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[Pd(NHC)(allyl)Cl] Complexes: Synthesis and Determination of the NHC Percent Buried Volume (%V_{bur}) Steric Parameter

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Complexes of palladium bearing NHC ligands (NHC=N-heterocyclic carbene) were synthesized and fully characterized. The [Pd(NHC)(allyl)Cl] series was obtained by simple cleavage of $[Pd(allyl)Cl]_2$ by using either the isolated free NHC or the in situ generated NHC. The NHC ligand sterics were varied by introduction of groups attached to the C4–C5 carbon atoms of the NHC backbone. Results of the X-ray diffraction study permitted determination of the NHC steric parameters within this series. It was observed that the NHC backbone induces variations in its percent buried volume (%V_{bur}) as a function of the N-substituents.

Introduction

N-heterocyclic carbene (NHC)-containing transition-metal complexes have attained a special status in organometallic chemistry.[1] Thus, they are now recognized to promote efficiently various reactions such as ruthenium-mediated metathesis,[2] copper-catalyzed cycloaddition and hydrosilylation,[3] gold-assisted transformations,[4] cross-coupling reactions using palladium complexes,[5] among others. Even if NHC ligands were initially considered as simple tertiary phosphane mimics in organometallic chemistry,[6] there is growing evidence highlighting the fact that NHC–metal catalysts can surpass their phosphane-based counterparts in both activity and scope.[1] Recent studies have described NHCs as being a very versatile class of ligands due to their interesting and tunable steric and electronic properties.[7] These ligands have several advantages over the commonly used tertiary phosphanes, as they have been found to greatly stabilize reactive intermediates, display higher thermal stability, and show good resistance to dissociation from the metal center. Particularly in the area of palladium-mediated cross-coupling reactions, NHC-containing Pd catalysts[5] have proven to be an excellent alternative to catalytic systems involving tertiary phosphanes.[8] The σ-donating character of NHC ligands allows the synthesis of well-defined, air- and moisture-stable NHC-bearing palladium(II). Moreover, NHC ligands provide stabilization of the low-coordinated catalytically active Pd^0 species, thus minimizing its degradation and side reactions. This has translated into the development of a number of structurally diverse NHC–Pd complexes adopting a dimeric structure,[9] or bearing an allyl,[10] cinnamyl,[11] palladacycle,[12] pyridine,[13] or acetylacetonato (acac)[14] ligand that exhibits good to excellent catalytic performance in numerous cross-coupling reactions.

In order to develop ever more efficient catalytic systems, a comprehensive study of the steric and electronic parameters (σ-donor and π-acceptor properties) associated with NHCs appears fundamental. By using the [Ni(NHC)-$(CO)_3$] system[14] (in a manner analogous to the seminal work of Tolman on tertiary phosphanes)[16] but also the $[Ir(NHC)(CO)_2Cl]$ complexes,[17] it has been possible to quantify both the NHC steric parameter θ and an electronic parameter ν. Little difference between the NHCs themselves was observed, showing the weak influence of N-substituents on electronic properties. However NHCs with chlorine atoms in their backbone or the triphenyltriazolylidene (TPT) group were found to be significantly less donating; unfortunately, their steric parameters were not determined.[17] In order to better define the steric pressure brought about by the use of NHC ligands, a model was proposed to measure the steric bulk of the NHC ("percent buried volume" or %V_{bur}) defined as the volume of a sphere with given dimensions that is occupied by atoms comprising the ligand.[18] This %V_{bur} is calculated from crystallographic data. In contrast, through calorimetric studies, it was shown that electronic and steric effects are intimately related and difficult to separate.[19] For these reasons, we thought it was important to explore if changes on the NHC

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backbone, which can lead to effective tuning of electronic properties, could also influence ligand steric bulk. Here, we report on the synthesis of a series of new [Pd(NHC)(allyl)Cl] complexes that include substitution on the NHC backbone. X-ray diffraction studies permit the determination of the steric parameter, $\%V_{bur}$, associated with each NHC ligand. For convenience, the structures of the NHC ligands examined in this work are depicted in Figure 1.

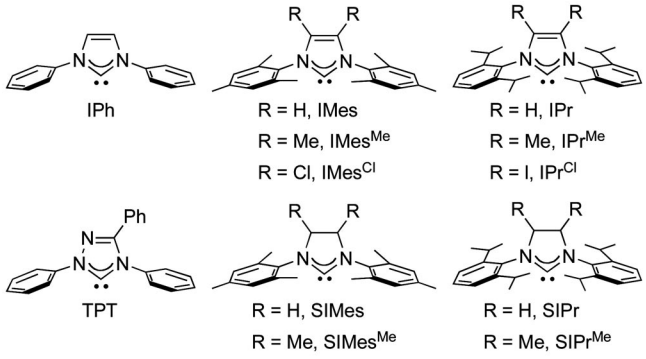
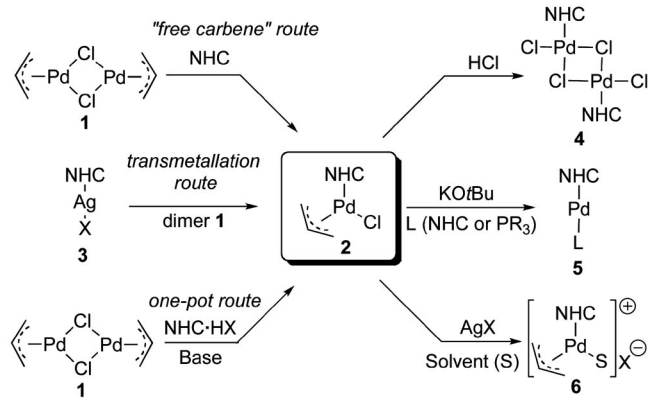


Figure 1. Structures of the NHCs investigated in this study.

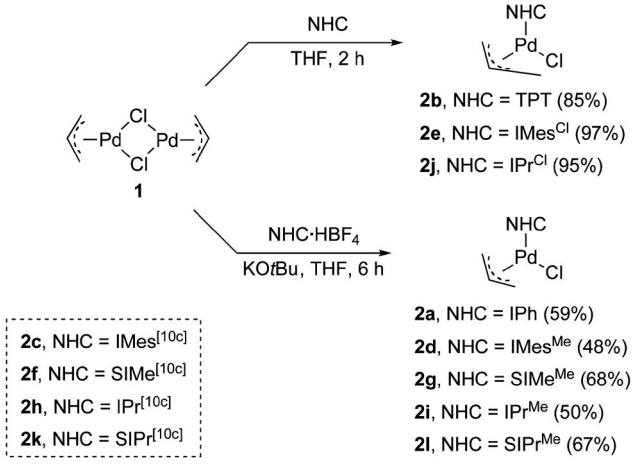
Results and Discussion

We have been interested in [Pd(NHC)(allyl)Cl] complexes **2** for a number of reasons. First, these complexes can be synthesized straightforwardly by using either the free carbene by simple cleavage of the dimer $[Pd(allyl)Cl]_2$ (**1**) [10a,10b,10d] through silver-mediated transmetallation from [Ag(NHC)X] **3**[20] or by using the imidazolium salt, which can be deprotonated in situ with a base and then treated with **1**[10c,21] (Scheme 1). Besides the fact that they are efficient precatalysts in various cross-coupling reactions,[10] these complexes can also be converted into other Pd-based complexes (Scheme 1). By protonolysis of the allyl group with HCl, $[Pd(NHC)Cl_2]_2$ complexes **4** can be obtained.[9] Reduction of [Pd(NHC)(allyl)Cl] with KO*t*Bu generates [Pd^0(NHC)], which can be subsequently trapped by an additional ligand L to give [Pd(NHC)(L)] series **5**.[22] Moreover, chlorine abstraction by using silver salts leads to the preparation of cationic complexes [Pd(NHC)(allyl)(S)]X **6** where S = solvent.[23]

The series of [Pd(NHC)(allyl)Cl] **2b**, **2e**, and **2j** complexes was synthesized in excellent to quantitative yield by using the free carbene in slight excess and dimer $[Pd(allyl)Cl]_2$ **1** (Scheme 2). Complexes **2a**, **2d**, **2g**, **2i**, and **2l** were obtained in moderated to good yields by using the in situ protocol followed by silica gel chromatography, which is a good testimony of the stability of such complexes. The synthesis of **2c**, **2f**, **2h**, and **2k** were previously described.[10c] The ^{1}H NMR spectra of complexes **2b**, **2d**–**e**, and **2i**–**j** show the absence of a low-field resonance around 7 ppm, corresponding to the imidazole protons of the nonsubstituted NHC ligand analogues such as **2a**. Complexes **2g** and **2l** bearing NHCs possessing a methyl-substituted saturated backbone were found to exist in two diastereoisomeric forms with a *cis*/*trans* ratio of 40:60. Of note, for the syntheses of **2g** and **2l**, imidazolium salts were used as a mixture of diastereomers, and we noticed that the *cis*/*trans* ratio was maintained during the synthesis of the complexes. Unfortunately, these diastereomers could not been separated. The ^{13}C NMR spectra of the unsaturated complexes have a characteristic resonance for the carbenic carbon atom around 180–190 ppm, whereas the resonance for the carbenic carbon atom of the saturated complexes (**2g** and **2l**) is found at lower field, around 210 ppm.



Scheme 1. Syntheses and applications of [Pd(NHC)(allyl)Cl] **2**.



Scheme 2. Synthesis [Pd(NHC)(allyl)Cl] **2a**–**j**.

Single-crystal X-ray diffraction was used to unambiguously determine the atom connectivity (Table 3). Ball-and-stick representations are shown in Figure 2. As depicted by their solid-state structures, palladium complex **2g** was obtained as the *cis* diastereomer, whereas **2l** was obtained as the *trans* diastereomer. For those complexes, the expected distorted square-planar coordination around the palladium center was observed. Bond lengths and angles in the complexes are rather unexceptional (Table 1). The value of the NHC–Pd–Cl angle (91–99°) indicates a mutual *cis* arrangement of the chloride anion and the NHC. The allyl group binds the palladium in a η^3 fashion with Pd–C lengths in the range 2.10–2.20 Å, which is similar to those reported for similar complexes.[10c] The longest distance belongs to the Pd–C_{allyl} bond opposite the carbene; this is due to the

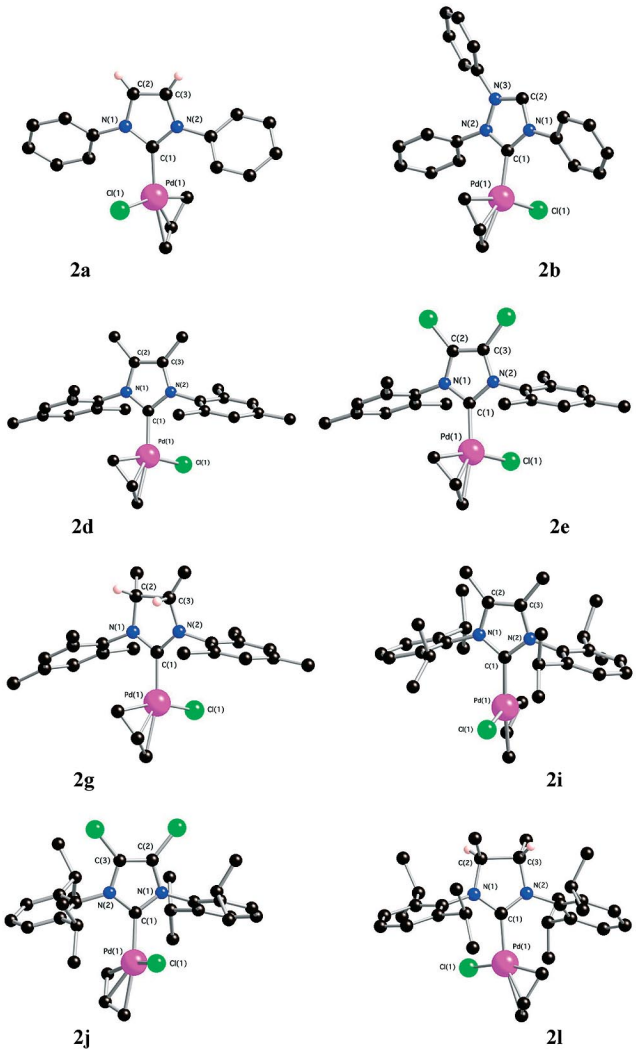


Figure 2. Ball-and-stick representation of the [Pd(NHC)(allyl)Cl] complexes. Most hydrogen atoms are omitted for clarity.

strong *trans* effect of the NHC ligand. For all NHC ligands, the Pd–C carbenic bond length is included in the narrow 2.00–2.04 Å range. Because it has been reported that IMes^{Cl}, IPr^{Cl}, and TPT exhibit a lower donating ability on the NHC scale,[17b] we expected more important differences. It is interesting to note that neither the nature of the N-substituents[10] nor the substitution of the NHC backbone seems to alter the Pd–NHC bond length. Noteworthy, a significant tilt of the aromatic N-substituents of the NHC was observed only for complexes **2a** and **2b**, that is, those containing the weakly congested phenyl groups.

In order to gain insight into the NHC geometry and into the NHC steric parameter, we examined more closely the planarity of the imidazolidene ring, that is, the N(1)–C(2)–C(3)–N(2) torsion angle (Table 1). As anticipated, the unsaturated NHC ligand showed a negligible degree of deviation due to the presence of sp^2 carbon or nitrogen atoms. Although SIMes^{Me} also presented good planarity, SIPr^{Me} was found particularly distorted (35°, and only 20° for SIPr). We believe the difference between SIMes^{Me} and SIPr^{Me} is more a result of the *cis*/*trans* diastereomer found for these complexes than any influence of the N-substituents.

To measure the steric factors characterizing these NHC ligands, we calculated the volume of a sphere, centered on the metallic center, occupied with atoms of the NHCs. This value we refer to as $\%V_{bur}$. The volume of this sphere represents the potential coordination sphere space around the metal that can be occupied by ligands. Consequently, the more-crowded NHCs would have a greater $\%V_{bur}$ value. We examined the DFT-optimized geometries of the free ligands by using software developed by Cavallo and co-workers, which is now available online as a user-friendly version.[24] Crystallographic information files (CIF) were easily transformed into Cartesian files (such as Crystalmaker Chem3D) by keeping only the atomic coordinates of ele-

Table 1. Selected bond lengths [Å], angles [°], and torsion angles [°] for [Pd(NHC)(allyl)Cl] **2**.

	2a	**2b**	**2d**	**2e**	**2g**	**2i**	**2j**	**2l**
				Bond lengths [Å]				
Pd(1)–C(1)	2.0438(10)	2.0285(12)	2.0306(16)	2.0366(11)	2.003(17)	2.0415(14)	2.0276(13)	2.041(2)
Pd(1)–Cl(1)	2.3734(3)	2.3596(3)	2.3560(4)	2.3556(3)	2.326(5)	2.3492(6)	2.3518(5)	2.3474(8)
Pd(1)-allyl	2.109(2)	2.1084(17)	2.1067(18)	2.1114(14)	2.096(16)	2.117(3)	2.111(2)	2.124(3)
	2.1011(14)	2.120(2)	2.1386(19)	2.1505(14)	2.108(18)	2.123(3)	2.119(10)	2.150(4)
	2.144(2)	2.1706(17)	2.1943(18)	2.1905(13)	2.170(17)	2.186(2)	2.133(2)	2.196(3)
	2.1821(13)	2.180(6)					2.1706(18)	
				Bond angles [°]				
C(1)–Pd(1)–Cl(1)	94.27(3)	95.39(4)	96.21(4)	96.44(3)	99.4(4)	97.99(5)	91.36(4)	92.28(4)
C(1)–Pd(1)–allyl	98.84(5)	96.93(6)	98.46(7)	98.24(5)	97.3(6)	99.27(10)	102.73(7)	103.38(11)
	167.15(5)	164.83(7)	166.85(6)	166.63(5)	165.6(6)	168.76(11)	170.10(8)	166.63(12)
N(1)–C(1)–N(2)	103.84(9)	102.80(10)	103.86(13)	104.88(10)	105.1(14)	104.13(12)	104.83(11)	108.02(18)
				Torsion angle [°]				
N(1)–C(2)–C(3)–N(2)	0.28(15)	–1.25(15)[a]	0.47(17)	0.07(14)	–4(3)	0	2.04(16)	–35.8(5)

[a] For **2b**, C(2) is replaced by N(3).

ments belonging to the NHC ligand. These were used as raw data for $\%V_{bur}$ calculations with a distance of 2 Å for the metal–ligand bond. A compilation of $\%V_{bur}$ values is presented in Table 2.

Table 2. Steric parameter buried volume ($\%V_{bur}$) calculated for the NHC in [Pd(NHC)(allyl)Cl] complexes.

Entry	Complex	NHC	$\%V_{bur}$
1	**2a**	IPh	28.1
2	**2b**	TPT	27.0
3	**2c**	IMes	26.5
4	**2d**	$IMes^{Me}$	27.0
5	**2e**	IMesCl	27.0
6	**2f**	SIMes	27.5
7	**2g**	$SIMes^{Me}$	27.7
8	**2h**	IPr	26.1
9	**2i**	IPr^{Me}	25.8
10	**2j**	IPr^{Cl}	30.1
11	**2k**	SIPr	33.0
12	**2l**	$SIPr^{Me}$	32.4

Burial volumes of the studied NHCs span the range from 25.7 to 33.0%. The triazolylidene TPT (Table 2, Entry 1) was found to be slightly larger than IPh, bearing the same *N*-phenyl groups (Table 2, Entry 2). The substituted backbone of TPT might hinder the distortion observed for the phenyl rings observed for IPh. Surprisingly, no effect on buried volumes for mesityl-containing NHCs was calculated (Table 2, Entries 3–7), showing a weak influence of backbone substitution on the NHC steric parameter. In contrast, calculations performed on 2,6-diisopropylphenyl–NHC revealed noticeable fluctuations (Table 2, Entries 8–12). Whereas introduction of methyl groups led to unchanged values of $\%V_{bur}$ for IPr, chlorine atoms demonstrated a noticeable increase in the value of V_{bur} by 4%. Furthermore, the values obtained for SIPr and $SIPr^{Me}$ point to a larger steric bulk of saturated NHCs and methylation of the backbone shows little influence.

Conclusions

In summary, we described the synthesis and structural characterization of a series of palladium complexes of the general formula [Pd(NHC)(allyl)Cl]. To gain insight into the steric factors governing NHC ligands, with special attention to NHC backbone substituents, the NHC ligands we employed in this study incorporate methyl and chlorine groups in the backbone or nitrogen in the ring structure (triazolylidene carbene). Analysis of the principal bond lengths in the various Pd–NHC complexes examined reveal very slight or no variations in ligand sterics. To quantify the steric factors characterizing these NHCs, calculations were conducted on the basis of structural data, leading to steric values measured as $\%V_{bur}$. Interestingly, the NHC backbone was found to have an influence on the ligand buried volume, but only as a function of N-substituents. To shed light on the NHC buried volume influence on catalysis, we are presently performing catalytic studies in cross-coupling reactions in order to establish a structure–activity relationship. These results will be disclosed in due course.

Experimental Section

General Considerations: All reagents were used as received. Tetrahydrofuran (THF) was dispensed from a solvent purification system from Innovative Technology. Syntheses of complexes were performed in an MBraun glove box containing dry argon and less than 1 ppm oxygen or on a Schlenk line. NHC ligands were synthesized by following literature procedures.[25] ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 Ultrashield NMR spectrometer. High-resolution mass spectroscopy (HRMS) analyses were performed at the ICIQ with a Waters LCT Premier spectrometer or a Waters GCT spectrometer. Elemental analyses were performed at the Universidad Complutense de Madrid. X-ray data see Table 3.

[Pd(IPh)(allyl)Cl] (2a): A Schlenk flask was charged with a stirring bar, **1** (293 mg, 0.8 mmol), the imidazolium salt IPh·HBF_4 (616 mg, 2 mmol), and KO*t*Bu (270 mg, 2.4 mmol). Three purge–vacuum–refill cycles were performed before adding dry THF (20 mL). The resulting mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated, loaded directly onto a silica gel column, and purified by flash chromatography (ether). The complex was then recrystallized from dichloromethane (DCM)/pentane to afford a white solid (380 mg, 59% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 [d, ^3J(H,H) = 7.7 Hz, 4 H, H^{Ar}], 7.50 [t, ^3J(H,H) = 7.9 Hz, 4 H, H^{Ar}], 7.45–7.41 (m, 4 H, H^{Ar} and H^{Im}), 4.90–4.84 (m, 1 H, H^{allyl}), 4.11 [dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.8 Hz, 1 H, H^{allyl}], 3.01 [d, ^3J(H,H) = 13.5 Hz, 1 H, H^{allyl}], 2.95 [d, ^3J(H,H) = 6.6 Hz, 1 H, H^{allyl}], 1.77 [d, ^3J(H,H) = 11.8 Hz, 1 H, H^{allyl}] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.2 (C, N-*C*-N), 140.2 (C, C^{Ph}), 129.2 (CH, CH^{Ph}), 128.4 (CH, CH^{Ph}), 124.9 (CH, CH^{Ph}), 122.4 (CH, CH^{Im}), 114.1 (CH, C^{allyl}), 71.6 (CH_2, C^{allyl}), 48.8 (CH_2, C^{allyl}) ppm. HRMS (ESI): calcd. for $C_{18}H_{17}ClN_2NaPd$ $[M + Na]^+$ 425.0013; found 425.0017. $C_{18}H_{17}ClN_2Pd$ (403.21): calcd. C 53.62, H 4.25, N 6.95; found C 53.48, H 4.21, N 6.97.

[Pd(TPT)(allyl)Cl] (2b): In a glove box, a scintillation vial was charged with a stirring bar triazolylidene (2.67 g, 9.0 mmol), dry THF (20 mL), and **1** (1 g, 2.7 mmol), and the mixture was stirred at room temperature for 2 h. Outside of the glove box, the solvent was evaporated in vacuo, and the remaining solid was triturated with pentane and collected by filtration through a sintered frit in air. The complex was then recrystallized from DCM/pentane to afford a white solid (3.25 g, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 [d, ^3J(H,H) = 7.7 Hz, 2 H, H^{Ar}], 7.66 (s, 4 H, H^{Ar}), 7.52 [t, ^3J(H,H) = 7.7 Hz, 2 H, H^{Ar}], 7.48–7.44 (m, 7 H, H^{Ar}), 7.36 [d, ^3J(H,H) = 7.4 Hz, 2 H, H^{Ar}], 4.98–4.96 (m, 1 H, H^{allyl}), 4.19 [d, ^3J(H,H) = 7.1 Hz, 1 H, H^{allyl}], 3.15 [d, ^3J(H,H) = 6.1 Hz, 1 H, H^{allyl}], 3.07 [d, ^3J(H,H) = 13.5 Hz, 1 H, H^{allyl}], 3.15 [d, ^3J(H,H) = 11.4 Hz, 1 H, H^{allyl}] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.0 (C, N-*C*-N), 153.6 (C, C^{Ar}), 139.6 (C, C^{Ar}), 137.2 (C, C^{Ar}), 130.8 (CH, CH^{Ar}), 129.6 (CH, CH^{Ar}), 129.4 (CH, CH^{Ar}), 129.0 (CH, CH^{Ar}), 128.9 (CH, CH^{Ar}), 128.7 (CH, CH^{Ar}), 128.6 (CH, CH^{Ar}), 127.6 (CH, CH^{Ar}), 124.8 (C, C^{Ar}), 123.2 (CH, CH^{Ar}), 114.6 (CH, C^{allyl}), 72.1 (CH_2, C^{allyl}), 50.6 (CH_2, C^{allyl}) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_3Pd$ $[M - Cl]^+$ 444.0692; found 444.0692. $C_{23}H_{20}ClN_3Pd$ (480.30): calcd. C 57.52, H 4.20, N 8.75; found C 57.20, H 4.32, N 8.57.

[Pd($IMes^{Me}$)(allyl)Cl] (2d): A Schlenk tube was charged with a stirring bar, **1** (176 mg, 0.5 mmol), the imidazolium salt $IMes^{Me}$·HBF_4

Table 3. Crystallographic data for the [Pd(NHC)(allyl)Cl] complexes.

	2a	**2b**	**2d**	**2e**
Chemical formula	$C_{18}H_{17}ClN_2Pd$	$C_{23}H_{21}ClN_3Pd$	$C_{26}H_{33}ClN_2Pd$	$C_{24}H_{27}Cl_3N_2Pd$
Fw	403.19	481.28	515.39	556.23
Space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
a [Å]	12.5911(3)	6.5033(2)	9.9528(3)	9.9696(6)
b [Å]	7.7151(2)	16.3290(4)	14.4363(5)	14.2759(9)
c [Å]	16.7517(14)	19.2449(4)	16.6477(6)	16.5092(11)
α [°]	90	90	90	90
β [°]	95.9000(10)	90	90	90
γ [°]	90	90	90	90
Z	4	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.654	1.564	1.431	1.572
μ (Mo) [mm^{-1}]	1.308	1.052	0.902	1.145
F(000)	808	972	1064	1128
θ range [°]	2.91 to 39.35	3.41 to 37.73	2.77 to 39.81	3.20 to 39.28
No. of reflections collected	27646	23551	32904	22055
No. of unique reflection / R_{int}	8679 / 0.0205	10018 / 0.0251	13619 / 0.042	11492 / 0.0307
No. of parameters / restraints	209 / 0	263 / 0	279 / 0	297 / 0
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0225$, $wR_2 = 0.0602$	$R_1 = 0.0240$, $wR_2 = 0.0605$	$R_1 = 0.0353$, $wR_2 = 0.0763$	$R_1 = 0.0228$, $wR_2 = 0.0578$
R indices (all indices)	$R_1 = 0.0251$, $wR_2 = 0.0616$	$R_1 = 0.0261$, $wR_2 = 0.0615$	$R_1 = 0.0410$, $wR_2 = 0.0788$	$R_1 = 0.0237$, $wR_2 = 0.0581$
Goodness-of-fit on F^2	1.062	0.932	0.999	1.061
Peak and hole [e Å^{-3}]	1.326 and –0.902	0.855 and –0.4451	1.897 and –0.526	1.394 and –0.668
	2g	**2i**	**2j**	**2l**
Chemical formula	$C_{26}H_{35}ClN_2Pd$	$C_{32}H_{45}ClN_2Pd$	$C_{30}H_{39}Cl_3N_2Pd$	$C_{32}H_{47}ClN_2Pd$
Fw	517.41	599.55	640.38	601.57
Space group	*Pccn*	*Pnma*	$P2_1/c$	$Pna2_1$
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
a [Å]	34.136(3)	17.9634(7)	12.8409(15)	22.7172(10)
b [Å]	16.2802(13)	17.4086(5)	12.3222(14)	8.6445(5)
c [Å]	8.8230(7)	9.8961(3)	19.284(2)	15.3732(8)
α [°]	90	90	90	90
β [°]	90	90	96.907(5)	90
γ [°]	90	90	90	90
Z	8	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.402	1.287	1.404	1.342
μ (Mo) [mm^{-1}]	0.881	0.707	0.898	0.725
F(000)	2144	1256	1320	1264
θ range [°]	2.69 to 25.35	3.28 to 40.00	3.26 to 36.62	2.85 to 36.27
No. of reflections collected	34412	41868	31920	29675
No. of unique reflection / R_{int}	4473 / 0.1206	8886 / 0.0288	14188 / 0.0351	9881 / 0.0271
No. of parameters / restraints	278 / 0	180 / 0	343 / 0	1344 / 31
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.1404$, $wR_2 = 0.2815$	$R_1 = 0.0354$, $wR_2 = 0.0913$	$R_1 = 0.0385$, $wR_2 = 0.1031$	$R_1 = 0.0347$, $wR_2 = 0.0878$
R indices (all indices)	$R_1 = 0.1500$, $wR_2 = 0.2860$	$R_1 = 0.0444$, $wR_2 = 0.0961$	$R_1 = 0.0466$, $wR_2 = 0.1079$	$R_1 = 0.0419$, $wR_2 = 0.0919$
Goodness-of-fit on F^2	1.178	1.061	1.0428	1.042
Peak and hole [e Å^{-3}]	1.380 and –2.612	1.904 and –0.909	2.333 and –1.799	1.504 and –0.710

(500 mg, 1.2 mmol), and KO*t*Bu (168 mg, 1.5 mmol). Three vacuum–backfill cycles were performed before adding dry THF (20 mL), and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated, loaded directly onto a silica gel column, and purified by flash chromatography (diethyl ether/pentane, 1:1 to 1:0). The complex was then recrystallized from DCM/pentane to afford a white solid (240 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.97 (s, 4 H, H^{Mes}), 4.87–4.77 [m, 1 H, H^{allyl}], 3.83 [dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 2.0 Hz, 1 H, H^{allyl}], 3.21 [d, ^3J(H,H) = 6.6 Hz, 1 H, H^{allyl}], 2.77 [d, ^3J(H,H) = 13.3 Hz, 1 H, H^{allyl}], 2.33 (s, 6 H, CH_3^{Mes}), 2.18 (s, 6 H, CH_3^{Mes}), 2.15 (s, 6 H, CH_3^{Mes}), 1.90 (s, 6 H, CH_3^{Mes}), 1.88 [d, ^3J(H,H) = 11.9 Hz, 1 H, H^{allyl}] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.8 (C, N-*C*-N), 138.5 (C, C^{Mes}), 135.9 (C, C^{Mes}), 135.8 (C, C^{Mes}), 134.3 (C, C^{Mes}), 129.1 (CH, CH^{Mes}), 129.0 (CH, CH^{Mes}), 126.0 (C, C^{NHC}), 114.0 (CH, C^{allyl}), 72.3 (CH_2, C^{allyl}), 48.7 (CH_2, C^{allyl}), 21.2 (CH_3, C^{Mes}), 18.3 (CH_3, C^{Mes}), 18.2 (CH_3, C^{Mes}), 9.2 (CH_3, C^{NHC}) ppm. HRMS (ESI): calcd. for $C_{26}H_{33}N_2Pd$ [M – Cl]$^+$ 479.1678; found 479.1702. $C_{26}H_{33}ClN_2Pd$ (515.43): calcd. C 60.59, H 6.45, N 5.43; found C 60.28, H 6.35, N 5.40.

[Pd(IMes^{Cl})(allyl)Cl] (2e): In a glove box, a scintillation vial was charged with a stirring bar, IMes carbene (1.72 g, 5.67 mmol), dry THF (15 mL), and dry CCl_4 (3 mL). The reaction mixture was stirred 3 h at room temperature before adding **1** (1 g, 2.7 mmol), and the mixture was stirred at room temperature for 2 h. Outside of the glove box, the solvent was evaporated in vacuo, and the remaining solid was triturated with pentane and collected by filtration through a sintered frit in air. The complex was then recrystallized from DCM/pentane to afford a white solid (2.9 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 (s, 4 H, H^{Mes}), 4.91–4.82 (m, 1 H, H^{allyl}), 3.91 [dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.8 Hz, 1 H, H^{allyl}], 3.31 [d, ^3J(H,H) = 5.6 Hz, 1 H, H^{allyl}], 2.83 [d, ^3J(H,H) = 13.4 Hz, 1 H, H^{allyl}], 2.35 (s, 6 H, CH_3^{Mes}), 2.23 (s, 6 H, CH_3^{Mes}),

2.21 (s, 6 H, CH_3^{Mes}), 1.88 [d, ^3J(H,H) = 12.0 Hz, 1 H, H^{allyl}] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.7 (C, N-*C*-N), 139.9 (C, C^{Mes}), 136.1 (C, C^{Mes}), 136.0 (C, C^{Mes}), 132.9 (C, C^{Mes}), 129.3 (CH, CH^{Mes}), 129.2 (CH, CH^{Mes}), 118.1 (C, *C*-Cl), 114.7 (CH, C^{allyl}), 72.6 (CH_2, C^{allyl}), 50.8 (CH_2, C^{allyl}), 21.2 (CH_3, C^{Mes}), 18.3 (CH_3, C^{Mes}), 18.2 (CH_3, C^{Mes}) ppm. HRMS (ESI): calcd. for $C_{24}H_{27}N_2Cl_2Pd$ [M – Cl]$^+$ 519.0586; found 519.0571. $C_{24}H_{27}Cl_3N_2Pd$ (556.26): calcd. C 51.82, H 4.89, N 5.04; found C 51.45, H 4.93, N 5.14.

[Pd(SIMes^{Me})(allyl)Cl] (2g): A Schlenk tube was charged with a stirring bar, **1** (183 mg, 0.5 mmol), the imidazolium salt SIMes^{Me}·HBF_4 (506 mg, 1.2 mmol), and KO*t*Bu (168 mg, 1.5 mmol). Three vacuum–backfill cycles were performed before adding dry THF (15 mL), and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated, loaded directly onto a silica gel column, and purified by flash chromatography (ether). The complex was then recrystallized from DCM/pentane to afford a white solid (350 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (s, 4 H, H^{Mes}), 4.76–4.71 (m, 1 H, H^{allyl}), 4.53–4.45 (m, 1 H, C*H*-CH_3), 4.40–4.34 (m, 1 H, C*H*-CH_3), 3.79 [dd, ^4J(H,H) = 2.1 Hz, ^3J(H,H) = 7.5 Hz, 1 H, H^{allyl}], 3.23 [d, ^3J(H,H) = 8.6 Hz, 1 H, H^{allyl}], 2.71 [d, ^3J(H,H) = 13.4 Hz, 1 H, H^{allyl}], 2.43 (s, 12 H, CH_3^{Mes}), 2.27 (s, 6 H, CH_3^{Mes}), 1.88 [d, ^3J(H,H) = 11.9 Hz, 1 H, H^{allyl}], 1.31–1.29 (m, 3 H, CH-CH_3), 1.21–1.20 (m, 3 H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.9 (C, N-*C*-N), 137.7 (C, C^{Mes}), 137.66 (C, C^{Mes}), 137.6 (C, C^{Mes}), 135.0 (C, C^{Mes}), 134.7 (C, C^{Mes}), 129.6 (CH, CH^{Mes}), 129.5 (CH, CH^{Mes}), 129.3 (CH, CH^{Mes}), 129.1 (C, C^{Mes}), 129.0 (C, C^{Mes}), 114.5 (CH, C^{allyl}), 72.8 (CH_2, C^{allyl}), 66.3 (CH, *C*H-CH_3), 61.9 (CH, *C*H-CH_3), 49.3 (CH_2, C^{allyl}), 21.0 (CH_3, C^{Mes}), 19.6 (CH_3, C^{Mes}), 18.5 (CH_3, C^{Mes}), 13.5 (CH_3, CH-*C*H_3), 12.7 (CH_3, CH-*C*H_3) ppm. HRMS (ESI): calcd. for $C_{26}H_{35}N_2Pd$ [M – Cl]$^+$ 481.1835; found 481.1842. $C_{26}H_{35}ClN_2Pd$ (517.44): calcd. C 60.35, H 6.82, N 5.41; found C 60.22, H 6.84, N 5.36.

[Pd(IPr^{Me})(allyl)Cl] (2i): A Schlenk tube was charged with a stirring bar, **1** (220 mg, 0.6 mmol), the imidazolium salt IPr^{Me}·HBF_4 (773 mg, 1.5 mmol), and KO*t*Bu (200 mg, 1.8 mmol). Three vacuum–backfill cycles were performed before adding dry THF (20 mL), and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated, loaded directly onto a silica gel column, and purified by flash chromatography (ether/pentane: 1:1). The complex was then recrystallized from DCM/pentane to yield a white solid (360 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 [t, ^3J(H,H) = 7.7 Hz, 2 H, H^{Ar}], 7.33 [d, ^3J(H,H) = 7.7 Hz, 4 H, H^{Ar}], 4.86–4.76 (m, 1 H, H^{allyl}), 3.90 [d, ^3J(H,H) = 7.4 Hz, 1 H, H^{allyl}], 3.10–2.89 [m, 5 H, H^{allyl} + C*H*(CH_3)$_2$], 2.84 [d, ^3J(H,H) = 13.4 Hz, 1 H, H^{allyl}], 1.97 (s, 6 H, CH_3^{NHC}), 1.36 [br. s, 13 H, H^{allyl} + CH(CH_3)$_2$], 1.13 [br. s, 12 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.7 (C, N-*C*-N), 146.5 (C, C^{Ar}), 134.6 (C, C^{Ar}), 129.7 (CH, C^{Ar}), 127.4 (C, C^{NHC}), 124.8 (C, C^{Ar}), 124.2 (C, C^{Ar}), 113.7 (CH, C^{allyl}), 73.5 (CH_2, C^{allyl}), 50.3 (CH_2, C^{allyl}), 28.3 [CH, *C*H(CH_3)$_2$], 25.1 [CH_3, CH(*C*H_3)$_2$], 25.0 [CH_3, CH(*C*H_3)$_2$], 24.8 [CH_3, CH(*C*H_3)$_2$], 24.1 [CH_3, CH(*C*H_3)$_2$], 10.7 (CH_3, *C*H_3^{NHC}) ppm. HRMS (ESI): calcd. for $C_{32}H_{45}N_2Pd$ [M – Cl]$^+$ 563.2617; found 563.2643. $C_{32}H_{45}ClN_2Pd$ (599.59): calcd. C 64.10, H 7.56, N 4.67; found C 63.72, H 7.49, N 4.76.

[Pd(IPr^{Cl})(allyl)Cl] (2j): In a glove box, a scintillation vial was charged with a stirring bar, IPr (2.2 g, 5.67 mmol), dry THF (15 mL) and dry CCl_4 (3 mL). The reaction mixture was stirred for 2 h at room temperature before adding **1** (1 g, 2.7 mmol), and the mixture was stirred at room temperature for 3 h. Outside of the glove box, the solvent was evaporated in vacuo, the remaining solid was triturated with pentane, and the solids were collected by filtration through a sintered frit in air. The complex was then recrystallized from DCM/pentane to yield a white solid (3.1 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 [t, ^3J(H,H) = 7.8 Hz, 2 H, H^{Ar}], 7.33 [d, ^3J(H,H) = 7.8 Hz, 4 H, H^{Ar}], 4.87–4.80 (m, 1 H, H^{allyl}), 3.97 [d, ^3J(H,H) = 6.5 Hz, 1 H, H^{allyl}], 3.17 [d, ^3J(H,H) = 5.7 Hz, 1 H, H^{allyl}], 3.08–3.01 [m, 2 H, C*H*(CH_3)$_2$], 2.87–2.79 [m, 3 H, H^{allyl} + C*H*(CH_3)$_2$], 1.66 [d, ^3J(H,H) = 12.0 Hz, 1 H, H^{allyl}], 1.42 [d, ^3J(H,H) = 6.6 Hz, 6 H, CH(CH_3)$_2$], 1.37 [d, ^3J(H,H) = 6.6 Hz, 6 H, CH(CH_3)$_2$], 1.26 [d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.18 [d, ^3J(H,H) = 6.6 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.1 (C, N-*C*-N), 146.8 (C, C^{Ar}), 146.7 (C, C^{Ar}), 133.0 (C, C^{Ar}), 130.8 (CH, C^{Ar}), 124.6 (CH, C^{Ar}), 124.3 (C, C^{Ar}), 119.7 (C, *C*-Cl), 114.5 (CH, C^{allyl}), 73.4 (CH_2, C^{allyl}), 51.9 (CH_2, C^{allyl}), 28.7 [CH, *C*H(CH_3)$_2$], 28.6 [CH, *C*H(CH_3)$_2$], 25.2 [CH_3, CH(*C*H_3)$_2$], 24.9 [CH_3, CH(*C*H_3)$_2$], 24.3 [CH_3, CH(*C*H_3)$_2$], 23.7 [CH_3, CH(*C*H_3)$_2$] ppm. HRMS (ESI): calcd. for $C_{30}H_{39}Cl_2N_2Pd$ [M – Cl]$^+$ 603.1525; found 603.1553. $C_{30}H_{39}Cl_3N_2Pd$ (640.42): calcd. C 56.26, H 6.14, N 4.37; found C 56.21, H 6.08, N 4.60.

[Pd(SIPr^{Me})(allyl)Cl] (2l): A Schlenk tube was charged with a stirring bar, **1** (183 mg, 0.5 mmol), the imidazolium salt SIPr^{Me}·HBF_4 (603 mg, 1.2 mmol), and KO*t*Bu (168 mg, 1.5 mmol). Three vacuum–backfill cycles were performed before adding dry THF (15 mL), and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated, loaded directly onto a silica gel column, and purified by flash chromatography (diethyl ether/pentane: 1:1). The complex was then recrystallized from DCM/pentane to yield a white solid (400 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 [t, ^3J(H,H) = 7.6 Hz, 2 H, H^{Ar}], 7.22 [d, ^3J(H,H) = 7.6 Hz, 4 H, H^{Ar}], 4.81–4.66 (m, 1 H, H^{allyl}), 4.49–4.35 (m, 1 H, C*H*-CH_3), 4.12–3.99 (m, 1 H, C*H*-CH_3), 2.89 [dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 2.8 Hz, 1 H, H^{allyl}], 3.53–3.44 [m, 3 H, C*H*(CH_3)$_2$], 3.29–3.26 [m, 3 H, C*H*(CH_3)$_2$], 3.08 [d, ^3J(H,H) = 6.4 Hz, 1 H, H^{allyl}], 2.79 [t, ^3J(H,H) = 12.8 Hz, 1 H, H^{allyl}], 1.52–1.21 (m, 30 H, CH_3), 1.01 [d, ^3J(H,H) = 11.8 Hz, 1 H, H^{allyl}] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.3 (C, N-*C*-N), 148.5 (C, C^{Ar}), 146.7 (C, C^{Ar}), 134.7 (C, C^{Ar}), 128.8 (CH, C^{Ar}), 124.6 (CH, C^{Ar}), 124.5 (CH, C^{Ar}), 124.4 (CH, C^{Ar}), 114.6 (CH, C^{allyl}), 73.1 (CH_2, C^{allyl}), 67.5 (CH, *C*H-CH_3), 63.2 (CH, *C*H-CH_3), 51.1 (CH_2, C^{allyl}), 28.9 [CH, *C*H(CH_3)$_2$], 28.2 [CH_3, CH(*C*H_3)$_2$], 26.7 [CH_3, CH(*C*H_3)$_2$], 26.0 [CH_3, CH(*C*H_3)$_2$], 25.4 [CH_3, CH(*C*H_3)$_2$], 23.9 [CH_3, CH(*C*H_3)$_2$], 20.1 (CH_3, *C*H_3^{NHC}) ppm. HRMS (ESI): calcd. for $C_{32}H_{47}N_2Pd$ [M – Cl]$^+$ 565.2774; found 565.2766. $C_{32}H_{45}ClN_2Pd$ (599.59): calcd. C 63.89, H 7.87, N 4.66; found C 63.70, H 7.54, N 4.67.

CCDC-711197 (for **2e**), -711198 (for **2j**), -711199 (for **2i**), -711200 (for **2l**), -711201 (for **2a**), -711202 (for **2b**), -711203 (for **2d**), -711204 (for **2g**) 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.

Supporting Information (see footnote on the first page of this article): Detailed procedures for the synthesis of the imidazolium salts.

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[1] a) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; b) S. P. Nolan (Ed.), *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, Weinheim, Germany, **2006**; c) F. Glorius (Ed.), *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer, Berlin, Germany, **2007**; d) H. Clavier, S. P. Nolan, *Annu. Rep. Prog. Chem. Sect. B: Org. Chem.* **2007**, *103*, 193–222; e) F. Boeda, S. P. Nolan, *Annu. Rep. Prog. Chem. Sect. B: Org. Chem.* **2008**, *104*, 184–210.

[2] a) R. H. Grubbs (Ed.), *Handbook of Metathesis*, Wiley-VCH, Weinheim, Germany, **2003**, vols. 1–3; b) E. Despagnet-Ayoub, T. Ritter, *Top. Organomet. Chem.* **2007**, *21*, 193–218; c) E. Colacino, J. Martinez, F. Lamaty, *Coord. Chem. Rev.* **2007**, *251*, 726–764.

[3] S. Díez-González, S. P. Nolan, *Synlett* **2007**, 2158–2167.

[4] a) I. J. B. Lin, C. S. Vasam, *Can. J. Chem.* **2005**, *83*, 812–825; b) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1782.

[5] a) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813; b) S. Díez-González, S. P. Nolan, *Top. Organomet. Chem.* **2007**, *21*, 47–82; c) N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440–1449; d) S. Würtsz, F. Glorius, *Acc. Chem. Res.* **2008**, *41*, 1523–1553.

[6] J. C. Green, R. G. Scur, P. L. Arnold, G. N. Cloke, *Chem. Commun.* **1997**, 1963–1964.

[7] For a comprehensive review on stereoelectronic parameters associated with NHC ligands, see: S. Díez-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874–883.

[8] a) R. Kuwano, M. Utsunomiya, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 6479–6486; b) M. W. Hooper, J. F. Hartwig, *Organometallics* **2003**, *22*, 3394–3403; c) M. W. Hooper, M. Utsunomiya, J. F. Hartwig, *J. Org. Chem.* **2003**, *68*, 2861–2873; d) X. Huang, K. W. Anderson, D. Zim, L. Jiang, A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 6653–6655; e) E. R. Strieter, D. G. Blackmond, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 13978–13980.

[9] a) Y. Ma, C. Song, W. Jiang, G. Xue, J. F. Cannon, X. Wang, M. B. Andrus, *Org. Lett.* **2003**, *5*, 4635–4638; b) D. R. Jensen, M. S. Sigman, *Org. Lett.* **2003**, *5*, 63–65.

[10] a) M. S. Viciu, R. F. Germaneau, S. P. Nolan, *Org. Lett.* **2002**, *4*, 4053–4056; b) M. S. Viciu, R. F. Germaneau, O. Navarro-Fernandez, E. D. Stevens, S. P. Nolan, *Organometallics* **2002**, *21*, 5470–5472; c) M. S. Viciu, O. Navarro, R. F. Germaneau, R. A. Kelly III, W. Sommer, N. Marion, E. D. Stevens, L. Cavallo, S. P. Nolan, *Organometallics* **2004**, *23*, 1629–1635; d) X. Luan, R. Mariz, M. Gatti, C. Costabile, A. Poater, L. Cavallo, A. Linden, R. Dorta, *J. Am. Chem. Soc.* **2008**, *130*, 6848–6858.

[11] a) N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111; b) O. Navarro, N. Marion, J. Mei, S. P. Nolan, *Chem. Eur. J.* **2006**, *12*, 5142–5148.

[12] a) M. S. Viciu, R. A. Kelly III, E. D. Stevens, F. Naud, M. Studer, S. P. Nolan, *Org. Lett.* **2003**, *5*, 1479–1482; b) S. Iyer, A. Jayanthi, *Synlett* **2003**, 1125–1128; c) G. D. Frey, J. Schütz, E. Herdtweck, W. A. Herrmann, *Organometallics* **2005**, *24*, 4416–4426; d) J. Broggi, H. Clavier, S. P. Nolan, *Organometallics* **2008**, *27*, 5525–5531.

[13] M. G. Organ, M. Abdel-Hadi, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. Sayah, C. Valente, *Chem. Eur. J.* **2008**, *14*, 2443–2452.

[14] a) O. Navarro, N. Marion, N. M. Scott, J. Gonzalez, D. Amoroso, A. Bell, S. P. Nolan, *Tetrahedron* **2005**, *61*, 9716–9722; b) N. Marion, P. de Frémont, I. M. Puijk, E. C. Ecarnot, D. Amoroso, A. Bell, S. P. Nolan, *Adv. Synth. Catal.* **2007**, *349*, 2380–2384.

[15] R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.

[16] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.

[17] a) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663–1667; b) R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202–210.

[18] For a review, see: a) L. Cavallo, A. Correa, C. Costabille, H. Jacobsen, *J. Organomet. Chem.* **2005**, *690*, 5407–5413; for examples, see: b) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, *Organometallics* **2003**, *22*, 4322–4326; c) P. Bazinet, T.-G. Ong, J. S. O'Brien, N. Lavoie, E. Bell, G. P. A. Yap, I. Korobkov, D. S. Richeson, *Organometallics* **2007**, *26*, 2885–2895; and ref.[10c,15,17b]

[19] a) J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 2370–2375; b) N. M. Scott, H. Clavier, P. Mahjoor, E. D. Stevens, S. P. Nolan, *Organometallics* **2008**, *27*, 3181–3186.

[20] a) S. Roland, M. Audouin, P. Mangeney, *Organometallics* **2004**, *23*, 3075–3078; b) C.-Y. Wang, Y.-H. Liu, S.-M. Peng, J.-T. Chen, S.-T. Liu, *J. Organomet. Chem.* **2007**, *692*, 3976–3983; c) O. Winkelmann, C. Näther, U. Lüning, *J. Organomet. Chem.* **2008**, *693*, 2784–2788; d) H. M. Peng, G. Song, Y. Li, X. Li, *Inorg. Chem.* **2008**, *47*, 8031–8043.

[21] a) S. Caddick, F. G. N. Cloke, G. K. B. Clentsmith, P. B. Hitchcock, D. McKerrecher, L. R. Titcomb, M. R. V. Williams, *J. Organomet. Chem.* **2001**, *617–618*, 635–6369; b) L. Xu, Y. Shi, *J. Org. Chem.* **2008**, *73*, 749–751; c) M. J. Cawley, F. G. N. Cloke, R. J. Fitzmaurice, S. E. Pearson, J. S. Scott, S. Caddick, *Org. Biomol. Chem.* **2008**, *6*, 2820–2825.

[22] S. Fantasia, S. P. Nolan, *Chem. Eur. J.* **2008**, *14*, 6987–6993.

[23] M. S. Viciu, F. Kauer Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2003**, *22*, 3175–3177.

[24] a) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759–1766; preceding paper; b) http://www.molnac.unisa.it/OMtools/sambvca.php.

[25] a) A. J. Arduengo III, R. Krafczyk, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534; b) S. P. Nolan, US patent 653688, **2003**; c) D. Enders, K. Breuer, U. Kallfass, T. Balensiefer, *Synthesis* **2003**, 1292–1295; d) Some NHCs such as IMes and IPr are commercially available from Strem Chemicals, Inc.

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