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N-Heterocyclic carbenes: deducing σ- and π-contributions in Rh-catalyzed hydroboration and Pd-catalyzed coupling reactions

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Dedicated to Professor John F. Hartwig in honor of his receipt of the 2007 Tetrahedron Young Investigator Award

ABSTRACT

The effect of tuning the electronic properties of *N*-heterocyclic carbene (NHC) ligands was evaluated in multiple, mechanistically distinct, metal-mediated reactions. Hydroboration and Heck reactions, catalyzed by Rh–NHC and Pd–NHC complexes, respectively, were found to result in yields that were up to ten times lower when π-withdrawing substituents were incorporated into the NHC backbone relative to analogues bearing σ-withdrawing groups.

1. Introduction

Over the past 40 years,[1] *N*-heterocyclic carbenes (NHCs) (**1**)[2] have blossomed into a class of ligands that have proven to be useful for a broad range of transition metals.[3,4] As strong, two-electron donors, they generally coordinate to metals in a fashion that is analogous to phosphines;[5] however, in many instances, they often produce complexes which are more thermally-stable[6] and/or exhibit higher catalytic activities.[3] Prime examples include the Grubbs second generation (**2**)[7] and PEPPSI[8] catalysts (**3**) (see Fig. 1), both of which show higher catalytic activities in olefin metathesis and cross-coupling reactions, respectively, than many of their phosphine-ligated counterparts. Considering the number of synthetic methods known to prepare these compounds,[9] NHCs are often the ligand of choice for applications ranging from metal-mediated catalysis to organometallic materials.[3,10]

In view of this breadth of utility, substantial efforts have been directed toward understanding the nature of the interactions formed between NHCs and transition metals. Like many other ligands,[11] both the steric and electronic components of NHCs can be independently modulated. Sterics are often modified by varying the N-substituents using relatively straightforward processes that typically involve standard alkylation or amination chemistries.[12] In many cases, the size of the NHC's N-substituents has been shown to significantly influence the catalytic activities of their respective NHC–metal complexes.[8] For example, in Pd-mediated coupling reactions, NHC ligands bearing bulky N-substituents have been found to drastically increase the stabilities and activities of the catalytically pertinent species.[13] Likewise, in NHC-ligated pre-catalysts, bulky NHCs have been shown to promote the dissociation of ancillary ligands and facilitate catalyst formation.[14] This feature is nicely exemplified in Ru-based olefin metathesis catalysts containing sterically encumbered NHC and phosphine ligands.[4e,15] Collectively, a broad range of highly active catalysts has resulted from judicious modification and optimization of the steric parameters of NHCs.[3]

Tuning the electronic components of NHCs is also of great interest for enhancing the catalytic activities of NHC–metal complexes.[16] Most NHC frameworks offer three distinct options for such purposes: (1) transposition of heteroatoms[17] (e.g., imidazole→oxazole or thiazole), (2) incorporation of additional heteroatoms into the backbone,[18] and (3) attachment of pendant electron-donating or electron-withdrawing groups. With rare exception,[16] varying the N-substituents (particularly, N-aryl substituents)

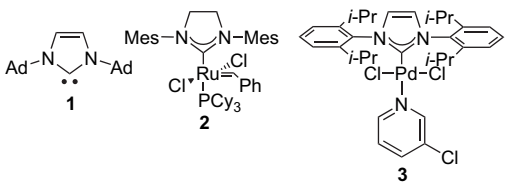

Figure 1. Representative examples of an *N*-heterocyclic carbene (NHC) (**1**) and catalytically active transition metal complexes bearing NHCs (**2** and **3**). Ad=adamantyl, Mes=2,4,6-trimethylbenzene, *i*-Pr=*iso*-propyl.

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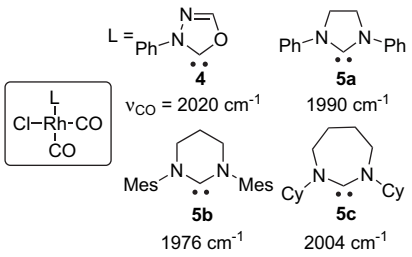


Figure 2. Representative complexes used for examining the electron-donating properties of *N*-heterocyclic carbenes. The number listed below each NHC refers to the stretching frequency (ν_{CO}) exhibited by the *trans*-CO group in their respective (NHC)RhCl(CO)$_2$ complexes.[20–22] Ph=phenyl, Mes=mesityl, Cy=cyclohexyl.

generally has little effect on the electronic properties of NHCs. Regardless, NHC electronics can often be modified without disrupting steric features, which effectively enables separation of these two key components.

The electronic properties of NHCs, particularly their electron-donating abilities, are routinely quantified by measuring the CO stretching frequencies (ν_{CO}) exhibited by their respective Rh carbonyl complexes, (NHC)RhX(CO)$_2$ (X=Cl, I).[19] Current data indicates that the largest changes in the electron-donating abilities of NHCs are achieved by incorporating one or more heteroatoms into their backbones. For example, a Rh carbonyl complex bearing an oxadiazolylidene (**4**; see Fig. 2) exhibited a ν_{CO}=2020 cm^{-1}, which corresponds to the CO ligand trans to the NHC and is among highest known frequencies for these types of complexes.[20] While incorporation of additional heteroatoms into NHC scaffolds likely changes their electronic structures with respect to typical imidazolylidenes, changes in sterics may contribute as well. For example, recent reports revealed that varying the ring size of NHC-type ligands[21] (i.e., **5a**→**5b**→**5c**) had substantial effects on the ν_{CO} exhibited by their respective Rh carbonyl complexes.[22] Hence, to properly study the effects of modifying the electronic components of NHCs, all other structural components should remain identical.

Adhering to this criteria, Organ and co-workers prepared a series of 1,3-diadamantyl-benzimidazolylidene precursors that differed only in the functional groups present at the distal 5- and 6-positions.[23] They then studied the ability of their respective NHCs to facilitate Pd-mediated Suzuki–Miyaura cross-coupling reactions[24] between various aryl chlorides and boronic acids (see Fig. 3).[23] This particular reaction was chosen because it is fairly well accepted that its rate-limiting step is oxidative addition of Pd^0 species with aryl chlorides;[25] hence, ligand electronics should strongly influence the outcomes of these reactions. As expected, complexes bearing electron rich 5,6-dimethoxy-benzimidazolylidenes were generally found to give higher yields of product than their electron deficient 5,6-difluoro analogues over the same time periods. This seminal contribution effectively paved a new avenue for tuning the activity of Pd-catalysts bearing NHC ligands.

While the installation of pendant functional groups onto NHC ligands clearly influences the electronic and catalytic properties of

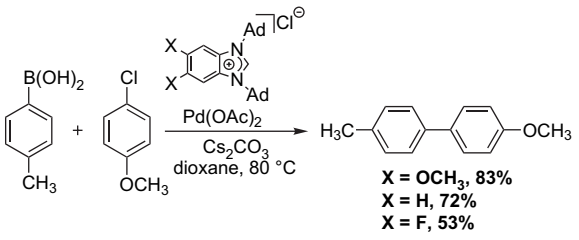


Figure 3. Previously reported Suzuki–Miyaura cross-coupling reactions using Pd complexes ligated to electronically different *N*-heterocyclic carbenes (generated in situ).[23a]

their respective transition metal complexes, the nature of these effects has not been studied in detail.[26] For example, NHCs are known to form σ- and π-bonding interactions with metals. Because the lone pairs on the nitrogen atom were believed to fill the empty p-orbital of the flanking carbene atom in preference to any ligated transition metal, π-backbonding interactions have historically been considered to be negligible.[27] However, that view has changed considerably over the past several years. For example, Meyer, Frenking, and others employed a combination of computational and crystallographic studies to conclude that π-backbonding interactions contribute up to 30% of the overall bonding character formed between NHCs and certain transition metals.[28] More recently, our group synthesized and characterized a series of Rh olefin and carbonyl complexes bearing NHCs with different σ- and π-withdrawing groups. Using NMR and FTIR spectroscopies, we were able to separate their relative electronic effects, which lead us to conclude that π-backbonding interactions were not only present in NHC–Rh complexes but, in some cases, tunable.[29]

Poised by these results, we sought to build upon Organ's initial investigation and gain insight into how various σ- and π-contributors influence the catalytic activities of NHC–metal complexes. Herein, we compare the abilities of a series of Rh- and Pd-complexes bearing uniquely functionalized NHCs to facilitate hydroboration and coupling reactions, respectively. We believe our results show that both σ- and π-interactions are formed between NHCs and transition metals and, in cases where one interaction dominates, can significantly influence the yields and outcomes of reactions catalyzed by such complexes. On a broader level, the results obtained from this fundamental investigation should help create new design parameters for optimizing reactions catalyzed by metal complexes containing NHC-type ligands.

2. Results and discussion

2.1. Synthesis and characterization of Rh complexes ligated to electronically different NHCs

In our previous study,[29] we prepared a series of Rh olefin (**6**) and carbonyl (**7**) complexes ligated to 1,3-dimethylimidazolylidenes bearing various functional groups in their 4- and 5-positions (see Fig. 4). We benchmarked 1,3-dimethyl-4,5-dichloroimidazolylidene as an NHC possessing predominately σ-withdrawing groups. However, due to known *ortho*-, *para*-directing effects of halo substituents in electrophilic aromatic substitutions (EAS), the π-donor abilities of the Cl substituents in this NHC may counteract, at least partially, their σ-withdrawing character. In order to strengthen our hypothesis that π-backbonding interactions are operative in NHC–Rh complexes and to ensure that the previously observed electronic effects were not due to weakened σ-donation, Rh olefin and carbonyl complexes ligated to 1,3-dimethyl-4-trifluoromethylimidazolylidene were prepared and studied. This particular NHC derivative was chosen because CF_3 and

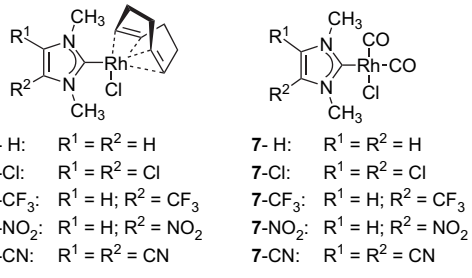


Figure 4. Structures of Rh olefin (**6**) and carbonyl (**7**) complexes synthesized and examined in this study.

Table 1
Spectroscopic properties of various NHC–Rh complexes

Complex	δ(=CH)[a] (ppm)	Complex	ν_{CO}[b] (cm^{-1})
6-H	5.00	**7-H**	2004
6-Cl	5.03	**7-Cl**	2010
6-CF_3	5.06	**7-CF_3**	2006
6-NO_2	5.12	**7-NO_2**	2012
6-CN	5.17	**7-CN**	2017

[a] Chemical shifts were determined using ^{1}H NMR spectroscopy (solvent=$CDCl_3$), reported downfield to tetramethylsilane and referenced to residual protio solvent.
[b] Carbonyl stretching frequencies (ν_{CO}) were determined using FTIR spectroscopy for compounds in solution ($CDCl_3$). Values reported are $\pm$0.5 cm^{-1}. The frequency indicated corresponds to the *trans*-CO moiety.

NO_2 groups possess identical group electronegativities (3.4).[30,31] Hence, while the electron-withdrawing capabilities of these two functional groups are virtually equal, they can be distinguished by the fact that CF_3 groups exhibit minimal π-interactions (i.e., they are *meta* directors in EAS reactions).

Rh complex **6-CF_3** was prepared in accord with our previously reported protocol.[29] 1,3-Dimethyl-4-trifluoromethylimidazolium iodide was treated with Ag_2O followed by transmetallation using $[Rh(cod)Cl]_2$ (cod=1,5-*cis*-*cis*-cyclooctadiene) to obtain pure **6-CF_3** as a yellow solid in 95% yield. Subsequently, pressurizing the solution of **6-CF_3** with carbon monoxide afforded Rh complex **7-CF_3** in quantitative yield. Analysis of these complexes using ^{1}H NMR and FTIR spectroscopies revealed that key signals were in accord with analogues bearing pendant H and Cl groups (see Table 1). Furthermore, despite the identical electronegativities of trifluoromethyl and nitro groups, **6-CF_3** and **7-CF_3** exhibited spectroscopic properties that were significantly different than **6-NO_2** and **7-NO_2**, respectively. In addition, the solid-state structure of **6-CF_3** (shown in Fig. 5) revealed bond distances that were similar to those found in the solid-state structures of **6-H** and **6-Cl** (not shown). For example, the distance of $C_{carbene}$–Rh in **6-CF_3** was found to be 2.018(4) Å, which is similar to $C_{carbene}$–Rh distances of 2.023(2) and 2.021(2) Å exhibited by **6-H** and **6-Cl**, respectively. For comparison, the solid-state structures of **6-NO_2** and **6-CN** revealed shorter $C_{carbene}$–Rh distances of 2.005(3) and 2.006(6) Å, respectively. Collectively these results provide additional support for our notion that π-backbonding interactions are operative in NHC–Rh complexes and may be tuned through derivatization of the NHC.[29] Moreover, we believe that by comparing metal complexes ligated to NHCs bearing trifluoromethyl groups to those with nitro groups should enable (1) a means to separate σ- and π-interactions formed between NHCs and transition metals and (2) insight into how each of these fundamental contributors influence the catalytic activities exhibited by these complexes.

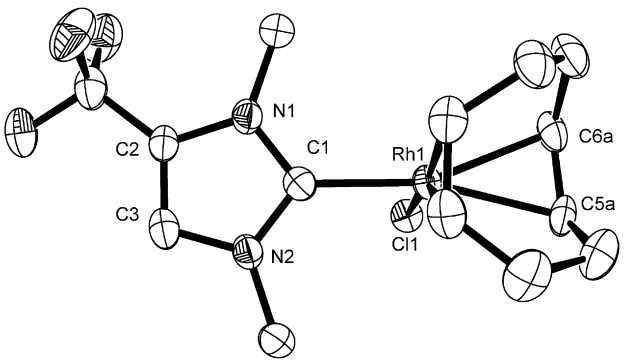


Figure 5. ORTEP drawing of **6-CF_3**. Selected bond lengths (Å) and angles (°): C1–Rh1, 2.018(4); C1–N1, 1.359(6); C1–N2, 1.353(3); N1–C2, 1.393(5); N2–C3, 1.373(5); C2–C3, 1.349(6); N1–C1–N2, 104.4(4).

2.2. Deducing σ- and π-contributions in hydroboration reactions catalyzed by Rh–NHC complexes

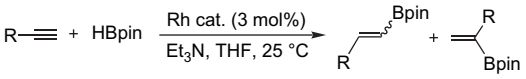
With a range of Rh complexes ligated to various functionalized NHCs in hand, attention turned toward exploring their abilities to catalyze hydroboration reactions. The hydroboration of terminal alkynes yields alkenylboronates, which ultimately provides direct access to vinyl boranes, a synthetically useful class of compounds.[24] Although this reaction proceeds uncatalyzed under certain conditions,[32] advantages of known[33] catalyzed variations include decreased reaction times and unique selectivities. In particular, Rh-catalyzed hydroborations of terminal alkynes with pinacol or catecholboranes were shown to be greatly facilitated by phosphine ligands and often provided (*Z*)-1-alkenylboronates in high yields.[34] Since NHC ligands have been shown to have similar metal-activating properties as phosphine ligands,[1–5] we explored the ability of analogous NHC–Rh complexes to catalyze various hydroboration reactions. In addition, NHC ligands bearing different functional groups were probed to deduce how σ- and π-contributions formed between NHCs and Rh influenced the outcomes of these reactions.

Initial efforts were directed toward studying the hydroborations of phenylacetylene and 1-octyne using pinacolborane and Rh olefin complexes **6**. In general, the reactions were performed under conditions analogous to those reported by Miyaura.[34] Mixtures of pinacolborane (1.0 equiv), alkyne (1.2 equiv), Rh catalyst (3 mol %), and an excess of triethylamine (5 equiv) were prepared in THF at 25 °C and then monitored over time by ^{1}H NMR spectroscopy using an internal standard (mesitylene or 1,3,5-trimethoxybenzene). As control experiments, uncatalyzed hydroborations, as well as those catalyzed with $[Rh(cod)Cl]_2$, were also performed under otherwise similar conditions. The results of these reactions are summarized in Table 2.

As shown in entry 1, Rh complex **6-H** was found to catalyze the hydroboration of phenylacetylene, affording a 55% yield of product, under the aforementioned conditions.[35] To the best of our knowledge, this is the first example demonstrating that Rh–NHC complexes are capable of catalyzing hydroboration reactions.[36] Complexes **6-Cl** and **6-CF_3** afforded slightly lower yields of products compared to **6-H** (see entries 2 and 3), which suggested to us that the Rh center was not strongly influenced by NHCs bearing strong σ-withdrawing groups. In contrast, significantly lower yields of product were obtained when **6-NO_2** or **6-CN** complexes, which contain NHCs bearing π-withdrawing groups, were used as catalysts (see entries 4 and 5). It is noteworthy that the yield of the reaction catalyzed by **6-CF_3** was nearly twice than that of the reaction catalyzed by **6-NO_2**. As mentioned above, the NHCs in these catalysts bear functional groups with identical group electronegativities; hence, we surmise that the observed difference in yields for these two complexes is due to differences in the nature of the interaction (σ vs π) formed between the NHC and Rh. Importantly, all of the Rh–NHC complexes examined catalyzed hydroborations significantly more efficiently than $[Rh(cod)Cl]_2$ or those performed without any added catalyst (cf., entries 6 and 7, respectively), which gave very low yields of product under otherwise identical conditions. Collectively, these results indicate, for the first time, that Rh complexes containing NHCs with σ-withdrawing groups can lead to different product outcomes than analogues bearing π-withdrawing groups.

Considerably different reaction outcomes were observed for hydroborations of 1-octyne catalyzed by the same set of Rh–NHC complexes. As shown in Table 2, preliminary experiments suggested that while **6-H** was capable of catalyzing the hydroboration of this substrate under the conditions described above, relatively low yields of product were obtained (see entry 8).[35] Comparison of entries 8–12 revealed that Rh complexes **6** afforded virtually the

Table 2
Hydroboration of alkynes catalyzed by various Rh complexes[a]



Entry	R	Rh catalyst	Yield[b] (%)	*E*/*Z*/*T*[c]
1	Ph	**6-H**	55	1.5:0.8:1.0
2	Ph	**6-Cl**	42	1.3:0.0:1.0
3	Ph	**6-CF$_3$**	50	1.3:0.2:1.0
4	Ph	**6-NO$_2$**	24	1.4:1.0:1.0
5	Ph	**6-CN**	24	1.5:0.0:1.0
6	Ph	[Rh(cod)Cl]$_2$	9[d]	2.2:1.1:1.0
7	Ph	None	0	nd
8	*n*-Hex	**6-H**	27	3.8:1.4:1.0
9	*n*-Hex	**6-Cl**	28	4.5:1.5:1.0
10	*n*-Hex	**6-CF$_3$**	21[d]	4.1:1.5:1.0
11	*n*-Hex	**6-NO$_2$**	18[d]	3.8:0.9:1.0
12	*n*-Hex	**6-CN**	21[d]	3.8:2.0:1.0
13	*n*-Hex	[Rh(cod)Cl]$_2$	10[d]	4.8:0.0:1.0
14	*n*-Hex	None	0	nd
15	Ph	(IMes)Rh(cod)Cl	26	4.5:1.6:1.0
16	*n*-Hex	(IMes)Rh(cod)Cl	50	4.3:0.7:1.0
17	4-MeO–Ph	**6-H**	60	1.4:0.7:1.0
18	4-NO$_2$–Ph	**6-H**	30	1.3:0.4:1.0
19	4-CN–Ph	**6-H**	33	1.3:0.3:1.0
20	4-MeO–Ph	**6-CF$_3$**	43	1.5:0.2:1.0
21	4-NO$_2$–Ph	**6-CF$_3$**	17	1.4:0.3:1.0
22	4-CN–Ph	**6-CF$_3$**	32	1.2:0.3:1.0
23	4-MeO–Ph	**6-NO$_2$**	31	1.9:0.8:1.0
24	4-NO$_2$–Ph	**6-NO$_2$**	20	1.7:0.4:1.0
25	4-CN–Ph	**6-NO$_2$**	28	1.2:0.4:1.0

cod=1,5-cyclooctadiene; IMes=1,3-dimesitylimidazolylidene; nd=not determined.
[a] General conditions: [pinacolborane]$_0$=0.33 M (1.0 equiv), [Et$_3$N]$_0$=1.65 M (5.0 equiv), [alkyne]$_0$=0.4 M (1.2 equiv), Rh complex (3 mol%), THF, 14 h, 25 °C, unless otherwise noted. All reactions were performed in triplicate.
[b] Combined yield of all possible isomers, as determined from ^{1}H NMR analysis of crude reaction mixtures using an internal standard (mesitylene or 1,3,5-trimethoxybenzene). Unless otherwise noted, reported yields are ±≤5%.
[c] Average ratios of the olefin regioisomers found; *E*: trans, *Z*: cis, *T*: terminal.
[d] Yield is ±≤8%.

same yield of product, within experimental error, regardless of the functional group installed on the NHC ligand. Furthermore, the activities of these Rh–NHC complexes were found to be only marginally more active than [Rh(cod)Cl]$_2$ (entry 13). Hence, any influence caused by the pendant functional groups on the NHC ligands in **6** appeared to have only a minimal effect on the performance of these particular hydroboration reactions. More broadly, this result suggested to us that the importance of relative σ- and π-contributions to the interactions formed between Rh and NHCs may be substrate dependent.

Although Rh complexes bearing bulky phosphine ligands have been reported to afford hydroboration products with high cis contents, very modest stereoselectivities were generally observed in the aforementioned hydroboration reactions catalyzed by **6**.[34] However, this disparity may, at least partially, be explained by the difference in sterics between the NHCs explored herein (which contain relatively small *N*-methyl groups) and the bulky phosphines (i.e., PCy$_3$) previously used.[34] This hypothesis is supported by the observation that (IMes)Rh(cod)Cl (IMes=1,3-dimesitylimidazolylidene),[37] a complex that bears bulky N-substituents, exhibited different selectivities, when compared to **6-H**, for the hydroboration of both phenylacetylene and 1-octyne (cf. entries 1 and 8 vs 15 and 16, respectively).

Based on a proposed mechanism of Rh-catalyzed hydroboration of alkenes, as reported by Männig and Nöth[38] and later supported by others,[39,40] an analogous mechanism for the hydroboration of alkynes is proposed in Figure 6. There are four key steps in this mechanism: (1) oxidative addition of a borane to Rh–NHC catalyst **A**, (2) alkyne coordination to the resulting Rh hydride **B**, (3) hydride

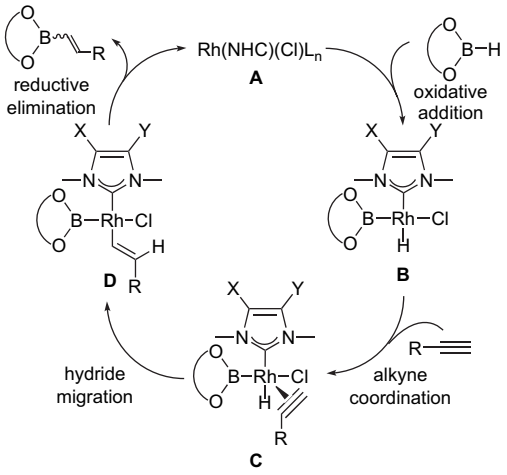


Figure 6. Proposed general reaction mechanism for the hydroborations of alkynes catalyzed by Rh–NHC complexes.

migration (**C**→**D**), and (4) reductive elimination, ultimately leading to an alkenylboronate product and **A**. The structures of the intermediates shown in Figure 6 are supported by analogous Ir hydride and Ir alkyl complexes bearing phosphine ligands, most of which have been characterized spectroscopically or crystallographically.[41,42]

While each of the steps in the proposed mechanism should be influenced by the electron density residing at the metal center, and therefore amenable to modulation by the coordinated NHC, it has been previously proposed that reductive elimination is the rate-limiting step in Rh-catalyzed hydroborations of alkenes.[39a,41,42] Based on the data shown in Table 2, we surmise that reductive elimination is also the limiting step for hydroboration of alkynes catalyzed by the Rh–NHC catalysts described herein. In particular, intermediate **D** features an NHC ligand situated trans to the alkenyl moiety. Electron-withdrawing groups on the carbene ligand are positioned to remove electron density from Rh, resulting in a stronger bond formed between the alkene carbon and the metal center. Hence, reductive elimination should be inhibited and result in decreased yields of product in accord with the nature and strength of the electron-withdrawing group. Indeed, as shown for phenylacetylene in Table 2, a Rh catalyst bearing an electron rich NHC ligand generally afforded higher yields of products than its electron deficient analogues (cf., entry 1 vs entries 2–5). Moreover, the nature of the interaction formed between NHCs and Rh appears to play an important role. Catalysts ligated to NHCs bearing σ-withdrawing CF$_3$ groups afforded higher yields of product compared to analogues bearing π-withdrawing NO$_2$ or CN groups (cf., entry 3 vs entries 4–5). These results suggested to us that π-withdrawing groups on the NHC ligand are more effective at decreasing electron density at the Rh center and therefore more significantly influencing its reactivity when compared to analogues bearing σ-withdrawing groups.

To gain additional support for the notion that reductive elimination is the rate-determining step in Rh–NHC catalyzed alkyne hydroborations, a series of functionalized phenylacetylene derivatives were synthesized and studied for their ability to react with pinacolborane under the conditions described above (entries 17–25). Using **6-H** as a catalyst, higher yields of hydroboration product were obtained when phenylacetylene (entry 1) or 4-methoxyphenylacetylene (entry 17) were used as substrates when compared to analogous reactions performed using relatively electron deficient alkynes, i.e., 4-nitro- or 4-cyanophenylacetylene (entries 18 and 19, respectively). In the former cases, the increased electron

density on the substrate may serve to weaken the bond formed between the Rh center and the coordinated alkenyl group, facilitating reductive elimination and resulting in higher yields of product. In contrast, the electron deficient nature of the latter substrates may result in the formation of relatively strong bonds between these two moieties, which hinders the reductive elimination process and ultimately product formation.

To explore whether the nature of the interaction formed between NHCs and Rh influence the yields of hydroboration products obtained from functionalized phenylacetylenes, the aforementioned reactions were repeated using **6-CF$_3$** and **6-NO$_2$** as catalysts (see entries 20–25). Compared to **6-H**, lower yields of product were observed, which is likely due to the decreased electron density on the Rh center. However, the yields of product obtained from either **6-CF$_3$** or **6-NO$_2$** were similar. Thus, we conclude that the pendant functional groups on these phenylacetylene derivatives modulate the strength of the Rh–alkenyl bond more strongly than the NHC ligand, thereby diminishing any noticeable effect caused by the latter.

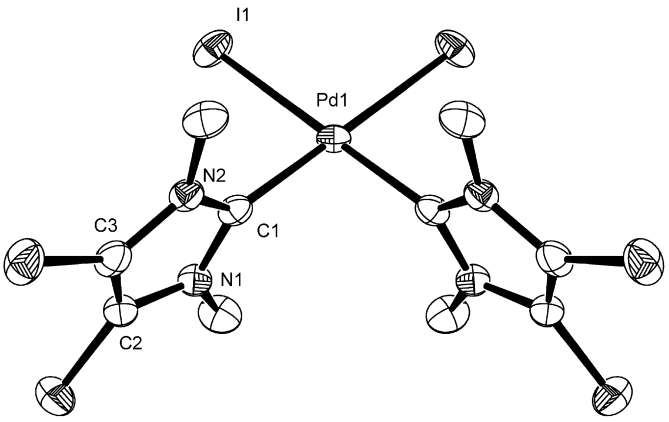
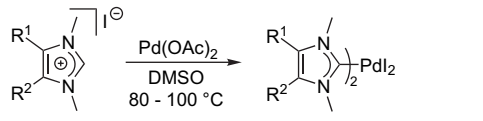


Figure 8. ORTEP diagram of **8-Cl**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths are listed in Table 3. The crystal structures of **8-CN** and **8-NO$_2$** were also obtained (not shown) and found to be similar to **8-Cl**. The crystal structure of **8-CF$_3$** (not shown) revealed that this complex adoped a trans geometry in the solid state.

2.3. Synthesis and characterization of Pd complexes ligated to electronically different NHCs

Next, attention was directed toward exploring how NHC-based ligands bearing different functional groups influenced Pd-catalyzed Heck-type cross-coupling reactions.[43] Using previously reported proctocols,[9a] (NHC)$_2$PdI$_2$ complexes (**8**) bearing the same NHCs as in the aforementioned Rh complexes (i.e., **6** and **7**) were prepared from their corresponding imidazolium salts and Pd(OAc)$_2$ (see Fig. 7). After 2 h at 80–100 °C in DMSO-d_6, NMR scale experiments indicated that the desired complexes formed in quantitative yields with concomitant formation of AcOH. Furthermore, electron deficient imidazoliums qualitatively reacted much faster than their electron rich analogues, supporting the notion that acetate functions as a base in these reactions.[9a] For syntheses performed on preparative scales, a 10 mol % excess of imidazolium salt was used to ensure complete consumption of Pd(OAc)$_2$.[44] Ultimately, Pd complexes **8** were obtained in excellent yields (90–96%) by pouring their corresponding reaction mixtures into excess water upon completion, which caused the precipitation of pale yellow solids that were later collected by filtration. Complexes **8** were found to be stable to ambient air and moisture and could be stored for months without any noticeable decomposition.

In addition to NMR and mass spectroscopy, Pd complexes **8** were characterized by X-ray crystallography. With the exception of **8-CF$_3$**, all complexes adopted pseudo-square planar geometries where the NHC ligands were cis to each other (an ORTEP of **8-Cl** is shown in Fig. 8 as a representative example). Although **8-CF$_3$**, which adopted a trans geometry, was different than the other complexes prepared, it has been previously shown that such differences do not influence ultimate product yields of coupling



8-H ($R^1 = R^2 = H$), 95%
8-Cl ($R^1 = R^2 = Cl$), 93%
8-CF$_3$ ($R^1 = H$; $R^2 = CF_3$), 92%
8-NO$_2$ ($R^1 = H$; $R^2 = NO_2$), 90%
8-CN ($R^1 = R^2 = CN$), 96%

Figure 7. Synthesis of Pd–NHC complexes **8**.

reactions mediated by (NHC)$_2$PdX$_2$-type pre-catalysts; however, initiation rates may vary.[45] Key bond lengths and angles for **8** are summarized in Table 3. Complexes **8-NO$_2$** and **8-CN** exhibited Pd–I and Pd–C$_{carbene}$ bond lengths that were shorter than the respective bond lengths in **8-H** and **8-Cl**. Similar differences were observed in the series of Rh complexes reported in our previous studies,[29] which were ultimately attributed to π-backbonding interactions.[46]

2.4. Deducing σ- and π-contributions in Heck reactions catalyzed by Pd–NHC complexes

With a range of Pd complexes in hand, attention turned toward exploring their utilities in catalyzing Heck-type coupling reactions.[47] In general, 1 mol % **8** was added to a DMF solution containing *tert*-butyl-acrylate (1.4 equiv) and an aryl halide (1.0 equiv), and then heated under nitrogen in the presence of NaOAc (1.5 equiv). Preliminary studies indicated that, in our hands, 120 °C was the optimal temperature for these coupling reactions. At lower temperatures (i.e., 100 °C), very low yields of product were obtained for all the Pd–NHC catalyst systems reported herein. At elevated temperatures (i.e., 140 °C), catalyst decomposition was observed, as evidenced by the formation of Pd^0. Due to the high temperatures employed, a series of control experiments involving Pd(OAc)$_2$ (no NHC ligand) were performed in parallel to see if ill-defined Pd species that may have formed over the course of the reaction are catalytically active.[44] Furthermore, initial studies revealed that all coupling reactions were complete in less than 18 h; hence, all reactions were performed for this amount of time (see below for additional details on the kinetics of these reactions). Product yields were determined by gas chromatography (GC) using an internal standard (mesitylene); results are summarized in Table 4.

Although no universal trend was observed amongst the catalysts studied, **8-CF$_3$** appeared to exhibit higher activities than **8-NO$_2$** when 4-bromobenzene or 4-bromoanisole was used as substrate. As described above, trifluoromethyl and nitro groups possess identical electronegativities;[30] hence, the relative activities exhibited by **8-CF$_3$** and **8-NO$_2$** may be attributed to σ- and π-contributions formed between their respective NHCs and Pd. The relatively high yields of product obtained with **8-CF$_3$** may be explained in terms of the overall donating ability of its respective NHC being similar to benzimidazolylidene, a ligand that has been reported to be highly efficient for Heck couplings.[48] Importantly,

Table 3
Selected bond lengths (Å) and angles (°) for Pd complexes **8**

Bond	**8-H**[a]	**8-Cl**	**8-CF_3**	**8-CN**	**8-NO_2**
Pd1–I1	2.6526(9)	2.6426(3)	2.5965(9)	2.6317(3)	2.6384(7)
Pd1–C1	1.993(3)	2.003(3)	2.006(9)	1.998 (4)	2.002(8)
C1–N1/2	1.351(4)	1.355(4)	1.342(11)	1.341(5)	1.338(10)
C2–C3	1.341(5)	1.340(4)	1.355(14)	1.353(6)	1.368(2)
N1–C1–N2	105.2(3)	105.2(3)	104.5(7)	105.7(3)	104.9(8)

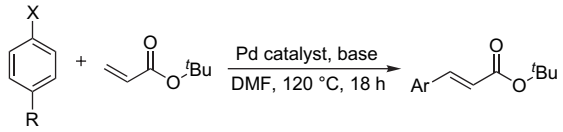
[a] Data reproduced from Ref. 3e.

these substrates produced very little product when $Pd(OAc)_2$ was used without NHC ligand, even at various loadings.[49]

While these results underscore the importance of differentiating σ- and π- components in NHCs to optimize yields, the overall activities displayed by these catalysts were relatively low, with many substrates, such as aryl chlorides (not shown), failing to react. However, 4-iodoanisole and aryl bromides bearing activating groups (e.g., CHO) afforded the expected products in excellent (>97%) yields. As expected for substrates containing deactivating functional groups, 4-bromoanisole afforded lower yields of product when compared to bromobenzene for all catalysts investigated.

Since the nature of the base used in Pd-mediated coupling reactions is known to often have a profound effect on reaction rates,[50] we envisioned that the use of stronger bases might facilitate regeneration of active Pd^0 species better than NaOAc and thus lead to higher yields of product. Indeed, as summarized in Table 4, improved yields were observed when the aforementioned coupling reactions were performed using K_2CO_3 as base.[51]

Table 4
Yields of products obtained by coupling *tert*-butylacrylate with various aryl halides using various Pd complexes as catalysts[a]



Entry	Catalyst	R:	H	OMe	OMe	CHO
		X:	Br	Br	Br	Cl
		Base:	NaOAc	NaOAc	K_2CO_3	K_2CO_3
1	**8-H**		19	8	47	1
2	**8-Cl**		11	4	42	1
3	**8-CF_3**		76	28	75	1
4	**8-NO_2**		8	4	22	3
5	**8-CN**		60	1	87	10
6[b]	**$Pd(OAc)_2$**		1	5	5	0
7	**9**		10	7	45	0

[a] General reaction conditions: catalyst (1 mol%), [aryl halide]$_0$=0.33 M, [*tert*-butylacrylate]$_0$=0.47 M, [base]$_0$=0.5 M, [mesitylene]$_0$=0.33 M (internal standard), DMF as solvent, 120 °C, nitrogen atmosphere, 18 h. All reactions were performed in triplicate. Reported yields were determined by GC and are ±5%. Notes: 4-MeO–PhI and 4-CHO–PhBr afforded >97% yield of product for all catalysts and bases studied. PhCl and 4-CHO–PhCl afforded no appreciable yield of product for all catalysts and bases studied.

[b] $Pd(OAc)_2$ was used without any NHC ligand. Similar results were obtained when these coupling reactions were loaded with 2, 0.1, or 0.01 mol% $Pd(OAc)_2$ (no NHC ligand or precursors).

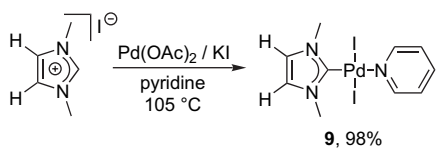


Figure 9. Synthesis of Pd–NHC complex **9**.

The active catalyst for the Heck reactions described above is believed to be a mono NHC-ligated Pd^0 complex, formed via in situ reduction of Pd^{II} and loss of a NHC ligand.[23b,52] To gain support for this hypothesis, complex **9**, which contains 1,3-dimethylimidazolylidene and pyridine, a ligand known[3a,53] to exhibit higher propensities toward dissociation, was prepared[8] as shown in Figure 9 and studied as a pre-catalyst. As shown in Table 4 (entry 7), complex **9** afforded coupled products in yields that were comparable to those obtained with **8-H**.[54]

Based on the generally accepted mechanism (see Fig. 10), the rate-limiting step of Pd-catalyzed Heck reactions is usually assigned to the oxidative addition of a Pd^0 species into an aryl halide.[25] Hence, it was surprising that **8-CF_3** and **8-CN** were the two most active catalysts studied as they appeared amongst the least likely to undergo rate-limiting oxidative addition. Furthermore, in similar studies, Organ demonstrated that benzimidazolylidenes bearing electron-withdrawing fluorines in their 4- and 5-positions resulted in the lowest yields of product.[23]

Hence, we surmised that the observed results may be explained by catalyst stability. To gain support for this hypothesis, a kinetic study comparing the activity of **8-H** (a Pd complex containing a relatively electron rich NHC that should favor oxidative addition) with **8-CN** (a Pd complex containing a relatively electron deficient NHC) over time was performed. The aforementioned catalysts were selected due to their large difference in electronic properies.[29] 4-Bromoanisole and *tert*-butylacrylate were chosen as coupling partners due to the relatively high yields of products obtained with these catalysts. The reaction conditions were analogous to those described in Table 4. As shown in Figure 11, it was apparent that while **8-H** initiated faster than **8-CN**, the former lost all catalytic activity after approximately 1.5 h. In contrast, despite relatively slow initiation kinetics, **8-CN** remained active for more than 8 h, which ultimately afforded a higher yield of product.[55] Assuming oxidative addition is the rate-limiting step, the resting state of the catalyst is likely to be a mono-ligated NHC Pd^0 complex (see above). Hence, we propose that the enhanced stability of **8-CN** is due to its π-withdrawing cyano groups, which serve to stabilize electron rich Pd^0.

Collectively, these results suggested to us that for catalysts bearing electron-withdrawing groups there is a fine balance between stabilizing Pd^0 intermediates and slowing down the rate of

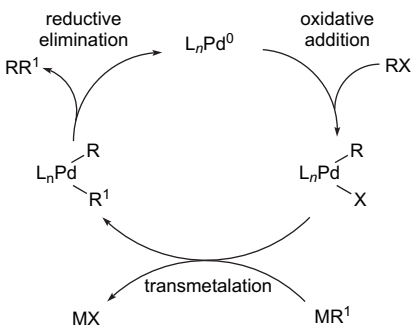


Figure 10. Generally accepted mechanism for Pd-catalyzed cross-coupling reactions.

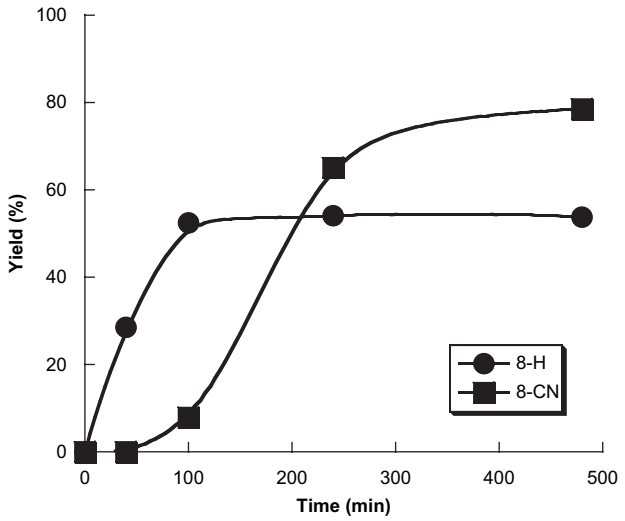


Figure 11. Plots of yield versus time for the Heck reaction of *tert*-butylacrylate with 4-bromoanisole, as catalyzed by **8-H** and **8-CN**. Conditions: catalyst (1 mol %), [4-bromoanisole]$_0$=1.0 M, [*tert*-butylacrylate]$_0$=1.1 M, [K_2CO_3]$_0$=2.0 M, [mesitylene]$_0$=1.0 M (internal standard), DMF as solvent, 120 °C, nitrogen atmosphere. Yields were determined by GC.

oxidative addition. Indeed, close examination of Table 4 reveals that **8-NO$_2$** generally afforded lower yields of product compared to **8-CF$_3$**. These subtleties highlight the sensitivity of catalytic activities toward electronic substitution and particularly the relative contributions of σ- and π-interactions present in NHC–Pd complexes.

3. Conclusions

In conclusion, we have synthesized and characterized a series of Rh and Pd complexes ligated to NHC ligands that bear different functional groups. These complexes were explored as catalysts for facilitating two important synthetic reactions: Rh-mediated hydroborations and Pd-mediated Heck reactions. Particular attention was directed toward exploring how the nature of the functional group appended to the NHC ligand influenced the outcomes of the aforementioned reactions. In Rh-catalyzed hydroborations involving phenylacetylene, NHCs bearing π-withdrawing groups were found to afford lower yields of products when compared to σ-withdrawing analogues. However, essentially no differences were observed in hydroborations of 1-octyne under otherwise identical conditions. Similar overall results were observed in Pd-catalyzed Heck reactions between *tert*-butylacrylate and certain aryl halides. Namely, differences in reaction yield were observed for Pd-catalysts bearing NHCs with π-withdrawing groups as compared to analogues bearing σ-withdrawing groups. Collectively, these results support the notion that NHCs not only participate in π-interactions with transition metals, an often disputed argument, but such interactions can influence catalytic activities. These results should also provide useful guidelines for the future design and optimization of metal catalysts bearing NHC ligands.[56]

4. Experimental

4.1. General

All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen filled glove-box. *N*,*N*-Dimethylformamide (DMF) was dried with molecular sieves and degassed by two freeze-pump-thaw cycles. Tetrahydrofuran and toluene were distilled from Na/benzophenone and degassed by two freeze-pump-thaw cycles. All reagents were purchased from commercial suppliers and were used without further purification. ^{1}H NMR spectra were recorded using a Varian Gemini (300 MHz or 400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio solvent as an internal standard ($CDCl_3$, 7.24 ppm; DMSO-d_6, 2.49 ppm). ^{13}C NMR spectra were recorded using a Varian Gemini (75 MHz or 100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as an internal standard ($CDCl_3$, 77.0 ppm; DMSO-d_6, 39.5 ppm). ^{13}C NMR spectra were routinely run with broadband decoupling. IR spectra were recorded using Perkin–Elmer Spectrum BX FTIR system. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument and are reported as *m*/*z* (relative intensity). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.2. 1,3-Dimethyl-4-trifluoromethylimidazolium iodide

A 30 mL vial was charged with 4-trifluoromethylimidazole (1.0 g, 7.35 mmol), $NaHCO_3$ (0.62 g, 7.35 mmol), 20 mL CH_3CN, 5 mL CH_3I, and stir bar. The vial was then sealed and the mixture was stirred at 60 °C. After 24 h, the solvent was removed, which afforded the desired product as a 1:1 (inseparable) mixture with NaI in quantitative yield. ^{1}H NMR (DMSO-d_6): δ 9.42 (s, 1H), 8.61 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 141.4, 126.5, 121.5 (q, J_{C-F}=41.3 Hz), 118.6 (q, J_{C-F}=267 Hz), 36.5, 35.1. ^{19}F NMR (DMSO-d_6): δ −60.28. HRMS [M]$^+$ calcd for $C_6H_9F_3N_2$: 166.0712; found: 166.0718.

4.3. 1,3-Dimethyl-4-trifluoromethylimidazolylidene AgI

A 30 mL pressure vessel was charged with a mixture of 1,3-dimethyl-4-trifluoromethylimidazolium iodide/NaI (0.44 g of material, 1.0 mmol azolium), Ag_2O (0.23 g, 0.55 mmol), CH_2Cl_2 (15 mL), and a stir bar. After sealing the vessel, the reaction mixture was stirred at 50 °C for 2 h. Subsequent cooling to ambient temperature caused solids to precipitate, which were later removed via filtration. Evaporation of the residual solvent under reduced pressure afforded 0.4 g (90% yield) of desired product as a white powder. ^{1}H NMR (DMSO-d_6): δ 8.25 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 189.2, 126.3, 121.5 (m), 37.0. ^{19}F NMR (DMSO-d_6): −59.76.

4.4. Rh complex 6-CF$_3$

A 20 mL flask was charged with 1,3-dimethyl-4-trifluoromethylimidazolylidene AgI (0.12 g, 0.30 mmol), $[Rh(cod)Cl]_2$ (73 mg, 0.15 mmol), THF (10 mL), and a stir bar. The resulting mixture was then stirred at 50 °C for 4 h. Afterward, the reaction mixture was cooled to ambient temperature and then filtered through a 0.2 μm PTFE filter. Removal of residual solvent under reduced pressure afforded 0.12 g (95% yield) of desired product as yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.19 (s, 1H), 5.06 (s, 2H), 4.17 (s, 3H), 4.10 (s, 3H), 3.27 (s, 2H), 2.39 (br, 4H), 1.96 (br, 4H). ^{13}C NMR ($CDCl_3$): δ 189.6 (d, J_{C-Rh}=51.3 Hz), 123.9, 120.7, 118.1, 99.8 (br), 68.3 (d, J_{C-Rh}=12.6 Hz), 38.3, 36.2, 32.9 (d, J_{C-Rh}=11.2 Hz), 28.8 (d, J_{C-Rh}=10.4 Hz). ^{19}F NMR ($CDCl_3$): δ −61.58. HRMS [M−Cl]$^+$ calcd for $C_{14}H_{19}F_3N_2Rh$: 375.0555; found: 375.0550. Crystals suitable for

X-ray analysis were obtained by slow diffusion of hexanes vapor into concentrated acetone solution of **6-CF_3**; CCDC 675951.

4.5. Rh complex 7-CF_3

A 5 mL flask was charged with **6-CF_3** (30 mg, 73 μmol), $CDCl_3$ (3 mL), and a stir bar. The resulting reaction mixture was then subjected to slight pressure of CO (using a balloon). After 1 h, the reaction was complete as determined by NMR spectroscopy. Removal of residual 1,5-cyclooctadiene (and solvent) was not attempted because (NHC)Rh(CO)$_2$Cl type complexes are generally unstable in the solid state.[57] ^{1}H NMR ($CDCl_3$): δ 7.37 (s, 1H), 4.00 (s, 3H), 3.94 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 184.8 (d, J_{C-Rh}=68.4 Hz), 180.8 (d, J_{C-Rh}=59 Hz), 124.57 (d, $_{C-F}$=5.1 Hz), 119.4 (q, J_{C-Rh}=355 Hz), 39.0, 37.0. ^{19}F NMR ($CDCl_3$): δ −61.51. HRMS $[M-2CO]^+$ calcd for $C_6H_7ClF_3N_2Rh$: 301.9305; found: 301.9310.

4.6. Pd complex 8-H

After charging a 25 mL flask with 1,3-dimethylimidazolium iodide (0.45 g, 2.0 mmol), $Pd(OAc)_2$ (0.21 g, 0.95 mmol), 15 mL DMSO, and a stir bar, the resulting reaction mixture was heated to 120 °C with stirring for 2 h. Subsequent cooling to ambient temperature followed by the addition of 40 mL of H_2O to the reaction vessel caused solids to precipitate. The solids were collected by filtration, washed with 20 mL of H_2O, and then dried under reduced pressure to afford 0.5 g (95% yield) of the desired product as yellow powder. Spectroscopic data matched the literature reports.[58]

4.7. Pd complex 8-Cl

After charging a 25 mL flask with 1,3-dimethyl-4,5-dichloroimidazolium iodide (0.59 g, 2.0 mmol), $Pd(OAc)_2$ (0.21 g, 0.95 mmol), 15 mL DMSO, and a stir bar, the resulting reaction mixture was heated to 80 °C for 1 h. Subsequent cooling to ambient temperature followed by the addition of 50 mL of H_2O to the reaction vessel caused solids to precipitate. The solids were collected by filtration, washed with 20 mL H_2O, and then dried under reduced pressure to afford 0.61 g (93% yield) of the desired product as a yellow powder. The solution structure of this complex was found to be predominantly (>95%) cis by ^{1}H NMR spectroscopy. ^{1}H NMR (DMSO-d_6): δ 3.88 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 162.6, 117.1, 37.5. HRMS $[M]^+$ calcd for $C_{10}H_{12}Cl_4N_4PdI_2$: 685.6946; found: 685.6946. Crystals suitable for X-ray analysis were obtained by slow cooling of saturated DMSO solution of **8-Cl**; CCDC 675948.

4.8. Pd complex 8-CF_3

After charging a 25 mL flask with 1,3-dimethyl-4-trifluoromethylimidazolium iodide (0.58 g, 2.0 mmol), $Pd(OAc)_2$ (0.21 g, 0.95 mmol), 15 mL DMSO, and a stir bar, the resulting reaction mixture was heated to 80 °C for 1 h. Subsequent cooling to ambient temperature followed by addition of 50 mL of H_2O to the reaction vessel caused solids to precipitate. The solids were collected by filtration, washed with 25 mL of H_2O, and then dried under reduced pressure to afford 0.60 g (92% yield) of the desired product as a yellow powder. A mixture of complexes with cis- and trans-geometries were found by ^{1}H NMR spectroscopy. Likewise, the ^{19}F NMR spectrum revealed that the product adopted a mixture of various geometrical isomers in an approximately 2:2:2:1 ratio. As noted in the text, X-ray crystallography revealed that **8-CF_3** adopted a trans geometry in the solid state. ^{1}H NMR (DMSO-d_6): δ 8.26 (m, 2H), 4.00–3.81 (m, 12H). ^{13}C NMR (DMSO-d_6): δ 173.7, 168.8, 127.2 (q, J_{C-F}=7.7 Hz), 126.6 (m), 122.5–121.7 (m), 119.6 (q, J_{C-F}=265 Hz), 119.4 (q, J_{C-F}=265 Hz), 38.2, 37.3, 37.1, 36.4. ^{19}F NMR (DMSO-d_6): δ −59.94 (s, 3F), −60.16 (s, 3F), −60.24 (s, 2F+0.8F from overlapping minor isomer), −60.34 (s, 0.8F). HRMS $[M]^+$ calcd for $C_{12}H_{14}F_6N_4PdI_2$: 685.8252; found: 685.8256. Crystals suitable for X-ray analysis were obtained by slow diffusion of water into a concentrated DMSO solution of **8-CF_3**; CCDC 675947.

4.9. Pd complex 8-NO_2

After charging a 25 mL flask with 1,3-dimethyl-4-nitroimidazolium iodide (0.54 g, 2.0 mmol), $Pd(OAc)_2$ (0.21 g, 0.95 mmol), 15 mL DMSO, and a stir bar, the resulting reaction mixture was heated to 80 °C for 1 h. Subsequent cooling to ambient temperature followed by addition of 50 mL of H_2O to the reaction vessel caused solids to precipitate. The solids were collected by filtration, washed with 50 mL of H_2O, and then dried under reduced pressure to afford 0.58 g (90% yield) of the desired product as a yellow powder. Although the solution structure of this complex was found to be predominantly (>95%) cis by ^{1}H NMR spectroscopy, equimolar quantities of two isomers exhibiting C_{2v} and S_2 symmetries were observed. ^{1}H NMR (DMSO-d_6): δ 8.78 (s, 1H), 8.77 (s, 1H), 4.19 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 169.4, 139.5, 127.40, 127.34, 39.6, 39.4. HRMS $[M]^+$ calcd for $C_{10}H_{14}N_6O_4PdI_2$: 641.8201; found: 641.8204. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexanes into a concentrated $CHCl_3$ solution of **8-NO_2**; CCDC 675951.

4.10. Pd complex 8-CN

After charging a 25 mL flask with 1,3-dimethyl-4,5-dicyanoimidazolium iodide (0.56 g, 2.0 mmol), $Pd(OAc)_2$ (0.21 g, 0.95 mmol), 15 mL DMSO, and a stir bar, the resulting reaction mixture was heated to 80 °C for 1 h. Subsequent cooling to ambient temperature followed by addition of 50 mL of H_2O to reaction vessel caused solids to precipitate. The solids were collected by filtration, washed with 50 mL of H_2O, and then dried under reduced pressure to afford 0.60 g (96% yield) of the desired product as a yellow powder. The solution structure of this complex was found to be predominantly (>95%) cis by ^{1}H NMR spectroscopy. ^{1}H NMR (DMSO-d_6): δ 4.04 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 172.5, 115.9, 107.2, 39.0. HRMS $[M+H]^+$ calcd for $C_{14}H_{13}N_8PdI_2$: 652.8387; found: 652.9391. Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a saturated DMF solution of **8-CN**; CCDC 675950.

4.11. Pd complex 9

After charging a 100 mL flask with 1,3-dimethylimidazolium iodide (0.54 g, 2.4 mmol), $Pd(OAc)_2$ (0.72 g, 3.2 mmol), KI (5 g, 30 mmol), 50 mL pyridine, and a stir bar, the resulting reaction mixture was heated to 105 °C for 4 h. Subsequent cooling to ambient temperature followed by removal of solvent afforded a yellow powder, which was triturated with chloroform (3×20 mL). Combined organic extracts were then passed through a short plug of silica gel (CH_2Cl_2 as eluent) to obtain 1.25 g (98% yield) of the desired product as a orange-yellow powder. ^{1}H NMR ($CDCl_3$): δ 9.02 (m, 2H), 7.72 (m, 1H), 7.31 (m, 2H), 6.90 (s, 2H), 3.95 (s, 6H). ^{13}C NMR (DMSO-d_6): δ 170, 153.8, 146.1, 137.6, 124.4, 123.0, 39.0. HRMS $[M-I]^+$ calcd for $C_{10}H_{13}IN_3Pd$: 407.9189; found: 407.9184. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexanes into a saturated $CHCl_3$ solution of **9**; CCDC 682401.

4.12. General procedure used for performing hydroboration reactions

A Rh complex (0.03 mmol) was first weighed into a glass vial containing a stir bar and then sealed with a 20:400 TFE/silicone (Alltech) septum followed by a plastic open-centered cap. THF

(3 mL), Et_3N (0.7 mL, 5 mmol), pinacolborane (0.14 mL, 1.0 mmol), and an internal standard such as 1,3,5-trimethoxybenzene (61 mg, 0.30 mmol) or mesitylene (0.17 mL, 1.2 mmol) were then added in succession. After stirring at ambient temperature for 30 min, phenylacetylene (0.13 mL, 1.2 mmol) or 1-octyne (0.18 mL, 1.2 mmol) was then added. After stirring the resulting mixture for an additional 14 h at 25 °C, any residual borane was quenched through the addition of excess MeOH (0.5 mL). An aliquot was then taken from the crude reaction mixture, diluted with $CDCl_3$, and analyzed using ^1H NMR spectroscopy.[59] To the best of our knowledge, the terminal olefin products shown in Table 2, entries 17–25, have not been previously reported. Hence, they were isolated by column chromatography (hexanes/ethyl acetate as eluent) and characterized.

1-p-Methoxyphenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene. ^1H NMR ($CDCl_3$): δ 7.43 (dt, J=9.0, 3.1 Hz, 2H), 6.48 (dt, J=9.0, 3.1 Hz, 2H), 5.99 (br, 1H), 5.94 (d, J=2.8 Hz, 1H), 3.79 (s, 3H), 1.30 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 156.8, 132.5, 127.6, 126.9, 112.7, 83.5, 55.8, 26.1. HRMS [M+H$^+$] calcd for $C_{15}H_{22}BO_3$: 261.1662; found: 261.1666.

1-p-Nitrophenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-ethene. ^1H NMR ($CDCl_3$): δ 8.16 (d, J=8.9 Hz, 2H), 7.60 (d, J=8.9 Hz, 2H), 6.23 (d, J=2.4 Hz, 1H), 6.18 (br, 1H), 1.31 (s, 12H). HRMS [M+H$^+$] calcd for $C_{14}H_{19}NO_4B$: 276.1407; found: 276.1411.

1-p-Cyanophenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-ethene. ^1H NMR ($CDCl_3$): δ 7.58 (d, J=8.5 Hz, 2H), 7.55 (d, J=8.5 Hz, 2H), 6.19 (d, J=2.7 Hz, 1H), 6.13 (br, 1H), 1.30 (s, 12H). ^{13}C NMR ($CDCl_3$): 146.1, 133.8, 132.0, 127.9, 119.2, 110.4, 84.2, 24.8. HRMS [M+H$^+$] calcd for $C_{15}H_{19}BNO_2$: 256.1509; found: 256.1513.

4.13. General procedure used for performing Heck coupling reactions

A stock solution of *tert*-butylacrylate (0.47 M), aryl halide (0.33 M), and mesitylene (0.33 M) (internal standard) was first prepared in DMF. In a separate vial, base (1.5 mmol), catalyst (0.01 mmol), and 3 mL of the aforementioned stock solution were combined under an atmosphere of nitrogen. The vial was then sealed and placed into an oil bath at 120 °C for 18 h. Afterward, an aliquot was removed, diluted with ethyl acetate, filtered, and then analyzed by GC.

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References and notes

1. (a) Wanzlick, H. W.; Schönherr, H. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141; (b) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42; (c) Cardin, D. J.; Çetinkaya, B.; Çetinkaya, E.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 514; (d) Bourissou, D.; Guerret, O.; Gabbaï, F. P. *Chem. Rev.* **2000**, *100*, 39.
2. Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.
3. For excellent reviews of catalytically active transition metal complexes containing *N*-heterocyclic carbenes, see: (a) Kantchev, E. A. B.; O'Briend, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768; (b) Díez-González, S.; Nolan, S. P. *Top. Organomet. Chem.* **2007**, *21*, 47; (c) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239; (d) Cavell, K. J.; McGuiness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671; (e) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290; (f) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.
4. For representative examples, see: (a) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101; (b) Navarro, O.; Marion, N.; Oonishi, Y.; Kelly, R. A., III; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 685; (c) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188; (d) Jørgensen, M.; Lee, S.; Liu, X.; Wolkowski, J. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 12557; (e) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.
5. Herrmann, W. A.; Mihalios, D.; Ofele, K.; Kipfor, P.; Belmedjahed, F. *Chem. Ber.* **1992**, *125*, 1795.
6. Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 2000.
7. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.
8. O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem.—Eur. J.* **2006**, *12*, 4743.
9. (a) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G. *Organometallics* **1999**, *18*, 4082; (b) Voutchkova, A. M.; Feliz, M.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 12834; (c) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **1998**, *251*, 642; (d) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.
10. (a) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496; (b) Khramov, D. M.; Boystron, A. J.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6186; (c) Boydston, A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073; (d) Boydston, A. J.; Rice, J. D.; Sanderson, M. D.; Dykhno, O. L.; Bielawski, C. W. *Organometallics* **2006**, *25*, 6087.
11. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, NY, 1988.
12. (a) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046; (b) Wolfe, J. P.; Wagaw, S.; Marcox, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805; (c) Prim, D.; Campagne, J.-M.; Joseph, D.; Andrioletti, B. *Tetrahedron* **2002**, *58*, 2041; (d) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195.
13. Glorius, F. *Top. Organomet. Chem.* **2007**, *21*, 1.
14. Courchay, F. C.; Sworen, J. C.; Coronado, A.; Wagener, K. B. *J. Mol. Cat. A: Chem.* **2006**, *254*, 111.
15. Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem.—Eur. J.* **2001**, *7*, 3236.
16. Leuthaeusser, S.; Schwazr, D.; Plenio, H. *Chem.—Eur. J.* **2007**, *13*, 7195.
17. Alcarazo, M.; Fernández, R.; Alvarez, E.; Lassaletta, J. M. *J. Organomet. Chem.* **2005**, *690*, 5979.
18. Präsang, C.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2005**, *127*, 10182.
19. Herrmann, W. A.; Schütz, J.; Frey, G. D.; Herdtweck, E. *Organometallics* **2006**, *25*, 2437.
20. For ranking of various carbenes according to their electron-donating properties, see: Fürstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 12676.
21. (a) Yun, J.; Marinez, E. R.; Grubbs, R. H. *Organometallics* **2004**, *23*, 4172; (b) Barinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 13314.
22. (a) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663; (b) Iglesias, M.; Beetstra, D. J.; Stasch, A.; Horton, P. N.; Hursthouse, M. B.; Coles, S. J.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Organometallics* **2007**, *26*, 4800.
23. (a) Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Org. Lett.* **2005**, *7*, 1991; (b) O'Brien, C. J.; Kantchev, E. A. B.; Chass, G. A.; Hadei, N.; Hopkinson, A. C.; Organ, M. G.; Setiadi, D. H.; Tang, T.-H.; Fang, D.-C. *Tetrahedron* **2005**, *61*, 9723.
24. For excellent reviews of cross-coupling reactions involving organoboron compounds see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457; (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.
25. For an excellent review on Pd-catalyzed cross couplings see: Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176.
26. For a theoretical analysis of a NHC–Ir complex where NHC π-donation was found to be significant, see: Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516.
27. (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2162; (b) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801; (c) Green, J. C.; Herbert, B. J. *J. Chem. Soc., Dalton Trans.* **2005**, 1214; (d) Lee, M.; Hu, C. *Organometallics* **2004**, *23*, 976; (e) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023; (f) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039; (g) Arduengo, A. J., III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812.
28. (a) Tulloch, A. D. D.; Danopoulous, A. B.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027; (b) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755; (c) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, *23*, 3640; (d) Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. *J. Organomet. Chem.* **2006**, *691*, 4350.
29. Khramov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, *26*, 6042.
30. Group electronegativities: H, 2.1; Cl, 3.0; CN, 3.3; CF_3, 3.4; NO_2, 3.4, see: (a) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111; (b) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006; p 16.
31. Furthermore, the pK_a of 3-trifluoromethylbenzoic acid (5.16) in a 1:1 mixture of CH_3OH/H_2O is very similar to that of its nitro analogue (4.85), see: De Maria, P.; Fontana, A.; Spinelli, D.; Dell'Erba, C.; Novi, M.; Petrillo, G.; Sancassan, F. *J. Chem. Soc., Perkin Trans. 2* **1993**, 649.
32. (a) Smith, K.; Pelter, A.; Brown, H. C. *Borane Reagents*; Academic: London, 1988; (b) Smith, K.; Pelter, A. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8; p 703; (c) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482.
33. (a) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179; (b) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957.
34. Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990.
35. At the conclusion of the hydroboration reaction between pinacolborane and phenylacetylene as catalyzed by **6-H** (Table 2, entry 1), the mass balance was

determined by ^{1}H NMR and mass spectroscopy to be as follows: 55% hydroboration product, 20% poly(phenylacetylene), 7% styrene, and 7% polystyrene. The remainder of the reaction mixture was indeterminant. For the analogous reaction with 1-octyne (entry 8), the mass balance was 27% product, 45% 1-octyne, and 10% 1-octene; the remainder of the reaction mixture was indeterminant. Pinacolborane was completely consumed in both cases.

36. Although to the best of our knowledge hydroborations using Rh–NHC complexes are unknown, diborylations of styrene have been demonstrated with Cu–NHC, Pd–NHC, Ag–NHC, Au–NHC, and Pt–NHC complexes and hydroborations mediated by Pt–NHC complexes have been reported. For examples of transition metal mediated diborylations involving NHC ligands, see: (a) Lillo, V.; Fructos, M. R.; Ramírez, J.; Braga, A. A. C.; Maseras, F.; Díaz-Requejo, M. M.; Pérez, P. J.; Fernández, E. *Chem.—Eur. J.* **2007**, *13*, 2614; (b) Corberán, R.; Ramírez, J.; Sanaú, M.; Peris, E.; Fernandez, E. *Chem. Commun.* **2005**, 3056; (c) Corberán, R.; Ramírez, J.; Poyatos, M.; Peris, E.; Fernandez, E. *Tetrahedron: Asymmetry* **2006**, *17*, 1759; (d) Lillo, V.; Mata, J.; Ramírez, J.; Peris, E.; Fernandez, E. *Organometallics* **2006**, *25*, 5829; For Pt–NHC hydroborations, see: Lillo, V.; Mata, J. A.; Segarra, A. M.; Peris, E.; Fernandez, E. *Chem. Commun.* **2007**, 2184.
37. Voutchkova, A. M.; Appelhans, L. N.; Chianese, A. R.; Crabtree, R. H. *J. Am. Chem. Soc.* **2007**, *127*, 17624.
38. Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878.
39. For detailed mechanistic studies of hydroboration reactions, see: (a) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6680; (b) Burgess, K.; van der Donk, W. A.; Farstfer, M. B.; Ohlmeyer, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 6139; (c) Widauer, C.; Grützmacher, H.; Ziegler, T. *Organometallics* **2000**, *19*, 2097; For ab initio studies of Rh catalyzed hydroborations of alkenes, see Ref. 42.
40. For mechanistic studies of catalyzed hydrometalation of terminal alkynes, see: (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127; (b) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984; (c) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177; (d) Maruyama, Y.; Yamamura, K.; Nakayama, I.; Yoshiuchi, K.; Ozawa, F. *J. Am. Chem. Soc.* **1998**, *120*, 1421.
41. Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.
42. Musaev, D. G.; Mebel, A. M.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10693.
43. Baker, M. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *J. Chem. Soc., Dalton Trans.* **2001**, 111.
44. Trace Pd is known to catalyze Heck-type coupling reactions without any ligand, see: (a) de Vries, A. H. M.; Lunders, J. M. C. A.; Mommers, J. H. M.; Henderickx, H. J. W.; de Vries, J. G. *Org. Lett.* **2003**, *5*, 3285; (b) Arvela, R. K.; Leadbeater, N. E.; Sangi, M. S.; Williams, V. A.; Granados, P.; Singer, R. D. *J. Org. Chem.* **2005**, *70*, 161.
45. For an analysis of reactivity differences exhibited by *cis* and *trans* bis-NHC Pd complexes, see: (a) McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Sketon, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165; (b) Huynh, H. V.; Ho, J. H. H.; Neo, T. C.; Kon, L. L. *J. Organomet. Chem.* **2005**, *690*, 3854.
46. For additional evidence of π-backbonding interactions in NHC–Pd complexes see: Hara, K.; Kanamori, Y.; Sawamura, M. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1781.
47. Efforts toward deducing σ- and π-effects in Suzuki–Miyaura reactions catalyzed by **8** are underway. Preliminary experiments indicate that coupling phenyl boronic acid to various aryl bromides, including deactivated 4-bromoanisole, are effectively catalyzed by ill-defined Pd species at elevated temperatures, which has obfuscated any conclusions regarding how electronic differences in NHC–Pd complexes affect their respective catalytic activities in these reactions.
48. The relative electron donor abilities of 1,3-dimethyl-benzimidazolylidene (δ=5.04–4.99 ppm) and 1,3-dimethyl-4,5-ditrifluoromethylimidazolylidene (5.06 ppm) were determined by comparing the chemical shifts of the *trans*-olefins in their respective NHC–RhCl(COD) complexes; see: Baker, M. V.; Brayshaw, S. K.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2841.
49. We acknowledge that ill-defined Pd species may form over the course of the reported coupling reactions, especially since high temperatures were required, and contribute to the observed catalytic activities.[44] However, our interpretation of the data presented is that this is not occurring to a significant degree.
50. (a) Shekhard, S.; Hartwig, J. F. *Organometallics* **2007**, *26*, 340; (b) Böhm, V. P. W.; Herrmann, W. A. *Chem.—Eur. J.* **2001**, *7*, 4191.
51. The use of other bases, including Na_2HPO_4, did not significantly improve the yields of these reactions.
52. (a) Campeau, L.-C.; Thansandote, P.; Fagnou, K. *Org. Lett.* **2005**, *7*, 1857; (b) Viciu, M. S.; Germaneau, R. F.; Navarro-Fernandez, O.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2002**, *21*, 5470.
53. Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035.
54. Under similar reaction conditions, a Pd complex containing 1,3-dimethylimidazolylidene and triphenylphosphine was found to couple alkyl acrylates with bromobenzene in nearly the same efficiencies as **8-H**, see: Schneider, S. K.; Roembke, P.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A. *Eur. J. Inorg. Chem.* **2005**, 2973.
55. Introducing a second bolus of *tert*-butylacrylate and 4-bromoanisole to the reactions catalyzed by **8-H** or **8-CN** after 1.5 h or 8 h, respectively, did not result in additional product formation.
56. For example, it is known that Pd complexes bearing NHCs with bulky N-substituents (e.g., 2,6-di-*iso*-propylphenylimidazolylidene) are more efficient in catalyzing cross coupling reactions than analogues with smaller NHCs; for examples, see: (a) Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866; (b) Fürstner, A.; Leitner, A. *Synlett* **2001**, 290. Efforts toward preparing and studying functionalized NHCs bearing bulky N-substituents in catalysis are underway.
57. Upon concentration, NHC–Rh carbonyl complexes are known to dimerize with concomitant loss of carbon monoxide, see: Sanderson, M. D.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2007**, *128*, 16514.
58. Herrman, W. A.; Fischer, J.; Öfele, K.; Artus, G. R. J. *J. Organomet. Chem.* **1997**, *530*, 259.
59. (a) Murata, B.; Kawakita, K.; Asana, T.; Watanabe, S.; Masuda, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 825; (b) Takai, K.; Shinomiya, N.; Kaihara, H.; Yoshida, N.; Moriwake, T.; Utimoto, K. *Synlett* **1995**, 963; (c) Stewart, S. K.; Whiting, A. *J. Organomet. Chem.* **1994**, *482*, 293; (d) Coapes, R. B.; Souza, F. E. S.; Thomas, R. L.; Hall, J. J.; Marder, T. B. *Chem. Commun.* **2003**, 614.