

Palladium(II) complexes bearing methylene and ethylene bridged pyrido-annelated *N*-heterocyclic carbene ligands as active catalysts for Heck and Suzuki–Miyaura cross-coupling reactions

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Received 12 January 2007; received in revised form 26 February 2007; accepted 26 February 2007

Available online 12 March 2007

Dedicated to Professor Peter Hofmann on the occasion of his 60th birthday.

Abstract

The synthesis and characterization of new bidentate *N*-heterocyclic carbene ligands is described. The ligands are derived from methylene (me) and ethylene (et) bridged imidazo[1,5-*a*]pyridine-3-ylidenes (impy) and can be synthesized readily from imidazo[1,5-*a*]pyridine and the respective dihaloalkanes. Palladium(II) dihalide complexes bearing these et(impy)₂ or me(impy)₂ ligands were prepared and also structurally characterized. The angle of the impy plane vs. the C–Pd–C plane is depending on the bridging unit as well as the halide ligands. In the solid state the me(impy)₂PdBr₂ complex forms a dimer by weak intermolecular Pd–hydrogen bridges. The activity of the Pd-complexes as catalysts for the Heck and Suzuki–Miyaura reactions was tested under various conditions. The catalysts show good activity at 120 °C in Heck and at 85 °C in Suzuki–Miyaura reactions.

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Keywords: *N*-Heterocyclic carbene; Imidazopyridinylidene; Bidentate ligands; Palladium complexes; Heck reaction; Suzuki–Miyaura reaction; C–C cross-coupling

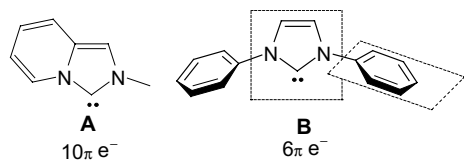
1. Introduction

Imidazo[1,5-*a*]pyridin-3-ylidenes **A** that belong to the Arduengo–Wanzlick carbene type [1,2], were first synthesized independently in the groups of Weiss [3], Lassaletta [4] and Glorius [5] and were used as ligands for transition metal catalysts. Their imidazolium salts were reported to be organocatalysts in the benzoin condensation in basic media [6], thus forming the imidazopyridine carbene *in situ*. Recently, we managed to resolve the first X-ray crystal structure of this carbene type and of a stable bipyridocarbene (see Scheme 1) [7]. The conjugated 10π-electron system that shows alternating single and double bonds in the imidazopyridine moiety is in conjugation with the empty p-orbital of the carbene atom thus increasing the electron density at

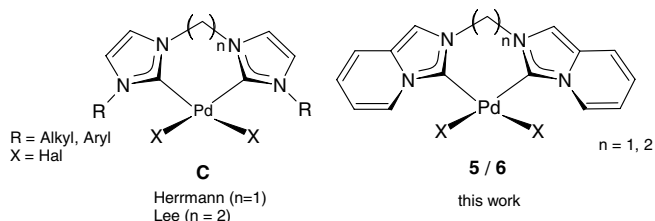
this center, which is displayed by the high-field shift of the carbene ¹³C NMR signals that lie in a range between 205 and 210 ppm [8]. Qualitatively the imidazopyridinylidenes should result slightly less basic as σ-donor and at the same time less π-acidic. In addition the geometry is different to imidazolinyliidenes **B**: while *N*-aryl substituents at imidazolinyliidenes are in a perpendicular orientation with respect to the imidazolin ring, the annelated pyrido moiety leads to a completely planar arrangement of the imidazopyridine carbenes. Therefore, additional substituents in position 5 would point towards the metal side upon coordination. We became interested in taking advantage of these qualities and use imidazopyridine carbenes as ligands for transition metal complexes and catalysts.

Our aim was to synthesize methylene and ethylene bridged bidentate impy ligands and their palladium(II) complexes **5/6** as they are analogous to the well established bis(imidazolinyliidene) ligand system first introduced by

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Scheme 1. Different electronic and structural features of imidazopyridine carbenes **A** and *N*-arylimidazolinylienes **B**.



Scheme 2. Catalytic active palladium complexes **C** with bis(imidazolinyliene) ligands by Herrmann and Lee, and the target complexes **5** and **6** of this work with bis(imidazopyridine carbene) ligands.

Öfele and Herrmann et al. for various transition metal complexes [9] (Scheme 2). Palladium dihalide complexes **C** ($n = 1$) with such bis(carbene) ligands were already shown to be active in various C–C cross-coupling reactions [10], the oxidative carbonylation of phenols [11] and even C–H activation [12]. The ethylene bridged palladium dihalide complexes **C** ($n = 2$) were tested by Lee in Heck and Suzuki–Miyaura reactions [13].

2. Results and discussion

2.1. Synthesis and characterization of the bridged bis(imidazopyridinium) salts **1a**, **1b**, **2**

Synthesis of the ligand precursor **1** and **2** is displayed in Scheme 3. Starting from imidazo[1,5-*a*]pyridine the bridged imidazolium salts were obtained in high yields by reaction with diiodomethane (**1a**), dibromomethane (**1b**) or dibromoethane (**2**) and could be isolated as white solids. Depending on the counterion the imidazolium salts could potentially serve as ionic liquids. However, the bis(impy*HX) compounds with bromide and iodide as counterions show rather high melting points (mp (dec.): 279 °C (**2**), 291 °C (**1b**), 265 °C (**1a**)).

The ^1H NMR spectra (DMSO- d_6) of the imidazolium salts **1a** and **1b**, and **2** are almost identical. The signal of the methylene protons is covered by the multiplet of the pyridinium moiety at 7.2–7.3 ppm. For imidazolium salt **2** the singlet of the 4 equiv. ethylene protons is detected at 5.14 ppm. The signals of the imidazolium proton 3-H are detected at 10.0 (**1a**) 10.1 (**1b**) and 9.69 (**2**) ppm, while the 1-H signals are observed at 8.53 (**1a**) and 8.58 (**1b**), 8.19 (**2**) ppm. This indicates a stronger acidity of proton 3-H. Therefore deprotonation is expected to occur preferentially at C3 (deprotonation at C1 would lead to an abnormal carbene) [14]. In the ^{13}C NMR spectrum (DMSO- d_6) of compounds **1a**, **1b** and **2**, the signals of

the imidazolium carbons C3 are found, upfield shifted by 7–10 ppm compared to other methyl- and ethyl bridged imidazolium salts [10,13] at a chemical shift of 127 ppm – an effect that is also observed for the free carbenes [8].

2.2. Molecular structures of the bis(imidazopyridinium) salts **1a** and **2**

Although the bis(imidazolium) salts in general could be important as ionic liquids, only very few molecular structures of methylene and ethylene bridged bis(imidazolium) salts are characterized so far [15]. Single crystals of **1a** were obtained from a saturated solution of **1a** in EtOH:MeOH:H₂O = 5:5:1. The X-ray analysis shows the two imidazolium rings not twisted, but roof-like oriented close to a C_{2v} framework symmetry. The formamidinium units are oriented cis [16]. Therefore the ligand precursor takes in already the same geometry as in the desired complex. (see Fig. 1) Other structures of bis(imidazolium) salts show the formamidinium functionalities pointing in opposite directions and/or the imidazolium moieties twisted [13,17].

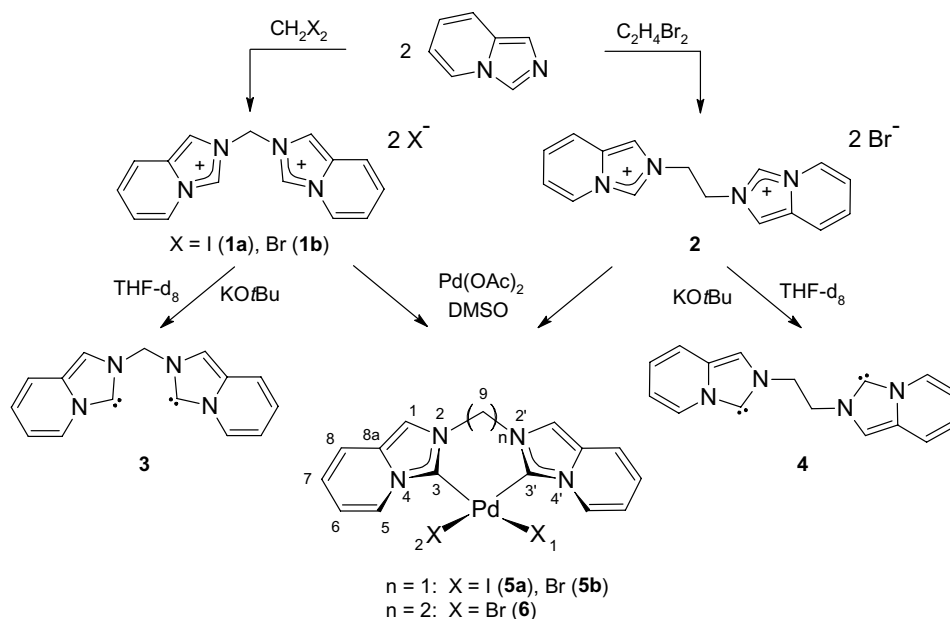
The molecular structure of the ethylene bridged bis(imidazopyridinium) salt **2** shows an anti conformation of the imidazopyridinium substituents on the ethylene bridge. In this case the formamidinium units are oriented in opposite directions. The bond lengths in the imidazopyridinium unit of **1a** and **2** are best represented by alternating single and double bonds, as it has been found already in other salts of this type [5,18], and also in the free carbene [7]. Compared with the free carbene **A** the N4–C3–N2 angle at the formamidinium unit is substantially larger (107.2° vs. 100.1° (**A**)) as it is generally found for imidazolium salts (Table 1).

2.3. In situ generation and characterization of the bis(imidazopyridinylienes) **3** and **4**

The free biscarbenes **3** and **4** were generated in situ by reaction with potassium *tert*-butanolate in THF- d_8 at room temperature and characterized by NMR experiments. Formation of the free carbenes **3** and **4** can already be observed in the ^1H NMR spectrum (THF- d_8) by the absence of the characteristic peak of the imidazolium proton 3-H at 10 ppm (**3**) and 9.7 ppm (**4**). The signal of the methylene protons in **3** is still covered by the 7-H signal at 6.60–6.65 ppm. However, proof for the formation of the carbene **3** and **4** can only be obtained in the ^{13}C NMR spectrum with the characteristic low field signals of the carbene C atoms at $\delta = 209.5$ (**3**) and 208.4 (**4**). These values lie in the typical range for imidazopyridinylienes (205–210 ppm).

2.4. Synthesis and characterization of bis(imidazopyridin-3-ylidene)palladium(II) dihalide complexes **5** and **6**

Synthesis of the palladium(II) complexes **5a** and **5b** is accomplished by reacting the bis(impy) salts **1a**, **1b** and **2**



Scheme 3. Synthesis of the new *N*-heterocyclic biscarbenes *me*(*impy*)₂ (**3**) and *et*(*impy*)₂ (**4**) and their palladium(II) complexes **5a**, **5b** and **6**.

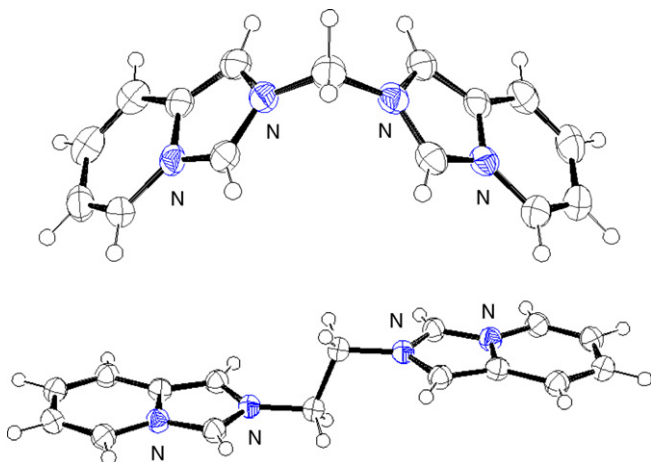


Fig. 1. ORTEP drawing of the structure of the bis(imidazopyridinium) salts with a methylene (**1a**, above) and an ethylene (**2**, below) bridge (the anions are omitted for clarity).

with palladium(II) acetate in DMSO at elevated temperature for 6–12 h. The poorly soluble carbene complexes precipitate upon cooling from DMSO and are isolated by filtration. After extraction with various organic solvents or recrystallization from DMSO and thorough drying in vacuo the product complexes can be obtained as light brown (**5a,b**) or bright yellow (**6**) solids in fair to good yields as DMSO adducts or – in the case of **5a** – without coordinated DMSO. All palladium complexes are thermally very stable (mp (dec.): 304–306 °C (**5a**), 335–339 °C (**5b**), 301–305 °C (**6**)).

Compared to the bis(imidazopyridinium) salts **1a** and **1b**, in the ¹H NMR spectrum all signals are shifted upfield by 0.3 ppm upon carbene formation and coordination to palladium. The only exception is the signal of proton 5-H

that is shifted downfield by 0.1 (**5a**) and 0.3 ppm (**5b**) which is possibly due to an influence of the palladium fragment. Upon coordination to palladium the protons of the meth-

Table 1
Crystal structure refinement for **1a** and **2**

	1a	2
Empirical formula	C ₁₇ H ₂₀ I ₂ N ₄ O	C ₁₆ H ₁₆ Br ₂ N ₄
Formula weight	550.17	424.15
Temperature (K)	200(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	2
Unit cell dimensions		
<i>a</i> (Å), α (°)	5.6573(5), 90.0	10.196(1), 90.0
<i>b</i> (Å), β (°)	13.4199(12), 100.429(2)	9.3253(9), 112.521(2)
<i>c</i> (Å), γ (°)	13.1539(12), 90.0	9.2031(9), 90.0
Volume (Å ³)	982.15(15)	808.3(1)
ρ _{calc.} (g/cm ³)	1.86	1.74
Absorption coefficient (mm ⁻¹)	3.21	5.02
Crystal colour/shape	Colorless/polyhedron	Colorless/block
θ Range (°)	1.6–28.4	2.2–28.3
Index ranges	−7 ≤ <i>h</i> ≤ 7, −17 ≤ <i>k</i> ≤ 17, −17 ≤ <i>l</i> ≤ 17	−13 ≤ <i>h</i> ≤ 13, −12 ≤ <i>k</i> ≤ 12, −12 ≤ <i>l</i> ≤ 12
Reflections collected	10478	8231
Independent reflections	4760 (<i>R</i> (int) = 0.0196)	2004 (<i>R</i> (int) = 0.0281)
Observed reflections	4508 (<i>I</i> > 2σ(<i>I</i>))	1920 (<i>I</i> > 2σ(<i>I</i>))
<i>T</i> _{max} , <i>T</i> _{min}	0.86 and 0.37	0.47 and 0.43
Data/restraints/parameters	4760/24/222	2004/0/132
Goodness-of-fit on <i>F</i> ²	1.04	1.08
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.026, <i>wR</i> ₂ = 0.060	<i>R</i> ₁ = 0.030, <i>wR</i> ₂ = 0.076
Largest difference peak and hole (e Å ⁻³)	0.76 and −0.39	0.92 and −0.32

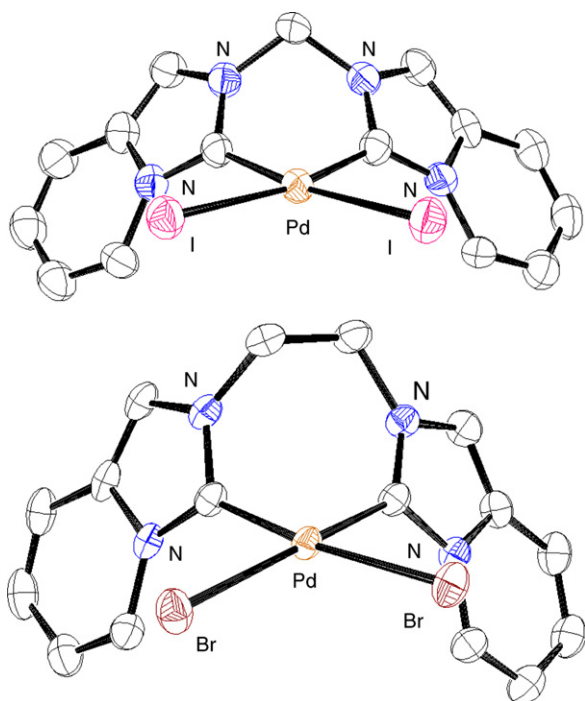


Fig. 2. ORTEP drawings of the methylene bridged bis(impy)palladium(II)diiodo complex **5a** (above) and the ethylene bridged bis(impy)palladium(II)dibromo complex **6** (below).

ylene group should no longer be chemically and magnetically equivalent, however the signals are covered by signal 7-H at 6.9–7.0 ppm. Therefore a possible equilibration of

the signals at higher temperatures as observed in the literature known complexes of Lee and Herrmann cannot be detected. The signal of carbene C3 was only detected for complex **5b** at 148.5 (C3) ppm. (Literature values for methylenebis(imidazolinyldene)PdBr₂-complexes: 172.2 ppm [10c] and 157–160 ppm [13].)

Upon coordination of the carbene ligand to palladium, the protons of the ethylene bridge are no longer magnetically equivalent. In the ¹H NMR spectrum (DMSO-*d*₆) of complex **6** the respective signal is split into two multiplets at 4.94 and 5.62 ppm. Like in complexes **5a** and **5b** upon coordination to palladium the chemical shift of the carbene proton signals is decreased by 0.3–0.4 ppm compared to ligand precursor **2**. Only proton 5-H is slightly deshielded by the influence of palladium resulting in a downfield shift of the signal 5-H by 0.13 ppm (δ 8.77).

In the ¹³C NMR spectrum (DMSO-*d*₆) of complex **6** the signal of the carbene carbon C3 is detected at 154.9 ppm, which is close to the value found for other ethylene bridged bis(carbene)PdBr₂ complexes (158–159 ppm) [13].

2.5. Structural characterization of the bis(imidazopyridin-3-ylidene)palladium complexes **5a**, **5b** and **6**

From concentrated solutions of **5a**, **5b** and **6** in boiling DMSO upon cooling we were able to get single crystals suitable for X-ray structure analysis. Fig. 2 shows the molecular structures of complexes **5a** and **6**.

Table 2

Selected bond lengths (Å) and angles (°) for complexes **5a**, **5b** and **6**, the precursor **1a** and **2**, and the free carbene **A**; labelling according to Scheme 3

	A	1a	5a	5b^a	2	6^b
C3–N4	1.393(4)	1.345(5)	1.350(10)	1.363(5)	1.341(2)	1.346(3) 1.363(3)
N4–C5	1.379(4)	1.394(5)	1.402(11)	1.393(6)	1.390(2)	1.389(3)
C5–C6	1.341(5)	1.340(6)	1.350(13)	1.346(6)	1.341(3)	1.343(3)
C6–C7	1.426(5)	1.416(7)	1.423(15)	1.434(7)	1.435(3)	1.431(4)
C7–C8	1.345(5)	1.338(7)	1.338(14)	1.339(6)	1.353(3)	1.343(4)
C8a–C8	1.413(5)	1.414(6)	1.448(13)	1.439(6)	1.425(2)	1.426(3)
N4–C8a	1.405(4)	1.387(5)	1.402(11)	1.409(6)	1.402(2)	1.408(3)
C8a–C1	1.356(5)	1.361(5)	1.361(13)	1.355(6)	1.368(2)	1.359(3)
C1–N2	1.374(4)	1.359(6)	1.377(10)	1.378(5)	1.373(2)	1.380(3)
N2–C3	1.356(4)	1.337(5)	1.350(10)	1.345(6)	1.329(2)	1.351(3)
C3–Pd	–	–	1.980(8)	1.982(4)	–	1.972(2)
C3'–Pd	–	–	1.994(8)	1.982(4)	–	1.990(2)
Pd–X1	–	–	2.6601(8)	2.4919(6)	–	2.4788(3)
Pd–X2	–	–	2.6693(8)	2.4919(6)	–	2.5034(3)
N4–C3–N2	100.2(3)	107.1(4)	103.7(7)	104.4(4)	107.24(15)	105.1(2) 104.1(2)
N2–C9–N2'	–	110.1(3)	106.9(6)	109.0(5)	–	–
C3–Pd–C3'	–	–	83.2(3)	84.0(3)	–	85.71(8)
C3–Pd–X2	–	–	90.4(2)	92.8(1)	–	90.51(6)
C3'–Pd–X1	–	–	92.2(2)	92.8(1)	–	91.12(6)
X1–Pd–X2	–	–	93.37(3)	89.90(3)	–	93.01(1)
C3'–Pd–C3–N2	–	–	45.4(7)	41.2(4)	–	–62.4(2)
C3–Pd–C3'–N2'	–	–	43.9(7)	41.2(4)	–	53.0(2)
C3–C3'–X1–X2	–	–	–1.4(2)	0	–	6.5(6)

^a Mean values of the dimer.

^b Mean values for the non-symmetric ligand halves; a second value indicates those cases with a significant deviation.

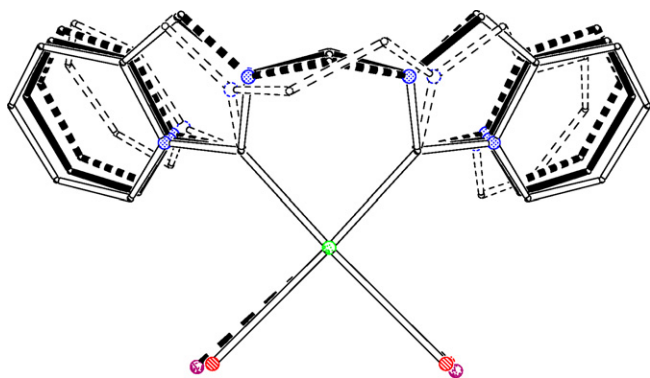


Fig. 3. Fit of the X-ray crystal structures of complexes **5b** (solid, molecule 1; open, molecule 2), **5a** (dashed solid) and **6** (dashed open).

As it could be already expected from the molecular structure of the imidazopyridine carbene **A** [7], the bonds of the imidazopyridine moiety do not show aromatic character, but are better described as alternating single and double bonds. A comparison with the free carbene reveals that upon coordination the NCN angle at the carbene increases by 4° which is realized by a shortening of the $C_{\text{carben}}\text{--N4}$ bond length $1.39 \rightarrow 1.36 \text{ \AA}$. All other bonds are of similar lengths to the carbene **A** and the imidazolium salts **1a** and **2** (see Table 2). Comparing the geometric differences of the molecular structures of complexes **5a**, **5b** and **6** (see Table 2 and Fig. 3), one can immediately recognize a different tilting of the impy plane vs. the $C3\text{--Pd--}C3'$ plane. In the dibromo complex **5b** the carbene moiety is tilted by only 41.2° ($N2\text{--}C3\text{--Pd--}C3'$), the angle at the

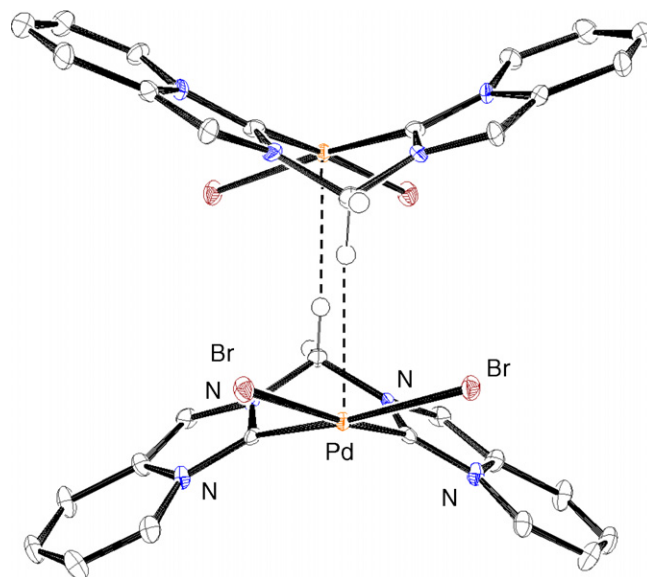


Fig. 4. ORTEP drawing of the palladium(II)dibromo complex **5b** as a dimeric species with weak hydrogen bridges in the solid state. Hydrogen atoms – except on the methylene bridge – are omitted for clarity.

methylene bridge measures 109.0° ($N2\text{--}C5\text{--}N2'$) and the bite angle 84.0° ($C3\text{--Pd--}C3'$). Tilting of the carbene plane against the palladium-ligand plane ($N2\text{--}C3\text{--Pd--}C3' = 45.4^\circ$) is bigger in the diiodo complex **5a** which results in a smaller angle at the methylene bridge ($N2\text{--}C9\text{--}N2' = 106.9(6)^\circ$) and a slightly smaller bite angle of 83.2° ($C3\text{--Pd--}C3'$). In both complexes the geometry around

Table 3
Crystal structure refinement for complexes **5a**, **5b** and **6**

	5a	5b	6
Empirical formula	$C_{17}H_{18}I_2N_4OPdS$	$C_{17}H_{18}Br_2N_4OPdS$	$C_{18}H_{20}Br_2N_4OPdS$
Formula weight	686.61	592.63	606.66
Temperature (K)	200(2)	100(2)	200(2)
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$Pnma$	$P\bar{1}$
Z	2	8	2
Unit cell dimensions			
a (\AA), α ($^\circ$)	8.898(1), 83.225(2)	17.1695(15), 90.0	8.7195(9), 96.068(2)
b (\AA), β ($^\circ$)	10.832(1), 78.819(2)	18.6162(13), 90.0	10.5698(11), 103.505(2)
c (\AA), γ ($^\circ$)	11.810(1), 70.521(2)	12.4753(9), 90.0	13.0996(14), 114.137(2)
Volume (\AA^3)	1051.0(2)	3987.5(5)	1043.38(19)
Density (calculated) (g/cm^3)	2.17	1.97	1.93
Absorption coefficient (mm^{-1})	3.93	5.06	4.84
Crystal colour/shape	Yellow/prism	Colorless/polyhedron	Yellowish/polyhedron
θ Range for data collection ($^\circ$)	1.8–28.4	2.0–28.4	1.6–28.3
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$	$-10 \leq h \leq 22$, $-22 \leq k \leq 24$, $-13 \leq l \leq 16$	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$
Reflections collected	10971	17395	11092
Independent reflections ($R(\text{int})$)	5157 (0.0283)	5075 (0.0765)	5152 (0.0215)
Observed reflections ($I > 2\sigma(I)$)	4650	3382	4672
Maximum and minimum transmission	0.86 and 0.6	0.82 and 0.63	0.64 and 0.40
Data/restraints/parameters	5157/0/237	5075/0/255	5152/26/281
Goodness-of-fit on F^2	1.24	0.97	1.03
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.063$, $wR_2 = 0.144$	$R_1 = 0.045$, $wR_2 = 0.069$	$R_1 = 0.022$, $wR_2 = 0.055$
Largest difference in peak and hole	1.67 and -1.39 e \AA^{-3}	1.01 and -0.68 e \AA^{-3}	0.68 and -0.51 e \AA^{-3}

the palladium is almost square planar and is similar compared with literature known methylenebis(imidazolinyldiene)PdBr₂ and -I₂ complexes [10,13,19] as well as bis(benzimidazolinyldiene)PdI₂ [20].

The biggest tilting of the carbene planes is found for complex **6** with 62.4° (C3'-Pd-C3-N2) and 53.0° (C3-Pd-C3'-N2'), which can be explained by an increased steric demand of the ethylene bridge. Compared to the methylene bridged complex **5b**, this has almost no effect on the bite angle of 85.71(8)° (C3-Pd-C3). This is consistent with the observations by Crabtree for bis(imidazolinyldiene)Rh complexes and Hahn for C₁ and C₃ bridged bis(benzimidazolin-3-ylidene)palladium complexes [21]. The almost square planar geometry at the palladium (C3-C3'-Br1-Br2 = 6.5°) is similar to the ethylene bridged complexes reported by Lee et al. [13].

A fit of the X-ray crystal structures (see Fig. 3) of the methylene bridged complexes **5b** and **5a** and the ethylene bridged complex **6** reveals nicely the different tilting of the imidazopyridine plane vs. the C_{Carbene}-Pd-C_{Carbene} plane.

Interestingly crystal structure **5b** reveals a dimeric form in the solid state (see Fig. 4). Two monomeric species are coordinated by intramolecular hydrogen bridges from the axial hydrogen of the methylene bridge of one molecule to the palladium of the second molecule* and vice versa. The bond distances of 3.665(7) Å (Pd-C9*) and

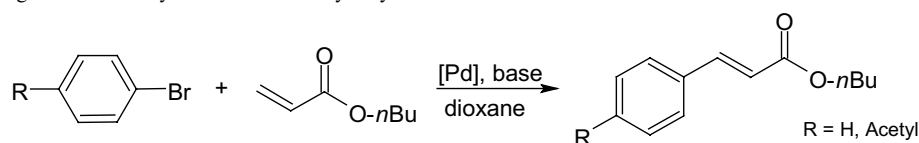
3.617(6) Å (Pd*-C9) can be interpreted as weak agostic Pd-H interactions (Table 3).

2.6. Catalysis

2.6.1. Heck reaction

As a comparison of the catalytic ability of our new complexes **5a**, **5b** and **6** with those of Herrmann and Lee, we tested them in C-C coupling reactions (see Table 4). Both complex types me(imp)₂PdX₂ (**5a**, **5b**) and et(imp)₂PdBr₂ (**6**) are active catalysts in the Heck reaction of bromobenzene with *n*-butylcinnamate at variable temperatures. At 150, 120 and 100 °C both complexes are active but the ethyl bridged complex **6** is more active than the methylbridged complexes **5**, as it was observed by Lee for electron withdrawing substrates in the Suzuki-Miyaura reaction. As a base we found Cs₂CO₃ in most cases to be superior to triethylamine: the yields are higher and no obvious reduction to Pd-black is observed during the course of reaction. Especially at a temperature of 100 °C the use of Cs₂CO₃ turned out to be essential. Only with a keto functionality in the substrate Cs₂CO₃ leads to side reactions and no desired product is observed. In these cases the product can be obtained with triethylamine as a base. The concentration of the catalyst was quite high, but can be reduced to 1% at 120 °C without any loss of activity.

Table 4
Pd-catalyzed Heck coupling reaction of arylhalides and *n*-butylacrylate^a



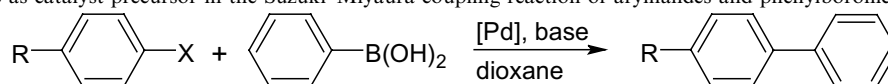
Entry	R _(Arylhalide)	Catalyst	(mol% Pd)	Base	T (°C)	Yield ^b (%)
1	C ₆ H ₅ -Br	6	1	Cs ₂ CO ₃	150	83
2	C ₆ H ₅ -Br	6	0.1	Cs ₂ CO ₃	150	57
3	C ₆ H ₅ -Br	6	3	NEt ₃	150	89
4	C ₆ H ₅ -Br	6	1	NEt ₃	150	49
5	C ₆ H ₅ -Br	6	0.1	NEt ₃	150	39
6	C ₆ H ₅ -Br	6	3	Cs ₂ CO ₃	120	87
7	C ₆ H ₅ -Br	6	3	NEt ₃	120	32
8	C ₆ H ₅ -Br	6	3	Cs ₂ CO ₃	100	85
9	C ₆ H ₅ -Br	6	1	Cs ₂ CO ₃	100	30
10	C ₆ H ₅ -Br	6	3	NEt ₃	100	7
11	C ₆ H ₅ -Br	5a	1	Cs ₂ CO ₃	150	67
12	C ₆ H ₅ -Br	5b	1	Cs ₂ CO ₃	150	44
13	C ₆ H ₅ -Br	5a	0.1	Cs ₂ CO ₃	150	35
14	C ₆ H ₅ -Br	5a	3	NEt ₃	150	19
15	C ₆ H ₅ -Br	5a	3	Cs ₂ CO ₃	120	44
16	C ₆ H ₅ -Br	5b	1	Cs ₂ CO ₃	120	14
17	C ₆ H ₅ -Br	5a	3	NEt ₃	120	9
18	C ₆ H ₅ -Br	5a	3	Cs ₂ CO ₃	100	13
19	4-Ac-C ₆ H ₄ -Br	6	0.1	NEt ₃	150	79 ^c
20	4-Ac-C ₆ H ₄ -Br	5a	0.1	NEt ₃	150	99 ^c
21	4-Ac-C ₆ H ₄ -Br	6	1	Cs ₂ CO ₃	120	0 ^c

^a Reaction conditions: arylhalide (1.00 mmol), *n*-butylacrylate (1.40 mmol), base (2.00 mmol), *n*-dodecane (30–50 mg), *N,N*-dimethylacetamide (3 ml), preheated oil bath, 16 h.

^b GC yield, based on *n*-dodecan as internal standard.

^c NMR yield, based on dodecahydrotriphenylene (20–40 mg) as internal standard.

Table 5

Preliminary screening of **6** as catalyst precursor in the Suzuki–Miyaura coupling reaction of arylhalides and phenylboronic acid^a

Entry	Arylhalide	Base	Yield ^b (%)
1	C ₆ H ₅ -Br	KOAc	39
2	C ₆ H ₅ -Br	Cs ₂ CO ₃	80
3	C ₆ H ₅ -Br	K ₃ PO ₄	40
4	4-Me-C ₆ H ₄ -Br	Cs ₂ CO ₃	49
5	C ₆ H ₅ -Cl	KOAc	0
6	C ₆ H ₅ -Cl	Cs ₂ CO ₃	0

^a Reaction conditions: arylhalide (1.00 mmol), phenylboronic acid (1.50 mmol), base (2.00 mmol), 1,4-dioxane (3 ml), preheated oil bath 85 °C, 16 h.^b Isolated yield.

2.6.2. Suzuki–Miyaura coupling

We also investigated complex **6** as a catalyst precursor in the Suzuki–Miyaura cross-coupling reaction of arylhalides and phenylboronic acid. In a first screening we tested various bases under standard conditions (85 °C, 16 h, 3 mol% **6**, 2 mmol base) and found again Cs₂CO₃ to be the base of choice compared to potassium phosphate and potassium acetate (see Table 5). Reaction of the less reactive bromotoluene resulted in lower yields (49%) whereas *p*-chlorotoluene did not react at all under these conditions.

It is not easy to compare the catalytic results with literature data due to the variety of different conditions, but a tentative comparison with the Herrmann system in the Suzuki–Miyaura reaction (1 mol% [CH₂(NHC)₂]PdI₂, bromobenzene, Ph–B(OH)₂, K₂CO₃, toluene, 12 h, 120 °C → 87% yield) [10a] implies, that complex **6** leads to a catalyst species of at least similar reactivity (longer reaction time, 3 fold catalyst loading, but reduced temperature for **6**).

3. Summary and outlook

In conclusion we were able to generate the first bis(imidazo[1,5-*a*]pyridin-3-ylidenes) and to synthesize and structurally characterize the respective Pd(II)dihalide complexes. Due to the special electronic structure of imidazopyridine carbenes the carbene remains electron rich upon coordination. The Pd complexes – upon activation – were found to be active catalysts in Heck and Suzuki–Miyaura cross-coupling reactions. The results of the catalytic experiments are a good basis to continue our work and to take now advantage of the special geometric possibilities that our bis(impy) ligand system provides, also in other catalytic applications.

4. Experimental

4.1. General comments

Unless otherwise noted all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried according to standard pro-

cedures and saturated with argon prior to use. Chemicals used were obtained from commercial suppliers and used without further purifications. Imidazo[1,5-*a*]pyridine was synthesized according to the literature procedure [22]. Infrared spectra were recorded on a Bruker Equinox 55 FT-IR-spectrometer as a KBr pellet or in solution. UV/Vis spectra were measured on a Hewlett-Packard HP 8452 spectrometer. Mass spectra were recorded on a Jeol JMS-700 with NBA (nitrobenzylalcohol) or dichloromethane as matrix. Melting points were determined with a Büchi Melting Point B 540 apparatus. NMR spectra were recorded using a Bruker DRX 300 or DRX 500 spectrometer. ¹H and ¹³C{¹H} NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard. Elemental analyses were carried out at Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

X-ray structural determinations: Frames corresponding to a sphere of data were collected with a Bruker APEX diffractometer using 0.3° ω scans and MoK_α radiation (λ = 0.71073 Å) in all cases. Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using the SADABS (V2.03) program [23] based on the Laue symmetry of the reciprocal space. Structure solutions and refinements were carried out with the SHELXTL (V6.12) program system [23] using direct methods and full matrix least squares refinement on F².

4.2. Synthesis of methylenebis(imidazo[1,5-*a*]pyridinium)-diiodide (**1a**)

In a sealed Schlenk tube 3.00 g (25.4 mmol) imidazo[1,5-*a*]pyridine and 1.03 ml (3.40 g, 12.7 mmol) diiodomethane are refluxed in 30 ml of toluene for a period of 20 h. The precipitate is filtered and washed three times with 20 ml of cold toluene. The residue is dried in vacuo to give 4.00 g (7.95 mmol, 63%) of the product as an off-white solid. ¹H NMR (DMSO-*d*₆): δ = 7.24–7.31 (m, 6H, 6-H, 7-H, CH₂), 7.95 (d, ³J_{HH} = 8.8 Hz, 2H, 8-H), 8.53 (s, 2H, 1-H), 8.75 (d, ³J_{HH} = 6.8 Hz, 2H, 5-H), 10.02 (s, 2H, 3-H). ¹³C NMR (DMSO-*d*₆): δ = 60.1 (CH₂), 113.3 (C1),

118.3 (C6), 118.5 (C8), 124.5 (C5), 125.2 (C7), 127.7 (C3), 129.4 (C8a). Mp: 265 °C (dec.). Anal. Calc. for $C_{15}H_{14}N_4I_2$: C, 35.74; H, 2.80; N, 11.11; I, 50.35. Found: C, 35.77; H, 2.90; N, 10.99; I, 50.18%. MS-ESI: $m/z = 377.1 [M-I]^+$.

4.3. Synthesis of methylenebis(imidazo[1,5-*a*]pyridinium)-dibromide (**1b**)

In a sealed Schlenk tube 1.00 g (8.48 mmol) imidazo[1,5-*a*]pyridine and 296 μ l (4.24 mmol) diiodoethane are refluxed in 10 ml of toluene for a period of 70 h. The precipitated product is filtered off and washed three times with 5 ml of cold toluene. The residue is dried in vacuo to give the product as an off-white solid. Yield: 18% (310 mg). 1H NMR (DMSO- d_6): $\delta = 7.23$ – 7.34 (m, 4H, 7-H, 6-H), 7.37 (s, 2H, CH₂), 7.95 (d, $^3J_{HH} = 9.1$ Hz, 2H, 8-H), 8.58 (s, 2H, 1-H), 8.67 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.1$ Hz, 2H, 5-H), 10.09 (s, 2H, 3-H). ^{13}C NMR (DMSO- d_6): $\delta = 60.1$ (CH₂), 113.2 (C1), 118.3 (C6), 118.5 (C8), 124.5 (C5), 125.2 (C7), 127.8 (C3), 129.4 (C8a). Mp: 291 °C (dec.). Anal. Calc. for $C_{15}H_{14}Br_2N_4$: C, 43.93; H, 3.44; N, 13.46. Found: C, 43.69; H, 3.48; N, 13.46%. MS-ESI: $m/z = 331.2/229.2 [M-Br]^+$, 249.2 $[M-H-2Br]^+$, 125.1 $[M-2Br]^2+$.

4.4. Synthesis of ethylenebis(imidazo[1,5-*a*]pyridinium)-dibromide (**2**)

In a sealed Schlenk tube 1.00 g (8.50 mmol) imidazo[1,5-*a*]pyridine and 800 mg (4.30 mmol) 1,2-dibromoethane are stirred in 17 ml of acetonitrile for a period of 20 h at 90 °C. Afterwards, the resulting suspension is filtered and the white product washed three times with 10 ml of cold acetonitrile and an additional 10 ml of *n*-pentane. After drying in vacuo the imidazolium salt can be isolated as a white solid. Yield: 44% (797 mg). 1H NMR (DMSO- d_6): $\delta = 5.14$ (s, 4H, CH₂), 7.19 (t, $^3J_{HH} = 6.9$ Hz, 2H, 6-H), 7.28 (dd, $^3J_{HH} = 6.9$ Hz, $^3J_{HH} = 9.2$ Hz, 2H, 7-H), 7.88 (d, $^3J_{HH} = 9.2$ Hz, 2H, 8-H), 8.19 (s, 2H, 1-H), 8.64 (d, $^3J_{HH} = 6.9$ Hz, 2H, 5-H), 9.69 (s, 2H, 3-H). ^{13}C NMR (DMSO- d_6): $\delta = 49.8$ (CH₂), 113.5 (C1), 117.5 (C6), 118.3 (C8), 124.3 (C5), 124.7 (C7), 127.0 (C3), 129.3 (C8a). Mp: 279–282 °C (dec.). Anal. Calc. for $C_{16}H_{16}N_4Br_2$: C, 45.31; H, 3.80; N, 13.21. Found: C, 45.51; H, 3.90; N, 13.24%. MS-ESI: $m/z = 132.1 [M-2Br]^2+$.

4.5. In situ generation of methylenebis(imidazo[1,5-*a*]pyridine-3-ylidene) (**3**)

In a Young-NMR tube 30 mg (60 μ mol) of the bisimidazolium salt methylenebis(imidazo[1,5-*a*]pyridinium)diiodide (**1a**) is dispersed in 0.5 ml of THF- d_8 . To the suspension, 20 mg (0.18 mmol) potassium-*tert*-butoxide is added and the tube is gently shaken for a few minutes until a dark solution can be obtained. 1H NMR (THF- d_8): $\delta = 6.31$ – 6.36 (m, 2H, 6-H), 6.60–6.65 (m, 4H, 7-H,

CH₂), 7.17 (d, $^3J_{HH} = 9.1$ Hz, 2H, 8-H), 7.45 (s, 2H, 1-H), 8.18 (d, $^3J_{HH} = 7.3$ Hz, 2H, 5-H). ^{13}C NMR (THF- d_8): $\delta = 66.8$ (CH₂), 109.5 (C1), 111.7 (C6), 118.3 (C8), 122.5 (C7), 131.8 (C5), 132.3 (C8a), 209.5 (C3).

4.6. In situ generation of ethylenebis(imidazo[1,5-*a*]pyridine-3-ylidene) (**4**)

In a Young-NMR tube 25 mg (60 μ mol) of the bisimidazolium salt ethylenebis(imidazo[1,5-*a*]pyridinium)dibromide (**2**) is dispersed in 0.5 ml of THF- d_8 . To the suspension, 20 mg (0.18 mmol) of potassium-*tert*-butoxide is added and the tube is gently shaken for a few minutes until a dark solution can be obtained. 1H NMR (500.13 MHz, THF- d_8): $\delta = 4.76$ (s, 4H, CH₂), 6.23 (dd, $^3J_{HH} = 7.3$ Hz, $^3J_{HH} = 6.2$ Hz, 2H, 6-H), 6.61 (dd, $^3J_{HH} = 9.3$ Hz, $^3J_{HH} = 6.2$ Hz, 2H, 7-H), 7.11 (s, 2H, 1-H), 7.16 (d, $^3J_{HH} = 9.3$ Hz, 2H, 8-H), 8.16 (d, $^3J_{HH} = 7.3$ Hz, 2H, 5-H). ^{13}C NMR (THF- d_8): $\delta = 53.9$ (CH₂), 110.9 (C1), 111.2 (C6), 118.1 (C8), 121.8 (C7), 131.4 (C5), 131.7 (C8a), 208.2 (C3).

4.7. Synthesis of diiodo(methylenebis(imidazo[1,5-*a*]pyridine-3-ylidene))palladium(II) (**5a**)

1.00 g (1.97 mmol) methylenebis(imidazo[1,5-*a*]pyridinium)diiodide (**1a**) and 441 mg (1.97 mmol) palladium(II) acetate are dissolved in 13 ml DMSO to give a dark red solution. This solution is heated to 80 °C and stirred overnight. The temperature is raised to 100 °C and the reaction mixture stirred for another 2 h. The precipitate is filtered and carefully recrystallised from DMSO in small portions to give after drying (54%, 700 mg) of a yellow crystalline material, which contains 1 equiv. of DMSO. The filtrate is concentrated until a light brown precipitate is formed which is filtered off and washed with 10 ml of acetonitrile, ethylacetate and petroleum ether. After drying in vacuo for a few days, the product (25%, 300 mg) can be obtained as a light brown powder that is free of DMSO. Overall yield: 79%. 1H NMR (DMSO- d_6): $\delta = 6.83$ – 7.02 (m, 6H, 7-H, 6-H, CH₂, CH₂'), 7.59 (d, $^3J_{HH} = 9.2$ Hz, 2H, 8-H), 8.21 (s, 2H, 1-H), 8.86 (d, $^3J_{HH} = 6.7$ Hz, 2H, 5-H). ^{13}C NMR (DMSO- d_6): $\delta = 64.5$ (CH₂), 112.9 (C6), 113.2 (C1), 118.0 (C8), 123.5 (C7), 129.5 (C5), 130.5 (C8a), the signal C3 could not be detected. Mp: 304–306 °C (dec.). Anal. Calc. for $C_{15}H_{12}N_4SOI_2Pd$: C, 29.74; H, 2.64; N, 8.16; I, 36.96. Found: C, 29.86; H, 2.70; N, 8.11; I, 37.13%. MS-FAB: $m/z = 608.0 [M]^+$, 481.1 $[M-I]^+$, 354.2 $[M-2I]^+$.

4.8. Synthesis of dibromo(methylenebis(imidazo[1,5-*a*]pyridine-3-ylidene))palladium(II) (**5b**)

250 mg (610 μ mol) methylenebis(imidazo[1,5-*a*]pyridinium)dibromide (**1b**) and 140 mg (610 μ mol) palladium(II) acetate are dissolved in 4 ml of DMSO. The solution is heated to 80 °C for 10 h, and then heated to 100 °C for another 2 h. The grey precipitate which is formed upon

cooling to room temperature is collected by filtration and extracted with dichloromethane in an ultrasonic bath to give a white powder. The product is filtered off and dried in vacuo to yield 21% (71 mg) of the complex, containing 0.75 equiv. of DMSO that could not be removed any further. Crystalline material can be obtained after recrystallisation from DMSO. ^1H NMR (DMSO- d_6): δ = 6.81 (dt, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 2H, 6-H) 6.91–7.00 (m, 4H, 7-H, CH_2 , CH'_2), 7.60 (d, $^3J_{\text{HH}} = 9.1$ Hz, 2H, 8-H), 8.16 (s, 2H, 1-H), 8.96 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H, 5-H). ^{13}C NMR (DMSO- d_6): δ = 64.2 (CH_2), 113.0 (C1), 113.2 (C6), 118.0 (C8), 123.3 (C7), 128.5 (C5), 130.3 (C8a), 148.5 (C3). Mp: 335–339 °C (dec.). Anal. Calc. for $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{N}_4\text{Pd} \cdot 0.75\text{C}_2\text{H}_6\text{SO}$: C, 34.58; H, 2.90; N, 9.78. Found: C, 34.61; H, 3.08; N, 9.61%. MS-FAB: $m/z = 433.0/453.0$ [$\text{M}-\text{Br}$] $^+$.

4.9. Synthesis of dibromo(ethylenebis(imidazo[1,5-*a*]pyridine-3-ylidene))palladium(II) (6)

1.00 g (2.35 mmol) ethylenebis(imidazo[1,5-*a*]pyridinium)dibromide (2) and 525 mg (2.35 mmol) palladium(II) acetate are stirred for 150 min in 20 ml DMSO at 50 °C. The reaction mixture is heated to 120 °C and stirred for another 150 min. The hot solution is then filtered and the residue extracted 10 times with 3 ml of boiling DMSO. The solvent of the combined fractions is evaporated by Kugelrohr distillation and the remaining green solid is carefully recrystallised in small portions from boiling DMSO to give after thorough drying in vacuo a bright yellow crystalline material containing 1 equiv. of DMSO. Yield: 44% (633 mg). ^1H NMR (DMSO- d_6): δ = 2.54 (s, 6H, H_{DMSO}), 4.94 (m, 2H, CH_2), 5.62 (m, 2H, CH'_2), 6.76 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 2H, 6-H), 6.91 (dd, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{HH}} = 9.3$ Hz, 2H, 7-H), 7.46 (d, $^3J_{\text{HH}} = 9.3$ Hz, 2H, 8-H), 7.89 (s, 2H, 1-H), 8.77 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H, 5-H). ^{13}C NMR (DMSO- d_6): δ = 48.1 (CH_2), 113.0 (C6), 113.9 (C1), 117.5 (C8), 123.0 (C7), 128.3 (C5), 130.9 (C8a), 154.9 (C3). Mp: 301–305 °C. Anal. Calc. for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{SOBr}_2\text{Pd}$: C, 35.56; H, 3.32; N, 9.24. Found: C, 35.76; H, 3.33; N, 9.31%. MS-FAB: $m/z = 447.2/449.2$ [$\text{M}-\text{Br}$] $^+$.

4.10. General setup for the Heck reaction

In a Schlenk tube, 157 mg (1.00 mmol) bromobenzene or 199 mg (1.00 mmol) bromoacetophenone, 179 mg (1.40 mmol) *n*-butylacrylate, 2.00 mmol of the corresponding base (652 mg Cs_2CO_3 , or 200 mg NEt_3) are mixed and the given amount of catalyst precursor is added, as well as a defined portion of *n*-dodecane (30–50 mg) as an internal GC standard or dodecahydrotriphenylene (20–40 mg) as an internal NMR standard and 3 ml of *N,N*-dimethylacetamide. The tube is sealed and placed in a preheated oil bath. The reaction mixture is stirred for 16 h and afterwards cooled to room temperature. The yield is determined by GC or NMR.

4.11. General setup for Suzuki reactions

In a Schlenk tube, 1.00 mmol of the aryle halide, 183 mg (1.50 mmol) phenylboronic acid, 30 μmol catalyst and 2.00 mmol of the given base are diluted in 3 ml of dioxane. The tube is sealed and placed into a preheated oil bath. The reaction mixture is stirred for 16 h and then allowed to cool to room temperature. The mixture is filtered over Celite[®], evaporated to dryness and the crude product is purified by column chromatography (silica, 20 * 2.5 cm, PE:EE 8:1).

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft (Emmy Noether Programm, Ku 1437/2-2) and the Fonds der Chemischen Industrie is gratefully acknowledged. D.K. thanks Professor Peter Hofmann for his continuous and generous support and Johnson Matthey for a loan of palladium salts. We thank Erik Johnsen for experimental assistance.

Appendix A. Supplementary material

CCDC 633262, 633260, 633263, 633264 and 633261 contain the supplementary crystallographic data for **1a**, **2**, **5a**, **5b** and **6**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.044.

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