ORGANOMETALLICS
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New Bidentate *Trans*-Chelating N-Heterocyclic Carbene Ligands for Palladium

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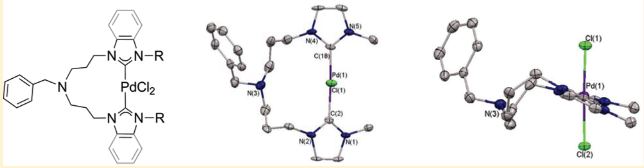
S *Supporting Information*

ABSTRACT:



A family of imidazolium salts of the type $[BnN(CH_2CH_2CH_2{}^{R}Im)_2]\cdot 2[Cl]$ (Bn = CH_2Ph; ^{R}Im = 1-methylimidazole (**1a**), 1-*tert*-butylimidazole (**1b**), 1-benzylimidazole (**1c**), 1-methylbenzimidazole (**1d**)), which contain a tertiary amine linking two imidazolium groups, has been synthesized. These imidazolium salts can be deprotonated with Ag_2O to generate the Ag carbene complexes $[\{BnN(CH_2CH_2CH_2{}^{R}Im)_2\}Ag]\cdot[AgCl_2]$ (^{R}Im = 1-methylimidazole (**2a**), 1-*tert*-butylimidazole (**2b**), 1-benzylimidazole (**2c**), 1-methylbenzimidazole (**2d**)). In the solid state **2d** exists as an unusual tetramer, which consists of an $[Ag_2Cl_4]^{2-}$ core bridging two Ag(NHC) cations. Subsequent reaction of the Ag complexes with $PdCl_2(MeCN)_2$ generates Pd species of the type $\{BnN(CH_2CH_2CH_2{}^{R}Im)_2\}PdCl_2$ (^{R}Im = 1-methylimidazole (**3a**), 1-*tert*-butylimidazole (**3b**), 1-benzylimidazole (**3c**), 1-methylbenzimidazole (**3d**)), which is a rare example of a family of Pd complexes that contain a bidentate *trans*-chelating N-heterocyclic carbene ligand. Compounds **3a** and **3c** were crystallographically characterized by X-ray crystallography and contain unusual 12-membered metallacycles. DFT calculations suggest that the preference for *trans* binding of the ligand is related to conformational effects of the linker. Compound **3b** reacts with excess MeI to form $\{BnN(CH_2CH_2CH_2{}^{tBu}Im)_2\}PdI_2$ (**5b**), a reaction in which we believe a Pd(IV) intermediate is generated. Compound **5b** was crystallographically characterized. Compounds **3a**−**d** are all active catalysts for the Heck reaction, and **3a** can also catalyze the Suzuki reaction.

INTRODUCTION

The isolation and crystallographic characterization of thermally stable N-heterocyclic carbenes (NHCs) by Arduengo et al.[1] initiated a considerable amount of research into the organometallic chemistry of these versatile ligands.[2−4] Since this discovery, a wide range of different NHC ligands have been prepared, including systems which incorporate NHCs in chelate and pincer scaffolds.[5−7] It has been shown that these ligands coordinate to most transition metals and can be utilized in a number of important catalytic reactions, particularly using Pd.[3−5,7] Surprisingly, given the plethora of research into bidentate chelating NHC ligands for Pd,[7] only a handful are known to coordinate in a *trans* fashion (NHC−M−NHC close to 180°).[8−18] Selected examples are shown in Figure 1. The first example (**i**) was described in 2000 by RajanBabu et al. and contains two dinapthyl groups.[8] This ligand readily coordinated to Pd but gave a mixture containing the carbene coordinated in both a *cis* and *trans* fashion; a problem which has been observed in other systems.[13,19] Although Baker and co-workers were able to separate the *cis* and *trans* isomers of a Pd complex supported by their *o*-xylyl-lined carbene (**ii**) on the basis of solubility, in most cases separation of *cis* and *trans* isomers has not been achieved.[19] Another problem in the preparation of *trans*-spanning bidentate NHC complexes was first encountered by Danopoulos and co-workers, who found that their ligand (**iii**) formed a mixture of inseparable monomeric, dimeric, and oligomeric Pd species upon metalation.[11] Recently, Burgess et al. successfully prepared a family of *trans*-spanning bidentate NHC ligands (**iv**), which feature a diamide linker.[9] This was one of the first families of *trans*-spanning bidentate NHC ligands, and Pd complexes supported by these ligands were able to catalyze the Heck reaction, albeit with low activity. In general, it appears that although there are many examples of tridentate pincer ligands coordinated to Pd, which feature *trans* carbenes,[20−29] it is difficult to synthesize *trans*-chelating bidentate NHC ligands. Furthermore, the electronic or steric properties of the ligand cannot be easily varied.

Received: September 15, 2010
Published: March 18, 2011

dx.doi.org/10.1021/om100890q | *Organometallics* 2011, 30, 1818–1829

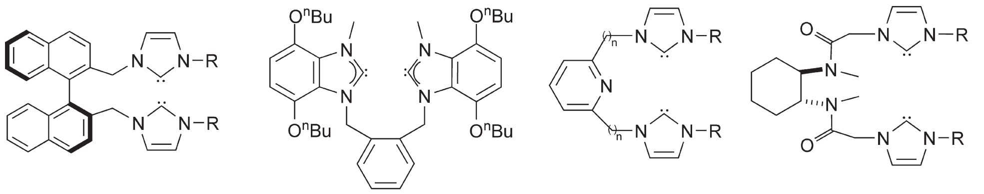

i ii iii (n= 1 or 2) iv

Figure 1. Previously synthesized bidentate *trans*-spanning NHC ligands.

Given that bidentate *trans*-chelating phosphines have been known since the 1970s and have found applications in many catalytic reactions of Pd,[30] our aim was to synthesize a series of easily accessible bidentate NHC ligands which coordinate to Pd in a *trans* fashion. Here, we build on pioneering work by Douthwaite and co-workers exploring flexible bis-NHC-amido ligands[14,31] to synthesize a family of new bidentate *trans*-chelating NHC ligands which contain a flexible linker incorporating a tertiary amine. The ligands readily bind to Pd(II) to form complexes which feature an unusual 12-membered palladacycle and are active catalysts for the Heck and Suzuki reactions.

RESULTS AND DISCUSSION

Ligand Synthesis and Metalation. Recently Douthwaite and co-workers synthesized a family of bis-NHC-amine (**v**) and bis NHC-amido ligands (**vi**) and showed that they coordinate to Pd(II) (Figure 2).[14,31] In almost all cases the amine or amido ligand was bound to Pd to form a tridentate pincer type ligand, except for one crystallographically confirmed example with a sterically bulky amine substituent and one example with a bulky substituent on the imidazole, which was not crystallographically characterized.[14] We postulated that by increasing the chain length of the linker from two carbons to three carbons and by utilizing a sterically bulky substituent on the amine, it would be possible to shut down coordination of the amine and generate a rare family of *trans*-chelating NHC ligands (**vii**) with easily varied properties (Figure 2).

Our synthesis of the new family of ligands is straightforward and high-yielding (Scheme 1). The synthesis allows for easy modification of the substituent on the imidazole ring, which we have demonstrated, and in principle it should also be possible to change the substituent on the central amine. Starting from commercially available benzylamine and ethyl acrylate, we performed a Michael addition to give the known ester (**a**). Reduction of the ester with $LiAlH_4$ generated the bis(alcohol) (**b**), which was converted into the bis(chloride) (**c**) using $SOCl_2$. The key step in the synthesis was an S_N2 reaction between the bis(chloride) (**c**) and a substituted imidazole to generate the imidazolium ligand precursors **1a**−**d**. Interestingly, in our system this reaction was significantly slower than in Douthwaite's system with a two-carbon linker, and it was critical to perform the reaction at high concentration.[14] The imidazolium salts **1a**−**d** were deprotonated using Ag_2O to generate the Ag carbenes **2a**−**d**. These species were characterized by ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. The ^1H NMR spectrum is consistent with C_s symmetry or an exchange process which equilibrates the methylene protons in the two $NCH_2CH_2CH_2N$ groups so that only three resonances are observed. The exchange process could involve inversion of the amine nitrogen and interconversion of conformations by twisting about C−C and C−N bonds, or even intermolecular exchange between the NHC−Ag groups. In all cases the benzylic protons on the central amine appear as a singlet.

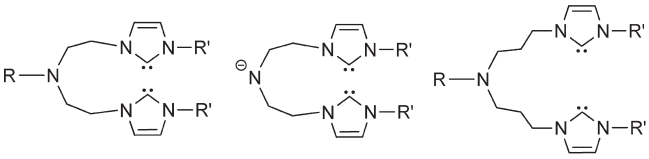

v vi vii

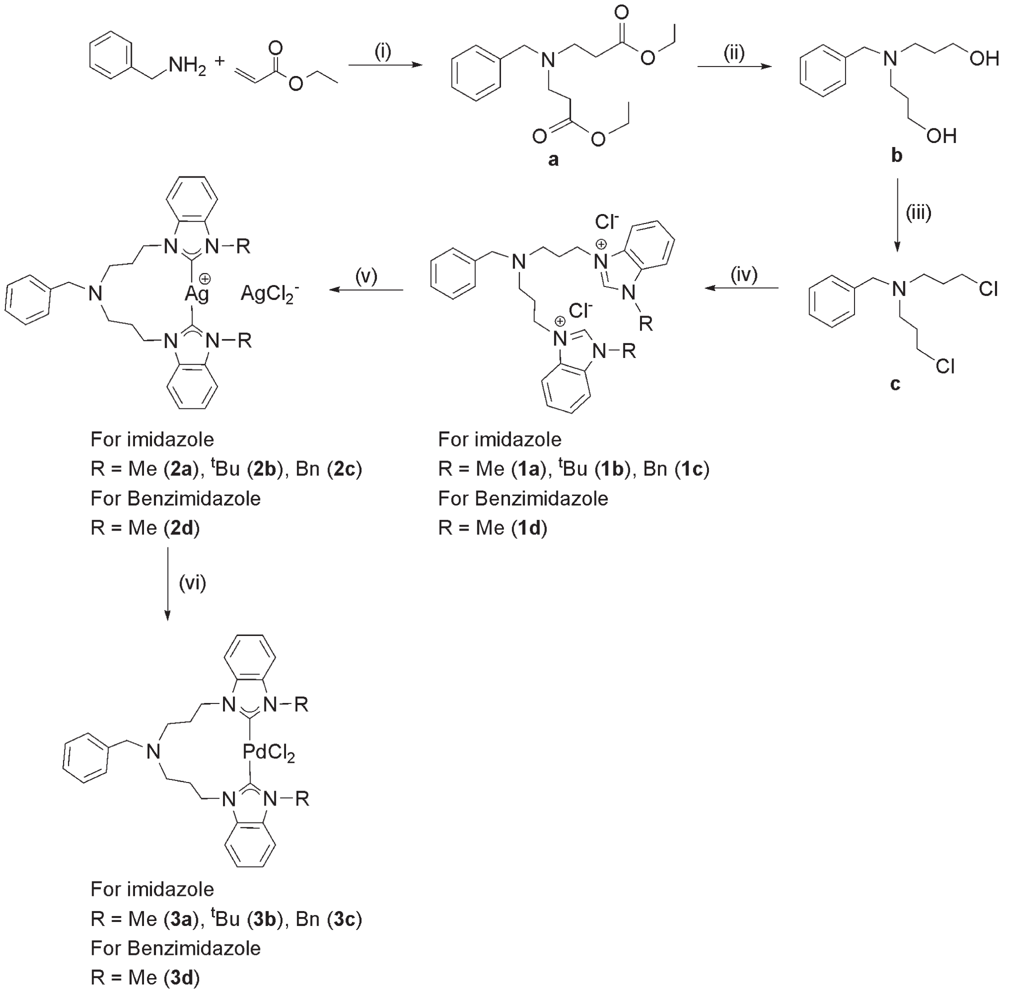
Figure 2. Douthwaite's bis-NHC-amine (**v**) and bis-NHC-amido (**vi**) and our target *trans*-chelating NHC ligands (**vii**).

It has previously been observed that silver carbenes can adopt a variety of different binding modes in the solid state.[17,32] Single crystals of **2d** were grown from a saturated solution of dichloromethane at room temperature, and the structure is shown in Figure 3. In the solid state **2d** exists as an unusual tetramer, which consists of an $[Ag_2Cl_4]^{2-}$ core bridging between two Ag(NHC) cations. There is a short Ag−Ag distance (2.9968(11) Å) between the silver atoms of the cation and anion, which is consistent with a weak interaction. In contrast, the Ag−Ag distance in the anionic core is 3.5706(8) Å, which is longer than the sum of the van der Waals radii of two silver atoms (3.44 Å).[33] Although this tetrameric Ag moiety has been observed in several Ag(NHC) complexes with Br or I as the halide,[17,32,34−39] to the best of our knowledge it is only the second example with Cl as the halide[34] and the first containing a bidentate ligand. The carbene ligand binds to the Ag with a *trans* geometry (C(1)−Ag(1)−C(29) = 162.52(15)°), and there is no binding from the central amine unit. The Ag−C distances of 2.055(3) and 2.057(4) Å are consistent with those observed in other silver carbenes.

Reaction between **2a**−**d** and $[PdCl_2(MeCN)_2]$ resulted in clean transmetalation of the carbene and generated the novel Pd complexes **3a**−**d**, with a *trans*-chelating NHC ligand. The relatively high yields observed for carbene transmetalation suggest that, in contrast to other systems, oligomerization is not a significant problem.[11,14] This may be related to the metalations being performed at low concentration. Furthermore, only one isomer is formed, whereas other systems give a mixture of *cis* and *trans* species or mono- and binuclear complexes.[11,13] The ^1H NMR spectra of **3a**−**d** suggest that the complexes possess C_s symmetry in solution or are undergoing exchange processes similar to those for the Ag species **2a**−**d**, as even at low temperature only three resonances were observed for the twelve $NCH_2CH_2CH_2N$ protons.

The X-ray structures of **3a** and **3c** were determined (Figures 4 and 5, respectively) and unequivocally confirm *trans* chelation of the bis-NHC ligand with no coordination from the central amine (Pd−N distances are approximately 4.35 Å in **3a** and 3.90 Å in **3c**). The C(2)−Pd(1)−C(18) bond angle in **3a** is 177.01(13)°, while the corresponding angles in **3c** are 174.9(2) and 177.1(2)°

Scheme 1[a]



[a] Legend: (i) MeOH, room temperature, 5 days, 99%; (ii) $LiAlH_4$, THF, 0 °C, 24 h, 85%; (iii) $SOCl_2$, CH_2Cl_2, room temperature, 1 h, 92%; (iv) imidazole, dioxane, 65 °C, 3−24 h, 82−94%; (v) Ag_2O, CH_2Cl_2, room temperature, 24 h, 70−98%; (vi) $PdCl_2(MeCN)_2$, CH_2Cl_2, room temperature, 3 h, 82−96%.

(two independent molecules are present in the unit cell). These are some of the largest bite angles reported for Pd complexes with *trans*-spanning ligands.[30] The complexes feature an unprecedented 12-membered palladacycle and the expected square-planar geometry around Pd. The bond lengths and distances are unexceptional, and the carbene ligands are oriented approximately perpendicular to the coordination plane, which is consistent with the structure of other *trans*-spanning bis-NHC ligands.[10,12,14] Both structures possess C_1 symmetry because the benzyl group is canted toward one of the propyl arms, but a fluxional process similar to those mentioned above presumably gives rise to the C_s-symmetric NMR spectra. Interestingly, in the structure of **3c** two different orientations of the amine nitrogen benzyl group are observed (as drawn in parts a and b of Figure 5, this corresponds to the amine nitrogen benzyl group pointing into or out of the page), whereas in the structure of **3a** only one orientation is present. This suggests that the flexible linker is able to support several different conformations, while the carbene ligands remain coordinated. In the structure of **3c** the central amine is below the Pd−NHC coordination plane and the benzyl group on the amine is directed above the plane. The benzyl substituents on the imidazole rings are also directed above the Pd−NHC coordination plane, and as a result all three benzyl groups are pointing in the same direction.

In order to further understand the factors that cause the *trans* isomer to be preferred, we performed density functional theory (DFT) calculations. Initially we looked at the model systems *cis*- and *trans*-$(NHC)_2PdCl_2$ (**viii**−**xi**), which contain two carbenes which are not linked (Figure 6). In all cases the *trans* isomer is lower in energy than the *cis* isomer, but the difference in energy is surprisingly small and does not even rise significantly as the steric bulk on the ligand is increased (Table 1). However, as the steric bulk of the NHC ligand increases, the five-membered imidazole ring tilts out of the coordination plane of Pd. This is shown for the *trans* isomers of **viii**−**xi** in Figure 7 (and in the Supporting Information for the corresponding *cis* isomers of **viii**−**xi**). In the case of both the *trans* and *cis* isomers the tilt increases as the steric bulk on the NHC increases. This suggests that electronically it is preferable to have the imidazole ligand coplanar with the coordination plane around Pd, but sterically it becomes preferable to have the imidazole ring almost normal to the coordination plane.

In contrast to the results from the unlinked case, calculations on the linked systems *trans*- and *cis*-**xii** and *trans*- and *cis*-**3a** revealed that the *cis* isomer is significantly higher in energy.[40] The optimized structure of *trans*-**3a** was a staggering 42.7 kJ mol^{-1} lower in energy than the optimized structure of *cis*-**3a** (Figure 8). Similarly, the calculations on *trans*- and *cis*-**xii** revealed that the *trans* isomer was 42.0 kJ mol^{-1} lower in energy. This indicates that the large difference in energy between the two structures is not related to the orientation of the benzyl group on the central amine or the methyl groups on the imidazole. We conclude that conformational effects relating to the orientation of the linker are responsible for the preference of **3a**−**d** to adopt a *trans* geometry. Interestingly, it has already been demonstrated that shorter linkers favor *cis* geometries,[41] and on the basis of these results and our current work we suggest that a linker of at least six atoms is required to favor *trans* coordination.

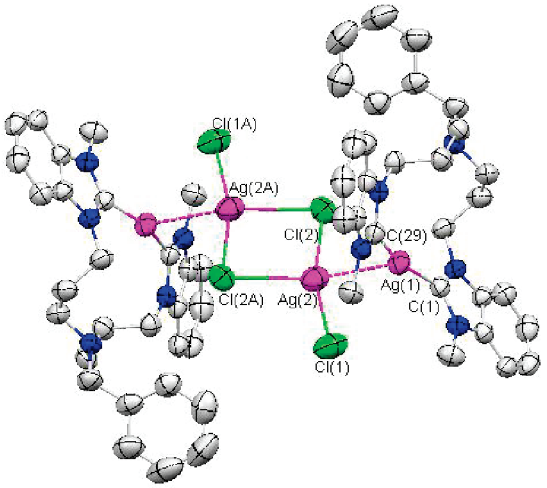


Figure 3. Molecular structure of **2d**. Hydrogen atoms and solvent molecules have been removed for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)−Ag(2) = 2.9968(11), Ag(2)−Ag(2A) = 3.5706(8), Ag(1)−C(1) = 2.055(3), Ag(1)−C(29) = 2.057(4), Ag(2)−Cl(1) = 2.3150(15), Ag(2)−Cl(2) = 2.3546(12), Ag(2)−Cl(2A) = 2.9551(14); C(1)−Ag(1)−C(29) = 162.52(15), Ag(2)−Ag(1)−C(1) = 102.52(11), Ag(2)−Ag(1)−C(29) = 94.92(11), Ag(1)−Ag(2)−Ag(2A) = 130.832(14), Ag(1)−Ag(2)−Cl(1) = 80.09(4), Ag(1)−Ag(2)−Cl(2) = 83.69(3), Ag(1)−Ag(2)−Cl(2A) = 151.35(3).

Oxidation and Catalysis. In recent years there has been significant interest in the synthesis of Pd(III) and Pd(IV) complexes, and they have been proposed as intermediates in several catalytic cycles.[42−44] In general NHC ligands are considered to be excellent donors, and we were interested in oxidizing our Pd(II) complexes **3a**−**d**. Electrochemical studies show that compounds **3a**−**d** all display irreversible oxidations between 1.4 and 1.7 V versus NHE (Figure 9).[40] In contrast, no oxidation of our starting material $PdCl_2(MeCN)_2$ is seen at potentials up to 2 V versus NHE, suggesting that our ligands make the oxidation of Pd(II) more facile in comparison with a commonly occurring Pd precatalyst. We believe that the oxidation is metal-centered, because the Ag complexes **2a**−**d** show no sign of significant oxidation, suggesting that the ligand is not readily oxidized.[40] At this stage there is no obvious explanation for the changes in oxidation potentials on the basis of the electronic effects of the substituents on the ligand. Surprisingly, compounds **3a**−**d** are also remarkably resistant to reduction, as no reduction was seen electrochemically. In contrast, $PdCl_2(MeCN)_2$ is easily reduced to Pd black.

Further support for our hypothesis that the new ligands make oxidation of Pd(II) easier was obtained from the reaction of **3b** with excess MeI. At 50 °C the diiodide species **5b** and MeCl are generated. The reaction presumably proceeds through oxidative addition of MeI to Pd(II) to generate an unstable Pd(IV) species, which then reductively eliminates MeCl (Scheme 2). NMR-scale experiments indicated the formation of an unsymmetrical intermediate, which we postulate as the mixed Pd(II) halide species (**4b**). Reaction of **4b** with MeI was clearly faster than reaction of **3b**, as significant concentrations of **4b** did not build up in the reaction mixture. Reductive elimination from the Pd(IV) is presumably facile, as no evidence for the proposed Pd(IV) intermediate was observed spectroscopically. Reaction between **3b** and EtI was significantly slower but also resulted in the formation of **5b** and EtCl. This is consistent with our proposal of oxidative addition. The X-ray structure of **5b** was determined (Figure 10) and again shows *trans* chelation of the bis-NHC ligand, with no coordination from the central amine (the Pd−N distance is approximately 4.69 Å). As expected, the Pd−I bonds in **5b** (Pd(1)−I(1) = 2.6164(7), Pd(1)−I(2) = 2.6288(8) Å) are significantly longer than the Pd−Cl bonds in either **3a** (Pd(1)−Cl(1) = 2.3217(7), Pd(1)−Cl(2) = 2.3230(7) Å) or

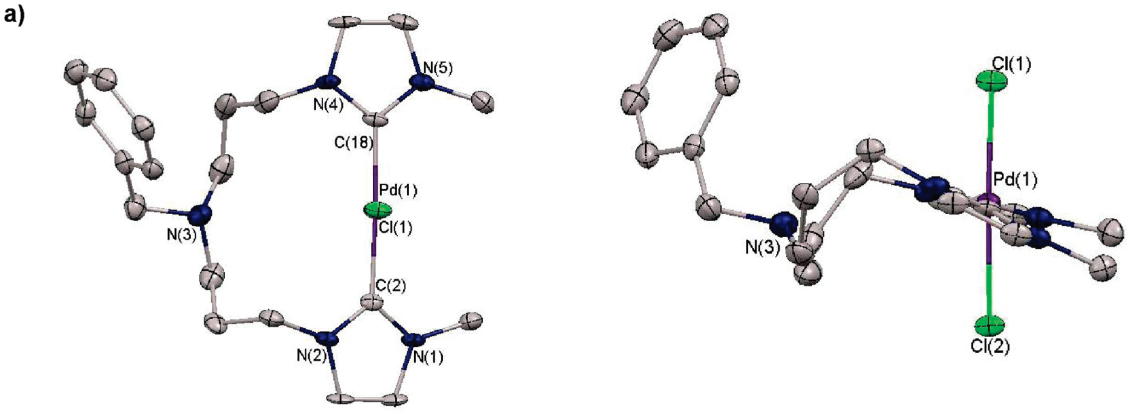


Figure 4. Molecular structure of **3a**: (a) view down the Cl(1)−Pd−Cl(2) axis; (b) view down the C(2)−Pd−C(18) axis. Hydrogen atoms and solvent molecules have been removed for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1) = 2.3217(7), Pd(1)−Cl(2) = 2.3230(7), Pd(1)−C(18) = 2.018(4), Pd(1)−C(2) = 2.021(4); Cl(1)−Pd(1)−Cl(2) = 177.73(3), C(2)−Pd(1)−C(18) = 177.01(13), C(2)−Pd(1)−Cl(1) = 91.63(8), C(2)−Pd(1)−Cl(2) = 89.20(8), C(18)−Pd(1)−Cl(1) = 90.37(8), C(18)−Pd(1)−Cl(2) = 88.88(8).

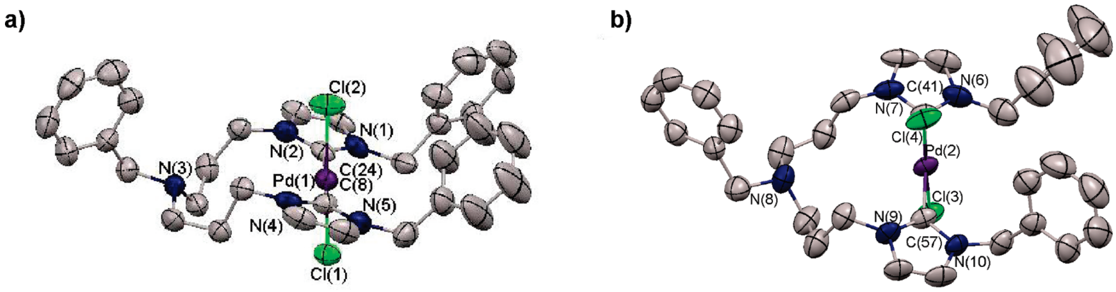


Figure 5. Molecular structure of **3c**: (a) first independent molecule in the unit cell; (b) second independent molecule in the unit cell. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1) = 2.2969(14), Pd(1)−Cl(2) = 2.2988(16), Pd(1)−C(8) = 2.033(5), Pd(1)−C(24) = 2.034(5); Cl(1)−Pd(1)−Cl(2) = 178.41(6), C(8)−Pd(1)−C(24) = 174.9(2), C(8)−Pd(1)−Cl(1) = 92.50(16), C(8)−Pd(1)−Cl(2) = 87.12(16), C(24)−Pd(1)−Cl(1) = 91.03(16), C(24)−Pd(1)−Cl(2) = 89.45(16); Pd(2)−Cl(3) = 2.2981(16), Pd(2)−Cl(4) = 2.2993(18), Pd(2)−C(41) = 2.016(7), Pd(2)−C(57) = 2.016(6); Cl(3)−Pd(2)−Cl(4) = 178.49(6), C(41)−Pd(2)−C(57) = 177.1(2), C(41)−Pd(2)−Cl(3) = 89.92(19), C(41)−Pd(2)−Cl(4) = 89.76(19), C(57)−Pd(2)−Cl(3) = 90.49(17), C(57)−Pd(2)−Cl(4) = 89.90(17).

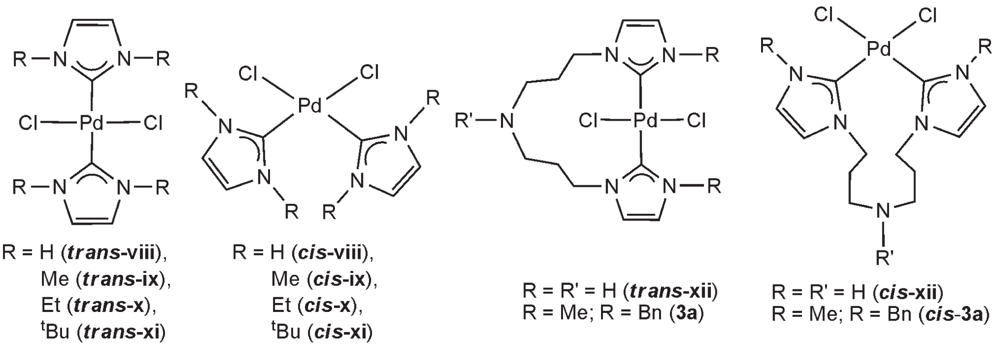


Figure 6. Compounds whose structures were optimized using DFT.

Table 1. Relative Energies of the Optimized Structures of viii−xi

compd	rel energy (kJ mol^{-1})[a]	tilt of NHC (deg)[b]
trans-**viii**	0	0, 0
cis-**viii**	2.51	23.2, 23.1
trans-**ix**	0	67.1, 67.1
cis-**ix**	1.21	68.8, 72.0
trans-**x**	0	68.3, 68.3
cis-**x**	1.16	73.2, 75.2
trans-**xi**	0	90.0, 90.0
cis-**viii**	2.67	69.7, 69.8

[a] Lowest energy isomer set to 0 kJ mol^{-1}. [b] Dihedral angle between Pd coordination plane and the plane of the imidazole ring.

3c (Pd(1)−Cl(1) = 2.2969(14), Pd(1)−Cl(2) = 2.2988(16), Pd(2)−Cl(3) = 2.2981(16), Pd(2)−Cl(4) = 2.2993(18) Å). In the structure of **5b** the plane formed by the five-membered NHC ring is exactly perpendicular to the Pd coordination plane, whereas there is some deviation from 90° in the structures of **3a**,**c**. The exact reason for this difference is unclear, but it adds further support to our proposal that the ligand is highly flexible.

Previously, it has been shown that Pd species with both bidentate *trans*-spanning phosphine and NHC ligands are competent catalysts for the Heck reaction.[8,14,17,18,45,46] We were interested in testing our complexes as catalysts. Initially it was demonstrated that **3a**−**d** all couple 4-bromoacetophenone with *n*-butyl acrylate using the conditions outlined by Douthwaite and co-workers (Table 2).[14] The maximum yield obtained was 80%, and no further conversion was observed at longer reaction times. Surprisingly, the substituent on the imidazole only made a minor difference in catalytic activity. However, the possibility that the ligand is decoordinating from the metal and that the reaction is catalyzed by colloidal Pd seems unlikely, as there was no increase in activity at lower catalyst loadings, which is a common feature of reactions that are catalyzed by Pd^0.[14]

The results described in Table 2 used previous literature conditions for the Heck reaction,[14] and we were interested in optimizing the conditions for our catalyst. A number of different parameters were varied using **3a** as the catalyst, including temperature, the absence or presence of the tetra-*n*-butylammonium bromide additive, the nature of the base, and the number of equivalents of *n*-butyl acrylate (Table 3). Our results (entries 1 and 2) indicated that, although the reaction could be run at lower temperatures, there was a significant decrease in rate as the temperature was decreased, suggesting that in a fashion analogous to that for other systems higher temperatures are required to achieve reasonable reaction rates. Surprisingly, our highest yield with 1.4 equiv of *n*-butyl acrylate was only 80% and we noticed that, even though it was present in excess, all of the *n*-butyl acrylate had been consumed at the end of the reaction. Increasing the amount of acrylate to 2 equiv resulted in an increased yield (entry 4), and changing the base from sodium acetate to sodium carbonate resulted in a yield of 100%. It has previously been reported that the addition of tetraalkylammonium bromide salts results in increased catalytic activity in the Heck

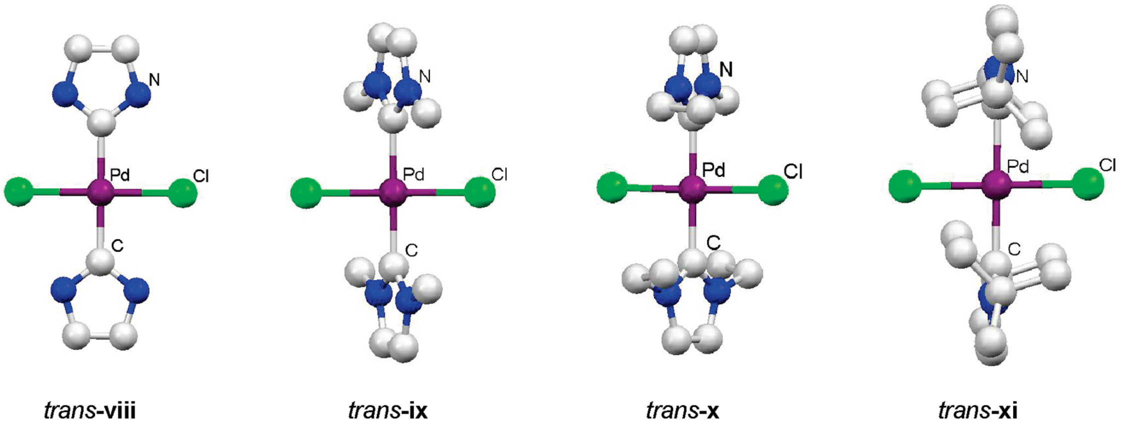


Figure 7. DFT optimized structures of *trans*-**viii**−**xi**. H atoms are omitted for clarity.

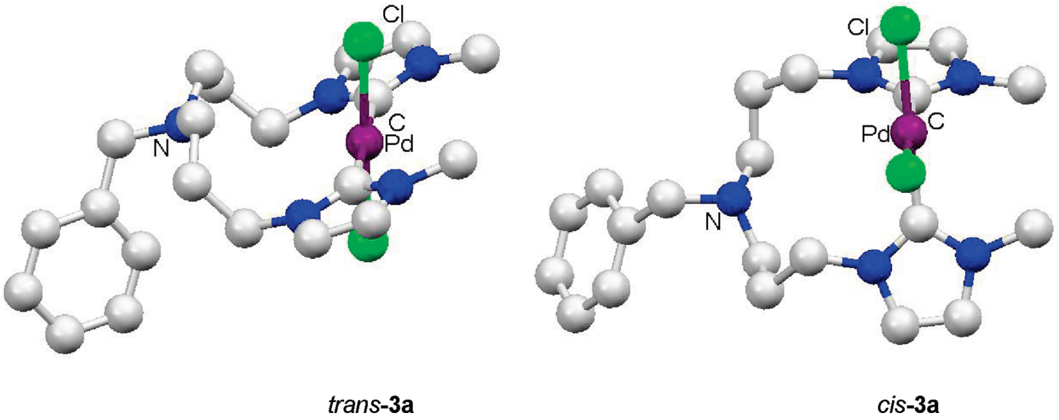


Figure 8. DFT optimized structures of *trans*-**3a** and *cis*-**3a**. H atoms are omitted for clarity.

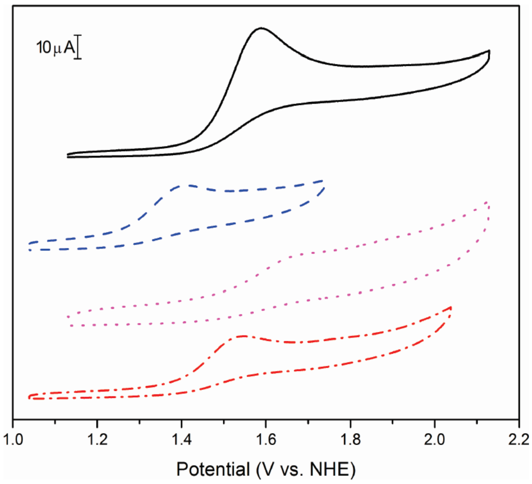


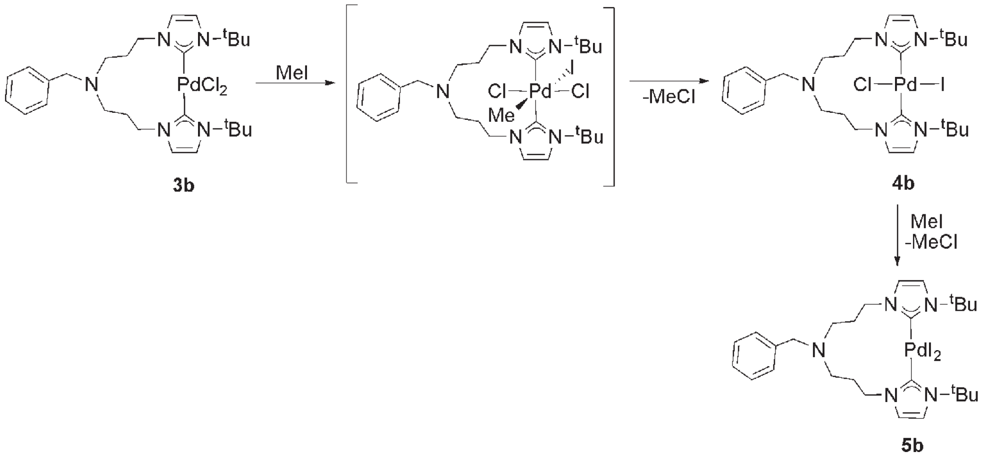
Figure 9. Cyclic voltammograms for **3a** (red, dashed/dotted line, bottom), **3b** (black, solid line, top), **3c** (blue, dashed line, second from top), and **3d** (pink, dotted line, second from bottom) in MeCN.

reaction,[47] and in our case removal of the additive also results in lower activity (entries 4 and 6).

The generality of our catalyst for the Heck reaction was investigated by exploring the substrate scope (Table 4). Compound **3a** can efficiently couple *n*-butyl acrylate with a variety of aryl iodides and aryl bromides but is unable to couple aryl chlorides. The coupling of aryl iodides is more efficient than that of aryl bromides. Electron-rich substituents which are less likely to undergo the Heck reaction are tolerated for aryl iodides but do not undergo efficient coupling with aryl bromides. Overall the performance of our catalyst for the Heck reaction is better than that of the Pd bidentate *trans*-spanning NHC system described by RajanBabu and co-workers[8] and is comparable with that described by Douthwaite et al.[14] All systems are vastly inferior to state of the art catalysts for the Heck reaction,[48] which presumably reflects the difficulty in performing oxidative addition to a square-planar Pd complex with a *trans*-spanning bidentate ligand.

It has also been demonstrated that Pd complexes with bidentate *trans*-spanning NHC ligands can be used as catalysts for the Suzuki reaction.[16,17] Using the optimized conditions described by Smith and co-workers,[17] we were able to demonstrate that **3a** is an active catalyst for the Suzuki reaction (Table 5). The substrate scope is again limited to aryl bromides and iodides, with no reaction observed with aryl chlorides. Our system is less active than Smith's, which is also capable of coupling aryl chlorides.[17] At this stage the reasons for the differences between systems are unclear, as there is almost no mechanistic information about how complexes with bidentate *trans*-spanning NHC ligands undergo the fundamental steps associated with the Suzuki reaction.

Scheme 2



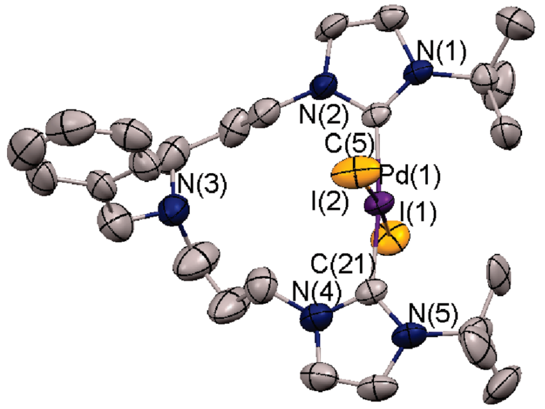


Figure 10. Molecular structure of **5b**. Hydrogen atoms and solvent molecules have been removed for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−I(1) = 2.6164(7), Pd(1)−I(2) = 2.6288(8), Pd(1)−C(5) = 2.051(4), Pd(1)−C(21) = 2.059(5); I(1)−Pd(1)−I(2) = 174.18(3), C(5)−Pd(1)−C(21) = 173.3(3), C(5)−Pd(1)−I(1) = 90.89(16), C(5)−Pd(1)−I(2) = 90.50(17), C(21)−Pd(1)−I(1) = 89.45(17), C(21)−Pd(1)−I(2) = 88.52(18).

Table 2. Results for the Heck Reaction between *n*-Butyl Acrylate and 4-Bromoacetophenone Using Complexes 3a−d as the Catalyst

cat. (amt (mol %))	time (h)	yield (%)[a]	TOF[b]
3a (0.1)	1	67	672
3a (0.01)	1	6.5	650
3a (0.01)	22	71	323
3b (0.1)	1	59	600
3c (0.1)	1	80	792
3d (0.1)	1	72	720

[a] The average of three runs determined by ^{1}H NMR using an internal standard; only the *trans* isomer was observed. No increase in yield was observed if the reaction was left for longer times, except where specified. [b] Turnover frequency (TOF) = (mol of product)/((mol of Pd) h)) Conditions: NaOAc (0.46 mmol), tetra-*n*-butylammonium bromide (0.041 mmol), 4-bromoacetophenone (0.41 mmol), *n*-butyl acrylate (0.57 mmol), dimethylacetamide (2 mL), 140 °C.

Table 3. Results for the Optimization of the Conditions for Heck Reaction between *n*-Butyl Acrylate and 4-Bromoacetophenone Using 3a as the Catalyst

entry	temp (°C)	additive	base	amt of acrylate (equiv)	time (h)	yield (%)[a]
1	120	yes	NaOAc	1.4	64	80
2	140	yes	NaOAc	1.4	4	67
3	140	yes	NaOAc	2	4	93
4	140	yes	NEt$_3$	2	4	22
5	140	yes	Na$_2$CO$_3$	2	4	100
6	140	no	NaOAc	2	4	39

[a] The average of three runs determined by ^{1}H NMR using an internal standard; only the *trans* isomer was observed. No increase in yield was observed if the reaction was left for longer times. Conditions: all reactions used 0.1 mol % **3a**, base (0.46 mmol), 4-bromoacetophenone (0.41 mmol), and dimethylacetamide (2 mL). The quantities of other reagents and the temperature are given in the table.

Table 4. Substrate Scope for Heck Reaction between *n*-Butyl Acrylate and Aryl Halides Using 3a as the Catalyst

entry	substrate	time (h)	yield (%)[a]
1	4-bromoacetophenone	4	100
2	4-bromonitrobenzene	4	100
3	bromobenzene	8	30
4	4-bromotoluene	8	50
5	4-bromoanisole	8	14
6	4-iodoacetophenone	<3	100
7	4-iodonitrobenzene	3	100
8	iodobenzene	4	99
9	4-iodotoluene	4	88
10	4-iodoanisole	4	94
11	4-chloroacetophenone	8	0
12	4-chlorotoluene	8	0

[a] The average of two runs determined by ^{1}H NMR using an internal standard; only the *trans* isomer was observed. No increase in yield was observed if the reaction was left for longer times. Conditions: all reactions used 0.1 mol % **3a**, Na$_2$CO$_3$ (0.46 mmol), substrate (0.41 mmol), 2 equiv of *n*-butyl acrylate, and dimethylacetamide (2 mL) at 140 °C.

Table 5. Substrate Scope for Suzuki Reaction between Phenylboronic Acid and Aryl Halides Using 3a as the Catalyst

entry	substrate	time (h)	yield (%)[a]
1	4-bromoacetophenone	12	100
2	4-bromonitrobenzene	6	84
3	bromobenzene	3	70
4	4-bromoanisole	24	20
5	4-iodoacetophenone	1	100
6	4-iodonitrobenzene	5	98
7	iodobenzene	3	89
8	4-iodoanisole	17	92
9	4-chloroacetophenone	8	0
10	4-chlorotoluene	8	0

[a] The average of two runs determined by ^{1}H NMR using an internal standard. No increase in yield was observed if the reaction was left for longer times. Conditions: all reactions used 1 mol % **3a**, Cs_2CO_3 (0.60 mmol), substrate (0.20 mmol), phenylboronic acid (0.30 mmol), and 1,4-dioxane (2 mL) at 100 °C.

CONCLUSIONS

We have generated one of the first families of bidentate *trans*-chelating NHC ligands and only the second series which contains a flexible linker.[9,15,16] The ligands are straightforward to synthesize, and both the sterics and electronics can be easily modified. The ligands preferentially appear to form monomeric species, and Pd complexes supported by the new ligands are catalytically active for the Heck reaction and Suzuki reactions. Electrochemical and chemical studies suggest the ligands may be able to support high-oxidation-state Pd species, and future work will focus on isolating complexes of this type.

EXPERIMENTAL SECTION

General Methods. Experiments were performed under a dinitrogen atmosphere using standard Schlenk techniques, unless otherwise noted. Solvents were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received, except where noted. Ethyl acrylate, benzylamine, $LiAlH_4$, 1-methylimidazole, 1-benzylimidazole, 1-methylbenzimidazole, *n*-butyl acrylate, 4-bromoacetophenone, and $PdCl_2(MeCN)_2$ were purchased from Aldrich. 1-*tert*-Butylimidazole was synthesized using a literature procedure.[49] Deuterated solvents were obtained from Cambridge Isotope Laboratories. CD_2Cl_2 and $CDCl_3$ were dried using P_2O_5 and vacuum-transferred prior to use. NMR spectra were recorded on Bruker AMX-400 and -500 spectrometers at ambient probe temperatures unless noted. Chemical shifts are reported in ppm with respect to residual internal protio solvent for ^{1}H and $^{13}C\{^1H\}$ NMR spectra; *J* values are given in Hz. All assignments are based on two-dimensional $^1H,^{13}C$-HMQC and HMBC experiments. HRMS were recorded at The Mass Spectrometry (MS) and Proteomics Resource of the W. M. Keck Foundation Biotechnology Resource Laboratory at Yale University. Robertson Microlit Laboratories, Inc., performed the elemental analyses.

Electrochemistry. Electrochemical experiments were carried out with a Princeton Applied Research Versastat 4-400 potentiostat/galvanostat using a standard three-electrode configuration. Experiments were carried out in still-dried acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate (Fluka, electrochemical grade) as the supporting electrolyte. A Pt wire and a Ag wire were used as the counter electrode and pseudo reference electrode, respectively. The reversible ferrocene/ferrocenium redox couple (Fc/Fc^+: +0.690 V vs NHE in MeCN) was used as an external standard and to reference the potential to the NHE. A basal plane carbon electrode was used as the working electrode to reduce background oxidation. The electrode consisted of a brass cylinder, sheathed in a Teflon tube. At the tip of the brass, a two-part Ag conducting epoxy (Alfa Aesar) was used to firmly attach the basal plane carbon electrode surface to the brass. Finally, the tip was sealed with the organic solvent resistant, electrically insulating, two-part epoxy Tra-bond 2151 (Emerson and Cuming, Canton, MA). Immediately prior to experiments, the working electrode was polished with 1 μm alumina paste, washed with copious amounts of water, and allowed to dry completely. Then, the surface of the working electrode was resurfaced with tape to restore the gray, basal surface.

DFT Calculations. Density functional calculations were carried out using Gaussian 09 Revision A.01.[50] Calculations were performed using the B3LYP functional and the LANL2DZ basis set for Pd and the 6-31G** basis set for all other atoms. The coordinates from X-ray structures were used where possible to generate the initial structure for optimization. In cases where no X-ray structures were available, several different initial structures were used to ensure that the lowest energy structure represented an overall minimum and not a local minimum. All optimized structures were verified using frequency calculations to check that they did not contain any imaginary frequencies.

X-ray Crystallography. The diffraction experiments were carried out on either a Bruker AXS SMART CCD three-circle diffractometer with a sealed tube using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) or a Rigaku Spider diffractometer equipped with a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Cu Kα radiation (λ = 1.541 87 Å). The software used were SMART for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT for integration of intensity of reflections and scaling, SADABS for empirical absorption correction, and SHELXTL for space group determination, structure solution, and least-squares refinements on $|F|^2$. The crystals were mounted at the end of glass fibers and used for the diffraction experiments. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions. Details of the crystal and refinement data for complexes **2d**, **3a**, **3c**, and **5b'**. are given in Table S1 in the Supporting Information.

Synthesis and Characterization of Compounds. *$BnN(CH_2CH_2C(O)OEt)_2$ (**a**).* This compound was prepared following a modified literature procedure.[51] Ethyl acrylate (21.9 g, 218.3 mmol) was added to a methanol solution (30 mL) of benzylamine (10.0 g, 93.3 mmol). The reaction mixture was purged with nitrogen, covered in aluminum foil, and stirred for 5 days. The solvent was removed in vacuo to give **a** as a colorless liquid. The product was stored under vacuum. Yield: 28.6 g, 99%. ^{1}H NMR data were consistent with those previously reported.[52]

*$BnN(CH_2CH_2CH_2OH)_2$ (**b**).* This compound was prepared following a modified literature procedure.[53] Under an atmosphere of nitrogen, $BnN(CH_2CH_2C(O)OEt)_2$ (**a**; 49.3 g, 160 mmol) was added dropwise over a period of 1 h to a solution of $LiAlH_4$ (7.61 g, 201 mmol) in dry THF at 0 °C. The reaction mixture was stirred at room temperature for 24 h. Methanol (15 mL) was then carefully added, followed by a 15% by weight NaOH(aq) solution (10 mL) and water (10 mL) (Fieser and Fieser method for quenching $LiAlH_4$ reactions[54]). The reaction mixture was stirred until the precipitate settled at the bottom of the flask. The solution was then filtered through a Buchner funnel and dried under vacuum to give **b** as a light yellow oil. Yield: 30.2 g, 85%. ^{1}H NMR data were consistent with those previously reported.[53]

*$BnN(CH_2CH_2CH_2Cl)_2$ (**c**).* A solution of $SOCl_2$ (20 mL) in dichloromethane (30 mL) was added dropwise to a solution of $BnN(CH_2CH_2CH_2OH)_2$ (**b**; 29.7 g, 133 mmol) in dichloromethane (200 mL) with stirring. The reaction mixture was stirred for 40 min and then purged with nitrogen to liberate the HCl gas. Water (6 mL) was

then added along with K_2CO_3 (20 g, 0.115 mol) to generate the free amine. BnN($CH_2CH_2CH_2Cl$)$_2$ (**c**) was isolated as a light yellow oil by vacuum distillation at 150 °C (0.1 Torr). Yield: 31.9 g, 92%. ^{1}H NMR data were consistent with those previously reported.[51]

*[^{Me}C(H)N(Bn)C(H)^{Me}]·2[Cl] (**1a**).* 1-Methylimidazole (0.91 g, 11.1 mmol) and BnN($CH_2CH_2CH_2Cl$)$_2$ (**c**; 1.02 g, 3.9 mmol) were mixed with dioxane (3 mL). The reaction mixture was heated at reflux under nitrogen for 3 h. The solvent was then removed in vacuo and the product dissolved in water and washed with toluene (3 × 15 mL). The water was removed by heating the crude reaction mixture for 12 h at 60 °C under reduced pressure to give **1a** as a yellow-orange glass. Yield: 1.35 g, 84%.

^{1}H NMR (400 MHz, CD_2Cl_2): 1.99 (4H, app p, $NCH_2CH_2CH_2N$, J_{H-H} = 7.0), 2.49 (4H, t, $CH_2CH_2CH_2NBn$, $^3J_{H-H}$ = 6.6), 3.55 (2H, m, NCH_2Ar), 3.80 (6H, s, NCH_3), 4.13 (4H, t, $NCNCH_2CH_2CH_2$, $^3J_{H-H}$ = 7.4), 7.32 (5H, m, C_6H_5), 7.43 (2H, s, HC=CH), 7.78 (2H, s, HC=CH), 10.69 (2H, s, NCHN). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 25.8, 35.7, 47.5, 49.2, 57.3, 122.0, 123.6, 127.7, 128.5, 129.8, 135.8, 137.3. HR FT-ICR MS: found (calcd for $C_{21}H_{33}Cl_2N_5$): m/z (M − Cl) 388.2263 (388.2263).

*[^{tBu}C(H)N(Bn)C(H)^{tBu}]·2[Cl] (**1b**).* 1-*tert*-Butylimidazole (1.27 g, 7.70 mmol) and BnN($CH_2CH_2CH_2Cl$)$_2$ (**c**; 1.00 g, 3.84 mmol) were mixed with dioxane (1 mL). The reaction mixture was heated at reflux under nitrogen for 24 h. The solvent was then removed in vacuo and the product dissolved in water and washed with toluene (2 × 20 mL) and pentane (20 mL). The water was removed by heating the crude reaction mixture for 12 h at 60 °C under reduced pressure to give **1b** as a yellow glass. Yield: 1.81 g, 94%.

^{1}H NMR (400.0 MHz, D_2O): 1.58 (18H, s, $NCCH_3$), 2.05 (4H, app p, $NCH_2CH_2CH_2N$, J_{H-H} = 7.0), 2.45 (4H, t, $CH_2CH_2CH_2NBn$, $^3J_{H-H}$ = 7.8), 3.59 (2H, s, NCH_2Ar), 4.16 (4H, t, $NCNCH_2CH_2CH_2$, $^3J_{H-H}$ = 6.8), 7.15 (2H, m, HC=CH), 7.24 (2H, m, HC=CH), 7.26 (1H, m, $C_6H_5CH_2N$), 7.33 (2H, app t, $C_6H_5CH_2N$, J_{H-H} = 1.8), 7.54 (2H, app t, $C_6H_5CH_2N$, J_{H-H} = 1.9) 8.80 (2H, s, NCHN). ^{13}C{^{1}H} NMR (126.0 MHz, D_2O): 26.2, 29.2, 48.0, 49.7, 57.7, 60.2, 120.6, 122.7, 128.2, 129.0, 130.1, 133.8, 137.4. ^{13}C{^{1}H} NMR (101 MHz, D_2O): 25.3, 33.3, 45.5, 49.9, 57.6, 113.4, 113.6, 127.4, 127.4, 127.8, 128.6, 129.6, 131.4, 132.4, 137.3, 141.2 HR FT-ICR MS: found (calcd for $C_{27}H_{43}Cl_2N_5$): m/z (M − Cl) 472.3208 (472.2896).

*[^{Bn}C(H)N(Bn)C(H)^{Bn}]·2[Cl] (**1c**).* 1-Benzylimidazole (0.66 g, 4.2 mmol) and BnN($CH_2CH_2CH_2Cl$)$_2$ (**c**; 0.50 g, 1.9 mmol) were mixed with dioxane (2 mL). The reaction mixture was heated at reflux under nitrogen for 3 h. The solvent was removed in vacuo, and the product was dissolved in water and washed with toluene (2 × 10 mL) and pentane (10 mL). The water was removed by heating the crude reaction mixture for 12 h at 60 °C under reduced pressure to give **1c** as a yellow oil. Yield: 0.88 g, 90%.

^{1}H NMR (400 MHz, $CDCl_3$): 2.17 (4H, app p, $NCH_2CH_2CH_2N$, J_{H-H} = 7.1), 2.57 (4H, t, $CH_2CH_2CH_2NBn$, $^3J_{H-H}$ = 6.4), 3.54 (2H, m, NCH_2Ar), 4.44 (4H, t, $NCNCH_2CH_2CH_2$, $^3J_{H-H}$ = 7.7), 5.51 (4H, s, $NCNCH_2Ar$), 7.12 (2H, s, HC=CH), 7.28−7−48 (15H, m, C_6H_5), 7.61 (2H, s, HC=CH), 10.71 (2H, s, NCHN). ^{13}C{^{1}H} NMR (101 MHz, D_2O): 25.6, 47.6, 49.0, 52.8, 57.2, 122.4, 122.6, 127.6, 128.5, 129.3, 129.3, 129.3, 129.7, 133.4, 133.6, 136.9. HR FT-ICR MS: found (calcd for $C_{33}H_{39}Cl_2N_5$): m/z (M − Cl) 540.2850 (540.2889).

*[^{Me}BzC(H)N(Bn)C(H)Bz^{Me}]·2[Cl] (**1d**).* 1-Methylbenzimidazole (1.02 g, 7.72 mmol) and BnN($CH_2CH_2CH_2Cl$)$_2$ (**c**; 1.00 g, 3.84 mmol) were mixed with dioxane (1 mL). The reaction mixture was heated at reflux under nitrogen for 24 h. The solvent was removed in vacuo, and the product was dissolved in water and washed with toluene (2 × 20 mL) and pentane (20 mL). The water was removed by heating the crude reaction mixture for 12 h at 60 °C under reduced pressure to give **1d** as a yellow oil. Yield: 1.62 g, 82%.

^{1}H NMR (400.0 MHz, $CDCl_3$): 2.38 (4H, app t, $NCH_2CH_2CH_2N$), 2.77 (4H, s br, $NCH_2CH_2CH_2NCN$), 3.63 (2H, s, $ArCH_2$), 4.27 (6H, s, $ImCH_3$), 4.74 (4 H, t, $BnNCH_2CH_2CH_2N$, $^3J_{H-H}$ = 15.4), 7.60 (13, Ar), 11.40 (2 H, s, NCHN). ^{13}C{^{1}H} NMR (101 MHz, D_2O): 25.3, 33.3, 45.5, 49.9, 57.6, 113.4, 113.6, 127.4, 127.4, 127.8, 128.6, 129.6, 131.4, 132.4, 137.3, 141.2. HR FT-ICR MS: found (calcd for $C_{29}H_{35}Cl_2N_5$): m/z (M − Cl) 488.2555 (488.2270).

*[(^{Me}CN(Bn)C^{Me})Ag]·[AgCl$_2$] (**2a**).* [^{Me}C(H)N(Bn)C(H)^{Me}]·2[Cl] (**1a**; 0.51 g, 1.19 mmol) was dissolved in dichloromethane (20 mL), and Ag_2O (0.43 g, 1.86 mmol) was added. The reaction vessel was covered in aluminum foil and the mixture stirred for 24 h. The reaction mixture was then filtered through Celite and the filtrate dried under reduced pressure to give **2a** as a white powder. Yield: 0.70 g, 93%.

^{1}H NMR (300 MHz, CD_2Cl_2): 2.14 (4H, app p, $NCH_2CH_2CH_2N$, J_{H-H} = 7.3), 2.52 (4H, t, $CH_2CH_2CH_2NBn$, $^3J_{H-H}$ = 6.4), 3.54 (2H, m, NCH_2Ar), 3.98 (6H, s, NCH_3), 4.40 (4H, t, $NCNCH_2CH_2CH_2$, $^3J_{H-H}$ = 7.7), 6.97 (2H, d, HC=CH, $^3J_{H-H}$ = 1.8), 7.01 (2H, d, HC=CH, J_{H-H} = 1.8), 7.35 (5H, m, C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 30.0, 38.9, 49.8, 51.4, 59.2, 121.6, 122.6, 127.3, 128.5, 129.1, 139.1, 180.2. Anal. Found (calcd) for $C_{21}H_{29}Ag_2Cl_2N_5$: C, 39.79 (39.53); H, 4.59 (4.58); N, 11.09 (10.97).

*[(^{tBu}CN(Bn)C^{tBu})Ag]·[AgCl$_2$] (**2b**).* [^{tBu}C(H)N(Bn)C(H)^{tBu}]·2[Cl] (**1b**; 250 mg, 0.492 mmol) was dissolved in dichloromethane (25 mL), and Ag_2O (285 mg, 1.23 mmol) was added. The reaction vessel was covered in aluminum foil and the mixture stirred for 24 h. The reaction mixture was then filtered through Celite and the filtrate dried under reduced pressure to give **2b** as a white powder. Yield: 297 mg, 98%.

^{1}H NMR (400 MHz, CD_2Cl_2): 1.71 (18 H, s, C(CH_3)$_3$), 2.03 (4 H, app p, $CH_2CH_2CH_2$, J_{H-H} = 7.0), 2.51 (4H, t, $CH_2CH_2CH_2$ $^3J_{H-H}$ = 6.5), 3.57 (2H, s, $PhCH_2N$), 4.21 (4 H, t, $CH_2CH_2CH_2$, $^3J_{H-H}$ = 6.5), 7.02 (2H, d, HC=CH, J_{H-H} = 1.9), 7.16 (2H, d, HC=CH, J_{H-H} = 1.9), 7.33 (5 H, $ArCH_2N$). ^{13}C NMR (126 MHz, $CDCl_3$): 29.9, 30.2, 31.1, 32.0, 51.0, 51.5, 57.8, 59.3, 119.1, 120.0, 127.3, 128.7, 129.2, 139.0, 177.3. HR FT-ICR MS: found (calcd for $C_{27}H_{41}Ag_2Cl_2N_5$): m/z (M − $AgCl_2$) 542.2409 (542.2402). Anal. Found (calcd) for $C_{27}H_{41}Ag_2Cl_2N_5$: C, 45.11 (44.83); H, 5.74 (5.85); N, 9.71 (9.68).

*[(^{Bn}CN(Bn)C^{Bn})Ag]·[AgCl$_2$] (**2c**).* [^{Bn}C(H)N(Bn)C(H)^{Bn}]·2[Cl] (**1c**; 130 mg, 23.7 mmol) was dissolved in dichloromethane (25 mL), and Ag_2O (110 mg, 47.5 mmol) was added. The reaction vessel was covered in aluminum foil and the mixture stirred for 24 h. The reaction mixture was then filtered through Celite and the filtrate dried under reduced pressure to give **2c** as a white powder. Yield: 151 mg, 83%.

^{1}H NMR (400 MHz, $CDCl_3$): 2.02 (4H, app p, $NCH_2CH_2CH_2N$, J_{H-H} = 7.2), 2.51 (4H, t, $CH_2CH_2CH_2NBn$, $^3J_{H-H}$ = 6.5), 3.56 (2H, m, NCH_2Ar), 4.16 (4H, t, $NCNCH_2CH_2CH_2$, $^3J_{H-H}$ = 7.4), 5.28 (4H, s, $NCNCH_2Ar$), 6.89 (2H, s, HC=CH), 7.05 (2H, s, HC=CH), 7.18−7−38 (15H, m, C_6H_5). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 29.9, 50.3, 51.1, 55.8, 59.2, 121.3, 122.0, 127.4, 128.0, 128.7, 128.7, 129.2, 135.8, 139.0, 179.7. HR FT-ICR MS: found (calcd for $C_{33}H_{37}Ag_2Cl_2N_5$): m/z (M − 2AgCl + H) 504.3099 (504.3127). Anal. Found (calcd) for $C_{33}H_{37}Ag_2Cl_2N_5$: C, 50.55 (50.13); H, 4.85 (4.72); N, 8.94 (8.86).

*[(^{Me}BzCN(Bn)CBz^{Me})Ag]·[AgCl$_2$] (**2d**).* [^{Me}BzC(H)N(Bn)C(H)Bz^{Me}]·2[Cl] (**1d**; 250 mg, 0.477 mmol) was dissolved in dichloromethane (25 mL), and Ag_2O (276 mg, 1.19 mmol) was added. The reaction vessel was covered in aluminum foil and the mixture stirred for 24 h. The reaction mixture was then filtered through Celite and the solvent removed under reduced pressure to give **2d** as a white powder. Yield: 247 mg, 70%.

^{1}H NMR (400 MHz, CD_2Cl_2): 2.12 (4 H, app p, $NCH_2CH_2CH_2N$, J_{H-H} = 7.0), 2.64 (4H, t, $NCH_2CH_2CH_2N$, $^3J_{H-H}$ = 6.5), 3.61 (2 H, s, $ArCH_2N$), 4.08 (6 H, s, NCH_3), 4.52 (4 H, t, $NCH_2CH_2CH_2N$ $^3J_{H-H}$ = 7.0), 7.21−7.26 (5H, m, C_6H_5), 7.31−7.35 (4H, m, C_6H_5), 7.36−7.42 (4H, m, C_6H_5). ^{13}C NMR (126 MHz, $CDCl_3$): 28.1, 35.8, 47.3, 51.5, 58.8, 111.2, 123.9, 127.0, 128.3, 128.8, 133.4, 134.4, 138.8, 189.8. HR FT-ICR MS: found (calcd for $C_{29}H_{33}Ag_2Cl_2N_5$): m/z (M − $AgCl_2$) 558.1780 (558.1776). Anal. Found (calcd) for $C_{29}H_{33}Ag_2Cl_2N_5$: C, 46.52 (47.18); H, 4.36 (4.51); N, 9.37 (9.49).

*$\{^{Me}CN(Bn)C^{Me}\}PdCl_2$ (**3a**).* $PdCl_2(MeCN)_2$ (21 mg, 0.080 mmol) and $[(^{Me}CN(Bn)C^{Me})Ag]\cdot[AgCl_2]$ (**2a**; 51 mg, 0.080 mmol) were dissolved in dichloromethane (50 mL) and stirred for 3 h. The reaction mixture was filtered through Celite and the solvent removed under reduced pressure to give **3a** as a white powder. Yield: 45 mg, 90%. X-ray diffraction quality crystals were grown from a ternary solution of dichloromethane, acetonitrile, and methyl isobutyl ketone.

^1H NMR (400 MHz, $CDCl_3$): 2.25 (app p, 4H, $CH_2CH_2CH_2$), 2.91 (t, 4H, $^3J_{H-H}$ = 5.6 Hz, $CH_2CH_2CH_2NMe$), 3.66 (s, 2 H, CH_2Ar), 4.11 (s, 6H, NCH_3), 6.63−4.67 (t, 4H, $^3J_{H-H}$ = 6.8 Hz, $NCNCH_2CH_2CH_2$), 6.78 (s, 4H, $HC{=}CH$), 7.31−7.36 (m, 3H, C_6H_5), 7.43−7.45 (m, 2H, C_6H_5). ^{13}C NMR (126 MHz, $CDCl_3$): 31.0, 37.7, 48.3, 53.6, 60.6, 121.0, 122.0, 127.1, 128.6, 128.8, 140.7, 169.6. HR FT-ICR MS: found (calcd for $C_{21}H_{29}Cl_2N_5Pd$): m/z (M + H) 530.0902 (530.0917). Anal. Found (calcd) for $C_{21}H_{29}Cl_2N_5Pd$: C, 48.05 (47.70); H, 5.20 (5.53); N, 13.10 (13.24).

*$\{^{tBu}CN(Bn)C^{tBu}\}PdCl_2$ (**3b**).* $PdCl_2(MeCN)_2$ (22 mg, 0.082 mmol) and $[(^{tBu}CN(Bn)C^{tBu})Ag]\cdot[AgCl_2]$ (**2b**; 58 mg, 0.082 mmol) were dissolved in dichloromethane (50 mL) and stirred for 3 h. The reaction mixture was filtered through Celite and the solvent removed under reduced pressure to give **3b** as a white powder. Yield: 40 mg, 95%.

^1H NMR (400 MHz, $CDCl_3$): 2.00 (18H, s, $C(CH_3)_3$), 2.33 (4H, s br, $NCH_2CH_2CH_2N$), 2.77 (4H, t, $NCH_2CH_2CH_2N^tBu$, $^3J_{H-H}$ = 5.9), 3.62 (2H, s, $ArCH_2$), 5.04 (4 H, s br, $BnNCH_2CH_2CH_2N$), 6.77 (2H, d, $HC{=}CH$, J_{H-H} = 2.0), 6.97 (2H, d, $HC{=}CH$, J_{H-H} = 2.0), 7.32 (5 H, C_6H_5). ^{13}C NMR (126 MHz, $CDCl_3$): 31.1, 32.2, 51.0, 54.2, 58.4, 62.1, 119.1, 120.1, 127.3, 128.6, 129.1, 140.2, 166.0. HR FT-ICR MS: found (calcd for $C_{27}H_{41}Cl_2N_5Pd$): m/z (M − Cl) 576.2051 (576.2080). Anal. Found (calcd) for $C_{27}H_{41}Cl_2N_5Pd$: C, 52.71 (52.90); H, 6.78 (6.74); N, 11.36 (11.43).

*$\{^{Bn}CN(Bn)C^{Bn}\}PdCl_2$ (**3c**).* $PdCl_2(MeCN)_2$ (21 mg, 0.080 mmol and $[(^{Bn}CN(Bn)C^{Bn})Ag]\cdot[AgCl_2]$ (**2c**; 63 mg, 0.080 mmol) were dissolved in dichloromethane (50 mL) and stirred for 2 h. The reaction mixture was then filtered through Celite and the filtrate dried under vacuum to give **3c** as a white powder. Yield: 45 mg, 82%. X-ray diffraction quality crystals were grown from a ternary solution of dichloromethane, acetonitrile, and methyl isobutyl ketone.

^1H NMR (500 MHz, CD_2Cl_2): 2.32 (m, 4H, $NCH_2CH_2CH_2N$, J_{H-H} = 7.2), 2.89 (m, 4H, $CH_2CH_2CH_2NBn$), 3.69 (m, 2H, NCH_2Ar), 4.67 (m, 4H, $NCNCH_2CH_2CH_2$), 5.65 (s, 4H, $NCNCH_2Ar$), 6.73 (s, 2H, $HC{=}CH$), 6.85 (s, 2H, $HC{=}CH$), 7.23−7.40 (m, 9H, C_6H_5), 7.42−7.55 (m, 6H, C_6H_5). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): 31.5, 49.0, 61.0, 120.7, 122.4, 127.4, 128.5, 128.8, 129.2, 129.2, 129.4, 137.3, 141.1, 170.9 (two peaks under CD_2Cl_2 as determined using ^1H,^{13}C-HSQC). HR FT-ICR MS: found (calcd for $C_{33}H_{37}Cl_2N_5Pd$): m/z (M + H) 682.1514 (682.1543). Anal. Found (calcd) for $C_{33}H_{37}Cl_2N_5Pd$: C, 58.08 (58.18); H, 5.40 (5.48); N, 9.90 (10.29).

*$\{^{Me}BzCN(Bn)CBz^{Me}\}PdCl_2$ (**3d**).* $PdCl_2(MeCN)_2$ (21 mg, 0.080 mmol) and $[(^{Me}BzCN(Bn)CBz^{Me})Ag]\cdot[AgCl_2]$ (**2d**; 53 mg, 0.080 mmol) were dissolved in dichloromethane (50 mL) and stirred for 8 h. The reaction mixture was then filtered through Celite and the solvent removed under reduced pressure to give **3d** as a white powder. Yield: 41 mg, 96%.

^1H NMR (400 MHz, $CDCl_3$): 2.28 (app t, 4 H, $NCH_2CH_2CH_2N$), 2.99 (t, 4H, $CH_2CH_2CH_2NBn$, $^3J_{H-H}$ = 5.6), 3.74 (s, 2H, $ArCH_2$), 4.37 (s, 6H, NCH_3), 5.07 (t, 4H, $NCNCH_2CH_2CH_2$, $^3J_{H-H}$ = 4.7), 7.26−7.33 (6H, C_6H_5), 7.33−7.43 (5H, C_6H_5), 7.48−7.54 (2H, C_6H_5). ^{13}C NMR (126 MHz, $CDCl_3$): 27.4, 33.5, 43.9, 52.4, 58.7, 109.1, 109.2, 121.8, 121.9, 126.0, 127.5, 129.9, 133.3, 134.0, 139.5, 180.1. HR FT-ICR MS: found (calcd for $C_{29}H_{33}Cl_2N_5Pd$): m/z (M − Cl) 592.1445 (592.1454). Anal. Found (calcd) for $C_{29}H_{33}Cl_2N_5Pd$: C, 54.40 (55.38); H, 5.13 (5.29); N, 11.00 (11.14).

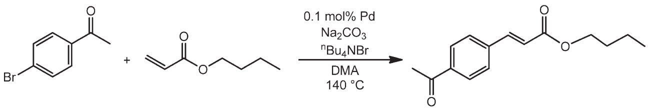
*$\{^{tBu}CN(Bn)C^{tBu}\}PdI_2$ (**5b**).* $\{^{tBu}CN(Bn)C^{tBu}\}PdCl_2$ (**3b**; 50 mg, 0.081 mmol) and MeI (115 mg, 0.814 mmol) were dissolved in chloroform (2.5 mL). The solution was heated at 50 °C for 50 h. The solvent was then removed under reduced pressure and the crude product dissolved in a minimum amount of dichloromethane. Pentane was then added to precipitate the product, which was collected by filtration and dried under reduced pressure to give **5b** as a yellow solid. Yield: 48 mg, 70%. X-ray diffraction quality crystals were grown by slow evaporation from a saturated chloroform solution at room temperature.

^1H NMR (400 MHz, $CDCl_3$): 1.92 (18H, s, $C(CH_3)_3$), 2.24 (4H, s br, $NCH_2CH_2CH_2N$), 2.73 (4H, t, $NCH_2CH_2CH_2N^tBu$, $^3J_{H-H}$ = 5.7), 3.58 (2H, s, $ArCH_2$), 4.88 (4 H, s br, $BnNCH_2CH_2CH_2N$), 6.85 (2H, d, $HC{=}CH$, J_{H-H} = 2.0), 7.07 (2H, d, $HC{=}CH$, J_{H-H} = 2.0), 7.22(1H, br, C_6H_5), 7.32 (2 H, t, C_6H_5, $^3J_{H-H}$ = 7.3), 7.39 (2H, d, C_6H_5, J_{H-H} = 7.3). ^{13}C NMR (126 MHz, $CDCl_3$): 28.6, 32.6, 51.9, 53.3, 38.2, 61.0, 120.3, 120.8, 127.3, 128.7, 129.2, 140.0, 161.4. HR FT-ICR MS: found (calcd for $C_{27}H_{41}Cl_2N_5Pd$): m/z (M − Cl) 688.144 (688.145).

When this reaction was performed in an NMR tube, an intermediate was observed, which we believe is $\{^{tBu}CN(Bn)C^{tBu}\}PdClI$ (**4b**). As mentioned in the text, this product could not be isolated. The chemical shifts for the ^1H NMR resonances of **4b** are listed below, and the actual ^1H NMR spectrum from the reaction is given in the Supporting Information.[40] Where possible, shifts were assigned using 2D NMR experiments.

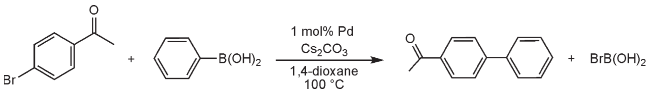
^1H NMR (400 MHz, $CDCl_3$): 2.01 (9H, s, $C(CH_3)_3$), 2.04 (9H, s, $C(CH_3)_3$), 2.28 (2H, br, $NCH_2CH_2CH_2N$, overlapping with **5b**), 2.37 (2H, br, $NCH_2CH_2CH_2N$), 2.63 (2H, br, $NCH_2CH_2CH_2N^tBu$), 2.79 (2H, t, $NCH_2CH_2CH_2N^tBu$, br, overlapping with **5b**), 3.65 (1H, s, $ArCH_2$), 3.66 (1H, s, $ArCH_2$), 4.64 (1H, s br, $BnNCH_2CH_2CH_2N$), 5.04 (2H, s br, $BnNCH_2CH_2CH_2N$, overlapping with **5b**), 5.68 (1H, s br, $BnNCH_2CH_2CH_2N$), 6.81 (1H, d, $HC{=}CH$, J_{H-H} = 2.0), 6.84 (1H, d, $HC{=}CH$, J_{H-H} = 2.0), 7.01 (1H, d, $HC{=}CH$, J_{H-H} = 2.0), 7.05 (1H, d, $HC{=}CH$, J_{H-H} = 2.0), 7.36 (3H, m, C_6H_5, overlapping with **5b**), 7.44 (3H, d, C_6H_5, overlapping with **5b**).

Representative Procedures for Catalysis. *Heck Reaction.*



This procedure was modified from the literature method of Douthwaite et al.[6] Tetra-*n*-butylammonium bromide (13.0 mg, 0.041 mmol) and Na_2CO_3 (48.7 mg, 0.46 mmol) were added to a dimethylacetamide (DMA; 1 mL) solution containing 0.1 mol % (relative to the aryl halide) of the Pd catalyst. This was heated under nitrogen with stirring until the temperature reached 140 °C. Subsequently a DMA solution (1 mL) of bromoacetophenone (81.6 mg, 0.41 mmol), *n*-butyl acrylate (73.1 mg, 0.57 mmol), and the internal standard trimethoxybenzene (69.0 mg, 0.41 mmol) were added. The catalytic mixture was stirred under nitrogen at 140 °C for the specified time. After it was cooled, a ^1H NMR spectrum was taken of the reaction mixture in $CDCl_3$.

Suzuki Reaction.



This procedure was modified from the literature method of Smith et al.[17] Cs_2CO_3 (196 mg, 0.60 mmol), phenylboronic acid (36.6 mg, 0.30 mmol), bromoacetophenone (39.8 mg, 0.20 mmol), 1 mol % (relative to the aryl halide) of the Pd catalyst, and the internal standard trimethoxybenzene (33.6 mg, 0.20 mmol) were added to a 10 mL round-bottom flask equipped with a stir bar. 1,4-Dioxane (1.4 mL) was then added to the reaction flask and the solution heated, with stirring, at 100 °C under nitrogen for the desired period of time. After it was cooled, a ^{1}H NMR spectrum was taken of the reaction mixture in $CDCl_3$.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Text, tables, figures, and CIF files giving X-ray data for **2d**, **3a**, **3c**, and **5b**'. and further details about electrochemical, NMR, and computational experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was partially (J.D.B.) supported by the ANSER EFRC under US DoE Award DE-PS02-08ER15944.

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