (b) effects of basicity of bases on SMR yields of sodium salts (Table S5: 10 minutes).

Figure 5

DFT-calculated gas-phase (in EtOH) bond dissociation free energy (BDFE in kcal/mol) for dissociation of NHC_{IPr} , PA_{tolyl} , and deprotonated $\text{PA}_{\text{tolyl}}^-$ in (a) **1a** and (b) deprotonated **1a⁻**; (c) molecular electrostatic potential isosurface and V_{min} (in kcal/mol) in EtOH in lone pair region of P atom; (d) Hirshfeld charge (in red) in EtOH for Pd(0) in $(\text{M}^+\cdots\text{O}^-)(\text{O}^-)(\text{tolyl})_2\text{P-Pd(0)}$.

Figure 6

(a) Full electrospray ionization mass spectrometry of **1a** precatalyst in negative mode at 275 °C inlet temperature. All **1a**-related ions are indicated with a blue star, and background ions from the solvent are indicated with a green star. Three expanded m/z regions of the possible precatalyst and ligand ions: (b) $\text{PA}_{\text{tolyl}}^-$ (m/z 229.23), (c) $(\text{O}^-)(\text{tolyl})_2\text{P}^+\text{Pd}(\text{II})\text{Cl}_2$ (m/z 407.08), and (d) the deprotonated **1a** ion (m/z 795.25). Spectra are fitted with calculated isotope distributions (blue bar) to verify that the elementary compositions match the detected ions. The anticipated m/z region of the $\text{PA}_{\text{tolyl}}^-$ (yellow) in spectrum (b) demonstrated an ion signal nearing background level.

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