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Imidazo[1,5-*a*]pyridine-3-ylidenes—pyridine derived N-heterocyclic carbene ligands

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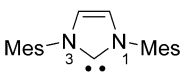
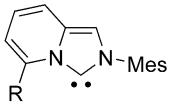
Abstract—The ready synthesis of differently substituted 2*H*-imidazo[1,5-*a*]pyridin-4-ium bromides is reported. These salts are precursors for a new class of N-heterocyclic carbene ligands. As a consequence of their bicyclic geometry, these ligands are capable of influencing the coordination sphere of a carbene bound metal. The usefulness of these ligands was demonstrated in the palladium-catalyzed Suzuki–Miyaura cross-coupling of sterically hindered aryl chlorides.

In the last 10 years, N-heterocyclic carbenes (NHCs) have become indispensable ligands for many areas of transition metal catalysis.[1] Many favorable characteristics render NHC to be attractive ligands for catalysis. They are electron rich donor ligands and generally form intriguingly stable complexes with many metals. Moreover, the geometry of NHC is different from other ligands, allowing the design of new ligand geometries. Therefore, it is rather surprising that most NHC ligands used in catalysis are 1,3-disubstituted imidazolylidenes like IMes, IiPr or their saturated analogues.[2] These ligands influence the metal's coordination sphere only to some extent. Ligand **1**, a hybrid between IMes and the NHC derived from **2**,[3] is different. As a result of its bicyclic structure the R substituent is placed in close proximity to a carbene bound metal, thus allowing significant shielding of the metal or, alternatively, stable or hemilabile coordination to the metal. Here we report on the flexible synthesis of pyridine derived imidazolium salts of type **1** and their first application in catalysis.



IMes



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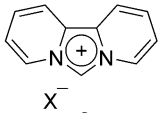

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1. Results and discussion

The synthesis of a range of differently substituted pyridine derived NHC ligands started with pyridine carboxaldehydes **3** which are commercially available or easily prepared following literature methods. Reaction of **3** with 2,4,6-trimethyl aniline resulted in the smooth formation of pyridine imines **4** in good yields (Table 1). The imidazolium salt formation of **2** from bispyridine relied on the use of the elaborated arsonium salt **6** as an alkylating agent, severely reducing the attractivity of this ligand class.[3] This might be the reason why no successive reports on the use of this particular carbene have appeared. On the other hand the successful usage of a commercially available or easily prepared alkylating agent would allow easy access to pyridine-derived carbenes. Therefore, we were pleased to find that a reagent formed from equal amounts of AgOTf and chloromethyl pivalate[4] resulted in the formation of the desired imidazolium triflates, isolated as the corresponding bromide **5** after anion exchange (Scheme 1). These bromide salts crystallize more readily, significantly facilitating the purification process. Overall, this route is efficient and flexible and allows the formation of differently substituted 2*H*-imidazo[1,5-*a*]pyridin-4-ium salts **5** (R=H, Me, Ph, OMe, Br).

Table 1. Yields for the synthesis of **5**

Ligand	R	Yield of **4** (%)	Yield of **5** (%)
a	H	90	53
b	Me	90	52
c	Ph	99	47
d	OMe	89	22
e	Br	88	54

Keywords: Ligand design; N-heterocyclic carbene; Suzuki–Miyaura cross-coupling.
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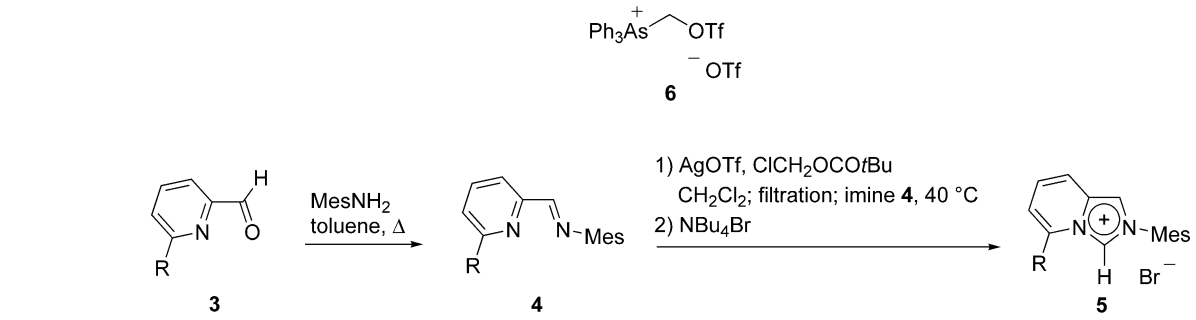


Scheme 1.

The structural identity of these compounds was unequivocally determined by X-ray structure analysis of **5a** and **5b** (Figs. 1 and 2).[5,6] These two compounds have similar bond lengths and angles. Most interestingly, on closer inspection of the bond lengths in **5a** and **5b** both molecules show the expected bond length alteration in the six-membered ring as expected from the canonical forms shown in Scheme 2. The two formal double bonds are approximately 0.08 Å shorter than the single bond in between. These three bonds and the bridging bond are identical within one σ in **5a** and **5b**.

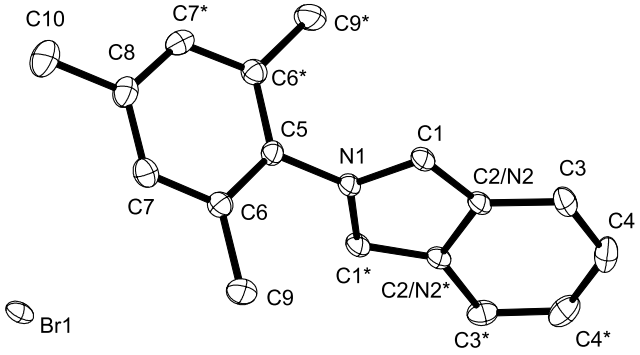


Figure 1. Molecular structure of **5a** which is situated on a crystallographic 2-fold axis. Atoms C2 and N2 share one position. Anisotropic displacement parameter ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°): C1–N1 1.356(2), C1–C2 1.357(2), C2–N2^{i} 1.403(3), C2–C3 1.412(2), C3–C4 1.351(3), C4–C4^{i} 1.435(5), C5–N1 1.453(3), symmetry code (i) $-x+1/4$, $-y+5/4$, z.

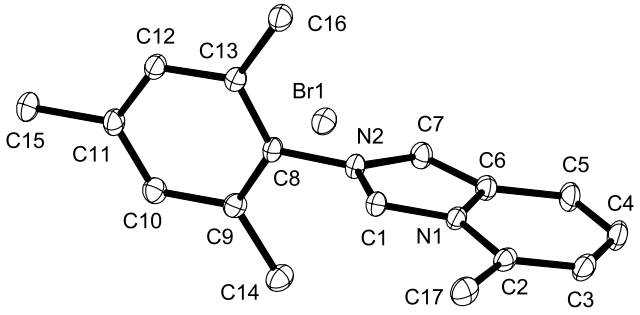
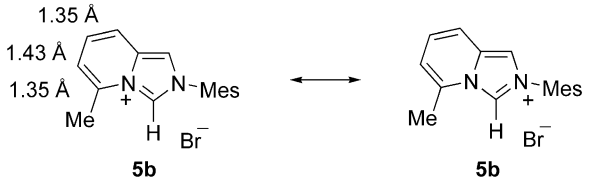


Figure 2. Molecular structure of **5b**. Anisotropic displacement parameter ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°): N1–C1 1.3484(17), N1–C2 1.4044(18), N1–C6 1.4061(18), C1–N2 1.3359(17), N2–C7 1.3761(17), N2–C8 1.4475(18), C2–C3 1.355(2), C3–C4 1.433(2), C4–C5 1.354(2), C5–C6 1.4222(19), C6–C7 1.3703(19).



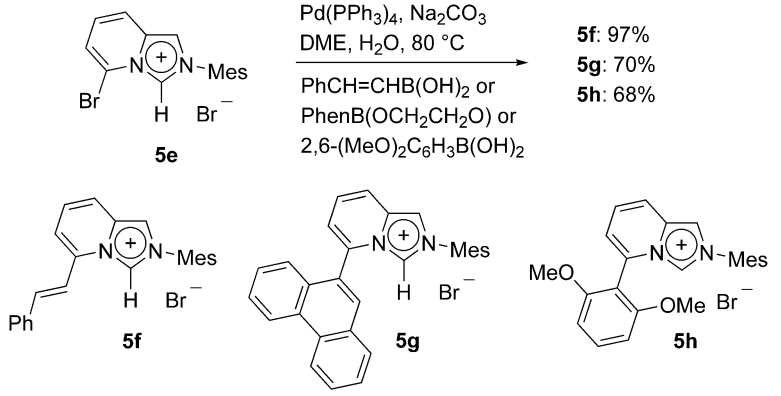
Scheme 2. Most important canonical forms of the imidazolium salts **5b**.

Interestingly, in **5c** the ^{1}H NMR signal of H–C(1) is shifted upfield compared to the other imidazolium salts **5a** and **5b** by more than 1 ppm This indicates that H–C(1) lies in the anisotropic cone of the phenyl ring. A similar interaction is envisioned to occur with a carbene bound metal.

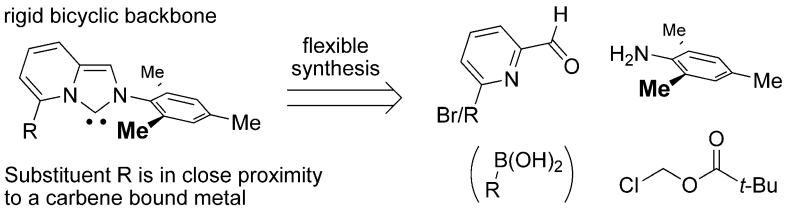
Ligand precursors **5a–e** can readily be synthesized. However, in order to introduce a new substituent R the whole sequence has to be repeated. A common synthetic precursor that could be manipulated to yield differently substituted products in one step would be highly desirable. In general, organic halides enable a plethora of synthetic transformations.[7] Therefore, we investigated the derivatization of bromide **5e**. Transition metal catalyzed coupling reactions seemed tempting, however, palladium catalyzed transformations of aryl halides in the presence of 2-unsubstituted imidazolium salts can provide potential pitfalls. Namely, deprotonation of the imidazolium salts might occur, providing sensitive NHCs or the corresponding palladium NHC complexes. Gratefully, after some optimization Suzuki cross-coupling of **5e** with different boronic acids or boronic acid esters provided the desired substituted imidazolium salts **5f**, **5g** and **5h** in good yields. This strategy allows the synthesis of a variety of differently substituted NHC-precursors in one step from **5e** (Schemes 3 and 4).

Compounds **5f** and **5g** can exist as atropisomers. Whereas the two *ortho*-methyl groups of the mesitylene moiety of **5f** give only one signal in ^{1}H and ^{13}C NMR, in compound **5g** they result in two individual signals. This implies that rotation of the 1-styryl moiety in **5f** is fast relative to the NMR time scale, whereas rotation of the phenanthrene unit in **5g** is slow. As a further indication for a relatively long life time, capillary electrophoresis of **5g** also results in two discrete base line separated peaks with diffusion times of 15.8 and 16.2 min. However, separation of the two atropisomers of **5g** by HPLC on a chiral phase was not successful.

Complexes of the NHCs derived from the ligand precursor **5** with R=H, Ph and C≡C–Ph have also been characterized by single crystal structure analysis in order to investigate their coordinational behavior. The differently substituted



Scheme 3. Suzuki–Miyaura cross-coupling of **5e**.



Scheme 4. Retrosynthetic analysis and ligand features.

ligands behave differently and the stability of the complexes formed depends strongly on the steric demand of the ligand.

Taking the unsubstituted **5a**, the stable $(NHC)_2PdI_2$ complex **7** smoothly forms in 52% yield under standard conditions (**5a**, $Pd(OAc)_2$, NaI, KO*t*Bu, THF).[8] In the distorted square planar complex **7** two carbene ligands (R = H) are *trans*-coordinated to the palladium (Fig. 3).[5] Both aza-indolizinyl ligands are rotated almost perpendicular to the coordination plane. The mesityl rings are oriented perpendicular to the heterocycles and adopt a proximal arrangement. The shortest non-bonding C···C distance is 3.537 Å, formed between C12 and C30. The bond lengths of the carbene ligand are all within three to four σ to those in **5b**, with the exception of the two carbene carbon–nitrogen atom bonds. These are, after averaging over both ligands in **7**, 1.357(3) and 1.367(3) Å long compared to 1.3359(19) and 1.3484(17) Å in the aza-indolizinium salt.

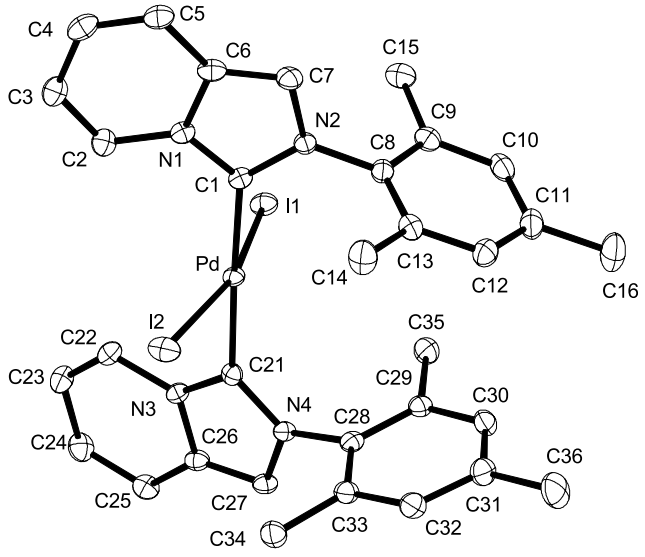
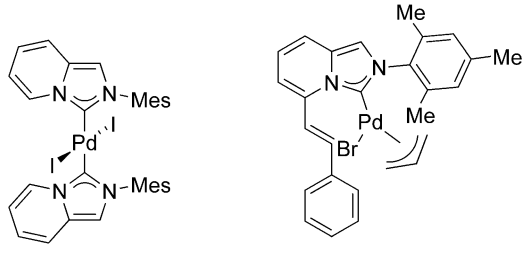
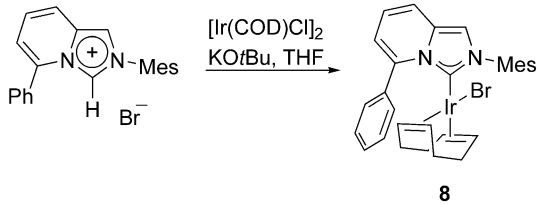


Figure 3. Molecular structure of **7**. Anisotropic displacement parameter ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°): Pd–C21 2.015(2), Pd–C1 2.033(2), Pd–I2 2.6062(2), Pd–I1 2.6289(2), N1–C1 1.369(3), N1–C2 1.391(3), N1–C6 1.411(3), N2–C1 1.358(3), N2–C7 1.381(3), N2–C8 1.446(3), N3–C21 1.364(3), N3–C22 1.393(3), N3–C26 1.407(3), N4–C21 1.356(3), N4–C27 1.388(3), N4–C28 1.458(3), C2–C3 1.345(4), C3–C4 1.436(4), C4–C5 1.347(4), C5–C6 1.428(3), C6–C7 1.357(4), C22–C23 1.350(4), C23–C24 1.436(4), C24–C25 1.351(4), C25–C26 1.427(3), C26–C27 1.359(3), C21–Pd–C1 177.68(9), C21–Pd–I2 88.45(6), C1–Pd–I2 92.45(7), C21–Pd–I1 87.41(6), C1–Pd–I1 92.30(6), I2–Pd–I1 163.418(10).



The isolation of the corresponding $(NHC)_2PdI_2$ complex of the sterically more demanding **5c** failed under standard conditions. However, sterically demanding **5c** (R = Ph) can also form complexes. Stirring $[Ir(COD)Cl]_2$ with



Scheme 5. Synthesis of complex **8**.

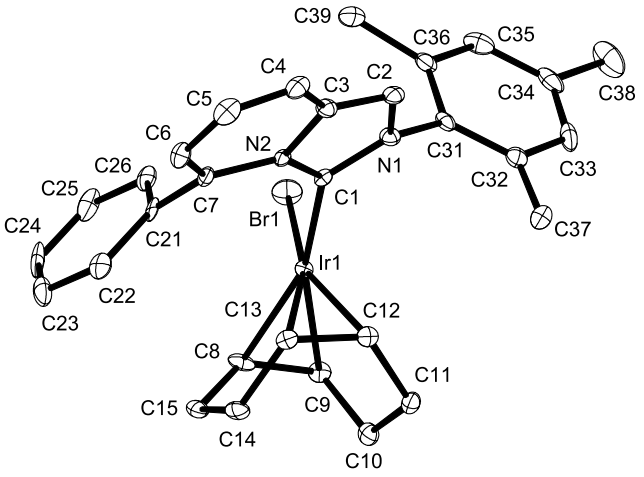


Figure 4. Molecular structure of **8**. Anisotropic displacement parameter ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°): C1–N1 1.366(7), C1–N2 1.382(6), C1–Ir1 2.046(4), C2–C3 1.362(7), C2–N1 1.370(7), C3–C4 1.407(7), C3–N2 1.438(6), C4–C5 1.343(8), C5–C6 1.438(7), C6–C7 1.360(6), C7–N2 1.414(6), C8–Ir1 2.163(5), C9–Ir1 2.190(4), C12–Ir1 2.099(5), C13–Ir1 2.106(5), C31–N1 1.470(6), Br1–Ir1 2.4975(5), C1–Ir1–C12 87.43(19), C1–Ir1–C13 89.11(18), C1–Ir1–C8 158.17(18), C12–Ir1–C8 97.2(2), C13–Ir1–C8 81.15(19), C1–Ir1–C9 163.04(18), C12–Ir1–C9 80.9(2), C13–Ir1–C9 89.83(18), C1–Ir1–Br1 96.58(12), C12–Ir1–Br1 153.83(16), C13–Ir1–Br1 164.88(13), C8–Ir1–Br1 88.62(15), C9–Ir1–Br1 88.73(13).

imidazolium salt **5c** and KO*t*Bu in THF results in the formation of Ir(COD)**5c**Br (**8**) (Scheme 5).[9] X-ray structural analysis reveals interesting features of this complex (Fig. 4, 5).[5] The iridium center is coordinated in a distorted pseudo-square planar arrangement. The carbene ligand and the bromine are *cis* to each other and the two remaining places of the co-ordination sphere are occupied by the midpoints of the two carbon–carbon double bonds of the cycloocta-1,4-diene. As expected, the phenyl-substituent of the ligand shields one of the two faces of the coordination plane of iridium. Most notable, there is an additional intramolecular interaction between two of the phenyl carbon atoms and the metal, resulting in a slight pyramidalization of C21 (Fig. 5). The distances to the iridium atom are 3.183 and 3.322 Å for C26 and C21, respectively.

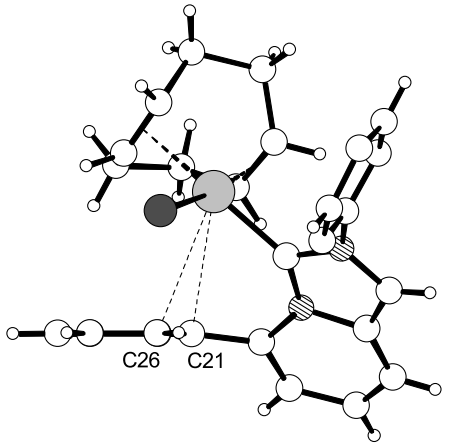


Figure 5. Molecular structure of **8**. Intramolecular contact between the iridium metal and carbon atom C21 (3.322 Å) and C26 (3.183 Å) shown as thin dashed lines. Carbon atom C21 is slightly pyramidalized, the sum of all bond angles for this atom is 359.59. The methyl groups of the mesityl ring have been omitted for clarity.

Secondary interactions, as observed in complex **8** between the phenyl group and the metal, arguably play an important role in catalysis.[10] This might result in a stabilization or activation of a catalytically active complex. This renders ligands **5c**, **5d**, **5f**, **5g** and **5h** especially valuable. It is obvious that the electronic and steric character of the R group can be fine tuned and also varied over a wide range.

We prepared palladium allyl complex **9** by stirring of the NHC derived from **5f** with palladium allyl chloride dimer.[9] It is important to note that the bromo and not the chloro complex is formed. The molecular structure is also distorted pseudo-square planar (Fig. 6).[5] The carbene ligand adopts a conformation similar to the one in **8** and the bond lengths follow the same trend as previously observed. The carbene carbon–nitrogen bonds are even more elongated than in **7**. In addition, a short contact is observed between the metal center and carbon atom C11 of the styrene substituent. With 3.081 Å, the distance is shorter than the sum of the van der Waals radii. A possible pyramidalisation of this carbon is not detectable from the X-ray crystal structure, due to the uncertainty of the hydrogen atom position. However, the torsion angle C5–C11–C12–C13 deviates by 4° from the ideal 180°, also indicating a weak interaction between palladium and C11.

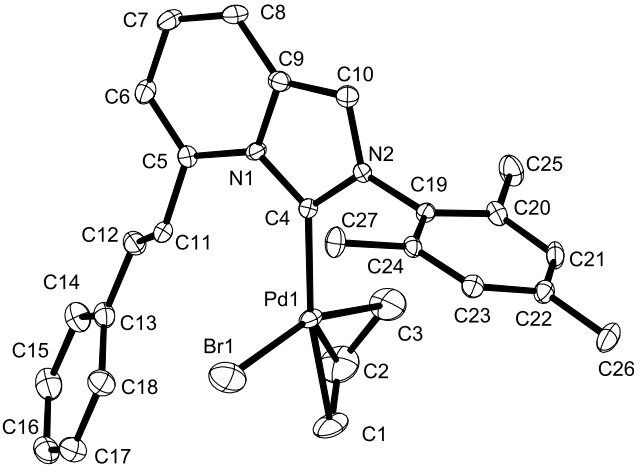
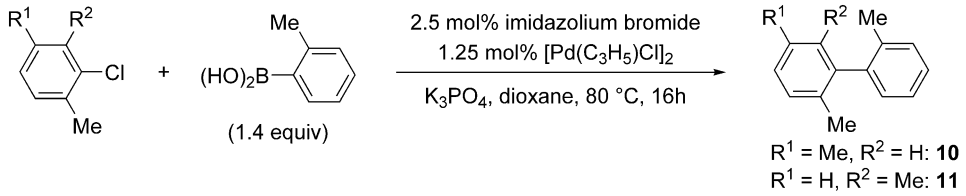


Figure 6. Molecular structure of **9**. Anisotropic displacement parameter ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°): C1–C2 1.359(9), C1–Pd1 2.186(5), C2–C3 1.385(9), C2–Pd1 2.133(6), C3–Pd1 2.123(6), C4–N2 1.360(5), C4–N1 1.377(5), C4–Pd1 2.059(4), C5–C6 1.361(6), C5–N1 1.405(5), C6–C7 1.429(6), C7–C8 1.353(7), C8–C9 1.420(6), C9–C10 1.369(6), C9–N1 1.412(5), C10–N2 1.375(6), C19–N2 1.448(5), C4–Pd1–C3 99.86(19), C4–Pd1–C2 132.2(2), C4–Pd1–C1 167.6(2), C3–Pd1–C1 67.7(2), C4–Pd1–Br1 98.08(11), C3–Pd1–Br1 161.81(16), C2–Pd1–Br1 126.6(2), C1–Pd1–Br1 94.31(16).

A more cationic metal with free coordination sites should result in much stronger interactions. Treatment of a CH_2Cl_2 solution of complex **9** with $AgSbF_6$ results in characteristic changes in the ^1H NMR spectrum, indicating a cationic palladium complex stabilized by double bond complexation. However, this complex decomposes on standing and no crystals suitable for X-ray structural analysis could be obtained.



Scheme 6.

2. Suzuki–Miyaura cross-coupling

The Suzuki–Miyaura cross-coupling is one of the most important method for the formation of unsymmetrical biaryls, substructures of many important compounds.[11] In general, aryl bromides and aryl iodides are used as coupling partner. However, the use of the cheaper but less reactive aryl chlorides under mild conditions is of great academic and practical interest and many research programs are devoted to this.[12] As a first test for the usefulness of this new ligand system we chose the Suzuki–Miyaura cross-coupling of sterically demanding aryl chlorides with aryl boronic acids to give di- and tri-orthosubstituted biaryls (Scheme 6, Table 2). Distinctive differences were found for the different ligands. Employing 2.5 mol% catalyst, most ligand/palladium combinations produced only low amounts of the desired product. In contrast, ligands **5g** and **5h** lead to the formation of di- and tri-orthosubstituted biaryls in respectable yields of up to 86% isolated yield.

Table 2. Suzuki–Miyaura cross-coupling of sterically hindered aryl chlorides resulting in di- and triortho-substituted biaryls[a]

Entry	Ligand	Product	Yield[a]
1	**5a**	**10**	(<10)
2	**5b**	**10**	(38)
3	**5c**	**10**	(39)
4	**5d**	**10**	(34)
5	**5f**	**10**	(22)
6	**5g**	**10**	86
7	**5h**	**10**	(67)
8	**5a**	**11**	<10
9	**5b**	**11**	30 (28)
10	**5c**	**11**	(27)
11	**5d**	**11**	(<10)
12	**5f**	**11**	(<10)
13	**5g**	**11**	78
14	**5h**	**11**	67 (69)

[a] Yield of isolated product; GC yield in brackets.

For Suzuki–Miyaura cross-couplings it is believed that a monoligated Pd-species is the active catalyst.[13] In order to increase the life time of this species steric shielding or hemilabile binding might be beneficial. Ligands derived from **5g** (R=phenanthryl) and **5h** (R=2,6-dimethoxyphenyl)[14] are suitable for this kind of interaction. The substituents R on the ligand shield the metal and in addition they can bind to the metal possibly resulting in a stabilization or activation of the catalytically active complex.

In conclusion we have reported a facile synthetic route to a new class of pyridine derived NHC ligands and transition metal complexes thereof. The first investigation of their catalytic activity has been reported, demonstrating the usefulness of this exciting ligand class.

3. Experimental

3.1. General remarks

All reactions were conducted in dried glassware under an atmosphere of argon. The solvents used were purified by distillation over the drying agents indicated and were transferred and stored under argon: tetrahydrofuran (THF) (Na), CH_2Cl_2 (P_4O_{10}), toluene (Na/K). For flash chromatography, Merck silica gel 60 (230–400 mesh) was used. NMR spectra were recorded on a DPX 300 or AV 400 spectrometer (Bruker) in the solvents indicated; chemical shifts (δ) are given in parts per million relative to tetramethylsilane, and coupling constants (J) are given in Hertz. For IR, a Nicolet FT-7199 spectrometer or Perkin–Elmer Fourier transform-IR Diamant Spectrum One (ATR) was used; wavenumbers (ν) are given in cm^{-1}. For MS (electron ionization (EI)), a FinniganMAT 8200 (70 eV) was used, and for high-resolution MS (HRMS), a Finnigan MAT 95 was used. All commercially available compounds were used as received. K_3PO_4 was ground with a mortar and flame dried.

3.1.1. 2-Bromo-6-methoxypyridine. To a stirred solution of 2,6-dibromopyridine (4.74 g, 20 mmol) in anhydrous MeOH (20 ml) was added NaOMe (2.16 g, 40 mmol) in anhydrous MeOH (8 ml) and the solution was refluxed for 24 h. The reaction mixture was poured into a cold aqueous 5% $NaHCO_3$ solution (40 ml), and extracted with ether (5× 10 ml). The organic layer was washed with brine (15 ml) and dried over Na_2SO_4. After evaporation of the solvent the remaining residue was purified by Kugelrohr distillation (2×10^{-2} mbar, 70 °C) to give the title compound (2.56 g, 68%) as a colorless liquid.

R_f=0.38 (hexane/EtOAc 9:1); IR (film) 2952, 1595, 1581, 1556, 1469, 1411, 1297, 1150, 1122, 1021, 855, 786; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 1H), 7.03 (d, J= 7.5 Hz, 1H), 6.66 (d, J=8.2 Hz, 1H), 3.92 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 163.7, 140.3, 138.6, 120.1, 109.3, 54.0; MS (EI) m/z (%) 189 (64), 188 (100), 187 (66), 186 (95), 160 (24), 159 (39), 158 (29), 157 (39), 108 (12), 93 (59), 78 (50), 76 (15), 65 (22), 64 (22), 53 (11), 76 (15), 65 (22), 64 (22), 53 (11), 51 (10), 50 (14), 39 (48), 38 (32), 37 (11); HRMS (ESI) calcd for $C_{27}H_{27}N_2$:186.9633, found 186.9631.

3.1.2. 6-Methoxypyridine-2-carbaldehyde (3d). To a solution of 2-bromo-6-methoxypyridine (2.56 g,

13.7 mmol) in anhydrous THF (50 ml) was added *n*-butyl lithium (1.6 M in THF, 8.9 ml, 14.2 mmol) at −78 °C and the solution was stirred for 1 h. DMF (1.18 ml, 15.2 mmol) was added dropwise, and the solution was stirred for 30 min at −78 °C. The cold solution was poured into an aqueous solution of 5% $NaHCO_3$ (130 ml) and extracted with ether (3×50 ml). The organic layer was dried over Na_2SO_4. After evaporation of the solvent the remaining residue was purified by column chromatography (3×12 cm, hexane/EtOAc 9:1) to give **3d** (1.0 g, 54%) as a colorless liquid.

R_f=0.68 (hexane/EtOAc 9:1); IR (film) 2986, 2954, 2828, 1720, 1702, 1599, 1473, 1331, 1274, 1219, 1028, 806, 779; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (m, 1H), 7.73–7.68 (m, 1H), 7.55–7.53 (m, 1H), 6.97–6.94 (m, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 164.4, 150.4, 139.0, 116.2, 115.4, 53.5; MS (EI) *m/z* (%) 137 (100), 136 (58), 108 (25), 107 (21), 94 (12), 93 (27), 80 (10), 79 (45), 78 (10), 66 (10), 65 (13), 52 (16), 51 (10), 39 (28), 38 (14); HRMS (EI) calcd for $C_7H_7NO_2$: 137.0478, found 137.0477.

3.1.3. 2-Bromo-6-formylpyridine (3e). A solution of *n*-butyl lithium (1.6 M in THF, 24.1 ml, 38.5 mmol) in toluene (30 ml) was cooled to −10 °C and *n*-butyl magnesiumbromide (2 M in THF, 10.95 ml, 21.9 mmol) was added dropwise. To this mixture was added a solution of 2,6-dibromopyridine (13 g, 55 mmol) in THF (40 ml). After stirring for 4 h at −10 °C the reaction mixture was poured into a solution of citric acid (21 g, 110 mmol) in water (45 ml), and extracted with MTBE (4×25 ml). The organic layer was dried over Na_2SO_4, and the solvent removed in vacuo. The remaining residue was purified by column chromatography (5×12 cm, hexane/EtOAc 10:1) followed by crystallization from MTBE/hexane to give **3e** (6.05 g, 60%) as colorless crystals.

R_f=0.45 (hexane/EtOAc 10:1); IR (KBr) 3040, 2872, 1732, 1574, 1436, 1413, 1291, 1213, 1120, 986, 856, 796; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99–9.98 (m, 1H), 7.92–7.90 (m, 1H), 7.76–7.70 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 191.6, 153.5, 142.6, 139.3, 132.6, 120.3; MS (EI) *m/z* (%) 187 (43), 185 (43), 159 (96), 158 (22), 157 (98), 156 (17), 78 (100), 77 (20), 76 (40), 75 (12), 52 (14), 51 (44), 50 (40), 29 (11); HRMS (ESI) calcd for C_6H_4BrO: 184.9476, found: 184.9474.

3.1.4. (*E*)-2,4,6-Trimethyl-*N*-((pyridin-2-yl)methylene)-benzenamine (4a). 2-Pyridinecarboxaldehyde (3.57 ml, 37.3 mmol) and 2,4,6-trimethylaniline (5.2 ml, 37.3 mmol) were dissolved in EtOH (50 ml) and heated to 90 °C for 30 min. Evaporation of the solvent in vacuo, followed by Kugelrohr distillation (2×10^{-2} mbar, 100–150 °C) of the remaining residue resulted in **4a** as a yellowish solid (7.5 g, 90%).

R_f=0.60 (EtOAc); IR (KBr) 3051, 2974, 2946, 2911, 2854, 1640, 1585, 1566, 1482, 1468, 1435, 1202, 1143, 876, 862, 770, 739; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (m, 1H), 8.35 (s, 1H), 8.29 (dt, *J*=1.0, 7.9 Hz, 1H), 7.84 (tdd, *J*=0.6, 1.7, 7.6 Hz, 1H), 7.41 (ddd, *J*=1.2, 4.9, 7.5 Hz, 1H), 6.91 (s, 2H), 2.31 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 154.6, 149.6, 147.8, 136.7, 133.4, 128.8, 126.8, 125.2, 121.2, 20.7, 18.2; MS (EI), *m/z* (%) 224 (69), 209 (100), 196 (9), 181 (6), 157 (20), 146 (36), 131 (17), 115 (6), 104 (8), 91 (18), 79 (20), 65 (8); HRMS (EI) calcd for $C_{15}H_{16}N_2$: 224.1313, found 224.1312.

3.1.5. (*E*)-2,4,6-Trimethyl-*N*-((6-methylpyridin-2-yl)-methylene)benzenamine (4b). Aldehyde **3b** (3.0 g, 24.8 mmol) and 2,4,6-trimethylaniline (3.5 ml, 24.8 mmol) were dissolved in EtOH (40 ml) and heated to 90 °C for 2 h. Evaporation of the solvent in vacuo, followed by Kugelrohr distillation (2×10^{-2} mbar, 100–140 °C) of the remaining residue resulted in **4b** as a yellow solid (5.3 g, 90%).

R_f=0.58 (EtOAc); IR (KBr) 3063, 2967, 2912, 2855, 1640, 1590, 1572, 1480, 1458, 1380, 1208, 1144, 987, 856, 837, 807, 732; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.10 (d, *J*=7.8 Hz, 1H), 7.72 (t, *J*=7.8 Hz, 1H), 7.26 (d, *J*=6.7 Hz, 1H), 6.90 (s, 2H), 2.65 (s, 3H), 2.31 (s, 3H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 158.3, 154.0, 147.9, 136.8, 133.2, 128.7, 126.8, 124.8, 118.2, 24.3, 20.7, 18.2; MS (EI), *m/z* (%) 238 (100), 223 (45), 196 (7), 157 (14), 146 (35), 131 (15), 119 (12), 103 (7), 93 (41), 77 (13), 65 (11); HRMS (ESIpos, CH_3OH and CH_2Cl_2) calcd for $C_{16}H_{19}N_2+H$: 239.1548, found 239.1550.

3.1.6. (*E*)-2,4,6-Trimethyl-*N*-((6-phenylpyridin-2-yl)-methylene)benzenamine (4c). 2-(6-Phenylpyridine)carboxaldehyde (2.9 g, 16.0 mmol) and 2,4,6-trimethylaniline (3.5 ml, 24.8 mmol) were dissolved in EtOH (25 ml) and heated to 90 °C for 1 h. Evaporation of the solvent in vacuo, followed by evaporation of the impurities by Kugelrohr distillation (2×10^{-2} mbar, up to 80 °C) resulted in **4c** as a yellow solid (4.8 g, 99%).

R_f=0.64 (EtOAc/hexane 1:1); IR (KBr) 3064, 3010, 2971, 2940, 2916, 2857, 1635, 1587, 1578, 1566, 1476, 1460, 1448, 1207, 1143, 850, 760, 685, 635; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J*=0.3 Hz, 1H), 8.27 (dd, *J*=1.1, 7.6 Hz, 1H), 8.10–8.08 (m, 2H), 7.91 (td, *J*=0.6, 7.8 Hz, 1H), 7.84 (dd, *J*=1.2, 7.8 Hz, 1H), 7.54–7.44 (m, 3H), 6.93 (s, 2H), 2.32 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.3, 154.5, 148.0, 138.9, 137.3, 133.3, 129.2, 128.8, 128.8, 127.0, 126.8, 121.9, 119.2, 20.7, 18.2; MS (EI), *m/z* (%) 300 (100), 285 (34), 155 (30), 144 (5), 131 (10), 91 (9), 77 (9); HRMS (EI) calcd for $C_{21}H_{20}N_2$: 300.1626, found 300.1629.

3.1.7. (*E*)-*N*-((6-Methoxypyridin-2-yl)methylene)-2,4,6-trimethylbenzenamine (4d). A solution of 2-methoxy-6-formylpyridine (**3d**) (831 mg, 6.0 mmol) and 2,4,6-trimethyl aniline (847 µl, 6.0 mol) in EtOH (13 ml) were refluxed for 4 h. The solvent was removed in vacuo and the residue purified by Kugelrohr distillation, yielding **4d** as yellow solid (1.59 g, 89%).

R_f=0.89 (hexane/EtOAc 9:1+1% NEt_3); IR (film) 3062, 3007, 2976, 2949, 2915, 2857, 1641, 1590, 1573, 1468, 1440, 1332, 1321, 1267, 1206, 1142, 1033, 987, 856, 841, 805, 731; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.17 (m, 1H), 7.86–7.84 (m, 1H), 7.73–7.68 (m, 1H), 6.89 (s, 2H), 6.86–6.83 (m, 1H), 3.99 (s, 3H), 2.29 (s, 3H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 163.6, 152.1, 148.1, 138.8, 133.2, 128.7, 126.8, 114.0, 112.5, 53.4, 20.7, 18.1; MS (EI) *m/z* (%) 255 (17), 254 (100), 253 (38), 238 (48),

196 (20), 195 (29), 146 (55), 145 (14),131 (18), 130 (11), 110 (18), 109 (25), 91 (16), 77 (12); HRMS (EI) calcd for $C_{16}H_{18}N_2O$: 254.1419, found 254.1421.

3.1.8. *N*-((6-Bromopyridin-2-yl)methylene)-2,4,6-trimethylbenzenamine (4e). A solution of 2-bromo-6-formylpyridine (2.96 g, 15.9 mmol) and 2,4,6-trimethyl aniline (2.24 ml, 15.9 mmol) in EtOH (30 ml) was refluxed for 4 h. The solvent was removed in vacuo and the residue purified by Kugelrohr distillation (2×10^{-2} mbar, 70–90 °C), yielding **4e** as yellow oil which solidifies upon standing (6.97 g, 88%).

R_f=0.82 (hexane/EtOAc 9:1); IR (KBr) 3065, 2912, 2854, 1645, 1550, 1478, 1440, 1334, 1206, 1123, 985, 853, 810; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.25 (dd, J= 7.7, 0.8 Hz, 1H), 7.68 (dd, J=7.8, 7.7 Hz, 1H), 7.59 (dd, J=7.8, 0.8 Hz, 1H), 6.90 (s, 2H), 2.29 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 155.7, 147.3, 141.7, 138.8, 133.7, 129.5, 128.8, 126.7, 119.6, 20.7, 18.1; MS (EI) *m/z* (%) 304 (30), 303 (16), 302 (30), 301 (12), 286 (3), 224 (18), 223 (100), 146 (66), 145 (14), 131 (20), 130 (11), 103 (9), 91 (13), 77 (11); HRMS (EI) calcd for $C_{15}H_{15}BrN_2$: 302.0419, found 302.0420.

3.1.9. Imidazolium bromide 5a. To a suspension of AgOTf (4.8 g, 18.7 mmol) in CH_2Cl_2 (50 mL) was added chloromethyl pivalate (2.78 mL, 18.7 mmol) and the resulting suspension was stirred for 45 min. After filtration the filtrate was added to pyridine imine **4a** (3.0 g, 13.4 mmol) and the solution was stirred in a sealed tube in the dark at 40 °C for 19 h. After the solution was cooled to rt MeOH (20 mL) was added, the solvent was removed in vacuo and the resulting oil was chromatographed on silica gel (2.5×10 cm, CH_2Cl_2/MeOH 50:1 to 10:1). The resulting foam was dissolved in CH_2Cl_2 (30 mL), NBu_4Br (6 g, 18.6 mmol) was added and the solution was stirred. After 2 h MTBE (100 mL) was added and the crystals were collected by filtration. Subsequent crystallisation from EtOH 2.75 g (53%, 7.1 mmol) of imidazolium triflate **5a** as colorless crystals.

R_f (of **5a**-OTf)=0.51 (CH_2Cl_2/MeOH 10:1); IR (KBr) 3070, 3045, 2992, 2917, 1649, 1607, 1537, 1497, 1449, 1212, 1158, 828, 763, 675; ^{1}H NMR (400 MHz, D_6-DMSO) δ 10.01 (d, J=1.0 Hz, 1H), 8.62 (dd, J=0.6, 7.1 Hz, 1H), 8.39 (s, 1H), 7.93 (d, J=9.2 Hz, 1H), 7.38 (dd, J=6.5, 8.8 Hz, 1H), 7.28 (td, J=0.9, 7.1 Hz, 1H), 7.18 (s, 2H), 2.35 (s, 3H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, D_6-DMSO) δ 140.7, 134.3, 131.7, 129.9, 129.4, 127.8, 125.4, 124.8, 118.5, 118.1, 114.8, 20.8, 17.0; MS (EI), *m/z* (%) 236 (59), 221 (16), 206 (7), 158 (100), 144 (14), 115 (7), 103 (5), 91 (6), 80 (9); HRMS (ESIpos, CH_3OH and CH_2Cl_2) calcd for $C_{16}H_{17}N_2$ (cation): 237.1391, found 237.1389.

3.1.10. Imidazolium bromide 5b. To a suspension of AgOTf (6.0 g, 23.5 mmol) in CH_2Cl_2 (60 mL) was added chloromethyl pivalate (3.5 mL, 23.5 mmol) and the resulting suspension was stirred for 45 min. After filtration the filtrate was added to pyridine imine **4b** (4.0 g, 16.8 mmol) and the solution was stirred in a sealed tube in the dark at 40 °C for 24 h. After the solution was cooled to rt EtOH (20 mL) was added, the solvent was removed in vacuo and the resulting oil was chromatographed on silica gel (3× 10 cm, EtOAc/MeOH 10:1 to 5:1). The resulting oil was dissolved in CH_2Cl_2 (90 mL), NBu_4Br (10.8 g, 33.6 mmol) was added and the solution was stirred. After 2 h the solvent was removed in vacuo. Subsequent crystallisation from EtOH/MTBE (1:4, 100 mL) gave 2.91 g (52%, 8.8 mmol) of imidazolium triflate **5b** as yellow/brown crystals.

R_f (of **5b**-OTf)=0.57 (CH_2Cl_2/MeOH 10:1); IR (KBr) 3131, 3115, 3064, 2986, 2969, 2914, 1659, 1561, 1505, 1482, 1455, 1317, 1224, 1200, 1157, 1084, 1039, 860, 811, 772, 752; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (m, 1H), 7.89 (d, J=1.7 Hz, 1H), 7.84 (d, J=9.3 Hz, 1H), 7.23 (m, 1H), 6.98 (s, 2H), 6.93 (t, J=0.9 Hz, 1H), 3.00 (s, 3H), 2.31 (s, 3H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 134.4, 134.0, 131.2, 130.9, 129.7, 126.5, 125.9, 117.0, 116.1, 114.5, 21.0, 19.9, 17.7; MS (ESIpos, CH_2Cl_2), *m/z* (%) 251 (100); HRMS (ESIpos, CH_3OH and CH_2Cl_2) calcd for $C_{17}H_{19}N_2$ (cation): 251.1548, found 251.1550. Anal. calcd For $C_{17}H_{20}BrN_2$: C, 61.64; H, 5.78; N, 8.46. Found C, 61.52; H, 5.72; N, 8.41.

3.1.11. Imidazolium bromide 5c. To a suspension of AgOTf (3.0 g, 11.7 mmol) in CH_2Cl_2 (30 mL) was added chloromethyl pivalate (1.75 mL, 11.7 mmol) and the resulting suspension was stirred for 45 min. After filtration the filtrate was added to pyridine imine **4c** (2.5 g, 8.3 mmol) and the solution was stirred in a sealed tube in the dark at 40 °C for 14 h. After the solution was cooled to rt EtOH (20 mL) was added, the solvent was removed in vacuo and the resulting oil was chromatographed on silica gel (3.5× 10 cm, CH_2Cl_2 to CH_2Cl_2/MeOH 10:1). The resulting oil was dissolved in CH_2Cl_2 (35 mL), NBu_4Br (5.0 g, 15.5 mmol) was added and the solution was stirred. After 12 h, the solvent was removed in vacuo and the resulting oil was chromatographed on silica gel (4×15 cm, EtOAc/MeOH 10:1 to 4:1). Subsequent crystallisation from CH_2Cl_2/MTBE (1:4, 100 mL) gave 1.52 g (47%, 3.9 mmol) of imidazolium triflate **5c** as colorless crystals.

R_f (of **5c**-OTf)=0.68 (CH_2Cl_2/MeOH 10:1); IR (KBr) 3065, 3029, 2998, 2916, 1651, 1608, 1549, 1491, 1448, 1154, 851, 806, 763, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J=1.1 Hz, 1H), 8.78 (d, J=1.8 Hz, 1H), 8.48 (d, J=9.3 Hz, 1H), 7.73–7.70 (m, 2H), 7.61–7.57 (m, 3H), 7.43 (dd, J=7.0, 9.3 Hz, 1H), 7.15 (dd, J=0.9, 7.0 Hz, 1H), 6.99 (s, 2H), 2.31 (s, 3H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 135.2, 133.9, 132.2, 131.3, 131.0, 130.6, 130.2, 129.7, 128.4, 125.8, 122.3, 119.6, 119.3, 117.6, 21.0, 17.7; MS (ESIpos, CH_2Cl_2), *m/z* (%) 313 (100); HRMS (ESIpos, CH_3OH and CH_2Cl_2) calcd for $C_{22}H_{21}N_2$ (cation): 313.1704, found 313.1699.

3.1.12. Imidazolium bromide 5d. To a suspension of AgOTf (2.06 g, 8 mmol) in CH_2Cl_2 (27 ml), chloromethyl pivalate (1.24 g, 8 mmol) was added and stirred in the dark for 45 min at rt. After filtration the filtrate was added to imine **4d** (1.46 g, 5.7 mmol) and stirred in the dark for 20 h at 45 °C. The solution was cooled to room temperature and quenched with EtOH (10 ml). The solvent was removed in vacuo and the resulting residue was purified by column chromatography (SiO_2, 2.5×12 cm, EtOAc/MeOH 9:1). Ion exchange with tetrabutylammonium bromide in CH_2Cl_2

and recrystallization from CH_2Cl_2/THF yielded **5d** (419 mg, 22%) as a greenish powder.

R_f=0.32 (EtOAc/MeOH 9:1); IR (KBr) 3058, 3031, 1656, 1555, 1374, 1281, 1200, 964, 854, 810, 772; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.65 (s, 1H), 8.17–8.07 (m, 1H), 7.69 (d, J=9.3 Hz, 1H), 7.43 (dd, J=7.6, 9.3 Hz, 1H), 7.10 (s, 2H), 6.59 (d, J=7.6 Hz, 1H), 4.28 (s, 3H), 2.38 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 147.1, 141.7, 132.1, 131.2, 134.1, 127.9, 122.3, 115.0, 110.5, 93.2, 129.7, 58.1, 20.9, 17.3; MS (ESI) *m/z* 267; HRMS (ESI) calcd for $C_{17}H_{19}N_2O$: 267.1497, found 267.1489.

3.1.13. Imidazolium bromide 5e. To a suspension of AgOTf (7.23 g, 28.14 mmol) in CH_2Cl_2 (100 ml) was added chloromethyl pivalate (4.24 g, 28.14 mmol), and the suspension was stirred in the dark for 45 min at rt. After filtration, the filtrate was added to imine **4e** (6.1 g, 20.1 mmol) and the solution was stirred in the dark for 17 h at 45 °C. The solution was cooled to room temperature and quenched with EtOH (40 ml). The solvent was removed in vacuo and the resulting residue was purified by column chromatography (SiO_2, 4.5×12 cm, CH_2Cl_2/MeOH 10:1). Ion exchange with tetrabutylammonium bromide in CH_2Cl_2 and recrystallization from CH_2Cl_2/diethyl ether yielded **5e** (4.3 g, 54%) as brownish crystals.

R_f=0.35 (CH_2Cl_2/MeOH 10:1); IR (KBr) 3053, 2974, 2914, 1646, 1523, 1307, 1297, 1184, 1154, 1037, 857, 812, 748, 648, 586; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94–9.91 (m, 1H), 8.76 (d, J=1.8 Hz, 1H), 8.48 (d, J=9.3 Hz, 1H), 7.47–7.45 (m, 1H), 7.24 (dd, J=9.2 Hz, 9.3 Hz, 1H, with $CHCl_3$), 6.99 (s, 2H), 2.31 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ?141.5, 133.8, 132.2, 130.8, 129.7, 126.1, 125.6, 123.1, 119.5, 118.4, 112.4, 21.0, 17.6; MS (ESI) *m/z* 315; HRMS (ESI) calcd for $C_{16}H_{16}N_2$: 315.0497, found 315.0499.

3.1.14. Imidazolium bromide 5f. A solution of imidazolium salt **5e** (793 mg, 2 mmol) and $Pd(PPh_3)_4$ (92 mg, 0.08 mmol) in 1,2-dimethoxyethane (8 ml) was degassed and stirred at room temperature for 30 min. To this suspension was added a solution of Na_2CO_3 (222.6 mg, 2.1 mmol) in degassed H_2O (2 ml) and 2-phenylvinylboronic acid (310 mg, 2.1 mmol). After 2.5 h, the reaction mixture was cooled to room temperature and water (10 ml) was added. The mixture was extracted with CH_2Cl_2 (5× 15 ml), and the organic layer was dried over Na_2SO_4. The solvent was removed in vacuo and the resulting residue was purified by column chromatography (SiO_2, 2.5×12 cm, CH_2Cl_2/MeOH 20:1) to give **5f** as a yellow solid (818 mg, 97%).

R_f=0.39 (CH_2Cl_2/MeOH); IR (KBr) 3400, 3030, 2919, 1647, 1623, 1535, 1497, 1449, 1198, 1155, 966, 852, 797, 753, 692; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 8.40 (d, J=15.8 Hz, 1H), 7.99–7.97 (m, 2H), 7.84–7.79 (m, 2H), 7.40–7.36 (m, 2H), 7.31–7.24 (m, 3H), 7.24–7.20 (m, 1H), 6.92 (s, 2H), 2.26 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.3, 135.7, 135.0, 133.9, 131.1, 129.6, 129.5, 128.8, 128.6, 127.2, 125.9, 117.3, 116.2, 114.1, 113.1, 131.2, 21.0, 17.7; MS (ESI) *m/z* 339; HRMS (ESI) calcd for $C_{24}H_{23}N_2$: 339.1861, found 339.1865.

3.1.15. 2-(Phenanthren-10-yl)-1,3,2-dioxaborolane. Magnesium turnings (1.94 g, 80 mmol) and a few crystals of iodine were heated with a heatgun. After cooling, a solution of 9-bromophenanthrene (12.8 g, 40 mmol) and ethyliodide (6.24 g, 40 mmol) in THF (40 ml) was added dropwise. After 1 h at room temperature this suspension was added dropwise to a solution of trimethylborate (8.31 g, 80 mmol) in THF (40 ml) at −78 °C. The reaction mixture was warmed to room temperature and the solvent removed in vacuo. To the resulting solid was added ethylene glycol (6.7 ml, 120 mmol) and toluene (120 ml). After refluxing overnight, toluene was removed in vacuo and the remaining solid recrystalized from CH_2Cl_2/MTBE, yielding the title compound as white crystals (7.01 g, 70%).

R_f=0.95 (CH_2Cl_2/MeOH) IR (KBr) 3053, 2982, 2905, 1444, 1402, 1384, 1328, 1267, 1212, 1028, 770, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86–8.80 (m, 1H), 8.75–8.67 (m, 2H), 8,46 (s, 1H), 7.95 (d, J=7.8 Hz, 1H), 7.75–7.57 (m, 4H), 4.51 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.0, 131.7, 130.6, 129.6, 129.1, 128.6, 127.6, 126.4, 126.2, 125.9, 122.3, 122.2, 65.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ ?33.2; MS (EI), *m/z* (%) 248 (100), 247 (25), 218 (4), 217 (8), 204 (16), 203 (7), 191 (10), 178 (5), 177 (6), 176 (9), 151 (4), 124 (4); HRMS (EI) calcd for $C_{16}H_{13}O_2B$: 248.1009, found 248.1011.

3.1.16. Imidazolium bromide 5g. A solution of imidazolium salt **5e** (300 mg, 0.756 mmol) and $Pd(PPh_3)_4$ (87.4 mg, 0.0756 mmol) in 1,2-dimethoxyethane (6 ml) was degassed and stirred at room temperature for 30 min. To this suspension was added a solution of Na_2CO_3 (84.2 mg, 0.794 mmol) in degassed H_2O (1.5 ml) and 2-(phenanthren-9-yl)-1,3,2-dioxaborolane (197 mg, 0.794 mmol). After 4 h at 80 °C the reaction mixture was cooled to room temperature and water (6 ml) was added. The mixture was extracted with CH_2Cl_2 (4×10 ml), and the organic layer was dried over Na_2SO_4. The solvent was removed in vacuo and the resulting residue was purified by column chromatography (SiO_2, 2.5×12 cm, CH_2Cl_2/MeOH 20:1) to give **5g** as a brownish solid foam (288 mg, 77%).

R_f=0.38 (DCM/MeOH 10:1) IR (KBr) 3382, 3145, 3056, 2955, 1653, 1553, 1450, 1311, 1187, 1153, 1039, 856, 809, 759, 729; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.96 (d, J=9.3 Hz, 1H), 8.82 (d, J=8.3 Hz, 1H), 8.74 (d, J= 8.3 Hz, 1H), 8.16 (s, 1H), 8.03–7.99 (m, 1H), 7.85–7.68 (m, 4H), 7.60–7.50 (m, 2H), 4.45–4.43 (m, 1H), 7.22 (d, J= 8.1 Hz, 1H), 6.90 (s, 2H), 2.25 (s, 3H), 1.96 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 141,8; 134,1; 134,0; 133,9; 132,1; 131,5; 131,4; 131,1; 131,0; 130,8; 129,7; 129,6; 129,6; 129,1; 128,1; 128,0; 127,9; 126,4; 126,0; 124,2; 124,2; 123,3; 122,9; 122,6; 120,9; 120,2; 118,0; 20,8; 17,3; 17,1; MS (ESI) *m/z* 413; HRMS (ESI) calcd for $C_{30}H_{25}N_2$: 413.2018, found 413.2019.

3.1.17. Imidazolium bromide 5h. A solution of imidazolium salt **5e** (595 mg, 1.5 mmol) and $Pd(PPh_3)_4$ (260 mg, 0.225 mmol) in 1,2-dimethoxyethane (12 ml) was degassed and stirred at room temperature for 30 min. To this suspension was added a solution of Na_2CO_3 (954 mg, 9 mmol) in degassed H_2O (3 ml) and 2,6-dimethoxyphenylboronic acid (819 mg, 4.5 mmol). After 18 h at

80 °C, more $Pd(PPh_3)_4$ (120 mg, 0.1 mmol), 2,6-dimethoxyphenylboronic acid (546 mg, 3 mmol) and Na_2CO_3 (636 mg, 6 mmol) were added to the reaction mixture. After heating for another 6 h at 80 °C, the reaction mixture was cooled to room temperature and water (10 ml) was added. The mixture was extracted with CH_2Cl_2 (5×15 ml), and the organic layer was dried over Na_2SO_4. The solvent was removed in vacuo and the resulting residue was purified by column chromatography (SiO_2, 2.5×12 cm, CH_2Cl_2/MeOH 10:1) to give **5h** as a brownish solid foam (462 mg, 68%).

R_f=0.25 (CH_2Cl_2/MeOH); IR (KBr) 3387, 3008, 2942, 2838, 1654, 1598, 1584, 1476, 1433, 1254, 1108, 783, 730; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (m, 1H), 8.50 (d, J=9.3 Hz, 1H), 8.36 (m, 1H), 7.51 (t, J=8.5 Hz, 1H), 7.39 (dd, J=9.3, 9.3 Hz, 1H), 7.12–7.10 (m, 1H), 7.00 (s, 2H), 6.7 (d, J=8.5 Hz, 2H), 3.77 (s, 6H), 2.33 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 141.4, 133.9, 133.5, 131.9, 131.1, 129.7, 128.7, 125.3, 123.0, 121.6, 119.4, 116.9, 107.1, 104.5, 56.0, 21.0, 17.3; MS (ESI) *m*/*z* 373; HRMS (ESI) calcd for $C_{24}H_{25}N_2O_2$: 373.1916, found 373.1920.

3.1.18. Synthesis of complex 7. A mixture of imidazolium triflate **5a** (100 mg, 0.26 mmol), $Pd(OAc)_2$ (23.2 mg, 0.10 mmol), NaI (62.2 mg, 0.41 mmol) and KO*t*Bu (31.4 mg, 0.28 mmol) in THF (7 ml) was stirred for 16 h at room temperature. The solvent was evaporated in vacuo and the remaining solid was purified by column chromatography (SiO_2, 1.5×15 cm, hexane/EtOAc 3:1) to give **7** (45 mg, 52%) as a yellow solid.

R_f=0.62 (EtOAc/hexane 1:1); IR (KBr) 3137, 3111, 3006, 2957, 2916, 2854, 1752, 1736, 1651, 1608, 1525, 1484, 1464, 1366, 1333, 1241, 1196, 1034, 855, 847, 744, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (m, 2H), 7.26–7.21 (m, 2H), 7.11 (s, 2H), 6.87 (s, 4H), 6.87–6.84 (m, 2H), 6.72–6.68 (m, 2H), 2.50 (s, 6H), 1.98 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 137.9, 135.5, 135.3, 131.3, 130.3, 129.1, 122.9, 116.8, 114.4, 111.8, 21.3, 20.8; MS (EI), *m*/*z* (%) 837 (1), 836 (2), 835 (1), 834 (3), 833 (2), 832 (4), 831 (3), 830 (1), 705 (32), 577 (9), 237 (100); HRMS (EI) calcd for $C_{32}H_{32}I_1N_4$: 705.0705, found 705.0704.

3.1.19. Synthesis of complex 8. $[Ir(COD)Cl]_2$ (60 mg, 0.09 mmol) and KO*t*Bu (25.3 mg, 0.23 mmol) were stirred for 10 min in THF (6 ml). Imidazolium bromide **5c** (73.9 mg, 0.19 mmol) was added and the reaction mixture was stirred for 1.5 h at room temperature. The solvent was removed in vacuo and the remaining solid was purified by column chromatography (SiO_2, 1×12 cm, hexane/EtOAc 3:1) to give **8** (96 mg, 77%) as a yellow solid. This material might contain a small amount of the corresponding chloro complex.

R_f=0.71 (EtOAc/hexane 1:3); IR (KBr) 3107, 3050, 2913, 2876, 2829, 1648, 1488, 1445, 1358, 1328, 1196, 1157, 1035, 780, 757, 710, 694.

3.1.20. Palladium complex 9. A solution of imidazolium salt **5f** (350 mg, 0.834 mmol) in THF (10 ml) was stirred with potassium *tert*-butoxide (86 mg, 0.77 mmol) for 1 h at room temperature. After addition of palladium allyl chloride dimer (134 mg, 0.348 mmol) and LiBr (183 mg, 2.1 mmol) the suspension was stirred for 3 h at room temperature. After evaporation of the solvent the remaining solid was purified by column chromatography (SiO_2, 2.5×10 cm, CH_2Cl_2/MeOH 95:5) to give **9** (326 mg, 83%) as a yellow solid.

R_f=0.95 (CH_2Cl_2/MeOH 10:1); IR (KBr) 3135, 3000, 2917, 1647, 1493, 1448, 1369, 1196, 1155, 956, 853, 782, 752, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, J=15.7 Hz, 1H), 9.26 (d, J=15.3 Hz, 1H), 7.74–7.65 (m, 4H), 7.41–7.24 (m, 10H), 7.08–6.71 (m, 10H), 4.80–4.66 (m, 1H), 4.66–4.52 (m, 1H), 4.04–3.91 (m, 2H), 3.52–3.38 (m, 2H), 2.88–2.79 (m, 1H), 2.70–2.60 (m, 1H), 2.38 (s, 3H), 2.33 (s, 6H), 2.24 (s, 3H), 2.17–2.11 (m, 1H), 2.03–1.96 (m, 1H), 1.85 (s, 6H); MS (ESI) *m*/*z* 485; HRMS (ESI) calcd for $C_{27}H_{27}N_2Pd$: 485.1208, found 485.1208.

3.1.21. Synthesis of a cationic complex from 9. A solution of complex **9** (40 mg, 0.0767 mmol) in CH_2Cl_2 (1 ml) was stirred with $AgSbF_6$ (27.7 mg, 0.081 mmol) in the dark for 1 h. The resulting suspension was filtered and the filtrate evaporated to dryness (40 mg, 73%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68–7.61 (m, 3H), 7.48–7.35 (m, 5H), 7.12–7.03 (m, 4H), 6.85–6.84 (m, 1H), 5.34–5.38 (m, 1H), 3.49–3.15 (m, 2H), 3.07–2.78 (m, 1H), 2.56–2.53 (m, 1H), 2.36 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H); MS(ESI) *m*/*z* 485.

3.2. General procedure for Suzuki–Miyaura cross-coupling

Preparation of the catalyst solution: in a glove box **5g** (24.7 mg, 0.025 mmol) and KO*t*Bu (5.6 mg, 0.025 mmol) were suspended in THF (0.6 ml) and stirred for 20 min. $[Pd(allyl)Cl]_2$ (9.7 mg, 0.0125 mmol) was added and the mixture was stirred for another 20 min at room temperature to give the catalyst solution.

To a vial containing the 2-methyl benzene boronic acid (0.7 mmol) and K_3PO_4 (1.5 mmol) in degassed dioxane (1.6 ml) was added the corresponding aryl halide (0.5 mmol), followed by addition of one half of the catalyst solution. After 16 h at 80 °C the solvent was removed in vacuo and the residue chromatographed on silica with hexane to give the biaryl product.

Note added in proof

In parallel to this work, the investigation of imidazo[1,5-*a*]pyridine derived NHCs has been reported by Lassaletta and co-workers: Alcarazo, M.; Roseblade, S. L.; Cowley, A. R.; Fernandez, R.; Brown, J. M.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3290.

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Supplementary data

Capillary electrophoresis plot for **5g** together with UV–vis spectra of the two atropisomers (peaks).

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.03.115

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5. Suitable crystals were obtained by recrystallization from methylenchloride/hexane (**5a**, **7** and **9**), ethanol/MTBE (**5b**) and MTBE/hexane (**8**). Data were recorded using an Enraf–Nonius KappaCCD diffractometer with graphite-monochromated Mo K_α-radiation ($\lambda=0.71073$ Å) and a rotating anode (FR 591) from the same manufacturer. The crystal was mounted on the tip of a glass fibre using viscous perfluoropolyether (Lancaster) and cooled in a stream of cold nitrogen gas. The structures were solved by direct methods (SHELXS-97; G.M. Sheldrick, Program for the determination of crystal structures, University of Göttingen, Germany, 1997) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97; G.M. Sheldrick, Program for least-squares refinement of crystal structures, University of Göttingen, Germany, 1997). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. Crystallographic data for **5a**: $C_{16}H_{17}BrN_2$, $M_r=317.23$ g mol^{-1}, colorless, crystal size $0.10\times0.09\times0.08$ mm, orthorhombic, *Fddd* [No. 70], $a=9.2195(2)$, $b=15.2969(4)$, $c=42.5886(11)$ Å, $V=6006.3(3)$ Å^3, $Z=16$, $D_{calc}=1.403$ mg m^{-3}, $\mu=2.726$ mm^{-1}, $T=100$ K, 26,654 reflections collected, 1546 independent reflections, 1499 reflections with $I>2\sigma(I)$, $\theta_{max}=26.43$(, Gaussian absorption correction (T_{min} 0.79/T_{max} 0.84), 91 refined parameters, $R=0.019$, $R_w=0.086$, $S=1.415$, largest diff. peak and hole$=0.4/-0.6$ e Å^{-3}. Crystallographic data for **5b**: $C_{17}H_{19}BrN_2$, $M_r=331.25$ g mol^{-1}, colorless, crystal size $0.21\times0.19\times0.05$ mm, monoclinic, $P2_1/n$ [No. 14], $a=9.49180(10)$, $b=12.3577(2)$, $c=13.2973(2)$ Å, $\beta=94.8220(10)°$, $V=1554.21(4)$ Å^3, $Z=4$, $D_{calc}=1.416$ mg m^{-3}, $\mu=2.637$ mm^{-1}, $T=100$ K, 43,271 reflections collected, 5929 independent reflections, 5048 reflections with $I>2\sigma(I)$, $\theta_{max}=33.2°$, Gaussian absorption correction (T_{min} 0.61/T_{max} 0.88), 185 refined parameters, $R=0.031$, $R_w=0.095$, $S=0.967$, largest diff. peak and hole$=0.5/-0.5$ e Å^{-3}. Crystallographic data for **7**: $C_{32}H_{32}I_2N_4Pd$, $M_r=832.82$ g mol^{-1}, yellow, crystal size $0.30\times0.09\times0.05$ mm, orthorhombic, *Pbca* [No. 61], $a=15.40640(10)$, $b=14.49290(10)$, $c=27.6507(2)$ Å, $V=6173.94(7)$ Å^3, $Z=8$, $D_{calc}=1.792$ mg m^{-3}, $\mu=2.629$ mm^{-1}, $T=100$ K, 72,369 reflections collected, 7659 independent reflections, 6531 reflections with $I>2\sigma(I)$, $\theta_{max}=28.30°$, Gaussian absorption correction (T_{min} 0.51/T_{max} 0.88), 358 refined parameters, $R=0.024$, $R_w=0.056$, $S=1.003$, largest diff. peak and hole$=0.7/-0.6$ e Å^{-3}. Crystallographic data for **8**: $C_{30}H_{32}BrIrN_2$, $M_r=692.69$ g mol^{-1}, orange, crystal size $0.16\times0.14\times0.14$ mm, orthorhombic, *Pbca* [No. 61], $a=12.78330(10)$, $b=17.9798(2)$, $c=21.8389(2)$ Å, $V=5019.48(8)$ Å^3, $Z=8$, $D_{calc}=1.833$ mg m^{-3}, $\mu=6.934$ mm^{-1}, $T=100$ K, 50,356 reflections collected, 5765 independent reflections, 4604 reflections with $I>2\sigma(I)$, $\theta_{max}=27.50°$, Gaussian absorption correction (T_{min} 0.46/T_{max} 0.53), 307 refined parameters, $R=0.032$, $R_w=0.149$, $S=1.139$, largest diff. peak and hole$=1.4/-1.7$ e Å^{-3}. Crystallographic data for **9**: $C_{27}H_{27}BrN_2Pd$, $M_r=565.82$ g mol^{-1}, yellow, crystal size $0.13\times0.09\times0.06$ mm, monoclinic, $P2_1/n$ [No. 14], $a=7.76490(10)$, $b=19.3896(2)$, $c=15.7751(2)$ Å, $\beta=93.0000(10)°$, $V=2371.82(5)$ Å^3, $Z=4$, $D_{calc}=1.585$ mg m^{-3}, $\mu=2.484$ mm^{-1}, $T=100$ K, 54,264 reflections collected, 5442 independent reflections, 5119 reflections with $I>2\sigma(I)$, $\theta_{max}=27.50°$, Gaussian absorption correction (T_{min} 0.88/T_{max} 0.95), 280 refined parameters, $R=0.052$, $R_w=0.175$, $S=1.147$, largest diff. peak and hole$=2.2/-3.5$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 256664 (**7**), CCDC 256665 (**5b**), CCDC 256666 (**8**), CCDC 256667 (**5a**), CCDC 256668 (**9**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 144-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
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