Supporting information:

"Pyridine-derived N-heterocyclic carbenes: An experimental and theoretical evaluation of the bonding in and reactivity of selected normal and abnormal complexes of Ni(II) and Pd(II)"

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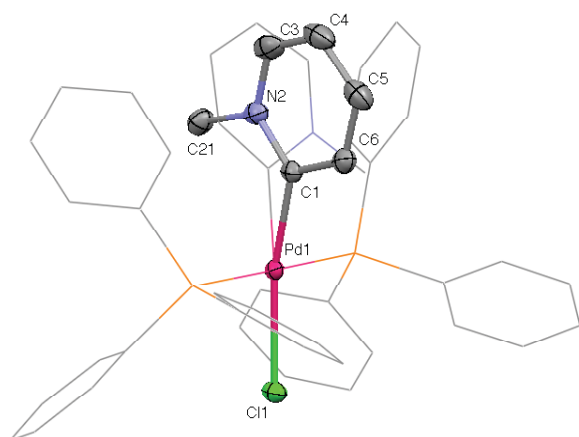
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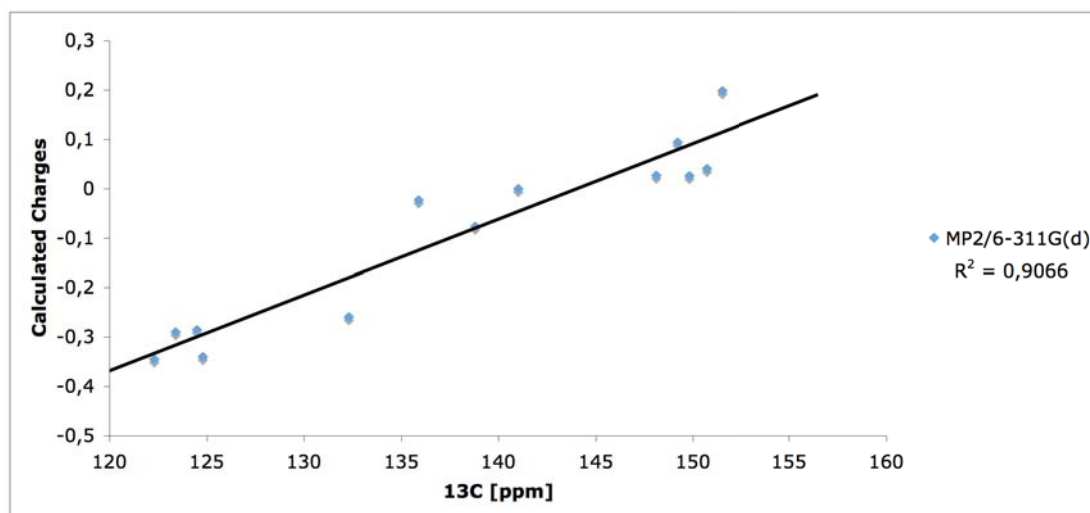
Figure S1. Correlation of calculated charges[1] and ^{13}C NMR shifts for carbon atoms in 2-, 3- and 4-chloropyridine.

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[1] Feshin, V. P.; Feshina, E. V.; Zhizhina, L. I. *J. Het. Chem.* **2006**, *42*, 1435.

Figure S2. Molecular structure of **3a** (in the BF$_4$ salt) with modeled disorder (s.o.f. 20%) that was missed previously.[2]

**Table S1.** Crystal Data, Data Collection and Structure Refinement Details.

	3a (in the BF4 salt)
Empirical formula	C$_{42}$H$_{37}$ClNP$_2$Pd·BF$_4$
M_r	846.33
Crystal system	Triclinic
Space group	*P-1*
a/Å	11.897 (2)
b/Å	13.008 (3)
c/Å	17.193 (3)
α/°	73.05 (3)
β/°	76.83 (3)
γ/°	65.23 (3)
V/Å^3	2293.8 (8)
ρ_{calc}/g cm^{-3}	1.225
Z	2
F(000)	860
μ (Mo-K$_\alpha$) (mm^{-1})	0.58
T/K	100
Refls. measured	26167
Refls. unique	10435 [R$_{int}$ = 0.020]
Refined param. /restraints	500/ 1
$R1$ [I≥2σ(I)]	0.035
$wR2^a$	0.082
Weighting scheme	a = 0.0275
	b = 3.4187
σ_{fin}(max/min)/eÅ^{-3}	0.92 / −0.61

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$

[2] Schneider, S. K.; Roembke, P.; Julius, G. R.; Raubenheimer, H. G.; Herrmann, W. A. *Adv. Synth. Catal.* **2006**, *348*, 1862.
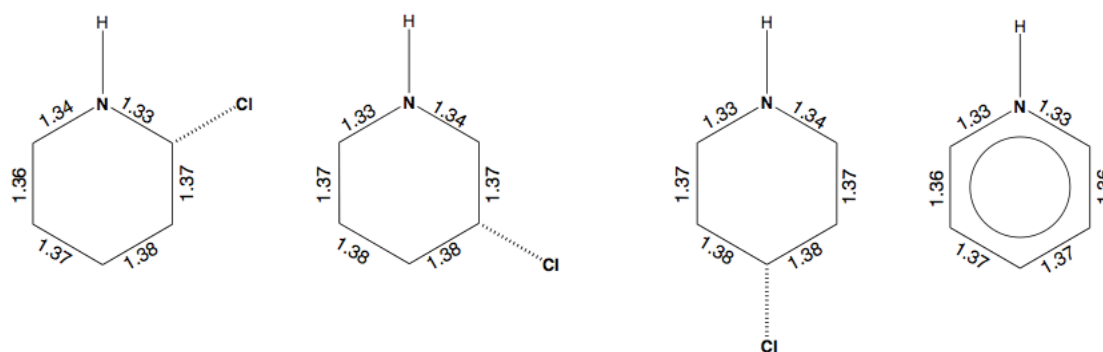
Figure S3. Average geometries of protonated chloropyridinium and pyridinium salts derived from available CCSD data.[3]
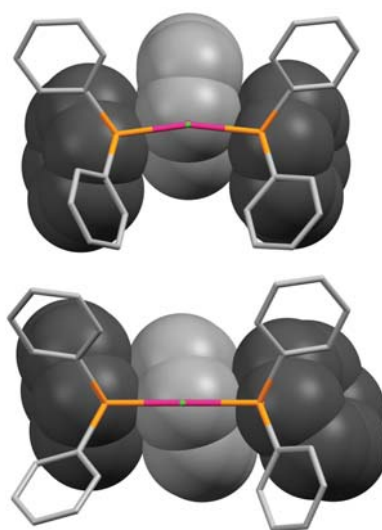
Figure S4: View along the Cl-Pd bond of **3b** (top) and **3c** (bottom)

As can be seen in Figure S4 (top), the asymmetric nature of the 3-pyridylidene ligand in **3b** results in a distortion of the square planar motif (*cf.* Table 1). Since four phenyl groups of the phosphines embrace the chloride in a staggered conformation, the carbene ligand becomes sandwiched between the remaining two phenyl groups. Thus, rotation is only possible in a concerted manner, which is hampered in the case of slipped stacking of the rings (Figure 4 - top). For the C_2-symmetric complexes **3c** and **4c**, where the rings align well, such a rotation is much more feasible (Figure 4 - bottom) and might be enforced by the phenyl rings. Therefore, a torsion angle analysis is not suitable for elucidation of electronic factors in this series.

[3] Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 389.

Table S2: Catalytic results for Suzuki-Miyaura cross-coupling reactions.

Entry	Catalyst	additive	Base	Conditions	T [°C]	Yield [%]^a
1	**3a**	none	K_2CO_3	air	130	78
2	**3b**	none	K_2CO_3	air	130	82
3	**3c**	none	K_2CO_3	air	130	86
4	$Pd(PPh_3)_4$	none	K_2CO_3	air	130	71
5	**3a**	[NBu$_4$]Br	Cs_2CO_3	inert	70	86
6	**3b**	[NBu$_4$]Br	Cs_2CO_3	inert	70	91
7	**3c**	[NBu$_4$]Br	Cs_2CO_3	inert	70	99
8	$Pd(PPh_3)_4$	[NBu$_4$]Br	Cs_2CO_3	inert	70	75

^{a} Determined by ^{1}H-NMR using diethyleneglycol-di-n-butylether as the internal standard (2:3:4 mixture of bromo acetophenone:phenylboronic acid:base with a catalyst loading of 0.1 mol% after 24h).