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Amination with Pd–NHC Complexes: Rate and Computational Studies on the Effects of the Oxidative Addition Partner

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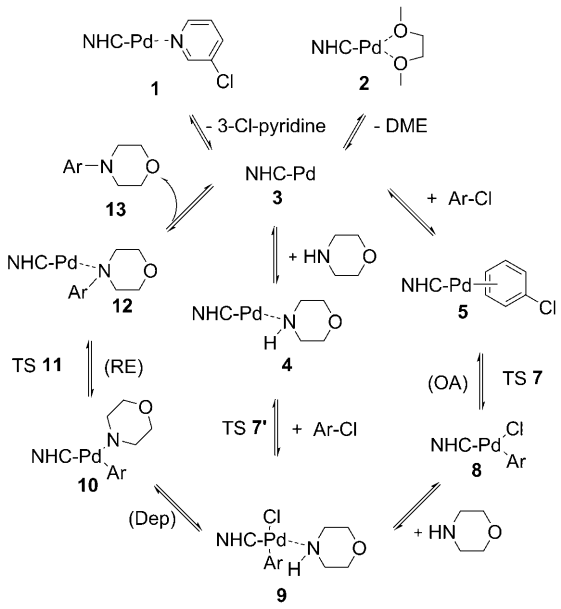
Pd-catalyzed amination has become an important and widely employed method to introduce nitrogen into an organic molecule.[1] By far the most commonly used supporting ligands for this reaction are phosphane based;[2] considerably fewer attempts have been made using N-heterocyclic carbene (NHC)-based ligands.[3] A general mechanism for this transformation,[4] which uses structures that are relevant to this study, is presented in Scheme 1.

The nature of the primary supporting ligand (depicted as an NHC in Scheme 1) plays a crucial role in determining which step in the cycle is rate limiting. NHC–Pd complexes



Scheme 1. The proposed mechanism for the coupling of aryl chlorides with morpholine (OA = oxidative addition, Dep = deprotonation, RE = reductive elimination). Complex **6** (Ar–Cl···Pd–NHC), which is lower in binding energy than **5**, has been omitted for clarity (see Table 1).

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are very adept at undergoing oxidative addition even with unactivated aryl chlorides in light of their comparatively strong σ-donating properties,[5] whereas phosphane-derived catalysts are more sluggish in this respect. By contrast, amine coordination is encouraged by a more electron-poor Pd center, making phosphanes well suited for this step. Recently, we illustrated that the electronic nature of the aryl moiety of the oxidative addition partner impacts the Pd center significantly following that step.[3d] Employing the moderately bulky *N*,*N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene NHC ligand (**17**, Figure 1, *Pd-PEPPSI-IPr*) in mildly basic conditions (e.g., Cs_2CO_3), electron-withdrawing groups (EWGs) led to good levels of conversion, whereas electron-donating groups (EDGs) slowed product formation.[3d] With NHC ligands, this would be consistent with amine-coordination (Scheme 1, **8**→**9**) or deprotonation of the subsequent complex (Scheme 1, **9**→**10**) being rate limiting. Further, KO*t*Bu, a relatively strong base, promoted good levels of amination seemingly irrespective of the electronic structure of the aryl halide.[6] This illustrates that amine coordination and deprotonation are not unrelated events. Under mildly basic conditions, strong amine coordination to the metal is necessary to lower the pK_a of the metal ammonium salt enough to allow deprotonation to take place. While these reaction conditions are strongly preferred by those working in the field, the procedure is only useful with electron-poor aryl halides, such as aryl rings decorated with EWGs or heterocycles.[7]

Here we have systematically evaluated the effects of steric and electronic properties of NHC ligands on catalyst performance and we believe that we have found a link between NHC bulk around the metal and the charge state of the metal. With the aid of spectroscopy and calculation, we have preliminary data to suggest that increasing the bulk around the coordination sphere of Pd leads to an increase in the positive charge on the metal.[8,9] Following this trend, we have further enhanced NHC bulk with the creation of *Pd-PEPPSI-IPent* (**18**, Figure 1)[10] and investigated this effect on amination reactions employing rate studies and computation; the results are detailed below.

Rate studies: To evaluate the above hypothesis, a rate study was conducted (Figure 1) on the amination of morpholine[3d,11,12] with a range of electron-poor to electron-rich aryl chlorides using complexes **17** and **18**. Clearly, the bulkier *IPent* catalyst **18** significantly outperforms *IPr* catalyst **17**.

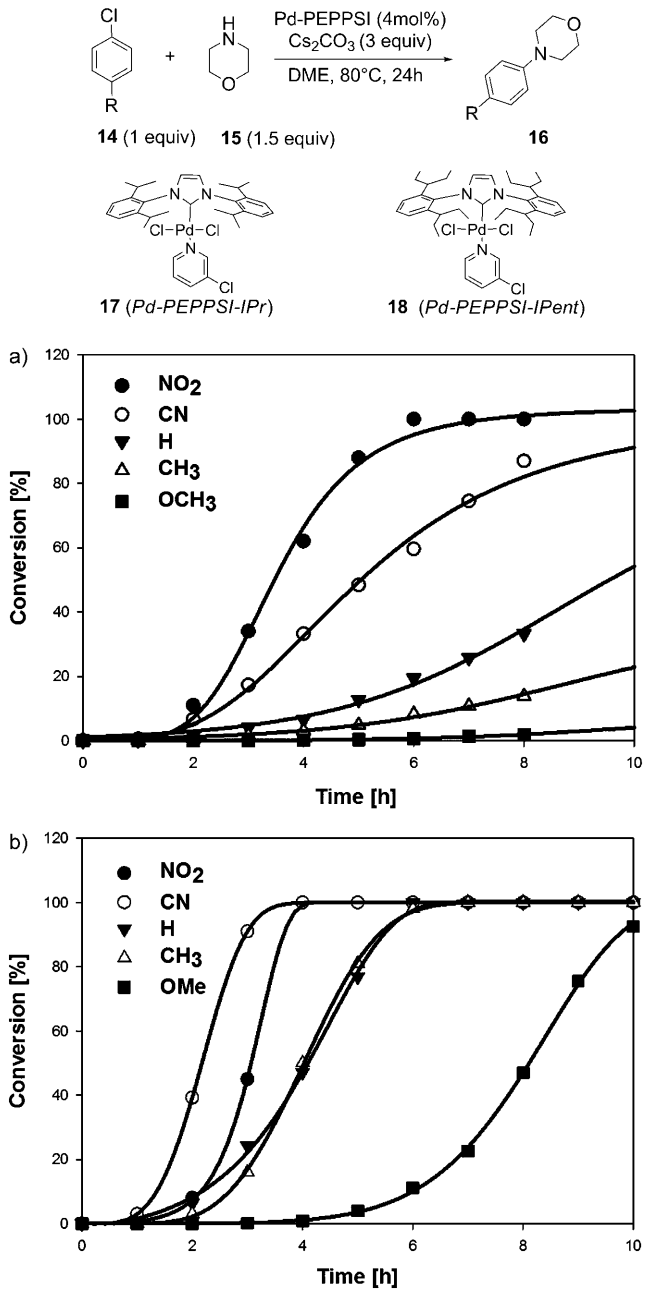


Figure 1. Substituent effects on the reaction of morpholine with *para*-substituted aryl chlorides as catalysed by *Pd-PEPPSI-IPr* (**17**) and *Pd-PEPPSI-IPent* (**18**). a) Rate study of test reaction using **17**. b) Rate study of test reaction using **18**. The final [**14**] is 1.0 mmol mL^{-1}.

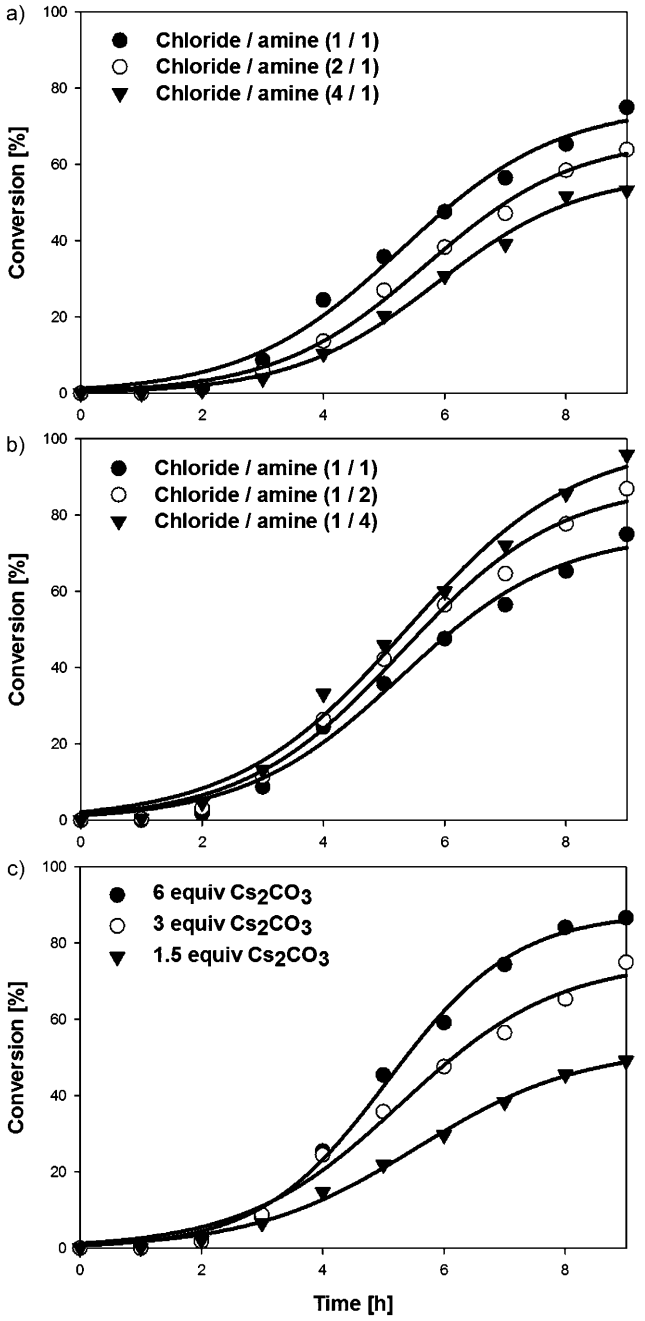


Figure 2. Effect of concentration of *p*NC-Ar-Cl, morpholine, and base on amination using catalyst **17**. a) Varying [*p*NC-Ar-Cl] ([**14b**] = 1.0, 2.0, and 4.0 mmol mL^{-1}, respectively); 3.0 equiv of Cs_2CO_3. b) Varying [morpholine]; 3.0 equiv of Cs_2CO_3. c) Varying [Cs_2CO_3]; 1.0 equiv of **14b**, 1.5 equiv of **15**. The final [**14b**] in runs b) and c) is 1.0 mmol mL^{-1}.

We knew that **17** readily oxidatively adds all five aryl chlorides used in this study from analogous Suzuki–Miyaura reactions that we had performed, supporting the notion that oxidative addition is not rate limiting (or at least not problematic).[3d]

To learn something about the order of the reactants and base, we conducted three additional studies keeping the catalyst fixed (**17**) while varying separately the concentrations of **14**, **15**, and Cs_2CO_3 (Figure 2).[12] Analysis was difficult as all reactions involving morpholine (and other alkyl amines) and the *PEPPSI* catalysts produced sigmoidal curves indicating that catalyst activation has an induction period. As a consequence, we looked at maximum rates, rather than initial rates, in a qualitative sense to spot trends. Surprisingly, the rate of the reaction decreases slightly with an increase in the concentration of the aryl chloride (Figure 2a), which further supports the idea that oxidative addition (i.e., Scheme 1, **5**→**8**) is not rate limiting. When the concentration

of morpholine was increased (Figure 2b), the maximum rate increased slightly (doubling morpholine concentration increased the maximum rate approx. 20%), but not sufficiently to claim that amine coordination (i.e., Scheme 1, **8**→**9**) by itself is rate limiting. However, increasing the amount of Cs_2CO_3 (Figure 2c), had a much more significant impact on the rate as we did see an approximate doubling of the rate when we doubled the amount of base present. This would support the notion that deprotonation (i.e., Scheme 1, **9**→**10**) is involved in the critical step. We have conducted solubility studies and found that essentially no Cs_2CO_3 dissolves in DME at 80°C; thus we believe that the deprotonation occurs at the surface of the heterogeneous base. This is consistent with results reported by Maes and co-workers who saw significant differences in yield when even different sources of the same reported quality Cs_2CO_3 were used in amination studies;[7a] presumably this points to differences in particle size and surface area. Nonetheless, the result suggests that the rate is heavily influenced by the amount of the base (i.e., deprotonation). To assess this, the reaction in Figure 2 using **17** was repeated with two variations: 1.5 equiv of KO*t*Bu were used (instead of 3.0 equiv Cs_2CO_3) and the reaction was performed at room temperature (instead of at 80°C); the reaction completed after just 15 s!

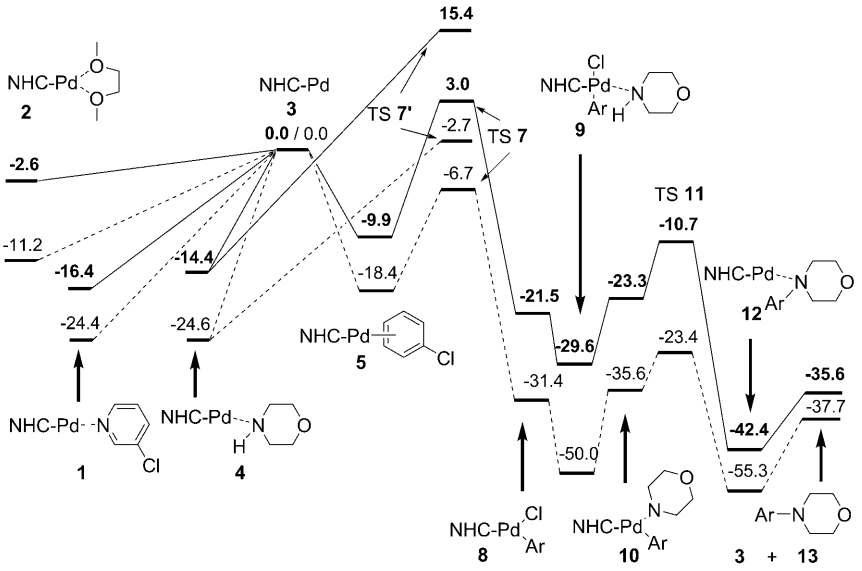


Figure 3. The potential energy surface for the coupling of chlorobenzene with morpholine using the *Pd-PEPPSI-IPr* (**17**) catalyst. Two sets of energies (kcal mol^{-1}) relative to NHC–Pd (**3**) are provided: bold face numbers are free energies at 80°C (solid line) and the lower set of numbers are enthalpies (dashed line).

Computational study: Density functional (B3LYP/LANL2TZ(f),6-31G*) calculations were used to examine important segments of the potential energy surface for the aminations reported above.[13] Computationally, it is difficult to study the deprotonation step and we have chosen to examine it qualitatively by the addition of KO*t*Bu and the corresponding elimination of KCl + HO*t*Bu. This provides a relative measure of the susceptibility to deprotonation for different catalyst/aryl chloride combinations.

Figure 3 depicts the potential energy surface (enthalpy and free energy at 80°C) for the *Pd-PEPPSI-IPr* (**17**)-catalyzed coupling of chlorobenzene and morpholine (the same was done for **18**, not shown, see Table 1 for values). One can consider the reaction in five steps: activation (not considered here), oxidative addition, amine adduct formation, deprotonation, and reductive elimination with the latter four repeated for catalysis. Introduction of the reduced precatalyst (**1**) into the catalytic cycle requires the dissociation of 3-Cl-pyridine, which binds more strongly to Pd than DME or the aryl chloride. However, the binding of morpholine is comparable to that of 3-Cl-pyridine, and given its much greater concentration, one would expect this complex (**4**) to be the resting state of the catalytic cycle, once activation is achieved. The activation process is complicated as there are other steps than those shown here, but the minimal 19.4 kcal mol^{-1} barrier (free energy from **1**→**TS-7**) could slow down activation. For the bare Pd^0Ln species (**3**) present during catalysis, morpholine binds by 14.4 kcal mol^{-1} and the pre-equilibrium relating the dissociation of morpholine and binding of chlorobenzene is endoergonic by 4.5 kcal mol^{-1} (**4**→**5**). This leads to an overall free energy barrier for oxidative addition (**4**→**7**) of 17.4 kcal mol^{-1}. Due to the strong binding of morpholine, we examined whether oxidative addition could occur with a bound amine. Transition states were located for this process (**4**→**TS-7′**→**9**) and the relative enthalpies are collected in Table 1. The enthalpy of **TS-7** is always lower than **TS-7′** and these values do not include the additional entropy associated with the binding of morpholine that will raise the free energy of **TS-7′** significantly. We conclude that the morpholine complex (**4**) is the likely resting state, but it must dissociate before oxidative addition can occur. Similarly, the reductive elimination step (**10**→**TS-11**→**12**→**3**+**13** via) has a barrier of 12.6 kcal mol^{-1}. Both these free energy barriers are low enough to be fast reactions and not reflective of a rate-limiting step that takes on the order of hours.

Everything taken together, deprotonation would seem to be the key step in the catalytic cycle and this was anticipated based on Figure 2 where the [Cs_2CO_3] was shown to be important in the rate-limiting step. Thus with poor deprotonating agents (due to pK_a or solubility), deprotonation becomes the rate-limiting step, while with stronger deprotonating agents, the rate-limiting step is calculated to be oxidative addition, which has a higher barrier than reductive elimina-

Table 1. DFT enthalpies (kcal mol^{-1}) relative to compound **3**, Pd^{0}Ln. See Scheme 1 and Figure 1 for the structures.

	Pd-PEPPSI-IPr (**17**)				
Ar–X	NO_2	CN	H	CH_3	OCH_3
1			−24.4		
2			−11.2		
3			0.0		
4			−24.6		
5[1]	−21.5	−20.4	−18.4	−18.0	−18.6
6[1]	−12.5	−12.4	−11.9	−12.4	−11.9
TS-7	−10.3	−9.6	−6.7	−6.4	−6.2
TS-7′	−9.0	−7.5	−2.7	−2.4	−2.0
8	−34.8	−34.3	−31.4	−31.1	−30.8
9	−53.9	−53.4	−50.0	−49.7	−50.2
10	−40.4	−39.6	−35.6	−35.0	−34.9
TS-11	−30.0	−28.6	−23.4	−22.7	−21.8
12	−57.8	−57.0	−55.3	−54.6	−54.4
13	−41.2	−40.4	−37.7	−37.4	−36.8
OA[2]	14.3	15.0	17.9	18.2	18.4
Dep[2]	−5.6	−5.3	−4.1	−3.9	−4.1
RE[2]	10.4	11.0	12.2	12.4	13.0
	Pd-PEPPSI-IPent (**18**)				
Ar–X	NO_2	CN	H	CH_3	OCH_3
1			−24.4		
2			−16.0		
3			0.0		
4			−23.9		
5[a]	−22.0	−20.9	−18.9	−17.5	−18.6
6[a]	−10.9	−10.7	−11.9	−11.7	−11.2
TS-7	−10.4	−9.7	−6.7	−6.4	−6.2
TS-7′	−8.4	−7.0	−2.2	−1.9	−1.5
8	−32.2	−31.7	−28.4	−28.0	−27.8
9	−53.1	−52.4	−49.2	−48.8	−48.9
10	−39.4	−38.7	−34.6	−34.7	−33.9
TS-11	−30.1	−28.7	−23.4	−22.6	−22.1
12	−58.0	−57.2	−55.1	−55.0	−54.8
13	−41.2	−40.4	−37.7	−37.4	−36.8
OA[b]	13.5	14.2	17.2	17.5	17.7
Dep[b]	−7.2	−7.0	−6.2	−6.7	−6.1
RE[b]	9.3	10.0	11.2	12.0	11.8

[a] Two different binding modes of the aryl chloride were found through the aromatic ring (**5**) and the chloride (**6**) with the former being lower in energy and only discussed in the figures and text. [b] **OA**: oxidative addition barrier from **4**→**7. Dep**: morpholine binding and deprotonation step from **8**→**10**; **RE**: reductive elimination barrier from **10**→**11**.

tion. However, both oxidative addition and reductive elimination have barriers that reflect reactions that should be complete very quickly; this is exactly what was seen with KO*t*Bu (vide supra) where the reaction completes within a matter of seconds.

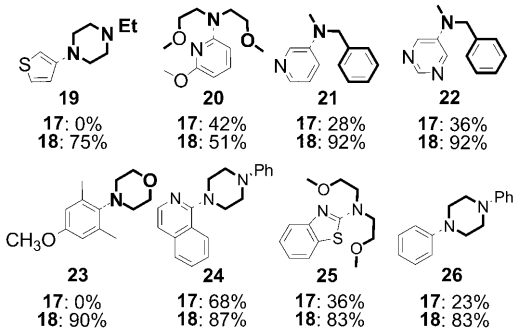
If deprotonation is rate-limiting, one can evaluate deprotonation based on the thermodynamics of the process leading from **8**→**10**. Since this step is slow, we assume the amine binding is reversible and the energy of this binding plays a role in its ability to be deprotonated. For this reason, we chose to consider **8**→**10** rather than **9**→**10**. The values for different aryl chlorides and the two catalysts are collected in Table 1. An interesting trend emerges: the reactions have higher exothermicities for *Pd-PEPPSI-IPent* compared with *Pd-PEPPSI-IPr*, which is consistent with the former having a faster rate of deprotonation, thus being a more active catalyst. In fact, if one assesses the relative rates of the *Pd-PEPPSI-IPr* catalysts based on experiments, the reactivities of aryl chlorides are $NO_2 > CN > H > CH_3 > OCH_3$ (Figure 1 a), whereas the computed deprotonation energies are −5.6, −5.3, −4.2, −3.9, −4.1 kcal mol^{-1}, respectively, in good agreement. Only the *Pd-PEPPSI-IPr* catalyzed NO_2-Ph-Cl has a reaction rate comparable to the slowest *Pd-PEPPSI-IPent* reaction suggesting that the deprotonation for *Pd-PEPPSI-IPent* for all substrates is at least as exothermic as this −5.6 kcal mol^{-1} value. Indeed, the deprotonation enthalpies with *Pd-PEPPSI-IPent* are between −7.2 kcal mol^{-1} and −6.1 kcal mol^{-1}.

While oxidative addition and reductive elimination appear not to be slow steps in these couplings, one can still look at the trends associated with para substitution of the aryl chloride as well as differences between the two catalysts. For oxidative addition, strongly electron-withdrawing groups on the aryl chloride lead to reduced barriers. In all cases, the *Pd-PEPPSI-IPent* has lower barriers for oxidative addition than *Pd-PEPPSI-IPr* by 0.7–0.8 kcal mol^{-1}. Relative to **3**, the corresponding sets of transition states (TS-**7**) for the two catalysts are almost eqi-energetic, thus the lower barriers for *Pd-PEPPSI-IPent* result from a 0.7 kcal mol^{-1} weaker binding of morpholine to this catalyst. That is, the *IPr* catalyst, which coordinates morpholine more tightly than does *IPent*, has a higher barrier from **4**. However, the overall oxidative energies are not in-line with the experimental data, which is consistent with this step not being rate-limiting in the overall coupling. The reductive elimination barriers are also reduced when strongly electron-withdrawing groups reside in the *para*-position of the aryl partner. For example for *Pd-PEPPSI-IPr*, these barriers are NO_2 (10.4) < CN (11.0) < H (12.2) < CH_3 (12.3) < OCH_3 (13.1). These results are consistent with previous work, where faster reductive elimination rates were observed when the aryl chloride partner had electron-withdrawing groups (note that the opposite trend was observed for para substitution of the amine partner, in aniline).[14] Once again, the reductive elimination step is slightly favored (0.4–1.2 kcal mol^{-1}) with the *Pd-PEPPSI-IPent* catalyst, possibly due to a reduction in the steric interactions of the more bulky *IPent* ligands.

Interestingly, while morpholine binds more tightly to *IPr* **3** than to *IPent* **3** (ca. 0.7 kcal mol^{-1}), which are both Pd^0 leading to resting state **4**, *IPent* **8** binds morpholine considerably more tightly (ca. 2 kcal mol^{-1}) than does *IPr* **8** (both now Pd^{II}). This much stronger binding occurs despite greatly increased hindrance; increased positive charge on the Pd of *IPent*, relative to *IPr*, could account for this as we have suggested (vide supra). This supports our contention that deprotonation is indeed rate limiting; this heightened coordination to Pd^{II} will assist in lowering the pK_a of the resultant metal ammonium salt to allow the weak base carbonate to deprotonate it. Thus, if we treat amine coordination and deprotonation as a single step, as we have needed to for the computational treatment, we can say that the transition state is quite late implying that coordination of alkyl amines to Pd must be tight and therefore significantly advanced

along the reaction coordinate in order for deprotonation to become possible.

Substrate study using *Pd-PEPPSI-IPr* and *Pd-PEPPSI-IPent*: By using the optimized conditions in the rate studies, a variety of especially challenging couplings of aryl halides to secondary amines was examined. For demonstration purposes, both **17** and **18** were used and the bulkier *IPent*-based catalyst consistently outperformed the less hindered (and believed to be more electron-rich) *IPr* system (Scheme 2).



Scheme 2. Sample challenging animation reactions using *Pd-PEPPSI-IPent* (**18**). All reactions were performed in duplicate using the reaction conditions outlined in Figure 2 and compared with *Pd-PEPPSI-IPr* (**17**). Reactions performed using $PdCl_2$ as a control showed no conversion to product.

In summary, *Pd-PEPPSI-IPent* (**18**)[15] is an incredibly reactive catalyst for the coupling of electronically-deactivated (i.e., electron-rich) and sterically hindered aryl chlorides to a wide array of secondary, hindered amines under very mild conditions. Rate studies have shown that *Pd-PEPPSI-IPr* (**17**) has a very strong dependence on the electron-withdrawing ability of the aryl chloride while **18** is more insensitive. Computational studies have shown that the difference in catalyst performance is closely associated with amine-coordination/deprotonation; thus, we conclude it to be the rate-limiting step. While the electron-rich Pd^0 complex **3** binds the amine more tightly as the *IPr* derivative, the *IPent* complex **8**, now electron-poor (i.e., Pd^{II}), binds the amine much more strongly than the *IPr* analogue of **8**. Both of these factors work in concert to make the *IPent* catalyst more reactive; IPent is less stable in resting state **4**, thus pushing it into the catalytic cycle, while stronger amine coordination in structure *IPent* **9** during deprotonation decreases the pK_a of the metal ammonium salt complex and lowers the barrier to this rate-limiting step.

Acknowledgements

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Keywords: amination · carbene ligands · catalysis · computational chemistry · kinetics · palladium

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[11] To ensure that there is no unique effect coming from morpholine in these studies, the reaction rates were studied by using piperidine as the amine with 4-chlorotoluene and the rates were essentially superimposable in the otherwise identical reaction with morpholine.

[12] All details of the amination reactions and rate studies are provided in the Supporting Information.

[13] All energies discussed in the text are free energies at 80 °C. Details of the computations and further energetic and structural information are provided in the Supporting Information.

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[15] *Pd-PEPPSI-IPent* is now commercially available through Sigma–Aldrich (Catalogue Number 732117).

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