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# Combining the Reactivity Properties of $PCy_3$ and $PtBu_3$ into a Single Ligand, $P(iPr)(tBu)_2$. Reaction via Mono- or Bisphosphine Palladium(0) Centers and Palladium(I) Dimer Formation

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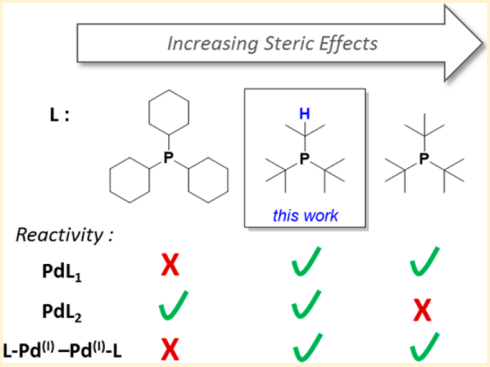
Supporting Information

**ABSTRACT:** Trialkylphosphine ligands are ubiquitous in catalysis. Via modulation of the steric bulk of these ligands, two central aspects that dictate reactivity and selectivity in catalysis can be controlled: i.e., the coordination sphere and favored oxidation state of the reactive metal center. Within this class of ligands, tricyclohexylphosphine ($PCy_3$) and tri-*tert*-butylphosphine ($PtBu_3$) are most widely used in catalysis. While the smaller $PCy_3$ favors reactivity via Pd bisphosphine species with the test substrate 4-chlorophenyl triflate **1** and does not form dinuclear Pd(I) complexes upon oxidation of Pd(0), $PtBu_3$ reacts via a monophosphine-ligated Pd complex with **1** and forms dinuclear Pd(I) complexes on oxidation. We herein report that the hybrid ligand $P(iPr)(tBu)_2$, characterized by a cone angle that is between those of $PCy_3$ and $PtBu_3$, features all of these reactivity properties in a single scaffold. This is exemplified in chemoselectivity studies with test system **1**, in which the site selectivity could be readily modulated. The novel Pd(I) dimer $\{[P(iPr)(tBu)_2]PdI\}_2$ has also been synthesized.




Over the past decades, the development of transition-metal-catalyzed transformations has greatly enhanced the synthetic chemist's toolbox and revolutionized the way bond-forming reactions are currently undertaken.[1] A key challenge in the development of organometallic reactivities is the control of the metal complex to steer toward desired reactivities and selectivities.[1,2] To this end, the ligand sphere encompassing the metal center is generally fine-tuned. While the modulation of steric and electronic properties of ligands has undoubtedly had a tremendous impact on organometallic catalysis, the precise effects and characteristics of these ligands are not always well understood.[3] Clearly there is no ligand available yet that allows for applications in a diverse set of transformations as an "all-round" ligand, and continuous re-evaluation of the potential utility of a given ligand in novel transformations has to be undertaken. Accordingly, methodology developments frequently rely on trial and error or screening approaches.[4]

Numerous organometallic transformations commence with the oxidative addition step.[1] The reactivity of this step is also dependent on the ligation state of the metal.[5] In general, with increasing steric bulk of the phosphine, fewer ligands will be coordinated. However, the overall mechanism of oxidative addition may also depend on the substrate identity.[6,7,10b,f,g,39] Given the diverse possibilities of pathways and intermediates, subtle modifications in the ligand framework may have more or less impact on the overall reaction speed. The study of site selectivity may allow indirect deduction of information on the nature of the reactive Pd species.[2b] In this context, the bulky and widely used trialkylphosphine[8] ligand $PtBu_3$ (cone angle[9] 182°) has been shown to involve a monophosphine metal complex in oxidative addition to ArCl.[5a,10] As a consequence of its steric bulk, the bisphosphine counterpart $Pd(PtBu_3)_2$ is itself unreactive and functions as a precursor for the monophosphine Pd, following ligand dissociation.[10] In competition experiments, this allows for selective functionalization of a C–Br[11] or C–Cl[12] bond over C–OTf, as shown by the groups of Hayashi, Brown, and Fu (see Figure 1). Smaller ligands, such as the ubiquitous tricyclohexylphosphine[13] $PCy_3$ (cone angle[9] 175°), result in typical reactivities of bisphosphine metal complexes, preferentially functionalizing the C–OTf bond in **1**.[10a,12]

In addition to the favored ligation state, the nature of the ligand may also impact the overall stability of the oxidation state of a metal complex. $PtBu_3$ shows the special characteristics of stabilizing palladium in the +1 oxidation state,[14,15] resulting in the dinuclear $Pd^I$ complex $\{LPd^IX\}_2$ (with X = Br, I and L = $PtBu_3$),[16] which $PCy_3$ does not.[17] It has been shown that these $Pd^I$ dimer complexes may have a significant role in catalysis, causing acceleration or inhibition,[18] and they may function as precatalysts[19,20] or be involved directly in transformations, displaying reactivities distinctly different from that of $Pd^0$.[21]

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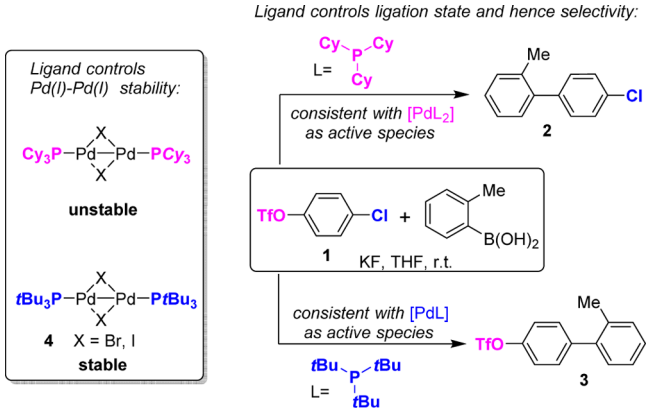


**Figure 1.** Distinct effect of ligands on selectivity via ligation state control and propensity to form $Pd^{I}$–$Pd^{I}$.

Moreover, the formation of +1 Pd species can also be a pathway of catalyst deactivation.[19a]

While the ligands P*t*Bu$_3$ and PCy$_3$ currently allow for either reactivity paradigm, i.e. monoligated active species and Pd(I) dimer for P*t*Bu$_3$ but bisligated Pd(0) reactive species and no Pd(I) stabilization for PCy$_3$, this report describes how a slight modification of the steric nature may combine the properties of these ligands in a single species: i.e., di-*tert*-butylisopropylphosphine, P(*i*Pr)(*t*Bu)$_2$.

Stimulated by our mechanistic studies of the effects of ligands on the ligation and favored oxidation state of a metal,[25,19a,18,23] we have recently begun to conduct additional computational studies.[24] These analyses suggested that replacement of a single methyl group by hydrogen in P*t*Bu$_3$ may allow for *either* a Pd–bisphosphine *or* a Pd–monophosphine complex to be reactive in catalysis. The reaction with 4-chlorophenyl triflate **1** (Figure 1) was computationally studied in this context. This substrate constitutes an ideal mechanistic probe to test for the active catalytic species, as a monoligated Pd species reacts at C–Cl, while the bisligated counterpart reacts with C–OTf.[25] The computational prediction for C–Cl versus C–OTf site selectivity for the reaction of PdL$_2$ (L= P(*i*Pr)(*t*Bu)$_2$) with **1** is illustrated in Figure 2. We applied the M06L/def2-QZVP method and the solvation model COSMO-RS (for THF), which have previously been shown to perform adequately in the study of similar systems.[26,27] A slight preference for C–Cl addition by monoligated Pd$^0$L was predicted in THF. The activation free energy difference ($\Delta\Delta G^{\ddagger}$) for the competing C–OTf addition by PdL$_2$ is very small (0.3 kcal/mol). Within the error margin of the calculations,[22] this would suggest that the favored ligation state might be changeable via alteration of the number of equivalents of ligand. In contrast, the bulkier analogue P*t*Bu$_3$ shows exclusive selectivity for C–Cl in THF, also in the presence of excess ligand, which is supported by computations that suggest a 11 kcal/mol preference for PdL addition to C–Cl over PdL$_2$ addition to C–OTf at the same level of theory.[28] PCy$_3$, which is smaller in steric bulk, does not access monoligated Pd and shows reactivity at C–OTf, consistent with PdL$_2$ as the active species.[12,25,10] This suggested that, depending on the number of equivalents of ligand, P(*i*Pr)(*t*Bu)$_2$ may feature the reactivity of either PCy$_3$ or P*t*Bu$_3$. To test for this as well as to explore other characteristic aspects, such as the potential to stabilize $Pd^{I}$–$Pd^{I}$, we subsequently undertook experiments.

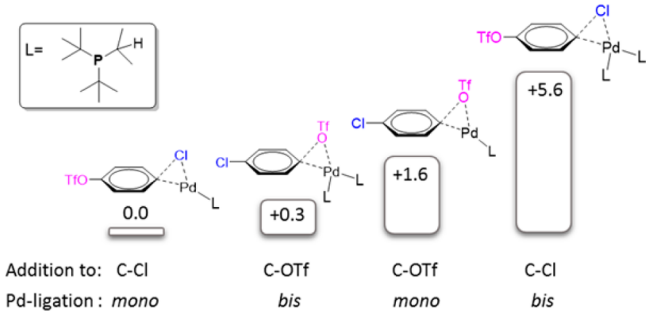


**Figure 2.** Calculated selectivity ($\Delta\Delta G^{\ddagger}$ in kcal/mol) for C–OTf vs C–Cl addition for the reaction of Pd[P(*i*Pr)(*t*Bu)$_2$]$_2$ with **1** in THF at the COSMO-RS (THF) M06L/def2-QZVP//ωB97XD/6-31G(d) level.[22]

Di-*tert*-butylisopropylphosphine, P(*i*Pr)(*t*Bu)$_2$,[29] was prepared according to Iwazaki's procedure: i.e., di-*tert*-butylchlorophosphine was reacted with isopropylmagnesium chloride.[30,31] Purification was performed in a glovebox to avoid oxidation of the ligand. With P(*i*Pr)(*t*Bu)$_2$ in hand, the synthesis of the bisphosphine Pd$^0$ complex Pd[P(*i*Pr)(*t*Bu)$_2$]$_2$ (**5**) was subsequently undertaken. This was accomplished via subjection of the ligand to the $Pd^{II}$ precursor complex [(tmeda)$Pd^0$(Me)$_2$]. Pd[P(*i*Pr)(*t*Bu)$_2$]$_2$ (**5**) was successfully obtained in good yield (63%) and characterized by $^1$H and $^{31}$P{H} NMR spectroscopy as well as X-ray diffraction. The X-ray crystallographic structure of **5** is depicted in Figure 3. The P–Pd–P axis is linear, and the Pd–P bond length was determined to be 2.265 Å. The C–P bond is 1.820 Å for the *i*Pr group and 1.913 and 1.881 Å for the two *t*Bu groups.

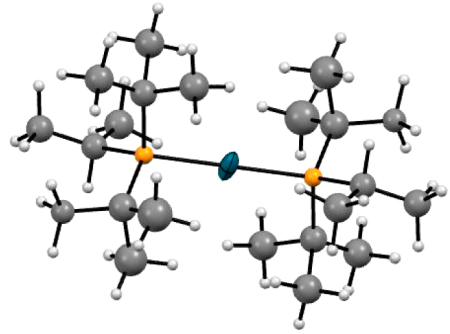

**Figure 3.** X-ray structure of Pd$^0$[P(*i*Pr)(*t*Bu)$_2$]$_2$ (**5**).

The reactivity of Pd$^0$[P(*i*Pr)(*t*Bu)$_2$]$_2$ was subsequently explored in the Suzuki cross-coupling of 4-chlorophenyl triflate (**1**), employing 3 mol % catalyst loading, KF as base, and 2-methylphenylboronic acid in THF. Reactivity was observed at room temperature, albeit slow, resulting in 15% of the C–Cl functionalization product **3**, along with recovered starting material (84%) (see Table 1). Modification to an overall 1:1 Pd to ligand ratio led to faster reaction, consistent with the reactivity previously seen with P*t*Bu$_3$.[12] Using Pd$_2$(dba)$_3$ (1.5 mol %)/P(*i*Pr)(*t*Bu)$_2$ (3 mol %) gave 86% of **3** (C–Cl addition) in 24 h at room temperature (Table 1, entry 2).

The selectivity for C–Cl addition would be in agreement with monoligated Pd[P(*i*Pr)(*t*Bu)$_2$] as the active catalytic species—a reactivity previously observed for P*t*Bu$_3$.

To further test for the reactivity of a bisphosphine Pd$^0$ complex, we repeated the experiments in the presence of excess phosphine ligand (10 equiv relative to Pd) that is expected to disfavor the required ligand dissociation for the monoligated


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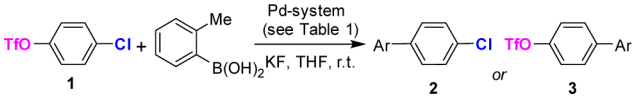
**Table 1. Selectivity Switch with Excess Ligand**




| entry | catalyst (amt (mol %)) | time (h) | yield (%) 2 | 3 |
|---|---|---|---|---|
| 1 | $Pd[P(iPr)(tBu)_2]_2$ (3) | 125 | | 15 |
| 2 | $Pd_2(dba)_3$ (1.5)/$P(iPr)(tBu)_2$ (3) | 24 | | 86 |
| 3 | $Pd[P(iPr)(tBu)_2]_2$ (3)/$P(iPr)(tBu)_2$ (30) | 125 | 10 | |
| 4 | $Pd_2(dba)_3$ (1.5)/$PtBu_3$ (30) | 169 | | 5 |

pathway, hence forcing the reaction to take place via a bisligated pathway (=C−OTf addition). Indeed, this led to exclusive functionalization of the C−OTf bond in **1**, consistent with the involvement of $Pd^0[P(iPr)(tBu)_2]_2$ as an active species. As a control, when we conducted the analogous experiment with $PtBu_3$ as ligand (also in excess), the reactivity was very low, and exclusive functionalization of C−Cl was observed (entry 4), consistent with the much greater energy differences predicted between mono- and bisligated pathways for this ligand. This suggests that $P(iPr)(tBu)_2$ may adopt and be utilized for the reactivity behavior of both very bulky ligands that typically favor monophosphine Pd species and for less bulky ligands in higher coordination spheres.

Another key difference between $PCy_3$ and $PtBu_3$ is the ability to form dinuclear $Pd^I$ complexes. We recently uncovered that additives commonly used in cross coupling, such as CuI and $CuBr_2$, rapidly oxidize $Pd^0L_2$ complexes bearing electron-rich phosphine ligands.[18] In the case of L = $PtBu_3$, the $Pd^I$ dimer **4** is obtained (Figure 1), the bridging halogens of which depend on the Cu salt employed and whose reactivities are consistent with several of the previously observed Cu effects in catalysis. On the other hand, for tricyclohexylphosphine, no stable $Pd^I$ dimer results upon oxidation and instead $Pd^{II}L_2$ is formed, highlighting the different abilities of the ligands in stabilizing the +1 Pd oxidation state.[17,18] Given that the hybrid ligand $P(iPr)(tBu)_2$ was able to adopt and mimic the reactivities of both $PtBu_3$ and $PCy_3$ in the Suzuki cross-coupling discussed above, we were intrigued to explore the propensity of $Pd^I$ dimer formation for $Pd^0[P(iPr)(tBu)_2]_2$ (**5**). In analogy to our previous report on the redox reactions involving $PCy_3$- and $PtBu_3$-derived $Pd^0$ complexes,[18] we subjected 1 equiv of CuI to **5** in THF at room temperature. Analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR after 1 h showed that a new species had formed at 88.8 ppm in addition to $Pd^0[P(iPr)(tBu)_2]_2$ (**5**) at 72.0 ppm. Since only 1 equiv of CuI was employed, a maximum of $^1/_2$ equiv of $Pd^I$ dimer could have potentially formed, consistent with the fact that $Pd^0$ was still detected by $^{31}P$ NMR spectroscopy. The same new species at 88.8 ppm was exclusively formed when we subjected **5** to a comproportionation with $PdI_2$ (see Figure 4). Subsequent isolation and characterization by X-ray crystallographic analysis confirmed that this species was the novel $Pd^I$ dimer $\{[P(iPr)(tBu)_2]PdI\}_2$ **6** (see Figure 5).[40]

In conclusion, di-*tert*-butylisopropylphosphine, $P(iPr)(tBu)_2$, was shown to feature reactivity properties of two of the most commonly used trialkylphosphine ligands ($PtBu_3$ and $PCy_3$). It was demonstrated that $P(iPr)(tBu)_2$ has the ability to stabilize the rare +1 oxidation state at Pd centers, paralleling the properties of $PtBu_3$. Moreover, computational and experimental reactivity data strongly support the notion that $P(iPr)(tBu)_2$

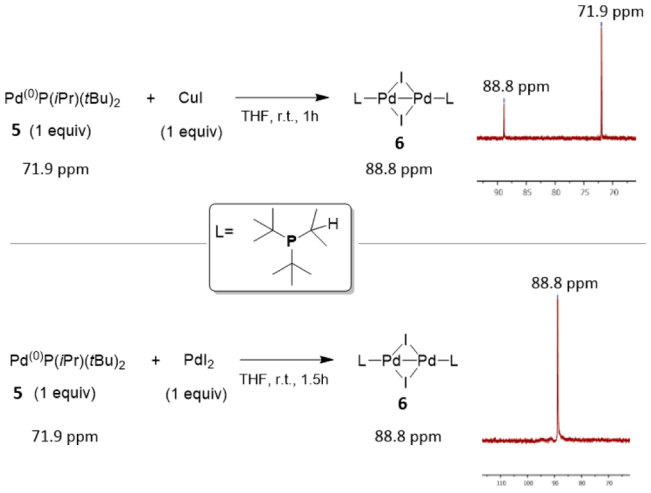



**Figure 4.** Formation of Pd(I) dimer $\{[PtBu_2(iPr)]PdI\}_2$ (**6**) from **5**.

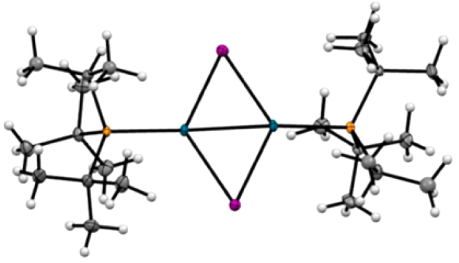


**Figure 5.** X-ray structure of Pd(I) dimer $\{[PtBu_2(iPr)]PdI\}_2$ (**6**).

may favor monoligated $Pd^0$ as the active species in the absence of excess ligand, paralleling the reactivity of $PtBu_3$ in preferentially reacting at the aromatic C−Cl over the generally more reactive C−OTf bond. However, in contrast to the case for $PtBu_3$, for $P(iPr)(tBu)_2$ modulation of the number of equivalents of ligand allows steering of the reactivity via a $Pd^0$ bisphosphine complex, in analogy to the case for $PCy_3$. This behavior is in line with the cone angles of the ligands, with the hybrid ligand $P(iPr)(tBu)_2$ being in between in steric bulk: $PtBu_3$ (182°) > $P(iPr)(tBu)_2$ (175°) > $PCy_3$ (170°).[9] We anticipate diverse applicability of this ligand on the basis of these properties.

## EXPERIMENTAL SECTION

**Chemicals and Reagents.** All reactions were performed under an atmosphere of nitrogen unless otherwise stated. All reactions were carried out in oven-dried glassware unless otherwise stated. THF and hexane were purified by an SP-105 solvent drying system from LC Technology Solutions Inc. under an atmosphere of nitrogen ($H_2O$ content <10 ppm as determined by Karl Fischer titration). Anhydrous solvents were purchased from Acros and were deoxygenated with a flux of nitrogen. Reagents and solvents were purchased at reagent grade from Acros, Aldrich, ABCR, and Fluka and were used as received unless otherwise stated; boronic acids were recrystallized and deoxygenated and aryl chlorides deoxygenated before their use.

**Physical Methods.** The $^1H$ NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra were recorded at 293 K on a Bruker ARX 300 or Bruker DRX 400 spectrometer. Residual solvent signals in the $^1H$ and $^{13}C$ NMR spectra were used as an internal reference, and trimethoxyphosphine oxide was used as an internal standard for $^{31}P$ NMR spectra. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer. The spectra were measured neat, and selected absorption bands are reported in wavenumbers ($cm^{-1}$). All cross-coupling reactions were monitored using an Agilent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Technologies 5975 series MSD mass spectrometer coupled with an Agilent Technologies 7820A gas chromatograph equipped with an Agilent 19091s-433 HP-SMS column (30 m × 0.250 μm × 0.25 μm). Melting points were obtained on a Büchi B540 and a Büchi M-560 apparatus in open capillary tubes. X-ray crystallographic data were obtained with a Bruker ApexIID8-Cu or Bruker APEX-II CCD diffractometer. CH elemental analysis was performed on a Elementar Vario EL analyzer.

*GC-MS conditions:* front inlet mode, split; temperature, 250 °C; pressure, 1.1066 psi; total flow, 50.474 mL/min; split ratio, 100:1; split flow, 50 mL/min; run time, 18.667 min; oven program, 50 °C for 2 min then 15 °C/min to 300 °C for 0 min; flow, 0.5 mL/min. Calibrations to obtain the relative ratios of products were achieved using a calibration curve generated using the supplied GC-MS software ("ChemStation"). Mesitylene was used as an internal standard.

**Preparation of Di-*tert*-butylisopropylphosphine.**[27] To a solution of di-*tert*-butylchlorophosphine (5.0 g, 27.7 mmol, 1.0 equiv) and copper(I) chloride (27.1 mg, 0.28 mmol, 0.1 equiv) in THF (20 mL) at 0 °C was added a solution of isopropylmagnesium chloride (2 M in THF, 21 mL, 41.5 mmol, 1.5 equiv) dropwise over 1 h. After the dropwise addition was completed, stirring was conducted at the same temperature for 3 h. The reaction mixture was warmed to room temperature and stirred overnight. A saturated solution of $NH_4Cl$ (20 mL, previously degassed) and $Et_2O$ (20 mL, previously degassed) were added. The aqueous phase was extracted with $Et_2O$ (20 mL, previously degassed). The organic layers were combined, washed with degassed water (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure to afford a colorless oil. The residue was transferred into the glovebox, dissolved in hexane, and filtered through a short pad of silica gel, and the compound was dried in vacuo to give the product (4.5 g, 88%) as a colorless oil: $\delta_H$ ($C_6D_6$, 300 MHz) 1.05−1.33 (2SH, m, C*H*); $\delta_P$ ($C_6D_6$, 126 MHz) 46.2. These data are consistent with those reported previously.[29]

**Preparation of (*N,N,N′,N′*-Tetramethylethylenediamine)-dichloropalladium(II).**[30] Palladium dichloride (2.53 g, 14.3 mmol, 1.0 equiv) was dissolved in MeCN (150 mL) at reflux for 1 h. The solution was cooled to room temperature, and *N,N,N′,N′*-tetramethylethylenediamine (15.5 mL, 104 mmol, 7.3 equiv) was added. The reaction mixture was stirred for 1 h at room temperature. The yellow precipitate that formed was filtered, washed with diethyl ether, and dried in vacuo to give the product (4.1 g, 98%), which was used without further purification.

**Preparation of (*N,N,N′,N′*-tetramethylethylenediamine)-dimethylpalladium(II).**[31] (*N,N,N′,N′*-Tetramethylethylenediamine)-dichloropalladium(II) (1.66 g, 5.64 mmol, 1.0 equiv) was dissolved in dry methyl *tert*-butyl ether (50 mL), and the resulting mixture was cooled to 0 °C. A solution of MeLi (1.6 M in THF, 10.5 mL, 16.9 mmol, 3.0 equiv) was added dropwise via syringe over 10 min. The solution was stirred at 0 °C for 30 min and then at room temperature for 1 h. The reaction mixture was cooled to 0 °C, and water (20 mL) was added to quench the excess MeLi. The resulting black solution was extracted with THF (5 × 30 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to give the product (1.2 g, 84%) as an off-white solid: $\delta_H$ ($C_6D_6$, 400 MHz) 0.45 (6H, s, Pd−C$H_3$), 1.69 (4H, s, C$H_2$), 2.05 (12H, s, N−C$H_3$); $\delta_C$ ($C_6D_6$, 100 MHz) −8.4, 47.9, 59.2. These data are consistent with those reported previously.[31]

**Preparation of Bis(di-*tert*-butylisopropylphosphine)-palladium(0) (5).** (*N,N,N′,N′*-Tetramethylethylenediamine)-dimethylpalladium(II) (0.61 g, 2.4 mmol, 1.0 equiv) and di-*tert*-butylisopropylphosphine (1.0 g, 5.3 mmol, 2.2 equiv) in THF (8 mL) were stirred at room temperature for 2 h. The solvent was removed in vacuo, and DMF (5 mL) was added. The precipitate that formed was collected by filtration, washed with hexane, and dried in vacuo to give the product (0.73 g, 63%) as white crystals: $\delta_H$ ($C_6D_6$, 300 MHz) 1.38−1.59 (50H, m, C*H*); $\delta_P$ ($C_6D_6$, 126 MHz) 71.3. Anal. Calcd for $C_{22}H_{55}P_2Pd$: C, 54.71; H, 10.43. Found: C, 54.28; H: 10.31.

**Preparation of 4-Chlorophenyl Trifluoromethanesulfonate (1).** 4-Chlorophenol (2.4 g, 18.7 mmol, 1.0 equiv) was dissolved in dichloromethane (15 mL). The solution was cooled to 0 °C, and triethylamine (10.0 mL, 71.7 mmol, 3.8 equiv) was added via syringe. Triflic anhydride (4.0 mL, 23.8 mmol, 1.3 equiv) was then added dropwise, and the reaction mixture turned brown. The reaction mixture was warmed to room temperature and stirred for 4 h. Water (50 mL) was then added and the phases were separated. The aqueous phase was extracted with dichloromethane (4 × 40 mL). The combined organic phases were washed successively with an aqueous solution of HCl (2 N, 2 × 50 mL), water (2 × 50 mL), and brine (50 mL), dried over $Na_2SO_4$, filtered, concentrated under reduced pressure, and purified by flash column chromatography (100% hexane) to yield a colorless oil (3.75 g, 80%): $\nu_{max}$ 1484 (C−H), 1424 ($SO_2$), 1205 ($SO_2$), 1135 (C−F), 1089 (C−Cl) $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 7.20−7.26 (2H, m, Ar*H*), 7.40−7.46 (2H, m, Ar*H*); $\delta_C$ ($CDCl_3$, 100 MHz) 118.7 (C−F, q, $J_{CF}$ 320.9), 122.7 (CH), 130.4 (CH), 134.3 (C), 147.9 (C); *m/z* (EI) 262 ([M]$^+$, 20%, $^{37}$Cl), 260 ([M]$^+$, 49%, $^{35}$Cl), 129 (33%, $^{37}$Cl), 127 (100%, $^{35}$Cl), 101 (16%, $^{37}$Cl) 99 (52%, $^{35}$Cl). These data are consistent with those reported previously.[10]

**General Procedure for the Suzuki Cross-Coupling Reactions.** Inside a glovebox, 4-chlorophenyl trifluoromethanesulfonate (**1**; 276.3 mg, 1.06 mmol, 1.0 equiv), 2-methylphenylboronic acid (145.5 mg, 1.07 mmol, 1.1 equiv), and KF (185.6 mg, 3.2 mmol, 3.0 equiv) were placed in an oven-dried vessel. THF (1 mL) was added, and the catalyst system in THF (1 mL) was then added to the reaction mixture. The reaction mixture was stirred in the glovebox for the indicated time at room temperature. At the end of the reaction, the reaction mixture was diluted with $Et_2O$ (50 mL), filtered through a short pad of silica gel, concentrated under reduced pressure, and purified by flash column chromatography. Ratios were then determined by calibrated GC-MS analysis, using mesitylene as an internal standard.[10]

*4′-Chloro-2-methyl-1,1′-biphenyl (2).* 4′-Chloro-2-methyl-1,1′-biphenyl (**2**) was isolated by flash column chromatography (95/5, hexane/EtOAc) as a colorless oil: $\nu_{max}$ 3020 (Ar−H), 1604 (Ar) $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.26 (3H, s, C$H_3$), 7.16−7.28 (6H, m, Ar*H*), 7.35−7.41 (2H, m, Ar*H*); $\delta_C$ ($CDCl_3$, 100 MHz) 20.4 ($CH_3$), 126.0 (CH), 127.6 (CH), 128.3 (CH), 129.7 (CH), 130.5 (CH), 130.6 (CH), 132.9 (C), 135.3 (C), 140.4 (C), 140.7 (C); *m/z* (EI) 204 ([M]$^+$, 31%, $^{37}$Cl), 202 ([M]$^+$, 100%, $^{35}$Cl), 167 (70%, $^{37}$Cl), 165 (58%, $^{35}$Cl), 152 (20%). These data are consistent with those reported previously.[10]

*4′-Trifluoromethanesulfonyloxy-2-methyl-1,1′-biphenyl (3).* 4′-Trifluoromethanesulfonyloxy-2-methyl-1,1′-biphenyl (**3**) was isolated by flash column chromatography (95/5, hexane/EtOAc) as a colorless oil: $\nu_{max}$ 1422 ($SO_2$), 1205 ($SO_2$), 1135 (C−F) $cm^{-1}$; $\delta_H$ ($CDCl_3$, 400 MHz) 2.26 (3H, s, C$H_3$), 7.16−7.35 (6H, m, Ar*H*), 7.37−7.45 (2H, m, Ar*H*); $\delta_C$ ($CDCl_3$, 100 MHz) 20.4 ($CH_3$), 118.8 (C−F, q, $J_{CF}$ 320.7), 121.0 (CH), 126.0 (CH), 128.0 (CH), 129.7 (CH), 130.6 (CH), 131.0 (CH), 135.2 (C), 139.9 (C), 142.4 (C), 148.5 (C); *m/z* (EI) 316 ([M]$^+$, 45%), 183 (100%). These data are consistent with those reported previously.[10]

**Computational Details.** All structures have been optimized with Gaussian 09 Revision A.02[22] in the gas phase using ωB97XD[32] with the basis sets 6-31G(d) and an effective core potential (ECP) for Pd (LANL2DZ[33]). Frequency calculations were performed on the same level of theory and were used to verify the nature of the stationary point as either a transition state or a minimum. Single-point energy corrections were then calculated with Gaussian 09 Revision D.01[22] at the M06L[34] level of theory with the basis set def2-QZVP. The solvent model COSMO-RS[35−38] has been used to describe the solvation influence of THF. The standard state was converted to 1 M in solution (+1.89 kcal/mol).

## ■ ASSOCIATED CONTENT

### Supporting Information

Text, figures, tables, and CIF and xyz files giving details on experimental procedures, spectroscopic and X-ray crystallographic data, computational information and Cartesian coordinates of calculated species, and the full ref 24. This


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material is available free of charge via the Internet at http://pubs.acs.org.

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### Author Contributions

E.L. and I.A.S. performed the calculations. M.A. provided the data for Figures 4 and 5. Except for entry 2 of Table 1 (done by E.L.), F.P. did all remaining experiments. F.S. wrote the manuscript.

### Notes

The authors declare no competing financial interest.

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