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A New Class of Stable, Saturated N-Heterocyclic Carbenes with *N*-Naphthyl Substituents: Synthesis, Dynamic Behavior, and Catalytic Potential

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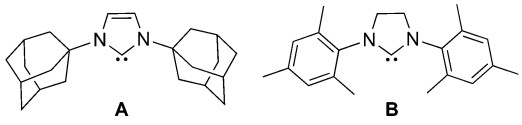
A new family of easily accessible and stable imidazolin-2-ylidenes has been synthesized, where the side chains are comprised of substituted naphthyl units. This generates C_2-symmetric (*anti*) and C_s-symmetric (*syn*) atropisomers. The interconversion between the isomers is studied in detail both for the N-heterocyclic carbene salts and the free carbenes through variable-temperature ^{1}H NMR spectroscopic studies; activation free energies are calculated and can be linked to the substitution pattern of the naphthyl moieties. Palladium complexes comprising the new N-heterocyclic carbenes are synthesized and preliminary data show that these compounds behave well as precatalysts in the Buchwald–Hartwig amination reaction of aryl bromides and aryl chlorides.

Introduction

Almost 30 years have elapsed between the proposal of stable N-heterocyclic carbenes (NHCs)[1] and the preparation of the first member of this class of compounds by Arduengo et al.[2] The isolation and characterization of the first stable and crystalline imidazol-2-ylidene **A**[2] and the saturated imidazolidin-2-ylidene derivative **B**[3] have sparked renewed interest in the chemistry of carbenes. To a large extent, research efforts in this area have been stimulated by the fact that NHCs can serve as ligand entities for transition-metal catalysts and often show increased stability and reactivity relative to their phosphane analogues.[4,5]



A **B**

Whereas dozens of structural variations of NHCs **A** and **B** exist nowadays, the overwhelming majority incorporate the unsaturated central N-heterocycle of **A**. The reason for this lies in the surprisingly different stabilities of unsaturated and saturated NHCs. Whereas dimerization of aromatically stabilized carbenes of type **A** is thermodynamically unfavorable even for small N-substituents like R = Me[6] and has only been observed for a special case of a covalently tethered bis-carbene,[7] formation of the enetetramine dimer of derivatives of **B** occurs readily. This renders saturated NHCs considerably less amenable to catalysis and restricts access to stable modifications of this ligand class, as the substituents at the nitrogen atoms need to be very bulky. The demarcation line separating stable from unstable carbenes may be established and lies somewhere between *t*Bu/*i*Pr for *N*-alkyl substituents and Mes/Ph for aromatic side chains.[8–10]

Among the NHC ligand architectures that behave well in catalysis, 2,4,6-mesityl- and 2,6-isopropylphenyl-substituted imidazol-2-ylidenes (IMes and IPr, respectively) and their saturated imidazolidin-2-ylidene counterparts (SIMes and SIPr) are by far the most versatile and reactive when used as bulky monodentate ligands and remain the only ligands representing a truly viable alternative to monodentate phosphanes. Presumably, the perpendicular arrangement of the aryl side chains, combined with the steric bulk on the aromatic rings, leads to a situation where these ligands confer stability to unsaturated, reactive metal centers during catalysis and where decomposition of the catalyst through unwanted metal–ligand interactions is rarely observed.

Recent work in our laboratory has led to the synthesis of promising members of a new family of stable, saturated NHCs that incorporate bulky naphthyl side chains.[11] The introduction of the naphthyl moieties generates atropisomeric ligands with C_2-symmetric (*anti*) and C_s-symmetric (*syn*) conformations (Scheme 1).[12] When used in catalysis, these systems seem to present versatility comparable to the reference systems SIMes and SIPr and show excellent catalytic activities, especially with one of the three ligands synthesized, which incorporates isopropyl groups at the C-2 and C-7 positions of the naphthyl side chains.

Following up on these preliminary data, we now report the synthesis of several new members of stable, saturated NHC structures that incorporate naphthyl side chains with different substitution patterns. We show that their chemical

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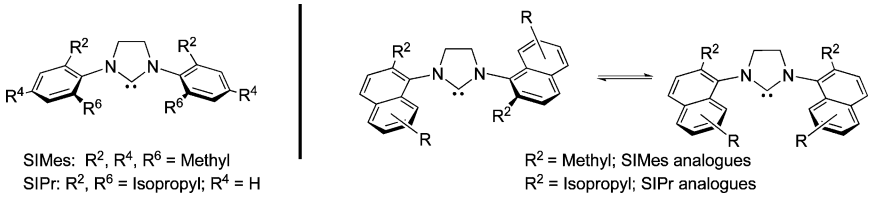


Scheme 1. Imidazolin-2-ylidenes with phenyl (left) and naphthyl (right) side chains.

behavior is similar and present a comparative study on their fluxional behavior. Further, the new ligands are used to synthesize new palladium complexes that are subsequently tested as precatalysts in the Buchwald–Hartwig amination reaction of aromatic bromides and chlorides.

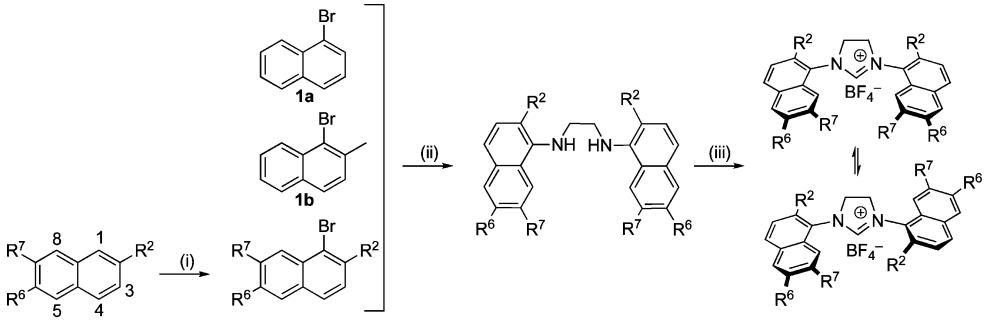
Results and Discussion

Synthesis and Characterization of *N*,*N*′-Binaphthyl-Substituted Imidazolinium Salts

Saturated NHCs with symmetrically substituted aromatic side chains are normally prepared from the reaction of triethyl orthoformate with the corresponding diamine, which in turn is either accessible through a condensation and reduction sequence starting from the corresponding aromatic amine,[9b,13] or through a palladium-catalyzed double C–N coupling of the aromatic bromide with ethylene diamine.[14] In our case, this latter reaction sequence appeared more straightforward when starting from alkyl-substituted naphthalene derivatives. Indeed, under optimized reaction conditions, the initial bromination turned out to be very selective for the C-1 position of the naphthyl derivatives, giving rise to expected isomers **1c**–**g** with selectivities of at least 80%. In some cases, small amounts of other brominated products were present, but these were conveniently eliminated through purification by column chromatography in the next step of the synthetic procedure. After a double Buchwald–Hartwig coupling with ethylenediamine in the presence of $Pd(dba)_2$, (±)-BINAP, and NaO*t*Bu, diamines **2a**–**g** were obtained as pure products after chromatographic workup. Finally, ring closing of **2a**–**g** with triethyl orthoformate in the presence of NH_4BF_4 by following an adapted synthetic procedure[15] afforded the corresponding imidazolinium salts **3a**–**g** in good yields and high purity (Scheme 2).

As a result of the presence of the alkyl substituents at C-2 of their naphthyl moieties, the (2)-SIMeNap·HBF_4 (**3b**), (2,7)-SIMeNap·HBF_4 (**3c**), (2)-SIPrNap·HBF_4 (**3d**), (2,6)-SIPrNap·HBF_4 (**3e**), (2,7)-SIPrNap·HBF_4 (**3f**), and (2)-SICyNap·HBF_4 (**3g**) salts were obtained as a mixture of C_2-(*anti*) and C_s-symmetric (*syn*) atropisomers, whereas SINap·HBF_4 (**3a**) adopts only one conformation. At room temperature ([D_6]DMSO), the ^{1}H NMR spectra of **3c**, **3d**, **3e**, and **3f** exhibit two distinct singlets in the region 9.6–9.5 ppm with an approximate ratio of 1.1:0.9, which correspond to the resonance of the imidazolinium protons. In the case of (2)-SICyNap·HBF_4 (**3g**), the presence of the bulky 2-cyclohexyl substituent significantly favors one of the two isomers, and the ^{1}H NMR spectrum shows two singlets centered at 9.56 and 9.64 ppm in a ratio of 3:1. Finally, the ^{1}H NMR spectrum of **3b** in [D_6]DMSO gives only one broad signal for the imidazolinium proton (9.47 ppm), but the presence of both isomers can be deduced from the presence of two signals for the aromatic H^8 protons of the naphthyl moieties (8.36 and 8.17 ppm).

In order to obtain more information on the dynamic behavior of the NHC salts, variable-temperature (VT) ^{1}H



Scheme 2. Synthesis of *N*,*N*′-binaphthyl-substituted imidazolinium salts. Reaction conditions: (i) Br_2, CH_2Cl_2, 0 °C; (ii) ethylenediamine, $Pd(dba)_2$, (±)-BINAP, NaO*t*Bu, toluene, 100 °C; (iii) NH_4BF_4, HCO_2H (cat.), $HC(OEt)_3$, 100 °C.

NMR spectroscopic studies were performed. Figure 1 schematically represents the rotation around the C–N bonds and the hydrogen atoms likely to be affected by the rotation (bold).[16]

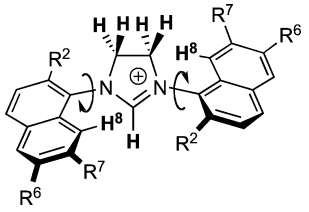


Figure 1. Schematic representation of the interconversion between the atropisomers of the imidazolinium salts.

First, VT ^{1}H NMR spectra of SINap·HBF$_4$ (**3a**) were measured in [D$_6$]acetone in the temperature range 183–303 K. Only one set of signals was observed for the whole temperature range, suggesting that the naphthyl substituents rotate freely even at low temperature (183 K). In the case of (2)-SIMeNap·HBF$_4$ (**3b**), the spectra were recorded in the temperature range 300–400 K in [D$_6$]DMSO. The results showed coalescence of the aromatic H^8 protons (8.17 and 8.36 ppm at room temperature) at 370 K, and above 380 K the backbone protons of the N-heterocycle appear as broad singlets, indicating fast interconversion. Note that the ease of rotation is almost unaffected by the introduction of the 7-methyl group, as the coalescence temperatures for (2)-SIMeNap·HBF$_4$ (**3b**) and (2,7)-SIMeNap·HBF$_4$ (**3c**) are almost identical. In the case of **3c**, the coalescence can be also observed for the imidazolinium proton, as its ^{1}H NMR spectrum shows two distinct singlets (8.05 and 8.10 ppm) at room temperature and only one signal at 370 K.

Contrary to **3b** and **3c**, the VT ^{1}H NMR spectra of (2)-SIPrNap·HBF$_4$ (**3d**), (2,6)-SIPrNap·HBF$_4$ (**3e**), (2,7)-SIPrNap·HBF$_4$ (**3f**), and (2)-SICyNap·HBF$_4$ (**3g**) revealed a static behavior, with no detectable line-shape modifications up to 400 K. As an example, Figure 2 shows the spectra of (2)-SICyNap·HBF$_4$ (**3g**) measured in [D$_6$]DMSO in the temperature range 300–400 K. Undoubtedly, the decrease in fluxionality is caused by the increased size of the C-2 substituents on the naphthyl moieties (isopropyl and cyclohexyl vs. methyl).

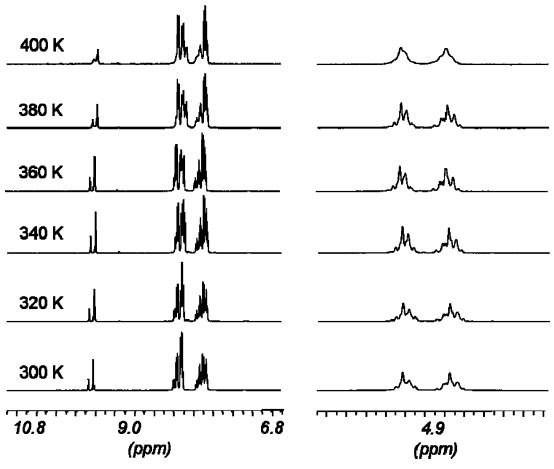


Figure 2. VT ^{1}H NMR spectra (400 MHz, [D$_6$]DMSO) of (2)-SICyNap·HBF$_4$ (**3g**).

Full characterization of these new imidazolinium salts includes single-crystal X-ray structure analysis of (2)-SIMeNap·HBF$_4$ (**3b**) and (2)-SICyNap·HBF$_4$ (**3g**). For **3b**, the crystals measured correspond to the C_s-symmetric (*syn*) species, whereas those of **3g** show the C_2-symmetric (*anti*) isomer (Figure 3).

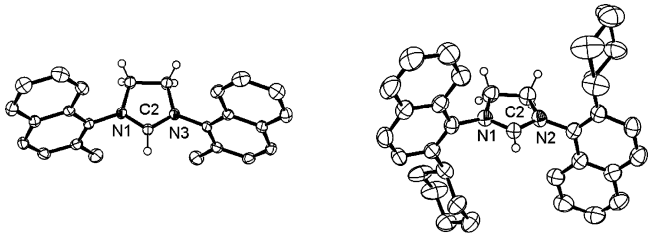
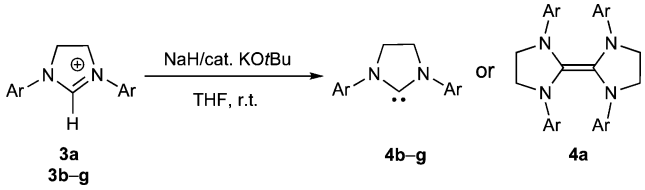


Figure 3. ORTEP views (50% probability ellipsoids) of **3b** (left) and **3g** (right). Hydrogen atoms (except for backbone and imidazolinium hydrogen atoms) and counterions (BF_4^-) are omitted for clarity.

Synthesis of *N*,*N*′-Binaphthyl-Substituted NHCs

Deprotonation of imidazolinium salts **3b**–**g** with NaH and a catalytic amount of potassium *tert*-butoxide led to the clean formation of free, monomeric carbenes **4b**–**g** in high yields. However, attempts to deprotonate SINap·HBF$_4$ (**3a**) with NaH/KO*t*Bu, KH/DMSO, or KHMDS invariably led to immediate formation of a bright orange solution containing the dimer SINap=SINap (**4a**) as the sole observable product (Scheme 3).



Scheme 3. Deprotonation of imidazolinium salts **3a**–**g**.

According to the ^{1}H and ^{13}C NMR spectra, deprotonated products **4a**–**c** adopt one conformation at 300 K. In the case of dimer **4a**, this implies that only one of the possible regioisomers is formed. For monomers (2)-SIMeNap (**4b**) and (2,7)-SIMeNap (**4c**), the results suggest that deprotonation of the imidazolinium salts leads to a situation where the naphthyl side chains are able to freely rotate due to the removal of the imidazolinium proton. Finally, examination of (2)-SIPrNap (**4d**), (2,6)-SIPrNap (**4e**), (2,7)-SIPrNap (**4f**), and (2)-SICyNap (**4g**) by ^{1}H NMR spectroscopy at 300 K revealed two sets of signals corresponding to the presence of two isomers in an approximate ratio of 1.1:0.9 in the case of **4d**–**f** and 3:1 in the case of **4g**. Thus, removal of the imidazolinium proton does not seem to alter the initial *syn*/*anti* ratio of the isomers, and we can therefore assume that a sufficiently high barrier to rotation between

the C_2- and C_s-conformations exists and no interconversion occurs during the deprotonation step. A straightforward experimental way to test this hypothesis comes from analysis of the nuclear Overhauser effects (2D NOESY NMR) between the respective isomers (Figure 4) and confirms our assumption for **3f/4f** and **3g/4g**. The major isomer in both cases is represented by the *anti* conformer (C_2 symmetry). This in turn means that the respective orientation of the side chains and the ratio between *anti* and *syn* isomers is determined during the ring-closing reaction leading to the NHC salts.

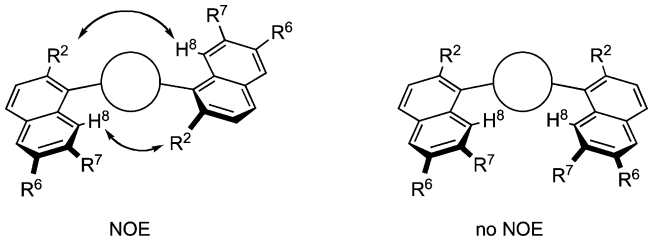


Figure 4. NOE signals expected for the C_2-symmetric conformation.

In order to evaluate the effect of the removal of the NHC–H bond on the dynamic behavior of carbenes **4b**–**g**, VT ^{1}H NMR studies were performed (Figure 5).

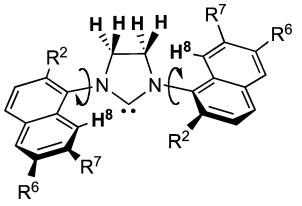


Figure 5. Schematic representation of the interconversion between the atropisomers of the free carbenes (hydrogen atoms affected by the rotation represented in bold).

As noted above, fast interconversion of the two conformations in (2)-SIMeNap (**4b**) and (2,7)-SIMeNap (**4c**) at room temperature leads to the observation of a single signal for the H^8 protons (8.18 ppm for **4b** and 8.02 ppm for **4c** in [D$_8$]toluene). Lowering the temperature showed gradual broadening of these signals with decoalescence at 273 K and 293 K for **4b** and **4c**, respectively. In the case of (2)-SIPrNap (**4d**), (2,6)-SIPrNap (**4e**), (2,7)-SIPrNap (**4f**), and (2)-SICyNap (**4g**), two sets of signals were observed at 300 K and fully attributed to the *anti* and *syn* forms. By raising the temperature, coalescence of the signals corresponding to the resonance of the H^8 protons was achieved at 330 (**4d** and **4e**), 360 (**4f**), and 340 K (**4g**). At 370 K, the signal appeared as a sharp doublet in all cases (Figures 6 and 7).

The identities of enetetramine **4a** and free NHCs **4c**, **4d**, and **4f** were unambiguously established by single-crystal X-ray structure analyses (Figure 8). The analyzed crystals of both (2,7)-SIMeNap (**4c**) and (2)-SIPrNap (**4d**) correspond to the *syn* form, whereas (2,7)-SIPrNap (**4f**) shows its C_2-symmetric (*anti*) conformer.[17]

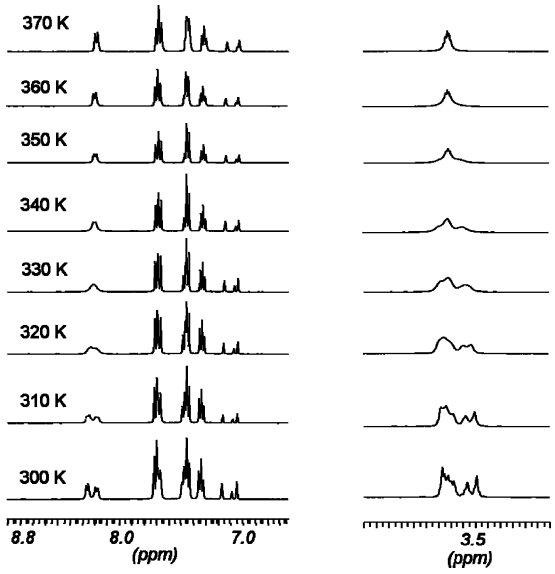


Figure 6. VT ^{1}H NMR spectra (400 MHz, [D$_8$]toluene) of (2)-SIPrNap (**4d**).

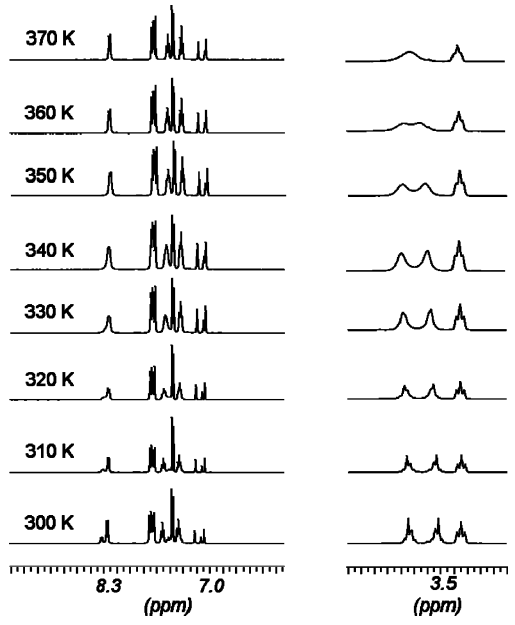


Figure 7. VT ^{1}H NMR spectra (400 MHz, [D$_8$]toluene) of (2)-SICyNap (**4g**).

A comparison of bond lengths and angles with the only two other crystallographically characterized saturated NHCs, namely, Arduengo's SIMes,[3] and Denk's SI*t*Bu,[9a] reveals a similar bonding situation for **4c**, **4d**, and **4f**. The N–C–N angles [104.8(2)° for **4c**, 104.5(2)° for **4f** and 104.8(1)° for **4d**] are almost identical to that for SIMes [104.7(3)°] but slightly smaller than that in SI*t*Bu [106.44(9)°]. A closer inspection of the planarity of the central N-heterocycle shows that different degrees of distortion exist in these saturated NHCs. Whereas the backbone carbon atoms in **4d**, SIMes, and SI*t*Bu deviate measurably from the plane of the other three ring atoms, the N-heterocycles in **4c** and **4f** are almost perfectly planar.

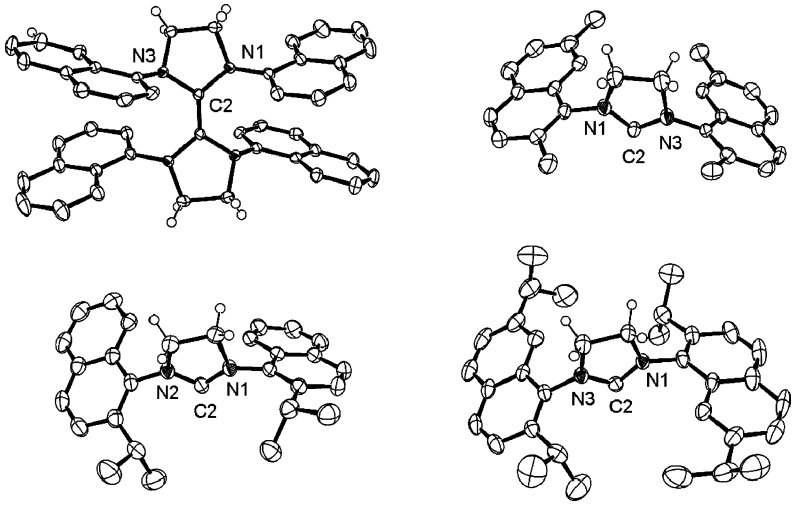


Figure 8. ORTEP views (50% probability ellipsoids) of **4a** (top, left), **4c** (top, right), **4d** (bottom, left), and **4f** (bottom, right). Hydrogen atoms (except for backbone hydrogens) are omitted for clarity.

Activation Free Energies

From the VT NMR analyses performed above, we calculated activation free energies for the interconversion of both imidazolinium salts and free carbenes by using complete line-shape analysis,[18] which gave the corresponding $\Delta G^{\ddagger}$ values (Table 1). The coalescence temperatures were calculated from the Gutowsky–Holm equation ($k_c = \pi\Delta\nu/2^{1/2}$). Assuming the transmission coefficient, κ, to be unity, the free energy activation ($\Delta G^{\ddagger}$) was calculated from the Eyring equation ($\Delta G^{\ddagger} = RT_c[\ln T_c - \ln k_c + 23.76]$).[19]

It is evident from the data that the rotational barriers decrease in the order **3d**–**g** > **3c** > **3b** > **3a** for the imidazolinium salts and **4d**–**g** > **4c** > **4b** for the free carbenes. These trends can be directly associated with the steric demand of the naphthyl side chains. More specifically, the size of the substituents at C-2 of the naphthyl moieties affect $\Delta G^{\ddagger}$ and limit the rotation about the C–N bonds. Surprisingly, introduction of the cyclohexyl substituent at C-2 (Table 1, Entry 13) does not affect the rotational barrier more than the introduction of an isopropyl substituent (Table 1, Entry 10). Overall, $\Delta G^{\ddagger}$ decreases by roughly 20 kJ mol^{-1} when removing the carbenic proton, that is, when going from the imidazolinium salts to the free carbenes. Furthermore, the values calculated for the rotational barrier of free carbenes **4d**–**g** validate our experimental conclusion that we have drawn above and clearly indicates that the respective symmetry (C_2 or C_s) is maintained in these structures at room temperature.

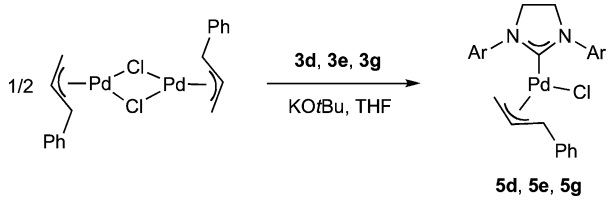
Catalytic Studies: Pd-Catalyzed Buchwald–Hartwig Amination

Pioneering work by Nolan et al. has shown that NHC-modified allyl–Pd catalysts are extremely active systems in various cross-coupling reaction protocols.[20] We previously demonstrated that the corresponding complexes incorporating ligands **4b**, **4c**, and **4f** showed very similar activity to the reference SIMes/SIPr modified systems.[11] We wanted therefore to establish how the new ligands reported here, namely, **4d**, **4e**, and **4g**, would behave in palladium-catalyzed reactions and chose the Buchwald–Hartwig coupling of both aryl bromides and aryl chlorides as the benchmark catalytic transformation. At the same time and to see whether a modification of the precatalyst structure would give a similar increase in reactivity as observed by Nolan et al.,[20d] we decided to incorporate the cinnamyl fragment

Table 1. Values of T_c and $\Delta G^{\ddagger}$ for **3a**–**g** (imidazolinium salts) and **4b**–**g** (free carbenes).

Entry	Compound	Solvent	T_c (K)	$\Delta G^{\ddagger}$ (kJ mol^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})
1	SINap·HBF_4 (**3a**)	[D_6]acetone	<183	<44.1	<10.5
2	(2)-SIMeNap·HBF_4 (**3b**)	[D_6]DMSO	370 (H^8)	74.6	17.8
3	(2,7)-SIMeNap·HBF_4 (**3c**)	$C_2D_2Cl_4$	353 (H^{im})	75.5	18.0
4	(2)-SIPrNap·HBF_4 (**3d**)	[D_6]DMSO	>410	>89.9	>21.5
5	(2,6)-SIPrNap·HBF_4 (**3e**)	[D_6]DMSO	>410	>89.9	>21.5
6	(2,7)-SIPrNap·HBF_4 (**3f**)	[D_6]DMSO	>410	>89.9	>21.5
7	(2)-SICyNap·HBF_4 (**3g**)	[D_6]DMSO	>410	>89.9	>21.5
8	(2)-SIMeNap (**4b**)	[D_8]toluene	273 (H^8)	56.9	13.6
9	(2,7)-SIMeNap (**4c**)	[D_8]toluene	293 (H^8)	59.8	14.3
10	(2)-SIPrNap (**4d**)	[D_8]toluene	350 (H^8)	80.6	19.2
11	(2,6)-SIPrNap (**4e**)	[D_8]toluene	350 (H^8)	80.4	19.2
12	(2,7)-SIPrNap (**4f**)	[D_8]toluene	360 (H^8)	82.6	19.7
13	(2)-SICyNap (**4g**)	[D_8]toluene	350 (H^8)	80.6	19.2

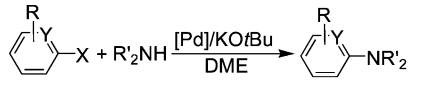
(instead of allyl) into the precatalyst structure. Thus, addition of $[Pd(cinnamyl)Cl]_2$ to NHC salts **3d**, **3e**, and **3g** in the presence of KO*t*Bu gave high yields of *syn*/*anti* mixtures of complexes [{(2)-SIPrNap}Pd(cinnamyl)Cl] (**5d**), [{(2,6)-SIPrNap}Pd(cinnamyl)Cl] (**5e**), and [{(2)-SICyNap}-Pd(cinnamyl)Cl] (**5g**) (Scheme 4). The new complexes were fully characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry. As expected, the *syn*/*anti* ratios of the NHC precursors were maintained in the complexes.

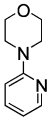
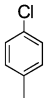
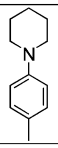
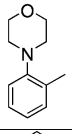
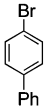
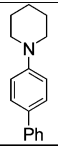


Scheme 4. Synthesis of complexes with general formula [(NHC)-Pd(cinnamyl)Cl].

The results of the catalytic reactions are summarized in Table 2 and compared to [(SIPr)Pd(cinnamyl)Cl] (**6**).[20d] The following conclusion can be drawn from these preliminary studies. Firstly, precatalysts **5d**, **5e**, and **5g** are active catalysts showing complete conversions at a catalyst loading of 1 mol-% and a reaction temperature of 80 °C. Second, among our complexes, [{(2)-SICyNap}Pd(cinnamyl)Cl] (**5g**), containing the most sterically demanding substituent at C-2, shows the best catalytic performance in all tested reactions. However, **5d**, **5e**, and **5g** present clearly lower catalytic activities relative to that of reference catalytic system **6**, which is able to efficiently transform all substrates studied at room temperature. Furthermore, we should note that **5d**, **5e**, and **5g** are not more active than our previously reported [{(2,7)-SIPrNap}Pd(allyl)Cl].[11] Whether this means that the somewhat different architecture of our naphthyl-substituted NHCs (as compared to SIPr/IPr) makes them insensitive to changes to the allyl moiety of the palladium precatalyst is not clear at present. Combining the data gathered in Table 2 with our earlier studies[11] indicates that whereas increased steric bulk at the 2-position of the naphthyl side chains translates into overall higher activity, the substitution pattern on the second naphthyl ring (C-6, C-7) also plays a role in the catalytic performance of these palladium complexes.

Table 2. Buchwald–Hartwig coupling reactions catalyzed by **5d**, **5e**, and **5g**.



Entry	Ar-X	Amine	Product	Catalyst (mol-%)	Time	*T* (°C)	Yield[a] (%)
1				**5d** (1)	1min	r.t.	97
2				**5d** (0.1)	6h	r.t.	42
3				**5e** (1)	1min	r.t.	100
4				**5e** (0.1)	6h	r.t.	53
5				**5g** (1)	1min	r.t.	100
6				**5g** (0.1)	6h	r.t.	59
7				**6** (1)	1min	r.t.	100[b]
8				**6** (0.1)	15min	r.t.	98[b]
9				**5d** (1)	22h	80	78
10				**5e** (1)	4h	80	94
11				**5g** (1)	15min	80	100
12				**6** (1)	1h	r.t.	100[b]
13				**5d** (1)	1h	80	96
14				**5e** (1)	1h	80	98
15				**5g** (1)	1h	80	100
16				**6** (1)	30min	r.t.	96[b]
17				**5d** (1)	1h	80	98
18				**5e** (1)	1h	80	98
19				**5g** (1)	10min	80	100
20				**6** (1)	5min	r.t.	83[b]

[a] Yield determined by GC against internal standard. [b] Data taken from ref.[20d]

Conclusions

The present work extends our previous results on the synthesis of a new class of saturated NHC ligands with naphthyl-derived side chains. Both imidazolinium salts and free carbene species were obtained in a straightforward manner and in good overall yield and high purity. The dynamic behavior of the salts and carbenes, that is, their interconversion between C_2-symmetric and C_s-symmetric conformations, was studied by VT NMR experiments and shows that the decrease in fluxionality is caused by the increased size of the substituents at C-2 of the naphthyl moieties (cyclohexyl and isopropyl vs. methyl). Steric considerations also played an important role in the catalytic activity of the palladium complexes derived from these new ligands. In representative Buchwald–Hartwig amination reactions, we identified the most bulky new NHC ligand as being superior to the other two NHC–Pd precatalysts tested.

Experimental Section

General Information: All manipulations were routinely carried out under an inert atmosphere of nitrogen by using Schlenk techniques or glove boxes (Mecaplex or Innovative Technology). Solvents were purged with argon and collected after passage through alumina columns in a solvent purification system (Innovative Technology). Deuterated NMR solvents were purchased from Armar Chemicals, degassed by purging with nitrogen, and dried with activated molecular sieves of appropriate size. NMR spectra were recorded with Bruker ARX-300, AV2–400, and AV-500 spectrometers and treated with MestReC. Mass spectra were recorded by the analytical services of the Chemistry Department of the University of Zurich. GC analyses of catalytic products were carried out with a Trace GC 2000 equipped with an FID detector. The column used was a 30-m ZB-5 capillary column with 0.25-mm inner diameter and 0.25-μm film thickness. Flow rate = 1.5 mL min^{-1} for He carrier

gas. Crystals were mounted on a glass fiber for low-temperature X-ray structure determinations. All measurements were made with a Nonius Kappa CCD area-detector diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. CCDC-715132 (for **3g**) and -715133 (for **4d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data for **3b**, **4a**, **4c**, and **4f** can be found in the Supporting Information of ref.[11] 2-Cyclohexylnaphthalene was prepared according to a published method.[21] Synthesis of compounds **1c**, **1f**, **2a**–**c**, **2f**, **3a**–**c**, **3f**, **4a**–**c**, and **4f** was reported elsewhere.[11] [Pd(cinnamyl)Cl]$_2$ was synthesized following a published procedure.[22] 2-Isopropylnaphthalene and 2,6-diisopropylnaphthalene were purchased from TCI Laboratory Chemicals and used without further purification.

1-Bromo-2-isopropylnaphthalene (1d): To a solution of 2-isopropylnaphthalene (30 g, 176 mmol) dissolved in CH_2Cl_2 (250 mL) and cooled to 0 °C was added a solution of Br_2 (28.13 g, 9.04 mL, 176 mmol) in CH_2Cl_2 (200 mL) dropwise over 90 min. The solution was then stirred for 1 h at room temperature. Subsequently, the reaction mixture was quenched by the addition of an aqueous solution of NaOH. After decantation, the orange organic phase was separated, washed with water, and dried with anhydrous $MgSO_4$. After filtration and concentration, the resulting yellow oil was subjected to a short silica gel plug (cyclohexane). The expected product was isolated as a light yellow liquid containing about 10% of a secondary brominated isomer and trace amounts of starting material. The material was used without further purification for the continuation of the experiments. Yield: 40.05 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (m, 1 H, H_{ar}), 7.79 (m, 2 H, H_{ar}), 7.57 (m, 1 H, H_{ar}), 7.46 (m, 2 H, H_{ar}), 3.78 [sept., ^3J = 6.9 Hz, 1 H, Ar-C*H*(CH$_3$)$_2$], 1.33 [d, ^3J = 6.9 Hz, 6 H, Ar-CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 145.1, 133.2, 132.5, 127.9, 127.8, 127.7, 127.2, 125.7, 124.1, 123.1 (C_{ar}), 33.8 [Ar-*C*H(CH$_3$)$_2$], 22.8 [Ar-CH(*C*H$_3$)$_2$] ppm. HRMS (EI): calcd. for $C_{13}H_{13}Br$ 248.0201; found 248.0200.

***N*,*N*′-Bis(2-isopropylnaphthalen-1-yl)ethane-1,2-diamine (2d):** In a glove box, a mixture of $Pd_2(dba)_3$ (261.4 mg, 0.285 mmol), (±)-BINAP (357.8 mg, 0.575 mmol), and NaO*t*Bu (1.651 g, 17.178 mmol) in toluene (50 mL) was stirred for a few minutes. Then, a solution of **1d** (3 g, 12.036 mmol) in toluene (30 mL) was added. Finally, ethylenediamine (383 µL, 5.729 mmol) was added. The volume of toluene was adjusted to 150 mL. The resulted dark red solution was heated at 100 °C for 20 h, subsequently cooled to room temperature, and filtered through a silica gel/Celite plug to remove insoluble residues. The filtrate was washed with CH_2Cl_2 until the eluent became colorless. After concentration in vacuo, the residue was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 10:1 to 1:1). Product **2d** was isolated from the last fraction as a yellow oil. Yield: 1.52 g (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (m, 2 H, H_{ar}), 7.82 (m, 2 H, H_{ar}), 7.62 (m, 2 H, H_{ar}), 7.46 (m, 6 H, H_{ar}), 3.97 (br., 2 H, N*H*), 3.53 [sept., ^3J = 6.8 Hz, 2 H, Ar-C*H*(CH$_3$)$_2$], 3.48 [s, 4 H, N(C*H*$_2$)$_2$N], 1.34 [d, ^3J = 6.8 Hz, 12 H, Ar-CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 140.7, 137.2, 133.2, 129.4, 128.3, 125.6, 125.1, 124.2, 123.8, 123.3 (C_{ar}), 52.0 [N(*C*H$_2$)$_2$N], 27.8 [Ar-*C*H(CH$_3$)$_2$], 23.9 [Ar-CH(*C*H$_3$)$_2$] ppm. HRMS (ESI): calcd. for $C_{28}H_{33}N_2^+$ [M + H]$^+$ 397.2644; found 397.2642.

1,3-Bis(2-isopropylnaphthalen-1-yl)imidazolinium Tetrafluoroborate [(2)-SIPrNap·HBF$_4$] (3d): A mixture of diamine **2d** (1.25 g, 3.152 mmol) and NH_4BF_4 (429.6 mg, 4.098 mmol) was dissolved in triethyl orthoformate (40 mL) and a few drops of formic acid were added. The solution was heated at 100 °C for 4 h. During the reaction, ethanol was regularly removed from the solution by applying a slight vacuum for a few second. The resulting white precipitate was filtered, washed with diethyl ether, and extracted with CH_2Cl_2 to remove the excess amount of NH_4BF_4. After evaporation and drying in vacuo, **3d** was obtained as a white powder. Yield: 1.12 g (72%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.62 (s, 0.55 H, N-C*H*=N of the major isomer), 9.58 (s, 0.45 H, N-C*H*=N of the minor isomer), 8.38–7.68 (series of m, 12 H, H_{ar}), 4.82 [m, 4 H, N(C*H*$_2$)$_2$N], 3.64 [sept., ^3J = 6.9 Hz, 0.9 H, Ar-C*H*(CH$_3$)$_2$ of the minor isomer], 3.41 [sept., ^3J = 6.7 Hz, 1.1 H, Ar-C*H*(CH$_3$)$_2$ of the major isomer], 1.51, 1.47, 1.34, 1.32 [series of d, 12 H, Ar-CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 161.5, 161.3 (N-*C*H=N), 144.4, 144.0, 132.3, 132.2, 130.9, 129.2, 129.1, 128.5, 128.4, 128.35, 128.3, 127.1, 127.0, 126.7, 126.6, 124.3, 124.2, 122.0, 121.3 (H_{ar}), 53.6, 53.5 [N(*C*H$_2$)$_2$N], 28.5, 28.3 [Ar-*C*H(CH$_3$)$_2$], 24.0, 23.2, 23.0 [Ar-CH(*C*H$_3$)$_2$] ppm. HRMS (ESI): calcd. for $C_{29}H_{31}N_2^+$ [M]$^+$ 407.2487; found 407.2491.

1,3-Bis(2-isopropylnaphthalen-1-yl)imidazolin-2-ylidene [(2)-SIPrNap] (4d): A suspension of NaH (60% dispersion in mineral oil, 67 mg, 1.675 mmol) and KO*t*Bu (10 mg, 0.089 mmol) in THF (10 mL) was added to a suspension of **3d** (750 mg, 1.516 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 24 h. The resulting yellow solution was filtered trough Celite, and the solvents were evaporated to dryness. After triturating with pentane, evaporation, and drying in vacuo, **4d** was obtained as a fine yellowish powder. Yield: 602 mg (98%). Crystals suitable for X-ray structure analysis were obtained by slow evaporation of a solution of **4d** in diethyl ether. M.p. 158–159 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.27 (d, J = 8.4 Hz, 1.10 H, H_{ar} of the major isomer), 8.19 (d, J = 8.3 Hz, 0.90 H, H_{ar} of the minor isomer), 7.70–7.27 (series of m, 10 H, H_{ar}), 3.78–3.35 [m, 6 H, N(C*H*$_2$)$_2$N and Ar-C*H*(CH$_3$)$_2$], 1.44–1.32 [series of four d, 12 H, Ar-CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]toluene): δ = 246.2, 246.0 (N-*C*-N), 143.8, 143.7, 136.8, 133.6, 132.4, 132.3, 128.4, 128.2, 126.7, 126.6, 125.5, 124.3, 124.0, 123.8 (C_{ar}), 53.6 [N(*C*H$_2$)$_2$N], 29.1, 29.0 [Ar-*C*H(CH$_3$)$_2$], 24.7, 24.6, 23.5 [Ar-CH(*C*H$_3$)$_2$] ppm.

1-Bromo-2,6-diisopropylnaphthalene (1e): To a solution of 2,6-diisopropylnaphthalene (37.4 g, 176 mmol) dissolved in CH_2Cl_2 (250 mL) and cooled to 0 °C was added a solution of Br_2 (28.13 g, 9.04 mL, 176 mmol) in CH_2Cl_2 (200 mL) dropwise over a period of 1 h. The solution was then stirred for 1 h at room temperature and subsequently quenched by the addition of an aqueous solution of NaOH. After decantation, the orange organic phase was separated, washed with water, and dried with anhydrous $MgSO_4$. After filtration and concentration, the resulting yellow oil was subjected to a silica gel plug (hexane). The expected product contained about 15% of a secondary brominated isomer. Yield: 45.61 g (89%). This starting material was used without further purification for the continuation of the experiments. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (m, 1 H, H_{ar}), 7.76 (m, 1 H, H_{ar}), 7.62 (m, 1 H, H_{ar}), 7.51 (m, 1 H, H_{ar}), 7.43 (m, 1 H, H_{ar}), 3.79 [sept., ^3J = 6.9 Hz, 1 H, Ar-C*H*(CH$_3$)$_2$], 3.11 [sept., ^3J = 6.9 Hz, 1 H, Ar-C*H*(CH$_3$)$_2$], 1.38 [d, ^3J = 6.9 Hz, 6 H, Ar-CH(C*H*$_3$)$_2$], 1.35 [d, ^3J = 6.9 Hz, 6 H, Ar-CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 146.3, 144.2, 133.4, 131.2, 127.7, 127.6, 127.1, 124.2, 124.1, 122.9 (C_{ar}), 33.9, 33.7 [Ar-*C*H(CH$_3$)$_2$], 23.9, 22.9 [Ar-CH(*C*H$_3$)$_2$] ppm. HRMS (EI): calcd. for $C_{16}H_{19}Br$ 290.0670; found 290.0668.

***N*,*N*′-Bis(2,6-diisopropylnaphthalen-1-yl)ethane-1,2-diamine (2e):** In a glove box, a mixture of $Pd_2(dba)_3$ (261.4 mg, 0.285 mmol), (±)-BINAP (357.8 mg, 0.575 mmol), and NaO*t*Bu (1.651 g,

17.178 mmol) in toluene (50 mL) was stirred for a few minutes. Then, a solution of **1e** (3.5 g, 12.022 mmol) in toluene (30 mL) was added. Finally, ethylenediamine (383 μL, 5.729 mmol) was added. The volume of toluene was adjusted to 150 mL. The resulting dark red solution was heated at 100 °C for 20 h, subsequently cooled to room temperature, and filtered through silica gel/Celite to remove the insoluble materials. The filtrate was washed with CH_2Cl_2 until the eluent became colorless. After concentration in vacuo, the residue was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 10:1 to 1:1). Product **2e** was isolated from the last fraction as a yellowish oil. Yield: 1.81 g (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.8 Hz, 2 H, H_{ar}), 7.68 (m, 2 H, H_{ar}), 7.61 (d, J = 8.8 Hz, 2 H, H_{ar}), 7.45 (m, 4 H, H_{ar}), 3.89 (br., 2 H, N*H*), 3.57 [sept., ^3J = 6.8 Hz, 2 H, Ar-C*H*$(CH_3)_2$], 3.52 [s, 4 H, N(CH_2)$_2$-N], 3.12 [sept., ^3J = 6.8 Hz, 2 H, Ar-C*H*$(CH_3)_2$], 1.40 [d, ^3J = 6.8 Hz, 12 H, Ar-CH(CH_3)$_2$], 1.38 [d, ^3J = 6.8 Hz, 12 H, Ar-CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 145.5, 140.7, 136.3, 133.4, 127.9, 125.4, 124.5, 124.2, 123.5, 123.3 (C_{ar}), 52.0 [N(*C*H$_2$)$_2$N], 34.0 [Ar-*C*H(CH$_3$)$_2$], 27.7 [Ar-*C*H$(CH_3)_2$], 23.95 [Ar-CH(*C*H$_3$)$_2$], 23.9 [Ar-CH(*C*H$_3$)$_2$] ppm. HRMS (EI): calcd. for $C_{34}H_{44}N_2Na$ 503.3402; found 503.3408.

1,3-Bis(2,6-diisopropylnaphthalen-1-yl)imidazolinium Tetrafluoroborate [(2,6)-SIPrNap·HBF$_4$] (3e): A mixture of diamine **2e** (1.17 g, 2.434 mmol) and NH_4BF_4 (306 mg, 2.919 mmol) was dissolved in triethyl orthoformate (30 mL) and a few drops of formic acid were added. The solution was heated at 100 °C for 4 h. During the reaction, ethanol was regularly removed from the solution by applying a slight vacuum for a few seconds. The resulting white precipitate was filtered, washed with diethyl ether, and then with water (to remove the excess amount of NH_4BF_4). After drying in vacuo for 2 d, **3e** was obtained as a white powder. Yield: 1.09 g (77%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.58 (s, 0.55 H, N-C*H*=N of the major isomer), 9.55 (s, 0.45 H, N-C*H*=N of the minor isomer), 8.28–7.71 (series of m, 10 H, H_{ar}), 4.81 [m, 4 H, N(CH_2)$_2$N], 3.61 [sept., ^3J = 6.8 Hz, 0.9 H, Ar-C*H*$(CH_3)_2$ of the minor isomer], 3.38 [sept., ^3J = 6.9 Hz, 1.1 H, Ar-C*H*$(CH_3)_2$ of the major isomer], 3.16 [m, 2 H, Ar-C*H*$(CH_3)_2$], 1.52–1.32 [m, 24 H, Ar-CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): δ = 161.4, 161.2 (N-*C*H=N), 146.9, 143.4, 143.0, 132.6, 132.5, 130.6, 128.1, 128.0, 127.8, 127.7, 127.0, 126.9, 124.6, 124.5, 124.2, 124.1, 122.1, 121.4 (C_{ar}), 53.6, 53.5 [N(*C*H$_2$)$_2$N], 33.3, 28.4, 28.2 [Ar-*C*H$(CH_3)_2$], 24.1, 24.0, 23.7, 23.6, 23.55, 23.5, 23.2, 22.9 [Ar-CH(*C*H$_3$)$_2$] ppm. HRMS (ESI): calcd. for $C_{35}H_{43}N_2^+$ [M]$^+$ 491.3426; found 491.3422.

1,3-Bis(2,6-diisopropylnaphthalen-1-yl)imidazolin-2-ylidene [(2,6)-SIPrNap] (4e): In a glove box, a suspension of NaH (60% dispersion in mineral oil, 45 mg, 1.125 mmol) and KO*t*Bu (7 mg, 0.062 mmol) in THF (10 mL) was added to a suspension of **3e** (576 mg, 0.995 mmol) in THF (10 mL) and stirred at room temperature for 24 h. The resulting yellow solution was filtered through Celite, and the solvents were evaporated to dryness. The residue was dissolved in ether and again filtered through Celite. After evaporation and drying in vacuo, **4e** was obtained as a fine yellowish powder. Yield: 470 mg (96%). M.p. 155–156 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.28 (d, J = 8.5 Hz, 1.10 H, H_{ar} of the major isomer), 8.19 (d, J = 8.3 Hz, 0.90 H, H_{ar} of the minor isomer), 7.71–7.40 (series of m, 8 H, H_{ar}), 3.85–3.43 [m, 6 H, N(CH_2)$_2$N and Ar-C*H*$(CH_3)_2$], 2.91 [sept., ^3J = 6.8 Hz, 2 H, Ar-C*H*$(CH_3)_2$], 1.48–1.25 [m, 24 H, Ar-CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]toluene): δ = 246.0, 245.9 (N-*C*-N), 145.8, 143.0, 142.9, 136.9, 134.0, 131.1, 131.0, 126.4, 126.3, 124.8, 124.3, 124.2, 124.1 (C_{ar}), 53.6 [N(*C*H$_2$)$_2$N], 34.4, 29.1, 29.0 [Ar-*C*H$(CH_3)_2$], 24.8, 24.7, 24.1, 24.0, 23.7, 23.6 [Ar-CH(*C*H$_3$)$_2$] ppm.

1-Bromo-2-cyclohexylnaphthalene (1g): To a solution of 2-cyclohexylnaphthalene (3.70 g, 17.6 mmol) dissolved in CH_2Cl_2 (100 mL) and cooled to 0 °C was added a solution of Br_2 (3.63 g, 22.7 mmol) in CH_2Cl_2 (100 mL) dropwise over 30 min. The solution was stirred for 1 h at room temperature and subsequently quenched by the addition of an aqueous solution of NaOH (200 mL). After decantation, the orange organic phase was separated, washed with water, and dried with anhydrous $MgSO_4$. After concentration, filtration through a plug of silica gel (hexane) and drying in vacuo, pure **1g** was obtained as a yellow liquid. Yield: 5.01 g (91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.37 (m, 1 H, H_{ar}), 7.80 (m, 2 H, H_{ar}), 7.59 (m, 1 H, H_{ar}), 7.48 (m, 2 H, H_{ar}), 3.40 (m, 1 H, H_{Cy}), 1.91 (m, 5 H, H_{Cy}), 1.53 (m, 4 H, H_{Cy}), 1.34 (m, 1 H, H_{Cy}) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 144.4, 133.5, 132.8, 128.1, 128.0, 127.9, 127.4, 126.0, 125.2, 123.6 (C_{ar}), 44.6, 33.4, 27.1, 26.5 (C_{Cy}) ppm. HRMS (EI): calcd. for $C_{16}H_{17}Br$ 288.0514; found 288.0514.

***N*,*N*′-Bis(2-cyclohexylnaphthalen-1-yl)ethane-1,2-diamine (2g):** In a glove box, a mixture of Pd(dba)$_2$ (442 mg, 0.769 mmol), (±)-BINAP (483 mg, 0.776 mmol), and NaO*t*Bu (2.217 g, 23.067 mmol) in toluene (50 mL) was stirred for a few minutes. Then, a solution of **1g** (4.7 g, 16.252 mmol) in toluene (30 mL) was added. Finally, ethylenediamine (414 μL, 7.685 mmol) was added. The volume of toluene was adjusted to 150 mL. The resulting dark red solution was heated at 100 °C for 20 h, cooled to room temperature, and filtered through silica gel/Celite to remove the insoluble materials. The filtrate was washed with CH_2Cl_2 until the eluent became colorless. After concentration in vacuo, the residue was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 10:1 to 1:1). The last fraction was collected and concentrated, and the residue was recrystallized from pentane to give **2g** as a yellowish solid. Yield: 2.50 g (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (m, 2 H, H_{ar}), 7.79 (m, 2 H, H_{ar}), 7.57 (m, 2 H, H_{ar}), 7.42 (m, 6 H, H_{ar}), 3.93 (br., 2 H, N*H*), 3.13 (m, 2 H, H_{Cy}), 1.86–1.26 (m, 20 H, H_{Cy}) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 141.3, 136.8, 133.4, 129.7, 128.5, 125.8, 125.3, 123.9, 123.5 (C_{ar}), 52.4 [N(*C*H$_2$)$_2$N], 39.1, 34.5, 27.4, 36.4 (C_{Cy}) ppm. HRMS (ESI): calcd. for $C_{34}H_{40}N_2Na$ 499.3089; found 499.3091.

1,3-Bis(2-cyclohexylnaphthalen-1-yl)imidazolinium Tetrafluoroborate [(2)-SICyNap·HBF$_4$] (3g): A mixture of diamine **2g** (2.00 g, 4.195 mmol) and NH_4BF_4 (440 mg, 4.197 mmol) was dissolved in triethyl orthoformate (45 mL) and a few drops of formic acid were added. The solution was heated at 100 °C for 4 h. During the reaction, ethanol was regularly removed by applying a slight vacuum for a few seconds. The resulting white precipitate was filtered, washed, redissolved in a mixture of acetone/CH_2Cl_2 (9:1, 60 mL), and precipitated by the addition of a mixture Et_2O/pentane (1:1). After drying in vacuo, **3g** was obtained as white powder. Yield: 1.89 g (78%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.64 (s, 0.25 H, N-C*H*=N, minor isomer), 9.56 (s, 0.75 H, N-C*H*=N, major isomer), 8.24–7.69 (series of m, 12 H, H_{ar}), 5.03–4.68 [m, 4 H, N(CH_2)$_2$-N], 3.07 (m, 1.5 H, cyclohexyl-C*H*, major isomer), 2.93 (m, 0.5 H, cyclohexyl-C*H*, minor isomer), 1.99–1.36 (m, 20 H, H_{Cy}) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 161.9, 161.3 (N-*C*H=N), 143.2, 142.8, 132.3, 132.2, 130.8, 130.7, 129.1, 129.0, 128.5, 128.45, 128.4, 128.2, 127.2, 127.1, 126.7, 126.6, 125.1, 125.0, 121.6, 121.4 (C_{ar}), 54.8 [N(*C*H$_2$)$_2$N], 53.5 [N(*C*H$_2$)$_2$N], 33.9, 33.1, 32.3, 26.2, 26.1, 26.0, 25.3, 25.2 (C_{Cy}) ppm. HRMS (ESI): calcd. for $C_{35}H_{39}N_2$ [M]$^+$ 487.3113; found 487.3110.

1,3-Bis(2-cyclohexylnaphthalen-1-yl)imidazolin-2-ylidene [(2)-SICyNap] (4g): In a glove box, a suspension of NaH (60% dispersion in mineral oil, 61 mg, 1.525 mmol) and KO*t*Bu (7 mg, 0.062 mmol) in THF (40 mL) was added to a suspension of **3g** (800 mg,

1.392 mmol) in THF (40 mL) and stirred at room temperature for 24 h. The resulting yellow solution was filtered through Celite, and the solvents were evaporated to dryness. After triturating with pentane, evaporation, and drying in vacuo, **4g** was obtained as a fine off-white powder. Yield: 640 mg (95%). M.p. 169–171 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.36 (d, J = 8.3 Hz, 0.5 H, H^8, minor isomer), 8.27 (d, J = 8.3 Hz, 1.5 H, H^8, major isomer), 7.72–7.26 (series of m, 10 H, H_{ar}), 3.73–3.31 [m, 6 H, N(CH_2)$_2$N and cyclohexyl-C*H*], 2.31–1.22 (series of m, 20 H, cyclohexyl-CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 245.6 (N-*C*-N), 143.3, 142.8, 137.1, 137.0, 133.8, 133.7, 132.5, 128.6, 128.1, 127.9, 127.4, 126.9, 126.6, 125.6, 125.5, 125.4, 124.2, 124.0 (C_{ar}), 54.0, 53.7 [N(CH_2)$_2$-N], 40.1, 39.8, 34.7, 34.6, 34.4, 34.0, 30.2, 28.0, 27.8, 27.5, 26.7, 26.6 (C_{Cy}) ppm.

{[(2)-SIPrNap]Pd(cinnamyl)Cl} (5d): In a glove box, a 20-mL vial was charged with (2)-SIPrNap·HBF$_4$ (**3d**; 200 mg, 0.404 mmol), [Pd(cinnamyl)Cl]$_2$ (100 mg, 0.190 mmol), KO*t*Bu (45 mg, 0.404 mmol), and THF (10 mL). The reaction mixture was stirred at room temperature for 16 h and subsequently filtered through a mixture of silica gel/Celite, and the filter was washed with hexane/EtOAc (1:1). After evaporation, the residue was subjected to column chromatography on silica gel (hexane/EtOAc, 2:1). Product **5d** (mixture of isomers) was obtained from the major fraction as a pale-yellow powder. Yield: 330 mg (94%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.17–6.70 (series of m, 17 H), 4.93 (m, 0.25 H), 4.40–4.19 (m, 4.75 H), 3.98–3.61 (m, 3 H), 2.71 (m, 1 H), 1.58–1.32 (series of m, 12 H), 1.28–1.15 (m, 1.2 H), 0.91–0.75 (m, 0.8 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 215.2, 146.2, 145.3, 139.1, 138.6, 134.1, 134.0, 133.8, 133.7, 133.5, 131.4, 131.3, 129.8, 129.7, 129.6, 129.1, 128.6, 128.5, 128.4, 127.5, 127.4, 127.2, 127.1, 126.9, 126.7, 126.3, 126.2, 126.1, 125.5, 125.3, 125.0, 124.8, 123.9, 110.1, 110.0, 90.2, 88.2, 87.9, 49.6, 48.6, 47.7, 34.7, 29.3, 26.0, 25.9, 25.8, 25.7, 24.0, 23.6, 22.9, 14.4 ppm. HRMS (ESI): calcd. for $C_{38}H_{39}{}^{104}PdN_2^+$ [M – Cl]$^+$ 627.2153; found 627.2161.

{[(2,6)-SIPrNap]Pd(cinnamyl)Cl} (5e): In the glove box, a 20-mL vial was charged with (2,6)-SIPrNap·HBF$_4$ (**3e**; 100 mg, 0.173 mmol), [Pd(cinnamyl)Cl]$_2$ (43 mg, 0.082 mmol), KO*t*Bu (20 mg, 0.173 mmol), and THF (8 mL). The reaction mixture was stirred at room temperature for 16 h and subsequently filtered through a mixture of silica gel/Celite, and the filter was washed with hexane/EtOAc (1:1). After evaporation, the residue was subjected to column chromatography on silica gel (hexane/EtOAc, 2:1). Product **5e** (mixture of isomers) was obtained from the major fraction as a pale-yellow powder. Yield: 180 mg (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06–6.72 (series of m, 15 H), 4.35–3.66 (series of m, 8.5 H), 3.16 (m, 2 H), 2.73–2.63 (m, 1 H), 1.62–1.31 (series of m, 24 H), 0.90 (m, 0.5 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 214.4, 146.2, 146.0, 144.8, 144.6, 138.4, 133.4, 133.2, 133.1, 133.0, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.0, 127.9, 127.6, 127.3, 127.0, 126.9, 126.7, 126.3, 126.2, 126.0, 124.9, 124.8, 124.7, 124.3, 124.1, 123.3, 109.6, 87.2, 53.9, 53.7, 53.4, 49.2, 34.0, 28.5, 25.6, 25.5, 24.1, 23.8, 23.7, 23.2, 22.3 ppm. HRMS (ESI): calcd. for $C_{44}H_{51}{}^{104}PdN_2^+$ [M – Cl]$^+$ 711.3092; found 711.3080.

{[(2)-SICyNap]Pd(cinnamyl)Cl} (5g): In a glove box, a 20-mL vial was charged with (2)-SICyNap·HBF$_4$ (**3g**) (200 mg, 0.348 mmol), [Pd(cinnamyl)Cl]$_2$ (86 mg, 0.166 mmol), KO*t*Bu (39 mg, 0.348 mmol), and THF (10 mL). The reaction mixture was stirred at room temperature for 16 h and subsequently filtered through a mixture of silica gel/Celite, and the filter was washed with hexane/EtOAc (1:1). After evaporation, the residue was subjected to column chromatography on silica gel (hexane/EtOAc, 2:1). Product **5g** (mixture of isomers) was obtained from the major fraction as a pale-yellow powder. Yield: 310 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16–6.67 (series of m, 17 H), 4.96 (m, 0.25 H), 4.41–3.23 (series of m, 6 H), 2.95–2.39 (series of m, 1.5 H), 2.21–1.26 (series of m, 21.5 H), 0.89 (m, 0.5 H), 0.72 (m, 0.25 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 214.3, 213.9, 212.1, 145.2, 145.1, 144.4, 144.3, 139.2, 138.6, 134.4, 134.3, 134.3, 134.1, 133.9, 133.6, 133.4, 133.3, 131.5, 131.4, 129.5, 129.4, 129.3, 129.0, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 127.4, 127.2, 127.1, 127.0, 126.9, 126.6, 126.5, 126.3, 126.2, 126.1, 126.0, 125.9, 125.8, 125.1, 125.0, 124.0, 110.1, 109.9, 90.4, 90.2, 88.3, 87.8, 51.2, 49.6, 48.0, 47.2, 40.3, 40.1, 40.0, 37.0, 36.9, 36.8, 36.5, 34.8, 33.7, 33.3, 33.2, 32.9, 28.2, 28.1, 28.0, 27.4, 27.3, 27.2, 27.0, 26.9, 26.8, 22.9, 14.4 ppm. HRMS (ESI): calcd. for $C_{44}H_{47}{}^{104}PdN_2^+$ [M – Cl]$^+$ 707.2779; found 707.2785.

Buchwald–Hartwig Cross-Coupling Reactions (General Procedure): In a glove box, to a vial closed with a screw cap fitted with a septum and equipped with a magnetic stir bar was sequentially added the catalyst (1 mol-%), KO*t*Bu (124 mg, 1.1 mmol), DME (1 mL), and dodecane (216 μL, 1 mmol). The mixture was then stirred at room temperature. After 5 min, the aryl chloride (1 mmol) and the amine (1.1 mmol) were injected. If the reaction was carried out at 80 °C, the aryl chloride and the amine were injected outside the glove box. The reaction was monitored by gas chromatography.

Buchwald–Hartwig Cross-Coupling Reactions at Low Catalyst Loading: In a glove box, the catalyst (0.01 mmol) was dissolved in DME (10 mL), providing catalyst solution A. To another vial closed with a screw cap fitted with a septum and equipped with a magnetic stir bar was sequentially added potassium KO*t*Bu (124 mg, 1.1 mmol), catalyst solution A (1 mL, 0.1 mol-%), and dodecane (216 μL, 1 mmol). The mixture was then stirred at room temperature. After 5 min, the aryl chloride (1 mmol) and the amine (1.1 mmol) were injected. The reaction was monitored by gas chromatography.

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