Organometallics **2004,** *23,* 1629−1635 1629

Synthetic and Structural Studies of (NHC)Pd(allyl)Cl Complexes (NHC = *N*-heterocyclic carbene)

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Received November 24, 2003

The synthesis and structural characterization of a series of palladium complexes bearing *N*-heterocyclic carbenes (NHC) as supporting ligands are described. The reaction of commercially available $[Pd(allyl)Cl]_2$ and isolated or in situ generated NHC leads to monomeric palladium complexes where one NHC is bound to the metal center, as indicated by spectroscopic and single-crystal X-ray diffraction studies. The relative reactivity trend for these complexes as catalysts in aryl amination is discussed in terms of ligand steric properties, which vary as a function of imidazole-nitrogen substituents and perturbation resulting in modulation of ring planarity. The concept of buried volume is used to quantify the steric demand of each NHC in the corresponding complexes.

Introduction

The potential offered by *N*-heterocyclic carbenes (NHC) as supporting ligands in palladium-mediated catalysis is evident by the continuously growing number of reactions mediated by such complexes.[1] Although few details are known concerning the exact mechanism and the nature of intermediates in Pd-NHC-assisted cross-coupling reactions, they have proven exceedingly versatile and useful. Recently, we reported a brief description of the synthesis and catalytic reactivity of (NHC)-Pd(allyl)Cl complexes.[2] Their reactivity profile varies substantially as a function of the nature of substituents on the NHC. We now present a study describing an extended family of complexes of general formula (NHC)-Pd(allyl)Cl (NHC = SIPr [*N*,*N*′-bis(2,6-diisopropylphenyl)4,5-dihydroimidazol)-2-ylidene] (**1**); IPr [*N*,*N*′-bis-(2,6-diisopropylphenyl)imidazol)-2- ylidene] (**2**); IMes [*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol)-2-ylidene] (**3**); SIMes [*N*,*N*′-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol)-2-ylidene] (**4**); I^{t}Bu [*N*,*N*′-bis *tert*-butylimidazol)-2-ylidene] (**5**); ICy [*N*,*N*′-bis(cyclohexylimidazol)-2-ylidene] (**6**); IAd [*N*,*N*′-bis(1-adamantylimidazol)-2-ylidene] (**7**); [*N*,*N*′-bis(1-*S*,*S*-phenylethylimidazol)-2-ylidene] (**8**)). The system is described and analyzed as a function of structural features. These parameters are observed to influence the catalytic reactivity profile of this family of complexes.

Results and Discussion

Synthesis of (NHC)Pd(allyl)Cl Complexes. Initial synthetic efforts revolved around the reaction of a free carbene (SIPr, for example) with $[Pd(allyl)Cl]_2$ under inert atmosphere in dry diethyl ether at −78 °C (dry ice/acetone). This protocol was adapted from a protocol employed in the synthesis of $(PCy_3)Pd(allyl)Cl$.[3] The solution is allowed to warm to room temperature with stirring for 1−2 h. After this time, the reaction is worked up by simply removing the ether solvent in vacuo and washing the resulting microcrystalline product with hexanes. The ^1H NMR spectrum of the crude material revealed the coordination of SIPr to the palladium center. This method afforded a 96%yield of **1**. In a simplified rendition of the synthetic protocol, the synthesis of **1**−**8** can be performed in dry THF for 1 h at room temperature with no decrease in yield (which is generally >90%). A protocol for the synthesis of **1**−**8** is presented in Scheme 1, and exact synthetic details can be found in the Experimental Section.

Usually a slight excess of NHC (1.05 equiv carbene to 1 equiv palladium) was used in order to simplify the workup procedure. The excess carbene can be easily washed away with hexanes. Despite the fact that NHC have a limited stability in moist air (for example, I^{t}Bu is pyrophoric), the workup procedure can be performed in air since the resulting palladium complexes are air-stable. All complexes were recrystallized from CH_2Cl_2/hexanes.

This direct reaction of NHC with $[Pd(allyl)Cl]_2$ leads to the desired complexes in high yield and purity but involves the isolation of free carbene as a preliminary step, making the overall synthesis a two-step process. Thus, we investigated a possible one-pot synthesis of

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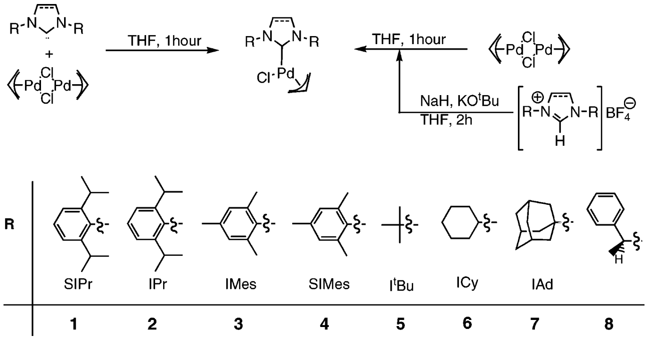
10.1021/om034319e CCC: $27.50
Publication on Web 02/25/2004

Scheme 1. Synthesis of (NHC)Pd(allyl)Cl Complexes (1−8)



1, **2**, and **3**. The appropriate imidazolium salts were first reacted with KO^{t}Am (potassium *tert*-amylate) in dry THF under argon atmosphere for 2 h.[4] The [Pd(allyl)Cl]$_2$ was then slowly added to the mixture, and the reaction was stirred at room temperature for two further hours. After filtration, the solvent was evaporated in vacuo and the solid obtained redissolved in CH_2Cl_2. The solution was passed through a plug of silica, and this plug was rinsed with two portions of 20 mL of CH_2Cl_2. Evaporation of the solvent CH_2Cl_2 in vacuo and trituration with hexanes yielded the desired complexes. The new protocol allowed to scale the synthesis of (IPr)Pd(allyl)Cl (**2**) to generate 21 g of the complex, representing a 97% yield.

In the case of complex **1**, single crystals of X-ray diffraction quality were obtained by slowly cooling a concentrated diethyl ether solution of **1**. Single crystals of **2** were obtained by slow evaporation of C_6D_6 solution, and single crystals of **4** from acetone solution. All other complexes were crystallized as single crystals from mixtures of 1,2-dichloroethane/hexanes or THF/hexanes in air. These experimental manipulations are a testament to the air and moisture stability of solutions of these (NHC)Pd(allyl)Cl complexes.

Structural Study of (NHC)Pd(Cl)allyl Complexes. Complexes **1**−**8** were analyzed by NMR spectroscopy and single-crystal XRD. The ^{1}H NMR region of the allyl moiety is a very sensitive indicator of reaction taking place on the metal center. The appearance of a characteristic pattern (one multiplet and four doublets) indicates the coordination of the carbene to the palladium center. The asymmetry in the structure is manifested as a magnetic inequivalency of allylic protons. Similar patterns have been observed for the equivalent phosphine complexes.[5]

The ^{13}C NMR signal of the carbenic carbon in the free carbene (ca. 210 ppm for unsaturated imidazol-2-ylidenes and 250 ppm for 4,5-dihydroimidazol-2-ylidenes) is shifted to higher field upon coordination to the palladium center by an average of 30 ppm, as a measure of electronic density transfer from the NHC carbenic center to the palladium(II) center. An interesting feature of the proton NMR spectra of the complexes is the upfield shifted position of imidazole backbone protons relative to the parent carbene precursors. In the case of **7**, the imidazolium chloride salt precursor has a resonance at 7.92 ppm, 6.91 ppm for the free carbene and 6.79 ppm (doublet) for the corresponding palladium complex.[6]

The structures of the complexes were unambiguously elucidated by single-crystal XRD (Table 1). In all cases distorted square-planar coordination around the palladium center was observed. The chloride anion is located *cis* to the carbene, and the allyl moiety is η^3 coordinated to the palladium with one terminal carbon *trans* to the carbene and the second terminal carbon *trans* to the chlorine. In all complexes, the palladium−C_{allyl} bonds opposite the NHC ligand are elongated by a strong *trans* effect. Selected bond distances are presented in Table 2. Saturated NHC have been described as better donors due to a delocalization of π-electronic density of the ring over three atoms (N−$C_{carbenic}$−N) compared to unsaturated counterparts, where π-electronic density is delocalized over the five members of the ring.[7] We have recently quantified this electron donation by solution calorimetry in a ruthenium system and have measured a difference of only 1 kcal/mol in donor ability between IMes and SIMes.[8] As a result of the increased donor property of the saturated NHC, a higher electronic density would be expected to reside on $C_{carbenic}$ in the saturated cases. We expected to observe some difference in the bonding distances from complexes bearing 4,5-dihydroimidazol-2-ylidene to imidazol-2-ylidene type of ligands, but no significant bond alteration was observed in two series of complexes, (IPr)Pd(allyl)Cl (**2**)/(SIPr)Pd(allyl)Cl (**1**) and (IMes)Pd(allyl)Cl (**3**)/SIMes)Pd(allyl)Cl (**4**). The Pd−$C_{carbenic}$ bonds were identical (2.04 and 2.03 Å, respectively) (Table 2). Among the eight complexes the bond length variation is small. The shortest distance is found for (SIMes)Pd(allyl)Cl (2.028 Å) and the longest for (ICy)Pd(allyl)Cl (2.072 Å). The distances between palladium and the carbenic center suggest a single-bond character, in good accordance with their exclusive σ-donor characteristics.[9]

Alkyl substituents on the nitrogen of the imidazole ring are expected to increase the electronic density at the carbenic center, making the carbene more electron rich, favoring a stronger bond between the NHC and the metal center. The palladium family revealed a slightly weaker interaction of alkyl-substituted carbenes and palladium center compared to *N*-aryl-substituted counterparts (Table 2).

It is interesting to note that Pd−Cl bond lengths follow the same trend as Pd−$C_{carbenic}$. The smallest bond distance is for the *N*-aryl-substituted unsaturated imidazole ring (IMes)Pd(allyl)Cl (2.358 Å) and the longest for the alkyl-substituted imidazol ring (ICy)Pd(allyl)Cl (2.419 Å). The imidazole ring of the carbene can be thought of as an aromatic system in which all atoms

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[4] For a similar protocol see: Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530−5534.

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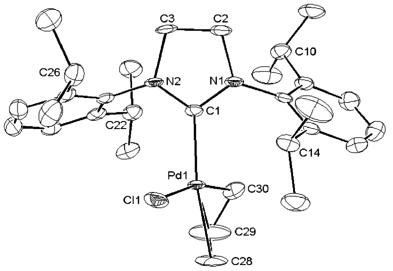
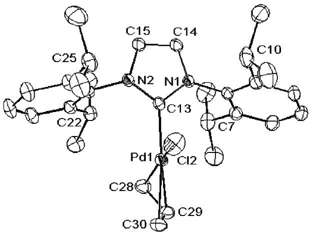
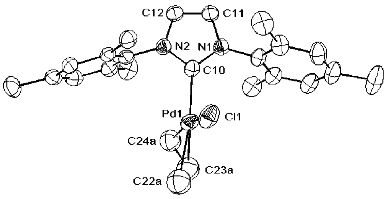
Table 1. ORTEP Structure for Complexes 1−8



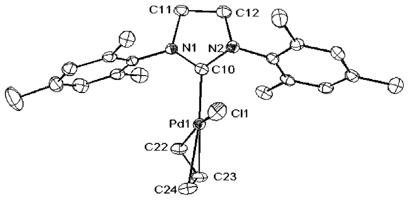
ORTEP of (SIPr)Pd(allyl)Cl (**1**)



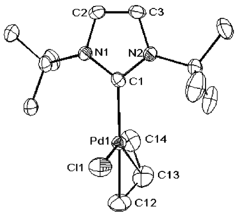
ORTEP of (IPr)Pd(allyl)Cl (**2**)



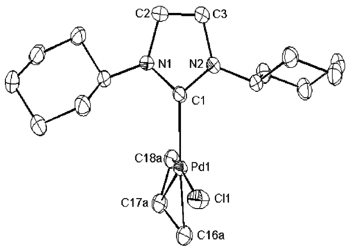
ORTEP of (IMes)Pd(allyl)Cl (**3**)



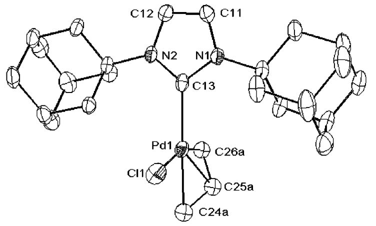
ORTEP of (SIMes)Pd(allyl)Cl (**4**)



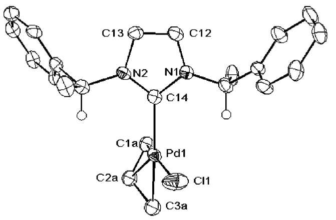
ORTEP of (I^{t}Bu)Pd(allyl)Cl (**5**)



ORTEP of (ICy)Pd(allyl)Cl (**6**)



ORTEP of (IAd)Pd(allyl)Cl (**7**)



ORTEP of (**8**)

are sp^2 hybridized. The planarity of the ring is affected by the substituents on the imidazole nitrogens. Aromatic substituents have a negligible effect on the imidazole torsion angle ($N_1C_4C_5N_2$): 0.1° for **2** and **3**; alkyl substituents, on the other hand, induce an important tension reflected in torsion angles up to 1.7° for both **5** and **6**. The saturated imidazole backbone, on the other hand, is expected to have some degree of deviation from planarity due to the presence of two sp^3 carbons in the heterocyclic ring.[10] The extended delocalization of the π-electronic cloud over two nitrogens and one carbon should minimize the torsion angle. Upon coordination to palladium, the torsion angle is 19.8° for **1** and 14.8° in complex **4**, while the torsion angle for free SIMes carbene is 13.4°. The general trend observed for the complexes reveals no differences in the Pd−C$_{\mathrm{carbenic}}$ bond length on moving from saturated to unsaturated imidazole rings, but there is a slight elongation of the bonds moving from aryl-substituted NHC to alkyl-substituted NHC.

Structure/Reactivity Relationship. The complexes were designed originally as catalyst precursors for various cross-coupling reactions.[2] They have the advantage of being stable to air and moisture and possess a well-defined, optimum metal-to-ligand ratio of 1:1. The oxidative addition of organic halides or pseudohalides to the “PdL” catalytic species relies on an associative mechanism, contrary to the required dissociative step(s) involved in the widely studied bis-phosphine palladium systems.[11] Furthermore, the elimination of products from palladium(II) centers is facilitated by a

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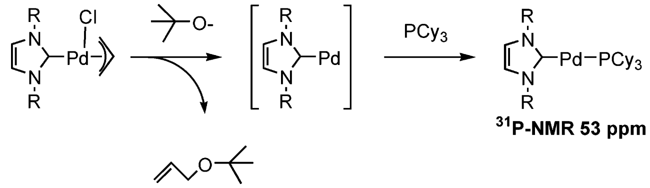
Table 2. Selected Bonds and Angles for Complexes 1−8

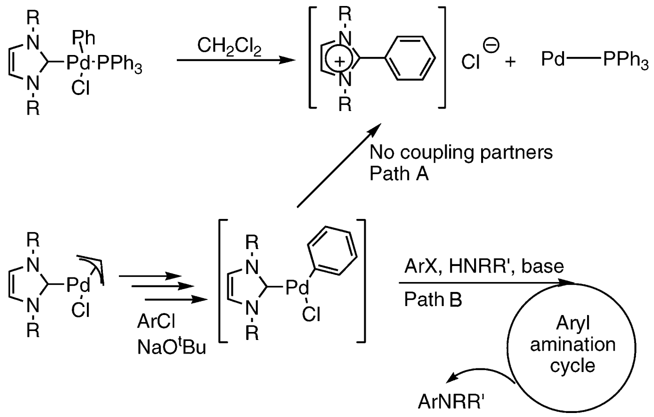
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Pd−C(2) (Å)	2.042(5)	2.040(11)	2.032(3)	2.028(4)	2.062(2)	2.072(2)	2.058(5)	2.040(9)
Pd−Cl (Å)	2.376(14)	2.37(5)	2.358(9)	2.373(12)	2.390(7)	2.419(8)	2.391(14)	2.380(2)
Pd−C_{allyl} (Å)	2.211(6)	2.201(17)	2.126(5)	2.115(5)	2.096(3)	2.137(4)	2.138(6)	2.160(10)
	2.124(7)	2.149(16)	2.148(5)	2.132(5)	2.125(3)	2.178(3)	2.134(7)	2.141(12)
	2.098(6)	2.110(16)	2.183(5)	2.202(5)	2.175(3)	2.236(4)	2.167(6)	2.192(11)
N(1)C(5)C(4)N(2) (deg)	19.8(6)	0.1(14)	0.2(4)	14.8(5)	1.7(3)	1.7(4)	0.8(7)	1.0(9)
C_4−C_5 (Å)	1.516(9)	1.346(17)	1.338(4)	1.512(7)	1.331(4)	1.359(4)	1.344(8)	1.355(12)
C_4−N_3 (Å)	1.489(7)	1.393(15)	1.394(4)	1.483(6)	1.386(3)	1.419(4)	1.37(7)	1.378(11)
C_2−N_1 (Å)	1.344(7)	1.359(14)	1.360(3)	1.347(6)	1.357(4)	1.388(3)	1.365(6)	1.369(11)
	1.346(6)	1.363(14)	1.356(3)	1.338(6)	1.380(5)	1.383(3)	1.375(6)	1.349(12)
$N_1C_2N_3$ (deg)	108.19(4)	103.78(9)	103.76(2)	107.89(4)	105.06(18)	104.89(2)	103.87(4)	104.7(7)

Y or T conformation of the metal center.[12] However, with (NHC)Pd(allyl/alkyl)Cl complexes the problem of stability of the precatalyst itself toward reductive elimination is present. Two decomposition pathways can be envisioned: one based on reductive elimination of allyl chloride and one based on formation of allyl imidazolium chloride salts. Thermal elimination of allyl chloride is less probable due to stabilization effect induced by η^3 coordination of the allyl moiety. Solutions of **2** in the presence of PCy_3 in CD_2Cl_2 are stable overnight with no sign of (IPr)Pd(PCy_3) formation or IPr displacement. Decomposition through C−C bond formation (2-alkyl/1,3-aryl imidazole hydrochloride salts as product) is documented in recent literature.[13] Unexpectedly, all complexes are stable in almost all solvents tested so far and in the solid state (**2** is stable up to 217 °C, when decomposition occurs). For instance, solutions of **2** in MeOH or technical grade 2-propanol decompose slightly over days. The same solutions heated to 40 °C for 48 h in air show little degradation of the precatalyst (5% by ^{1}H NMR). It is unclear at this time if the slight decomposition of **2** in MeOH is due to a lower activation barrier in polar solvents or nucleophilic attack of RO^- as previously mentioned by Grushin.[14] Nucleophilic attack of RO^- in the form of NaO^tBu on the precatalyst is known[2b] and was used as the method to generate (NHC)-Pd(0) species by the elimination of allyl-*tert*-butyl ether. The existence of the transient 12-electron species (NHC)Pd(0) is supported by trapping experiments conducted in the presence of tertiary phosphines[15] (Scheme 2).

Scheme 2. Generation of Pd(0) Species through Nucleophilic Attack of Alkoxides on (NHC)Pd(allyl)Cl



Scheme 3. Decomposition through NHC-aryl Elimination and Suppression in the Presence of Coupling Partners



The generation of Pd(0) species can be achieved using other reagents (metal hydrides and alkoxides, for instance). NaO^tBu is convenient since it can play the dual role of base for the cross-coupling reaction and activator for the catalyst. Once the catalyst is activated, its stability during a cross-coupling catalytic cycle is an issue that should be mentioned. Our study on cross-coupling of aryl chlorides/triflates and amines mediated by (NHC)Pd(allyl)Cl complexes demonstrated reactivity even at room temperature.[2b] Our attempts to isolate oxidative addition products of general formula (NHC)-Pd(Cl)Ph invariably failed when initiated from the allyl palladium species. Cloke recently isolated such a species from a bis-NHC palladium complex bearing very bulky NHC substituents.[16] Grushin recently investigated the stability of σ-aryl palladium complexes bearing IPr as supporting ligand and observed the facile elimination of $[IPrPh]^+X^-$ even at room temperature.[11a] The reaction is accelerated by the dissociation of PPh_3 (Scheme 3, path a), making that system identical to the one described here if no coupling partner is added (Scheme 3, path b). This experiment might explain our failure to isolate the oxidative addition product. The high reactivity of some (NHC)Pd(allyl)Cl complexes in aryl amination seems to contradict access to this decomposition pathway. The experiments conducted by Grushin were performed in a simplified system where coupling partners are missing. Under catalytic conditions, oxidative

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(14) Grushin, V. V. *Organometallics* **2000**, *19*, 1888−1900.

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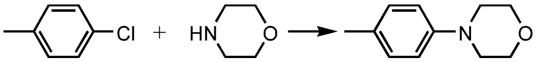
(16) (a) Caddick, S.; Cloke, F. G. N.; Hitchcock, P. B.; Leonard, J.; de Lewis, A. K.; McKerrecher, D.; Titcomb, L. R. *Organometallics* **2002**, *21*, 4318−4319. (b) De Lewis, A. K.; Caddick, S.; Cloke, F. G. N.; Billingham, N. C.; Hitchcock, P. B.; Leonard, *J. Am. Chem. Soc.* **2003**, *125*, 10066−10073.

Table 3. Standard Aryl Amination: Catalyst Performance[a]



catalyst	temperature (°C)	time (h)	yield (%)
(IPr)Pd(allyl)Cl	80	0.25	100
	RT	6	95
(SIPr)Pd(allyl)Cl	80	0.25	100
	RT	1.25	100
(IMes)Pd(allyl)Cl	80	2	100
(ItBu)Pd(allyl)Cl	80	3	99
(SIMes)Pd(allyl)Cl	80	1.6	100
(ICy)Pd(ally)Cl	80	no reaction	
(IAd)Pd(allyl)Cl	80	2	100
8	80	no reaction	

[a] 1 mol % catalyst, 1.5 mmol of NaO^{t}Bu, 1 mmol of 4-chlorotoluene, 1.2 mmol of morpholine, 4 mL of DME. GC yields.

addition, transmetalation, and reductive elimination take place at a rate that precludes decomposition through C−C bond formation involving the NHC ligand. Difficult substrates for aryl amination, such as electron-rich aromatic *N*-heterocycles, support this hypothesis: a slow transmetalation step (with all other conditions held constant) leads to catalyst deactivation or to the formation of an oxidative addition product (Scheme 3, path a) that decomposes with precipitation of inactive Pd.[17]

We compared the effectiveness of the palladium/NHC complexes in cross-coupling of morpholine and 4-chlorotoluene trying to find a correlation between the structure of the precursors and their catalytic activity. The nearly identical Pd−$C_{carbenic}$ bond length in all complexes indicates similar electronic effects, and we consider them not to be the origin of the large differences in activity between complexes in cross-coupling reactions, particularly in aryl amination (Table 3). Recent infrared characterization of Ni(NHC)(CO)$_n$ (n = 2, 3) systems showed small differences in infrared ν_{CO} shift among the different NHC nickel complexes.[18]

High steric crowding by the ligand(s) coordinated to the metal center is known to facilitate reductive elimination of the product in the last step of the catalytic cycle.[19] The “fence” or “fan” type shape associated with NHC makes inappropriate the use of the classical “cone angle” steric description.[20] The “wing span” of **3** is 13.263 Å, the largest of all ligands (wing span angle C(8)−Pd(1)−C(20) = 152.45°), and **5** offers the most “crowded” environment around palladium (Pd(1)−C(7) = 3.113 Å; Pd(1)−C(11) = 3.240 Å), but both failed to provide optimum efficiency in a standard aryl amination reaction (see Table 3).

The steric factor of NHC was conceptualized as a sphere of imposed radius (3 Å) centered around the palladium atom and the volume occupied by the ligand (Figure 1). This method allowed a realistic comparison with other ligands, particularly tertiary phosphines. A similar approach was used recently to estimate the steric factor for a series of ruthenium *N*-heterocyclic carbene complexes.[8] The buried volume (Table 4) was calculated for (NHC)Pd(allyl)Cl complexes for an imposed 2 Å distance Pd−$C_{carbenic}$ and for real bond lengths experimentally obtained from X-ray measurements.

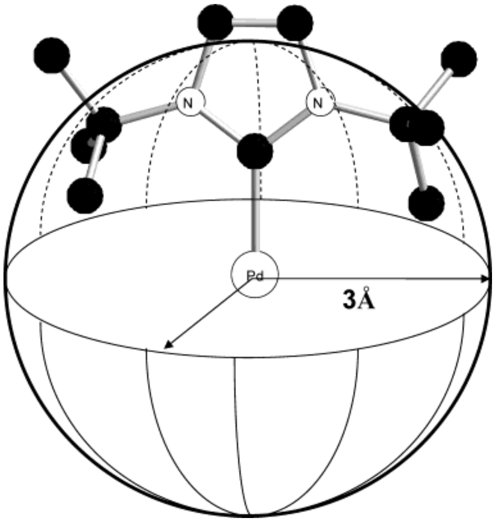


Figure 1. Buried volume calculated as the volume of the ligand confined inside a sphere of 3 Å radius centered on palladium.

Table 4. Calculated Buried Volume for (NHC)Pd(allyl)Cl Complexes

complex	buried volume[a] (%)	buried volume[b] (%)
(IPr)Pd(allyl)Cl	26.10	24.99
(SIPr)Pd(allyl)Cl	33.03	32.27
(IMes)Pd(allyl)Cl	26.50	25.87
(ItBu)Pd(allyl)Cl	33.37	32.25
(SIMes)Pd(allyl)Cl	27.49	26.91
(ICy)Pd(ally)Cl	25.17	23.90
(IAd)Pd(allyl)Cl	33.56	32.20
8	23.61	22.93

[a] Buried volume calculated for a fixed distance Pd−$C_{carbenic}$ of 2 Å. [b] Buried volume calculated based on crystallographic distances.

The most demanding ligands are I^{t}Bu, IAd, and SIPr. The catalytic performance of palladium complexes bearing these NHC greatly fluctuates within this subgroup. It is interesting to note another striking reactivity difference between IPr-containing **2** and the SIPr analogue **1** despite almost identical structures. Complexes **1** and **2** performed best in the reaction of morpholine and 4-chlorotoluene with complete conversions even at room temperature. The marked difference in reactivity between these two ligands appears when the reaction is carried out at lower temperature. At room temperature, **1** mediated the above-mentioned reaction 4 times faster than **2**. We associated this difference in reactivity among catalysts with the shape of bound carbene and not with the electronic donating ability. We mentioned before an upfield shift of imidazole backbone protons that can be associated with a decrease in aromaticity of the ring[21] where there is no longer a delocalized and

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(17) Reductive elimination of electron-rich *N*-heterocycle from Pd(II)/phosphine centers has been discussed in detail: (a) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860. (b) Mann, G.; Hartwig, J. F.; Driver, M. S.; Fernandez-Rivas, C. *J. Am. Chem. Soc.* **1998**, *120*, 827−828. (c) Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575−5580. (d) Grasa, G. A.; Viciu, M. S.; Huang, J.; Nolan, S. P. *J. Org. Chem.* **2001**, *66*, 7729−7737. It is assumed to be slow, but it is accelerated for low ratio phosphines/palladium (T or Y configuration for 1:1 ratio) or chelating bis-phosphines that force product elimination.

(18) Dorta, R.; Stevens, D. S.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490−10491.

(19) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: New York, 2001.

(20) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(21) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913−921.

rigid π system. The presence of bulky substituents and asymmetric environment around palladium complexes lead to an increase of the torsion angle $N_1C_5C_4N_2$[22] and a rearrangement of the nitrogen substituents.

The presence of two sp^3 carbon atoms in the backbone of **1** and **4** induces a deformation of the dihydroimidazol-2-ylidene ring of 19.8° and 14.8°, respectively. The twisted ring affects the orientation of aryl substituents on nitrogen, inducing a supplementary rotation of the aryl moiety around the $N-C_{aryl}$ bond. The substantially shorter distances between the metal center and aryl groups of the ligand, compared to **2**, increase the steric hindrance around palladium and facilitate reductive elimination in the last step of the catalytic cycle.[23] A similar explanation can be proposed for the higher reactivity of **4** compared to **3**, but there is no definitive answer why **5** has a limited activity in aryl amination. We speculate that the longer $Pd-C_{carbenic}$ bond found in all alkyl-substituted imidazoles may make the ligand more susceptible to decomposition. The chiral complex **8** is inactive in all cross-coupling chemistry tested so far, maybe due to an unfavorable spatial distribution of substituents that are "further removed" from the reaction center, inducing a minimum steric impact.

Conclusions

The synthesis and structural characterization of a series of palladium complexes of general formula (NHC)-Pd(allyl)Cl is described. An analysis of principal bond distances shows very little or no variations when imidazole-based carbenes were substituted by their saturated homologues. Unexpected weaker (longer) $Pd-C_{carbenic}$ bonds were observed for electron-donating alkyl-substituted NHC. The stability of the complexes has been examined in terms of steric parameters recently described. The shape of ligands and $Pd-C_{carbenic}$ bond lengths were used to explain the trend in reactivity in cross-coupling involving amines and aryl halides.

Experimental Section

General Considerations. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-300 or a Varian-400 MHz spectrometer at room temperature. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Elemental analysis was performed at Desert Analysis, Tucson, AZ. 4-Chlorotoluene and morpholine were used as received (Aldrich). 1,2-Dimethoxyethane (anhydrous and technical grade) was purchased from Aldrich. Synthetic procedures for the imidazolium salts and corresponding carbenes are reported in the Supporting Information.

Catalytic Aryl Amination Reactions: General Procedure. Catalyst (1 mol %), NaO^{t}Bu (1.52 mmol, 150 mg), and dry DME (4 mL) were loaded, inside the drybox, into a vial. 4-Chlorotoluene (1 mmol, 118 μL), morpholine (1.2 mmol, 100 μL), and di-*tert*-butyl ether (1 mmol) were added through the septum using a syringe. The reactions were run at the indicated temperature and monitored by GC. After consumption of reactants or no further conversion, the reactions were stopped by quenching with an aqueous solution of NH_4Cl. The organic layer was extracted with CH_2Cl_2 and dried over Na_2SO_4, mixed with a small amount of silica gel. The solvent was evaporated in vacuo, and for identification purpose the product/silica gel mixture was placed on top of a flash chromatographic column and eluted with hexanes/ethyl acetate (90/10). The product 4-(4-tolyl)morpholine was obtained in all reactions as a viscous yellow oil with higher than 95% purity by ^{1}H NMR.[24]

(SIPr)Pd(allyl)Cl (1). SIPr[25] (780 mg, 2 mmol) and [Pd(allyl)Cl]$_2$ (365.8 mg, 1 mmol) were charged together in a Schlenk tube in the drybox. At −78 °C, dry Et_2O (20 mL) was added by cannula and the reaction mixture was stirred for 30 min at this temperature. The solution was allowed to warm to room temperature with stirring during the course of 2 h. The ether was then removed in vacuo, and 40 mL of anhydrous hexane was added to triturate the product. The mixture was filtered in air and washed with hexane. This method led to 1.1 g of **1** (96% yield). Crystals suitable for the diffraction study were grown from a saturated Et_2O solution. ^{1}H NMR (400 MHz $CDCl_3$): 7.6 (t, J = 7.6 Hz, 2H), 7.261 (d, J = 5.2 Hz, 2H), 7.204 (s, 2H), 4.749 (pentet, J = 7.2 Hz, 1H), 4.0−4.07 (m, 4H), 3.878 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 3.394−3.536 (m, 4H), 3.019 (d, J = 6 Hz, 1H), 2.743 (d, J = 13.6 Hz, 1H), 1.548 (d, J < 1 Hz, 1H), 1.465 (d, J = 6.8 Hz, 6H), 1.366 (d, J = 6.8 Hz, 6H), 1.291 (d, J = 6.8 Hz, 6H), 1.251 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, C_6D_6): 24.206, 24.388, 26.952, 29.030, 29.136, 50.013, 54.321, 72.740, 109.896, 114.553, 124.870, 129.740, 137.265, 147.886, 148.144, 215.385. Anal. Calcd: C, 62.8; H, 7.51; N, 4.89. Found: C, 62.61; H, 7.51; N, 5.13.

(IPr)Pd(allyl)Cl (2). In glovebox, a Schlenk flask equipped with a magnetic bar was loaded with the imidazolium salt IPr·HCl (40 g, 94.26 mmol), K^{t}OAm (8 g, 62.84 mmol), and dry THF (400 mL), and the mixture was stirred for 2 h at 50 °C. After allowing it to cool to room temperature, (Pd(allyl)Cl)$_2$ (7.19 g, 19.64 mmol) was added slowly, and the reaction mixture stirred again for 2 h at room temperature. The mixture was filtered in air, and the precipitate washed with THF (2 × 25 mL). The solvent was evaporated on a rotoevaporator and redissolved in CH_2Cl_2. The solution was passed through a plug of silica gel, previously wetted with hexane. The silica was washed with CH_2Cl_2 (2 × 25 mL), and all the portions were placed together in a rotoevaporator. The solvent was evaporated in vacuo and the solid triturated with hexanes, yielding 21.81 g of (IPr)Pd(η^3-allyl)Cl (97% yield). Crystals suitable for diffraction study were grown from benzene by slow evaporation. ^{1}H NMR (400 MHz, $CDCl_3$): 7.434 (t, J = 8 Hz, 2H), 7.287 (d, J = 3.6 Hz, 4H), 7.16 (s, 2H), 4.817 (pentet, J = 6.4 Hz, 1H), 3.903 (d, J = 7.2 Hz, 1H), 3.133 (pentet, J = 6.8 Hz, 2H), 3.045 (d, J = 6 Hz, 1H), 2.867 (pentet, J = 6.8 Hz, 2H), 2.782 (d, J = 3.6 Hz, 1H), 1.584(d, J = 12.4 Hz, 1H), 1.397 (d, J = 7.2 Hz, 6H), 1.341 (d, J = 7.2 Hz, 6H), 1.183 (d, J = 7.2 Hz, 6H), 1.093 (d, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, C_6D_6): 23.401, 23.493, 26.269, 26.845, 29.061, 29.167, 49.603, 72.103, 114.113, 124.369, 124.476, 124.552, 130.544, 136.871, 146.854, 147.021, 188.531. Anal. Calcd: C, 63.1; H, 7.18; N, 4.9. Found: C, 62.84; H, 7.18; N, 4.85

(IMes)Pd(allyl)Cl (3). The imidazolium salt IMes·HCl (2 g, 5.87 mmol) was reacted with NaH (211 mg, 8.80 mmol) and NaO^{t}Bu (5.63 mg, 5.87×10^{-2} mmol) in dry hexanes (20 mL) under an inert atmosphere, at room temperature for 20 h. The mixture was then filtered under inert atmosphere and washed with dry hexanes. The filtrate was evaporated in vacuo, yielding 0.834 g of the carbene IMes (2.75 mmol, 47%). After adding 20 mL of dry THF under inert atmosphere, (Pd(allyl)-Cl)$_2$ (503.3 mg, 1.375 mmol) was added slowly and allowed to react for 1.5 h. The mixture was filtered and washed with THF

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[22] N1, N3 denote the nitrogens and C4, C5 the backbone carbon atoms of imidazole (dihydroimidazole ring). The torsion angles were calculated from crystallographic data.

[23] For instance, $Pd-C_{(CHMe2)}$ bond distances in **2** are 4.562, 4.050, 4.401, and 4.262 Å. $Pd-C_{(CHMe2)}$ bond distances in **1** are 3.710, 3.543, 4.902, and 4.956 Å. As observed, the ligand environment around the metal center is substantially different.

[24] Tsuji, Y.; Huh, K. T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365−1370.

[25] The synthesis of the NHC from the corresponding imidazolium salts is adapted from a previously reported protocol: see ref 6.

(2 × 5 mL). The solvent was evaporated in vacuo and the complex triturated with hexanes. After filtration, 1.10 g of (IMes)Pd(η^3-allyl)Cl was obtained (82% yield). Crystals suitable for diffraction study were grown from THF/hexanes solution. ^{1}H NMR (400 MHz, C_6D_6): 6.745 (d, $J = 6.8$ Hz, 4H), 6.200 (s, 2H), 4.476 (pentet, $J = 6.8$ Hz, 1H), 3.733 (dd, $J = 7.2$ Hz, $J = 2$ Hz, 1H), 3.072 (d, $J = 6.4$ Hz, 1H), 2.713 (d, $J = 13.2$ Hz, 1H), 2.274 (s, 6H), 2.226 (s, 6H), 2.069 (s, 6H), 1.800 (d, $J = 12$ Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6): 18.771, 18.812, 21.337, 48.984, 72.099, 114.095, 122.956, 129.632, 136.226, 136.281, 136.936, 139.175, 185.677. Anal. Calcd: C, 59.3; H, 5.96; N, 5.75. Found: C, 60.07; H, 5.90; N, 5.6.

(SIMes)Pd(allyl)Cl (4). The imidazolium salt SIMes·HCl (4.0 g, 11.68 mmol) is converted into the HBF_4 salt by reaction with HBF_4 (54% solution in ether, 15 mL) in 100 mL of distilled water for 1 h. After collection by filtration and washing with water (2 × 20 mL), the precipitate was dried under vacuum. This method leads to the isolation of 3.32 g of SIPr·HBF_4 (72% yield). Out of this reaction, 2 g (5.1 mmol) of the salt was reacted with NaH (183 mg, 7.62 mmol) and NaO^{t}Bu (4.9 mg, 5.1×10^{-2} mmol) in dry THF (20 mL) under an inert atmosphere at 60 °C for 20 h. The solvent was evaporated in vacuo, followed by the addition of dry hexanes (30 mL). The mixture was filtered, under inert atmosphere, and washed with dry hexanes. The filtrate was evaporated in vacuo, yielding 1.03 g of the carbene SIMes (3.37 mmol, 66%). After adding 20 mL of dry THF under inert atmosphere, [Pd(allyl)-Cl]$_2$ (514 mg, 1.41 mmol) was added slowly and allowed to react for 1.5 h. The mixture was filtered and washed with THF (2 × 5 mL). The solvent was evaporated in vacuo and the complex triturated with hexanes. After filtration, 0.626 g of (SIMes)-Pd(allyl)Cl was obtained (45% yield). Crystals suitable for diffraction study were grown from acetone solution. ^{1}H NMR (400 MHz, $CDCl_3$): 6.93 (s, 4H), 4.758 (pentet, $J = 6$ Hz, 1H), 3.99 (s, 4H), 3.82 (dd, $J = 5.2$ Hz, $J = 2$ Hz, 1H), 3.231 (d, $J = 6.8$ Hz, 1H), 2.72 (d, $J = 13.2$ Hz, 1H), 2.42 (s, 12H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 211.53, 138.23, 136.55, 129.55, 114.83, 73.21, 51.41, 49.52, 21.24, 18.65, 18.59. Anal. Calcd: C, 58.78; H, 6.58; N, 5.71. Found: C, 58.92; H, 6.45; N, 5.48.

(I^{t}Bu)Pd(allyl)Cl (5). The imidazolium salt I^{t}Bu·HBF_4 (2 g, 7.46 mmol) was reacted with NaH (269 mg, 11.19 mmol) and NaO^{t}Bu (7.2 mg, 7.46×10^{-2} mmol) in dry hexanes (25 mL) under an inert atmosphere at room temperature for 20 h. The solvent was then evaporated in vacuo, and the free carbene sublimed with the aid of a coldfinger, under static vacuum, leading to the isolation of 636 mg (47%) of I^{t}Bu. After addition of 20 mL of dry THF under inert atmosphere, (Pd(allyl)Cl)$_2$ (641.6 mg, 1.75 mmol) was added slowly and the reaction allowed to proceed for 1.5 h. The mixture was filtered in air and the precipitate washed with THF (2 × 5 mL). The filtrate was evaporated in vacuo and the complex triturated with hexanes. After filtration, 1.206 g of (I^{t}Bu)Pd(η^3-allyl)Cl was obtained (95% yield). Crystals suitable for diffraction study were grown from CH_2Cl_2/hexanes solutions. ^{1}H NMR (400 MHz, C_6D_6): 6.618 (s, 2H), 4.911 (heptet of doublets, $J = 7.2$ Hz, $J = 0.8$ Hz, 1H), 4.171 (ddt, $J = 7$ Hz, $J = 2.4$ Hz, $J = 0.8$ Hz, 1H), 3.241 (doublet of pentets, $J = 13.2$ Hz, $J = 0.8$ Hz, 1H), 3.053 (dddd, $J = 6.8$ Hz, $J = 2.4$ Hz, $J = 1.4$ Hz, $J = 0.8$ Hz, 1H), 2.01 (ddd, $J = 6.8$ Hz, $J = 2.4$ Hz, $J = 1.2$ Hz, 1H); 1.668 (s, 9H); 1.493 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6): 32.431, 32.710, 52.154, 59.217, 59.351, 69.413, 112.828, 118.848, 119.224, 179.255. Anal. Calcd: C, 46.3; H, 6.89; N, 7.72. Found: C, 46.3; H, 6.92; N, 7.52.

(ICy)Pd(allyl)Cl (6). ICy[23] (515 mg, 2.2 mmol) and (Pd(allyl)Cl)$_2$ (365.8 mg, 1 mmol) were mixed together in a Schlenk tube in the drybox. Dry THF (20 mL) was added by cannula and the mixture stirred at room temperature for 1 h. The solvent was removed in a vacuum, and 20 mL of anhydrous hexane was added to triturate the product. The product was filtered in air and washed with hexane. Yield: 85% (706 mg). Crystals suitable for diffraction study were grown from CH_2Cl_2/hexanes solutions. ^{1}H NMR (400 MHz, $CDCl_3$): 6.88 (s, 2H); 5.38 (pentet, $J = 3.2$ Hz, 1H); 4.15 (d, $J = 6.8$ Hz, 1H), 3.37 (d, $J = 6.8$ Hz, 1H), 3.23 (d, $J = 6.8$ Hz, 1H), 2.41 (d, $J = 11.6$ Hz, 1H), 2.072 (m, 4H), 1.85 (m, 8H), 1.72 (d, $J = 12$ Hz, 4H), 1.58−1.16 (m, 8H). ^{13}C NMR (100 MHz, CD_2Cl_2): 178, 119.57, 118.03, 114.96, 72.02, 61.0, 60.87, 47.82, 34.65, 34.59, 26.16, 25.89. Anal. Calcd: C, 51.93; H, 7.26; N, 6.73. Found: C, 52.11; H, 7.38; N, 6.65.

(IAd)Pd(allyl)Cl (7). IAd[23] (740 mg, 2.2 mmol) and (Pd(allyl)Cl)$_2$ (365.8 mg, 1 mmol) were mixed together in a Schlenk tube in the drybox. Dry THF (5 mL) was added by cannula and the mixture stirred at room temperature for 2 h. The solvent was removed in a vacuum, and 20 mL of anhydrous hexane was added to triturate the product. The reaction mixture was filtered in air and the solid washed with hexane. The procedure yielded 945 mg of (IAd)Pd(allyl)Cl (91% yield). Crystals suitable for diffraction study were grown from THF/hexanes solutions. ^{1}H NMR (400 MHz, C_6D_6): 6.79 (dd, $J = 8$ Hz, $J = 2.4$ Hz, 2H), 5.08 (pentet, $J = 6$ Hz, 1H), 4.22 (dd, $J = 6.8$ Hz, $J = 2.4$ Hz, 1H), 3.32 (d, $J = 12.8$ Hz, 1H), 3.21 (d, $J = 6.4$ Hz, 1H), 2.58 (d, $J = 1.6$ Hz, 6H), 2.43 (d, $J = 11.6$ Hz, 3H), 2.27 (d, $J = 11.6$ Hz, 3H), 2.18 (d, 1H), 2.00 (d, $J = 11.6$ Hz, 6H); 1.62−1.47 (m, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): 30.101; 30.192; 36.170; 36.200; 44.022; 44.340; 52.571; 59.217; 69.443; 111.964; 115.941; 117.426; 175.598. Anal. Calcd: C, 60.00; H, 7.36; N, 5.38. Found: C, 59.72; H, 7.19; N, 5.20.

[*N*,*N*′-Bis(1-*S*,*S*-phenylethylimidazol)-2-ylidene]Pd(allyl)Cl (8). [*N*,*N*′-Bis(1-*S*,*S*-phenylethylimidazol)-2-ylidene]carbene[23] (303.6 mg, 1.1 mmol) and (Pd(allyl)Cl)$_2$ (182.9 mg, 0.5 mmol) were mixed together in a Schlenk tube in the drybox. Dry THF (20 mL) was added and the mixture stirred at room temperature for 2 h. The solvent was removed in a vacuum, and 20 mL of anhydrous hexane was added to triturate the product. The product was filtered in air and washed with hexane. The procedure yielded 376.3 mg of the title compound (82% yield). Crystals suitable for diffraction study were grown from THF/hexanes mixture. ^{1}H NMR (400 MHz, CD_2Cl_2): 7.38 (t, $J = 12$ Hz, 2H), 7.28−7.21 (m, 4H), 6.817 (d, $J = 6.4$ Hz, 4H), 6.05 (s, $J = 5.6$ Hz, 2H), 5.19 (quartet, $J =$ Hz, 2H), 4.94 (pentet, $J = 6.4$ Hz, 1H), 4.04 (d, $J = 7.2$ Hz, 1H), 3.07 (d, $J = 12$ Hz, 1H), 2.99 (d, $J = 14$ Hz, 1H), 2.83 (d, $J = 6$ Hz, 1H), 1.74 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (400 MHz, CD_2Cl_2): 182.40,-130.52, 120.42, 116.872, 116.52, 73.32, 61.26, 49.90, 22.71. Anal. Calcd: C, 57.40; H, 6.58; N, 5.71. Found: C, 57.21; H, 6.40; N, 5.55.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation and the Louisiana Board of Regents.

Supporting Information Available: Experimental details for the synthesis of (NHC)Pd(allyl)Cl, catalysis protocol for cross-coupling of morpholine and 4-chloro toluene, and full crystallographic tables including atomic positions and bond distances, angles, and torsion angles are available free of charge via the Internet at http://pubs.acs.org.

OM034319E