Comparison of the catalytic activity for the Suzuki–Miyaura reaction of \((\eta^5\text{-Cp})\text{Pd(IPr)}\text{Cl}\) with \((\eta^3\text{-cinnamyl})\text{Pd(IPr)}\text{(Cl)}\) and \((\eta^3\text{-1-t-Bu-indenyl})\text{Pd(IPr)}\text{(Cl)}\)

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Abstract

Complexes of the type \((\eta^3\text{-allyl})\text{Pd(L)(Cl)}\) and \((\eta^3\text{-indenyl})\text{Pd(L)(Cl)}\) are highly active precatalysts for the Suzuki–Miyaura reaction. Even though allyl and indenyl ligands are similar to cyclopentadienyl (Cp) ligands, there have been no detailed comparative studies exploring the activity of precatalysts of the type \((\eta^5\text{-Cp})\text{Pd(L)(Cl)}\) for Suzuki–Miyaura reactions. Here, we compare the catalytic activity of \((\eta^5\text{-Cp})\text{Pd(IPr)}\text{Cl}\) \(\text{(IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene, Cp)}\) with two commercially available catalysts \((\eta^3\text{-cinnamyl})\text{Pd(IPr)}\text{(Cl)}\) \(\text{(Cin)}\) and \((\eta^3\text{-1-t-Bu-indenyl})\text{Pd(IPr)}\text{(Cl)}\) \(\text{(tBuInd)}\). We show that \(\text{Cp}\) gives slightly better catalytic activity than \(\text{Cin}\), but significantly inferior activity than \(\text{tBuInd}\). This order of activity is rationalized by comparing the rates at which the precatalysts are activated to the monoligated Pd(0) active species along with the tendency of the starting precatalysts to comproportionate with monoligated Pd(0) to form inactive Pd(I) dimers. As part of this work the Cp supported Pd(I) dimer \((\mu\text{-Cp})(\mu\text{-Cl})\text{Pd}_{2}(\text{IPr})_{2}\) \(\text{(CpDim)}\) was synthesized and crystallographically characterized. It does not readily disproportionate to form monoligated Pd(0) and consequently \(\text{CpDim}\) is a poor catalyst for the Suzuki–Miyaura reaction.

Introduction

The Suzuki–Miyaura reaction is a powerful synthetic method for forming C–C bonds between aryl halides or pseudo halides and organoborane containing species [1-5]. The most active catalysts are generally based on Pd and feature strongly electron-donating and sterically bulky phosphate or N-heterocyclic carbene (NHC) ancillary ligands [6,7]. In particular, precatalysts of the type \((\eta^3\text{-allyl})\text{Pd(NHC)(Cl)}\) have shown excellent activity for the Suzuki–Miyaura reaction, with systems incorporating an \(\eta^3\text{-cinnamyl}\) moiety giving the best catalytic results (Figure 1) [8-12]. Recently, we showed that the excellent activity of the cinnamyl system is related to two factors: (i) the rate at which the Pd(II) precatalyst is reduced to the...
active monoligated Pd(0) species; and (ii) the difficulty of comproportionation between L-Pd(0) and the starting precatalyst, which generates a Pd(I) μ-cinnamyl dimer of the form (μ-cinnamyl)(μ-Cl)Pd₂(L)₂, and removes L-Pd(0) from the reaction mixture [13,14]. Furthermore, we used this mechanistic information to design an improved precatalyst scaffold featuring an η₃-indenyl ligand [15]. In particular, precatalysts based on the (η₃-1-t-Bu-indenyl)Pd(L)(Cl) scaffold were highly active because Pd(I) dimer formation was effectively suppressed and the rate of reduction from Pd(II) to Pd(0) was increased [16].

In organometallic chemistry, allyl and indenyl ligands are considered to be closely related to cyclopentadienyl (Cp) ligands [17]. Nevertheless, to the best of our knowledge there are only two reports describing the catalytic activity of complexes of the type (η⁵-Cp)Pd(NHC)(Cl) for the Suzuki–Miyaura coupling, as well as related cross-coupling reactions [18,19]. These preliminary reports indicate that (η⁵-Cp)Pd(NHC)(Cl) precatalysts are highly active. For example, full conversion at room temperature was achieved using simple aryl chlorides as the substrate in Suzuki–Miyaura couplings at relatively low catalyst loadings (1 mol %) [18]. However, despite this impressive activity, a direct comparison of the performance of (η⁵-Cp)Pd(NHC)(Cl) type precatalysts with the related commercially available (η³-allyl)Pd(NHC)(Cl) and (η³-indenyl)Pd(NHC)(Cl) systems under the same reaction conditions has never been performed. Here, we directly assess the activity of (η⁵-Cp)Pd(IPr)(Cl) (IPr = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene, Cp) to the analogous (η³-cinnamyl)Pd(IPr)(Cl) (Cin) and (η³-1-t-Bu-indenyl)Pd(IPr)(Cl) (tBuInd) precatalysts [20]. We show that the performance of Cp fits into our model of precatalyst performance based on the speed at which a scaffold is reduced from Pd(II) to Pd(0) and its tendency to undergo comproportionation.

Results and Discussion

Catalytic comparison of (η⁵-Cp)Pd(IPr)Cl, (η³-cinnamyl)Pd(IPr)Cl and (η³-1-t-Bu-indenyl)Pd(IPr)Cl

The IPr supported precatalyst for the Suzuki–Miyaura reaction Cp was synthesized using a literature method starting from the commercially available Pd(II) dimer (μ-Cl)₂Pd₂(η³-allyl)₂(Scheme 1) [18]. It is notable that in this synthesis dimeric {(IPr)Pd(Cl)}₂(μ-Cl)₂ is prepared as an intermediate, followed by treatment with two equivalents of NaCp to generate the monomer Cp. This synthesis makes rapid ligand screening using the Cp supported scaffold difficult as the Cp group is introduced after the ligand. In contrast, the syntheses of both Cin and tBuInd involve the initial preparation of dimers of the form {(η³-cinnamyl)Pd}₂(μ-Cl)₂ or {(η³-1-t-Bu-indenyl)Pd}₂(μ-Cl)₂, respectively [11,15], which can then be treated with a ligand to generate the ligated precatalyst. Despite repeated attempts we were unable to synthesize a related unligated Cp containing dimer, which could be used for ligand screening [21].

The catalytic activity of Cp for Suzuki–Miyaura reactions with different substrates under both strong (KOr-Bu) and weak (K₂CO₃) base conditions is compared to Cin and tBuInd in Figure 2 and Figure 3. In general, the performance of Cp is slightly better than Cin, but considerably worse than tBuInd. At
Figure 2: Comparison of catalytic performance of Cin, Cp and tBuInd for a series of Suzuki–Miyaura reactions using KOt-Bu as the base. Yields for Cin and tBuInd are from previous literature results [15]. All yields were determined using GC and are the average of two runs.

Understanding the relative activity of (η⁵-Cp)Pd(IPr)Cl (Cp)

In order to understand the relative activity of Cp in comparison to Cin and tBuInd, we measured both the rate at which it is activated to monoligated Pd(0) and its tendency to undergo comproportionation to a Pd(I) dimer. The rate of activation was measured using the same procedure that we have previously used for Cin and tBuInd [16]. Cp was treated with base in the presence of ten equivalents of 1,3-divinyl-1,1,3,3-tetramethyl-disiloxane (dvds) under a variety of conditions which are relevant to the Suzuki–Miyaura coupling and the reaction followed using ¹H NMR spectroscopy (Table 1). The metal containing product of this reaction is the Pd(0) complex (IPr)Pd(dvds) [22]. The rate of formation of (IPr)Pd(dvds) can be used as a model for the rate of Pd(0) formation in catalysis. In all cases Cp is
activated slower than \( \text{tBuInd} \) [16], consistent with its inferior catalytic performance. For example, under the reaction conditions used in Table 1, entry 4, the rate of activation for \( \text{tBuInd} \) is \( 7.6 \pm 0.1 \times 10^{-4} \text{ s}^{-1} \) compared to \( 3.4 \pm 0.1 \times 10^{-4} \text{ s}^{-1} \) for \( \text{Cp} \) [16]. In contrast, \( \text{Cp} \) is generally activated faster than \( \text{Cin} \). The rate of activation for \( \text{Cin} \) under the conditions used in Table 1, entry 3 is \( 4.2 \pm 0.1 \times 10^{-4} \), less than half the rate of that observed for \( \text{Cp} \). The conditions used in Table 1, entry 4 are the most relevant to the catalysis described above, but although in this case it appears that \( \text{Cp} \) is activated faster than \( \text{Cin} \) (\( 3.4 \pm 0.1 \times 10^{-4} \text{ s}^{-1} \) vs \( 1.4 \pm 0.2 \times 10^{-4} \text{ s}^{-1} \)), the relatively large error associated with these numbers makes a firm conclusion difficult.

The mechanism of activation of \( \text{Cp} \) appears to be analogous to that previously described for \( \text{Cin} \) and \( \text{tBuInd} \) as the organic byproducts of \( \text{Cp} \) activation, cyclopentadiene and either acetone (in the case of reactions performed in iPrOH) or formaldehyde (in the case of reaction performed in MeOH), are consistent with the previously reported pathway (Scheme 2) [16]. In this mechanism initial substitution of a Cl\(^-\) ligand in \( \text{Cp} \) by the solvent gives rise to the alkoxide complex A. Subsequently, the \( \eta^5\)-Cp ring can undergo slippage to form complex B, with an \( \eta^1\)-Cp ligand. The \( \eta^1\)-Cp ligand is nucleophilic and can abstract a \( \beta \)-hydrogen from the alkoxide ligand to generate a Pd(0) species with a coordinated cyclopentadiene ligand (C). In this step the formaldehyde or acetone byproduct originating from...
Table 1: Rates of activation of Cp under different conditions in the presence of dvds.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>PhB(OH)(_2) present</th>
<th>Rate of activation (k_{obs} (s^{-1}))b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KOi-Bu</td>
<td>iPrOH-d(_8)(^c)</td>
<td>No</td>
<td>2.8 ± 0.1 × 10(^{-3})</td>
</tr>
<tr>
<td>2</td>
<td>KOi-Bu</td>
<td>MeOH-d(_4)</td>
<td>No</td>
<td>1.1 ± 0.1 × 10(^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>K(_2)CO(_3)</td>
<td>MeOH-d(_4)</td>
<td>No</td>
<td>9.2 ± 0.2 × 10(^{-4})</td>
</tr>
<tr>
<td>4</td>
<td>K(_2)CO(_3)</td>
<td>MeOH-d(_4)</td>
<td>Yes(^a)</td>
<td>3.4 ± 0.1 × 10(^{-4})</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: 0.0087 mmol Cp, 0.087 mmol of base, 0.087 mmol of dvds in 500 μL of solvent. \(^b\)All rates are the average of at least two runs and were measured using \(^1\)H NMR spectroscopy. \(^c\)100 μL of THF-d\(_8\) was added along with only 400 μL of iPrOH. \(^d\)Two equivalents of 18-crown-6 (relative to K\(_2\)CO\(_3\)) were added to solubilize the K\(_2\)CO\(_3\). \(^e\)0.0087 mmol precursor, 0.087 mmol phenylboronic acid, 0.096 mmol base, 0.087 mmol dvds in 500 μL MeOH-d\(_4\).

The considerably faster rate of activation for Cp compared to Cin, suggests that Cp should be a much better precatalyst than Cin, which is inconsistent with our catalytic results (Figure 2 and Figure 3). In our model for precatalyst performance, catalytic activity is also related to the ease at which the starting precatalyst undergoes comproportionation with monoligated Pd(0) to form a Pd(I) dimer \([13]\). The reaction of Cp with a weak base, K\(_2\)CO\(_3\), in an alcohol solvent (MeOH) provided the dimeric complex, (μ-Cp)(μ-Cl)Pd\(_2\)(IPr)\(_2\) (Cp\(_{Dim}\)), in excellent yield (82%, Scheme 3). This is the same procedure we previously described for the preparation of Pd(I) dimers with a bridging chloride ligand and one bridging allyl or indenyl ligand \([13]\).

Cp\(_{Dim}\) was characterized by NMR spectroscopy and X-ray crystallography (see Figure 4). The binding of the bridging Cp ligand is similar to that observed in other Pd(I) dimers supported by a bridging Cp or indenyl ligand \([23-39]\). The two Pd centers are bound to three carbon atoms of the bridging Cp ligand. Two of the three carbon atoms are bound to only one Pd center, while the central carbon atom binds to both Pd centers. Pd–C bond distances of almost 3 Å clearly indicate that there is no interaction between the Pd centers and the other two carbon
atoms of the bridging Cp ligand. Consistent with this pseudo η³-binding, the C–C bond distances relating to two long bonds, two bonds of intermediate length and one short bond in the bridging Cp ligand are similar to those observed in monomeric η³-systems [40]. Strong evidence for a Pd–Pd single bond is provided by the Pd–Pd distance of 2.5669(4) Å [41]. Presumably for steric reasons the NHC ligands are bent away from the bridging Cp ligand and the C–Pd–Pd (C of IPr) bond angles are significantly less than 180° (Pd(1)–Pd(2)–C(7) 164.9(1) and Pd(2)–Pd(1)–C(6) 171.1(1)).

To determine if CpDim is catalytically relevant modified conditions were used to allow for the reaction to be monitored by 1H NMR spectroscopy (Scheme 4). In order to observe the Pd containing species, an increased catalyst loading was used, 4 mol % Cp, compared to the loadings described in Figure 2 and Figure 3. Peaks consistent with the formation of CpDim are observed during catalysis, and approximately 40% of the Pd is in the form of CpDim upon completion of the catalytic reaction. In contrast, for Cin under the same conditions, only a small amount of Pd was determined to be in the form of a Pd(I) dimer [13]. This suggests that Cp is more likely to undergo dimerization than Cin. CpDim was confirmed to be a poor catalyst under the conditions employed in Figure 2 (Scheme 5). This result is indicative of CpDim as an off-cycle deactivation product, which reduces the amount of the active Pd(0) species in solution.

Previously, we have demonstrated that the comproportionation of Pd(0) and Pd(II) species to IPr supported Pd(I) dimers with one bridging allyl and one bridging chloride ligand is reversible [13,14]. One method to measure the rate of disproportionation of Pd(I) dimers is to react these species with a trapping agent for Pd(0), such as dvds. This results in the formation of the Pd(I) species (IPr)Pd(dvds) and a Pd(II) species of the form (η³-allyl)Pd(IPr)(Cl). We examined the tendency of CpDim to undergo disproportionation in the presence of dvds. The disproportionation of CpDim is extremely difficult and at 60 °C the
half-life for the formation of \( \text{Cp} \) and \((\text{IPr})\text{Pd(dvds)}\) is 60 minutes (Scheme 6). In contrast, in the presence of dvds \((\mu\text{-cinnamyl})(\mu\text{-Cl})\text{Pd}_2(\text{IPr})_2\) undergoes full disproportionation in approximately 40 minutes at 40 °C, while for \((\mu\text{-allyl})(\mu\text{-Cl})\text{Pd}_2(\text{IPr})_2\) the reaction is complete in less than 10 minutes at room temperature [13]. Although these results show that disproportionation of \(\text{CpDim}^{\text{Dim}}\) is more difficult than related allyl species, they provide no information on whether this is related to thermodynamic or kinetic effects.

To probe the relative thermodynamic favorability of dimer formation between allyl and \(\text{Cp}\) systems we performed a crossover experiment (Scheme 7a). In this experiment \((\mu\text{-allyl})(\mu\text{-Cl})\text{Pd}_2(\text{IPr})_2\) was mixed with \(\text{Cp}\). The products of crossover are \(\text{CpDim}^{\text{Dim}}\) and \((\eta^3\text{-allyl})\text{Pd(IPr)(Cl)}\) and our experiments indicate that the equilibrium favors these species. The crossover reaction can be described as the combination of the disproportionation of the allyl dimer and the comproportionation of \(\text{Cp}\) with \(\text{IPr-Pd(0)}\) (Scheme 7b). From these results, we conclude that the comproportionation reaction to form \(\text{CpDim}^{\text{Dim}}\) is more exergonic than in the allyl case (\(|\Delta G^{\circ}_{\text{Cpdimerformation}}| > |\Delta G^{\circ}_{\text{allyldimerformation}}|\) in Scheme 7b). The results of this experiment indicate that in part disproportionation of \(\text{CpDim}^{\text{Dim}}\) to form \(\text{Cp}\) and \(\text{L-Pd(0)}\) is more challenging than the corresponding allyl dimer for thermodynamic reasons.

**Conclusion**

We have performed the first detailed comparative investigation of the catalytic activity for the Suzuki–Miyaura reaction of \((\eta^5\text{-Cp})\text{Pd(IPr)(Cl)}\) (\(\text{Cp}\)), with the related commercially available catalysts \((\eta^3\text{-cinnamyl})\text{Pd(IPr)(Cl)}\) (\(\text{Cin}\)) and \((\eta^3\text{-1-t-Bu-indenyl})\text{Pd(IPr)(Cl)}\) (\(\text{tBuInd}\)). We found that \(\text{Cp}\) is a slightly more efficient catalyst than \(\text{Cin}\), but significantly less active than \(\text{tBuInd}\). The low activity of \(\text{Cp}\) in comparison to \(\text{tBuInd}\) is related both to its slower rate of activation to the monoligated Pd(0) active species and its tendency to form a significant amount of the inactive Pd(I) dimer \((\mu\text{-Cp})(\mu\text{-Cl})\text{Pd}_2(\text{IPr})_2\) \((\text{CpDim})\) under catalytic conditions. The formation of this inactive dimer also explains why \(\text{Cp}\) is only a slightly more active precatalyst than \(\text{Cin}\), which activates slower than \(\text{Cp}\), but is less likely to form the corresponding inactive Pd(I) dimer. In principle, the addition of steric bulk to \(\text{Cp}\) could prevent the formation of a Pd(I) dimer and result in a more active precatalyst. However, an additional challenge that must be overcome if

![Scheme 6: Disproportionation of \(\text{CpDim}^{\text{Dim}}\) with dvds.](image)

![Scheme 7: a) Crossover experiment between \(\text{Cp}\) and \((\mu\text{-allyl})(\mu\text{-Cl})\text{Pd}_2(\text{IPr})_2\), b) Crossover experiment expressed as the sum of disproportionation and comproportionation half reactions.](image)
practical precatalyst scaffolds based on a Cp ligand are to be developed is that the synthetic routes to these species are currently not amenable to rapid ligand screening in an analogous fashion to Cin and tBuInd.

Experimental
General methods
As previously described in [13] and [15], experiments were performed under a dinitrogen atmosphere in an M-Braun dry box or using standard Schlenk techniques unless otherwise stated. Under standard glovebox conditions, purging was not performed between uses of pentane, benzene and toluene; thus when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles. Stainless steel cannulas were used to transfer moisture- and air-sensitive liquids on a Schlenk line or in a dry box. THF, diethyl ether, and toluene were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received; exceptions where noted. MeOH (J. T. Baker), and iPrOH (Macron Fine Chemicals) were not dried but were degassed by sparging with dinitrogen for one hour and stored under dinitrogen. Potassium tert-butoxide (99.99%, sublimed) was purchased from Aldrich. Potassium carbonate was purchased from Mallinckrodt and ground up with a mortar and pestle and stored in an oven at 130 °C prior to use. 1,3-Divinyltetramethyltetrasiloxane was purchased from Cambridge Isotope Laboratories. MeOH-d$_4$ and THF-d$_6$ were not dried but were degassed prior to use through three freeze-pump-thaw cycles. Agilent-400, -500 and -600 spectrometers were used to record NMR spectra at ambient probe temperatures. Gas chromatography analyses (GC) were performed on a Shimadzu GC-2010 Plus apparatus equipped with a flame ionization detector and a Shimadzu SHRXI-5MS column (30 m, 250 μm inner diameter, film: 0.25 μm). The following conditions were utilized for GC analyses: flow rate 1.23 mL/min constant flow, column temperature 50 °C (held for 5 min), 20 °C/min increase to 300 °C (held for 5 min), total time 22.5 min. Literature procedures were used to prepare the following compounds: (η$^3$-cinnamyl)Pd(iPr)(Cl) (Cin) [11], (η$^3$-1-t-Bu-indenyl)Pd(iPr)(Cl) (tBuInd) [15], (η$^3$-Cp)Pd(iPr)(Cl) (Cp) [18] (μ-allyl)(μ-Cl)Pd$_2$(iPr)$_2$ [13].

X-ray crystallography
X-ray diffraction experiments were carried out on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα radiation (λ = 1.54178 Å) at −180 °C. The crystals were mounted on MiTeGen polyimide loops with immersion oil. The data frames were processed using Rigaku CrystalClear and corrected for Lorentz and polarization effects. Using Olex2 [42] the structure was solved with the XS [43] structure solution program by Patterson methods and refined with the XL [43] refinement package using least-squares minimization. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model unless otherwise stated.

Synthetic procedures and characterizing data
(μ-Cp)(μ-Cl)Pd$_2$(iPr)$_2$ (CpDim)$^\text{a}$ (η$^5$-Cp)Pd(iPr)(Cl) (Cp) (0.250 g, 0.42 mmol) and K$_2$CO$_3$ (0.116 g, 0.84 mmol) were added to a 100 mL Schlenk flask. Degassed MeOH (30 mL) was added to the flask via cannula. The reaction mixture was stirred at room temperature for 2 hours. The precipitate was filtered in air and washed with water to remove excess salts. The solid was washed with pentane and dried under vacuum to give CpDim as a red solid. Yield: 0.188 g, 82%. X-ray quality crystals were grown from a saturated toluene solution layered with pentane (V(toluene):V(pentane) = 1:2) at −35 °C. $^1$H NMR (CD$_3$OD, 400 MHz) 7.18 (t, J = 7.7 Hz, 4H), 7.11 (d, J = 7.7 Hz, 8H), 6.62 (s, 4H), 4.39 (s, 5H), 3.13 (sept, J = 6.8 Hz, 8H), 1.35 (d, J = 6.9 Hz, 24H), 1.11 (d, J = 6.9 Hz, 24H). $^{13}$C($^1$H) NMR (CD$_3$OD, 100 MHz) 186.5, 146.0, 137.3, 128.9, 123.4, 122.2, 84.3, 28.5, 25.3, 23.1.

Representative procedures for catalytic Suzuki–Miyaura reactions with Cp KOt-Bu conditions
Reactions were performed under dinitrogen in a 1 dram vial containing a flea stir bar and sealed with a septum cap. To the vial was added 950 μL of a MeOH stock solution, containing 0.5263 M aryl chloride, 0.5525 M boronic acid, 0.5789 M KOt-Bu and 0.2632 M naphthalene. The vial was then heated using an aluminum block heater set to 25 °C. After thermal equilibration, the reaction was initiated via the addition of 50 μL of the appropriate precatalyst solution in THF (0.1 M [Pd]). Aliquots (~50–100 μL) were removed at reaction times indicated. The aliquots were purified by filtration through pipet filters containing approximately 1 cm of silica and eluted with 1–1.2 mL of ethyl acetate directly into GC vials. Conversion was determined by comparison of the GC response of the internal naphthalene standard. Biaryl products were initially synthesized using literature procedures [15], identified using NMR spectroscopy by comparison to the literature chemical shifts [11] and then these pure samples used to generate calibration plots for the GC.

K$_2$CO$_3$ conditions
Potassium carbonate (0.75 mmol) was transferred on the benchtop into a 1 dram vial containing a flea stir bar. The vial was sealed with a septum cap, and placed under dinitrogen (by
cycling three times between vacuum and dinitrogen) on a Schlenk line through a needle. To the vial was added 950 μL of a MeOH stock solution, containing 0.5263 M aryl chloride, 0.5525 M boronic acid and 0.2632 M naphthalene. The vial was then heated using an aluminum block heater set to 25 °C. After thermal equilibration, the reaction was initiated via the addition of 50 μL of the appropriate precatalyst solution in THF (0.1 M [Pd]). Aliquots (≈50–100 μL) were removed at reaction times indicated. The aliquots were purified by filtration through pipet filters containing approximately 1 cm of silica and eluted with 1−1.2 mL of ethyl acetate directly into GC vials. Conversion was determined by comparison of the GC responses of product and the internal naphthalene standard. Biaryl products were initially synthesized using literature procedures [15], identified using NMR spectroscopy by comparison to the literature chemical shifts [11] and then these pure samples used to generate calibration plots for the GC.

Experiments on activation of Pd(II) to Pd(0)

Experimental details for Table 1: Rates of activation of Cp under different conditions in the presence of dvds

iPrOH-ď8/KOr-Bu experiments: KOr-Bu (9.8 mg, 0.087 mmol) was dissolved in 300 μL of iPrOH-ď8 along with 100 μL of a 0.87 M solution of dvds in iPrOH-ď8. Cp (5.2 mg, 0.0087 mmol) was dissolved in 100 μL of THF-ď8. These solutions were combined in a J. Young NMR tube at −78 °C. The reaction mixture was degassed on a Schlenk line, after which dinitrogen was introduced into the NMR tube. An array of 1H NMR spectra was taken at 25 °C over the course of 3 hours. During this time, the growth of the methyl protons of the (IPr)Pd(dvds) [22] product were monitored.

MeOH-ď4/KK2C2O5 experiments: K2C2O5 (12.0 mg, 0.087 mmol) and 18-crown-6 ether (46.0 mg, 0.174 mmol) were dissolved in 300 μL of MeOH-ď4 along with 100 μL of a 0.87 M solution of dvds in MeOH-ď4. Cp (5.2 mg, 0.0087 mmol) was dissolved in 100 μL of MeOH-ď4. These solutions were combined in a J. Young NMR tube at −78 °C. The reaction mixture was degassed on a Schlenk line, after which dinitrogen was introduced into the NMR tube. An array of 1H NMR spectra was taken at 25 °C over the course of 3 hours. During this time, the growth of the methyl protons of the (IPr)Pd(dvds) [22] product were monitored.

Catalysis using Cp under NMR conditions: In a glovebox, phenylboronic acid (10.0 mg, 0.082 mmol), 4-chlorotoluene (9.2 μL, 0.0781 mmol), KOr-Bu (9.6 mg, 0.0859 mmol) and 2,6-dimethoxytoluene (6.0 mg, 0.039 mmol) were dissolved in 400 μL of MeOH-ď4. Cp (1.8 mg, 0.0031 mmol) was dissolved in 100 μL of THF-ď8. These solutions were combined in a J. Young NMR tube and the reaction was monitored by 1H NMR spectroscopy for one hour at 25 °C. After this time, the solvent mixture was removed on a Schlenk line and benzene-đ6 was added. A final 1H NMR spectrum was recorded to identify the Pd containing products of the reaction. CpDim was observed as the main Pd containing product, with a yield of 40% compared to the internal standard 2,6-dimethoxytoluene.
Disproportionation of \( \text{Cp}^{\text{Dim}} \) using dvds: In a nitrogen filled glovebox, \( \text{Cp}^{\text{Dim}} \) (5.5 mg, 0.005 mmol), dvds (9.2 mg, 0.05 mmol) and 2,6-dimethoxytoluene (0.8 mg, 0.005 mmol) were added to a vial. MeOH\( \cdot d_4 \) (300 \( \mu \)L) and deuterated benzene (200 \( \mu \)L) were added and the homogeneous mixture was transferred to a J. Young tube and sealed. The contents were heated at 60 °C for one hour, at which time an NMR spectrum was recorded. The methyl protons of the product (IPr)Pd(dvds) [22] were compared to the internal standard. At one hour, the reaction had reached 50% conversion.

Crossover experiment using Cp and (\( \mu \)-allyl)(\( \mu \)-Cl)\( \text{Pd}_2 \)(IPr)\(_2\): In a nitrogen-filled glovebox, (\( \mu \)-allyl)(\( \mu \)-Cl)\( \text{Pd}_2 \)(IPr)\(_2\) (4.0 mg, 0.00375 mmol) and Cp (2.2 mg, 0.00375 mmol) were added to a vial. \( \text{C}_6\text{D}_6 \) (0.5 mL) was added and the solution was transferred to a J. Young tube and sealed. The mixture was heated to 60 °C and allowed to equilibrate over 36 hours. At this time, an NMR spectrum was recorded at room temperature. The equilibrium constant was calculated by using relative integrations of the Cp protons from Cp and \( \text{Cp}^{\text{Dim}} \) to yield a \( K \) of 1.1.

Supporting Information

Supporting Information File 1
1\( H \) NMR spectrum for the \( \text{Ind} \), \( \text{Cp} \) and \( \text{Cp}^{\text{Dim}} \) and crystallographic information for \( \text{Cp}^{\text{Dim}} \).
[http://www.beilstein-journals.org/bjoc/content/ supplementary/1860-5397-11-269-S1.pdf]

Supporting Information File 2
Crystallographic information file for \( \text{Cp}^{\text{Dim}} \).
[http://www.beilstein-journals.org/bjoc/content/ supplementary/1860-5397-11-269-S2.cif]

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References
20. Even though the structure of \( \text{Cp} \) is drawn with an \( \eta^5 \)-Cp ligand, the \( \text{Pd} \)–C bond distances in the crystal structure (see reference [18]) show 3 \( \text{Pd} \)–C bonds which are \( \approx 0.1 \) Å shorter than the other 2 \( \text{Pd} \)–C bonds. Thus, the bonding is probably best described as intermediate between an \( \eta^5 \)- and an \( \eta^3 \)-Cp ligand and the analogy between \( \text{Cp} \) and \( \text{Al} \) and \( \text{IBr}_{\text{Ind}} \), where the allyl and 1-t-Bu-indenyl ligands are unambiguously \( \eta^3 \)-coordinated, is even stronger upon detailed analysis of the \( \text{Cp} \) structure.
21. Most of our attempts to synthesize an unligated \( \text{Cp} \) dimer focused on using a similar synthetic method to that used to prepare (\( \eta^3 \)-cinnamyl)\( \text{Pd}_2 \)(Cl)\(_2\) or (\( \eta^3 \)-1-t-Bu-indenyl)\( \text{Pd}_2 \)(Cl)\(_2\). See references [11] and [15] for more information.

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