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Influence of pyrido-annulation on *N*,*N*′-dineopentyl-imidazolin-2-ylidene and associated transition metal complexes; comparison with benzo-, naphtho- and quinoxalino-annulation

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ABSTRACT

The syntheses of isolable *N*,*N*′-dineopentyl-substituted non- and pyrido-annulated imidazolin-2-ylidenes and selected Ag, Rh and Pd complexes thereof, in part earlier communicated, are now reported in full detail. The compounds were structurally characterized by multinuclear NMR and in part by crystal structure analyses. Diagnostic structural and NMR data were compared with those of analogously *N*,*N*′-dineopentyl-substituted benzo-, naphtho- and quinoxalino-annulated compounds, and the influence of the annulation was tested by L/Pd-and L_2/Pd-catalyzed Suzuki-Miyaura couplings of $PhB(OH)_2$ with *p*-bromotoluene.

1. Introduction

The chemistry of *N*-heterocyclic carbenes (NHCs) has attracted considerable attention in the last two decades. After the initially investigations of imidazol-2-ylides (imy), a variety of related annulated systems and their complexes were studied [1,2]. The exceptionally high interest in the NHCs is attributed to their multiple use as nucleophilic reagents, organocatalysts or ligands for main group elements, f-block and, in particular, transition metal compounds and catalysts. Examples are NHC silver complexes, applied in transmetalation reactions, catalysis and medicinal chemistry [3] and Rh or Pd NHC complexes, allowing a broad spectrum of homogenous transition-metal catalyzed organic transformations [2–5]. Furthermore, various transition-metal NHC complexes were found to be useful in medicinal chemistry [6] or material sciences [7].

We studied a variety of annulated imidazole-2-ylidenes (Chart 1) [8,9] as part of long-standing investigations of carbo- and heterocyclically annulated π-excess-aromatic *N*-heterocycles with (p-p)π-bonded heavier main group elements (As, P [10]; Si, Ge, Sn [11]). Results for non- and *N*-pyrido-annulated imidazolin-2-ylidenes and some complexes thereof were partly communicated earlier with a focus on the different electronic structure of pyrido-annulated *N*-heterocyclic carbenes and silylenes [9]. This final report will provide a detailed description of the syntheses, structure, screening in a Suzuki-Miyaura test-coupling and comparison of the results with those of closely related benzo- [12], naphtho-, quinoxaline and phenanthrene-annulated NHCs [8] to illustrate the influence of annulation.

2. Results and discussion

2.1. Syntheses

For comparison with our previously studied annulated NHC

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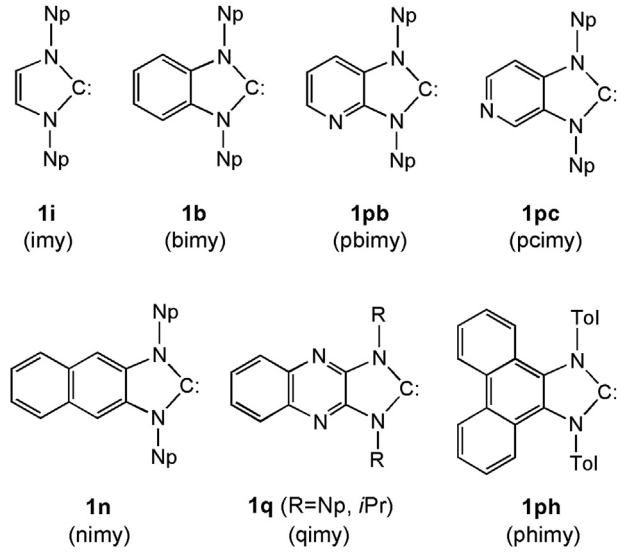
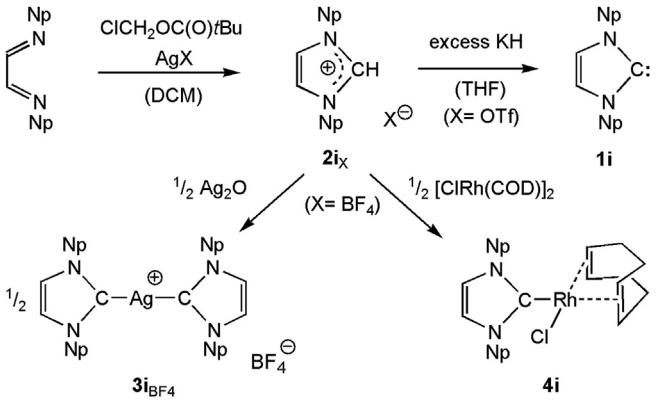


Chart 1. Types of non-, carbo- and heterocyclically annulated imidazole-2-ylidenes **1**, included in our studies [8,9].

systems, we focussed on *N,N′*-dineopentyl-substituted compounds. These are advantageous because of the facile accessibility of the precursors, significant steric stabilization of the benzo- [12a] and naphtho[b]-annulated [8a] NHCs as monomers and, last but not least, by straightforward NMR reaction monitoring and product identification. Attempts to synthesize non-annulated dineopentylimidazolium salts did not succeed by classic procedures, such as bis-alkylation of sodium imidazolide with neopentyl bomide in DMF, or by one-pot condensation of the primary amine $NpNH_2$ with glyoxal and formaldehyde [13]. However, a protocol introduced by Glorius et al. for the synthesis of bis-oxazoline-annulated imidazolium salts [14] allowed us to obtain **2i$_{OTf}$** and **2i$_{BF4}$** in reasonable yields (ca. 70%) by reaction of glyoxal bis(neopentylimine) [15] with AgOTf or $AgBF_4$ and chloromethyl pivalate. Conversion of **2i$_{OTf}$** with excess KH in THF and of **2i$_{BF4}$** with Ag_2O and $[Rh(COD)Cl]_2$ in CH_2Cl_2 (DCM) led to the dineopentylimidazolin-2-ylidene **1i** and its silver and rhodium complexes **3i$_{BF4}$** and **4i**, respectively (Scheme 1).

The pyrido[b]- and pyrido[c]-annulated imidazolium salts **2pb$_{PF6/Cl}$** and **2pc$_{PF6/Cl}$** were obtained in the classic way by heating the corresponding diaminopyridines with triethylorthoformate in the presence of NH_4PF_6 or NH_4Cl, and allowing ethanol to distill off. Reaction of the hexafluorophosphates **2pb$_{PF6}$** and **2pc$_{PF6}$** with excess potassium hydride (at least 2 equivalents) in dry THF under strictly inert conditions provides a high-yield (90–95%) access to



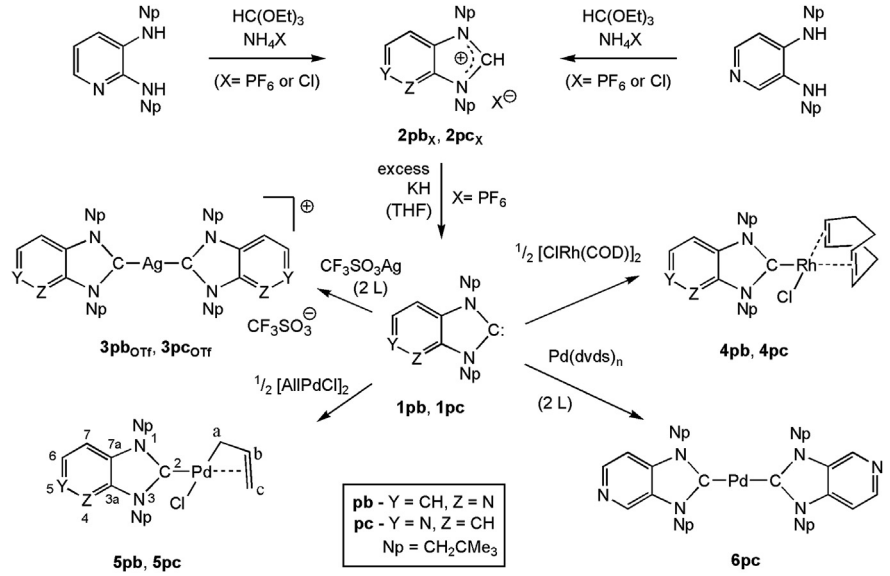
Scheme 1. Synthesis of Np_2imy salts **2i$_{OTf/BF4}$**, **1i** and the complexes **3i$_{BF4}$** and **4i**.

the pyridoimidazolin-2-ylidenes **1pb** and **1pc**. Both carbenes are monomeric at r.t., without noticeable interactions between the N-donor atom of the pyridine ring and the divalent carbon atom. The thermal stability is sufficient to allow distillation of the colorless oils under vacuum without detectable decomposition. Thus they differ from their higher homologues with more electropositive group 14 elements, which are less stable as monomers [16]. Nevertheless they are highly reactive and very sensitive to moisture or air. For this reason it is more convenient to use the crude carbenes for application in further reactions immediately after separation from excess KH and insoluble potassium salts. The free carbenes **1 pb** and **1pc**, crude or distilled, are suitable for direct conversion with various transition metal compounds. Examples are the reactions with ionic silver salts such as AgO_3SCF_3 or with μ-chloro-bridged complexes such as $[Rh(1,5\text{-}COD)Cl]_2$ and $[Pd(Allyl)Cl]_2$ in THF, or replacement of the labile π-donor/acceptor-ligands from $Pd(dvds)_n$ (8–10% Pd, dvds = divinyltetramethyldisiloxane) in hexane, leading to **3pb$_{OTf}$** and **3pc$_{OTf}$**, **4pb** and **4pc**, **5pb** and **5pc**, and **6pc** (Scheme 2). In the reaction of **1pb** and **1pc** with $[Rh(PPh_3)_2(CO)Cl]$, the replacement of one Ph_3P ligand was strongly preferred but was accompanied by competing slow replacement of Cl as a minor side reaction [9a].

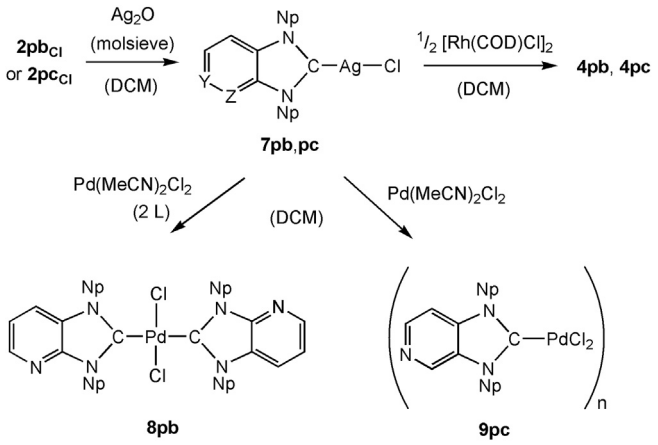
Alternative routes to transition metal complexes of **1pb** and **1pc** are realized via the synthesis of the AgCl complexes **7pb** and **7pc**, readily available from the pyridoimidazolium chlorides **2pb$_{Cl}$** and **2pc$_{Cl}$** by reaction with Ag_2O in the presence of a molecular sieve (according to the protocol of Wang and Lin [17]) and subsequent transmetalation in DCM. Examples are the conversions with $[Rh(1,5\text{-}COD)Cl]_2$ or with $Pd(MeCN)_2Cl_2$ to **4pb** and **4pc** or to **8pb** and **9pc**, respectively (Scheme 3).

In all these complexes, the transition metal coordinates at the nucleophilic NHC carbene center, as shown by the upfield coordination chemical shifts of the $^{13}C(II)$ nuclei in the $^{13}C\{^1H\}$ solution NMR spectra (Table 1) and in the solid state by crystal structure analyses of **3pb$_{OTf}$**, **4pb**, **4pc**, **7pb** and **7pc**.

Almost all of the complexes were readily soluble in CD_2Cl_2, $CDCl_3$ or d_8-THF. Only **9pc** was insoluble in these solvents and sparingly soluble even in DMSO-d_6. Single crystals that would have provided more direct information on its structure and possible coordinative interactions of the pyridine N-atom could therefore not be obtained. For evaluation of effects of the pyridine N-atom on structural data and properties of pyrido-imy compounds, the benzannulated carbene **1b** and a few benzanellated complexes were included in the comparison. The new compounds **5b**, **8b** and **10/11b** were prepared by transmetalation of the bimy-AgCl complex **7b** [8b] with appropriate Pd-precursor complexes (Scheme 4). The transmetalation of **7b** with palladium acetate in a 2:1 M ratio (referred to monomer formula unit) led to a mixture of two bimy-$Pd(OAc)_2$ complexes **10b** and **11b**, characterized by ^1H and ^{13}C NMR data with typical chemical shifts for C^{II} and COO^-, $\delta^{13}C = 181.58$, 183.75 (C^{II}, integral 5:3), 175.73, 175.80 (CO), and with the HRMS isotopic pattern of the $[Pd(\mathbf{1b})_2(OAc)]^+$ cation. However, separation and/or growing single crystals for structure proof by XRD have so far failed. A literature report on related compounds suggests facile isomerization and control of the *cis*/*trans*-preference by steric factors. Thus, for the reaction of the *trans*-$(R_2bimy)_2PdX_2$ complexes (R = Me, X = I and R = *i*Pr, X = Br) with two equivalents AgOAc in acetonitrile, rapid isomerization of the initially formed *trans*-$(Me_2bimy)_2Pd(OAc)_2$ to the thermodynamically more stable *cis*-isomer was observed, whereas for the more bulky $(iPr_2bimy)_2Pd(OAc)_2$ a final *trans*/*cis*-ratio of 3.5:1 was determined by ^1H NMR spectroscopy. The major *trans*-isomer, also characterized by crystal structure analysis, displays only one set of signals for the *N*-isopropyl group, indicating free rotation around the Pd-C^{II} bonds [18]. The same behavior was observed for the *N*-neopentyl signals



Scheme 2. Syntheses of **1pb** and **1pc** and direct conversion to Ag, Rh and Pd complexes.



Scheme 3. Synthesis and transmetallation reactions of **7pb** and **7pc**.

of **10b**, assigned as the *trans*-isomer, whereas AB-splitting of the NCH_2 protons of **11b** hint at the *cis*-isomer.

2.2. Structural aspects

The electronic structure of the pyrido[b]-, pyrido[c]- and benzimidazolin-2-ylidenes **1pb**, **1pc** and **1b** was determined by He(I)-photoelectron studies and correlation of the experimental IP_v values with calculated ionization potentials (ROVGF/cc-pVDZ on geometries optimized at the B3LYP/cc-pVTZ level of theory) of the respective *N,N′*-di-*tert*-butyl substituted model compounds [9b]. These studies reveal that the C-lone pair occupies the HOMO (IP_v exp./calc. 7.9/7.72, 8.0/7.83, 7.9–8.5(superimp.)/7.57 eV), while the pyridine N-lone pair of **1pb** and **1pc** is much lower in energy (HOMO-3) and requires higher energies for ionization (IP_v exp./calc. 9.65/9.53, 9.3/9.53 eV) and interactions with empty orbitals of electrophiles. This may explain the strongly preferred coordination of the transition metals at carbon.

2.2.1. Crystal structures

XRD analyses of **3pb**, **4pb**, **4pc**, **7pb** and **7pc** (Figs. 1–5) give detailed information on the molecular structures of these pbimy and pcimy complexes, and also on interactions between neighboring molecules. The complexes **4pb** and **4pc** are not isotypic, nor are **7pb** and **7pc**. For the LAgCl complexes **7pb** and **7pc** μ-chloro-bridged dimers were observed. A short HLN# contact (2.57 Å) was observed in **7pc** (C4-H4LN5), whereas other short distances to neighboring molecules in **4pb** and **4pc** and in **7pb** and **7pc** were observed mainly between C-H groups and the chloro ligands. Coordinative interactions between the pyridinic N atom and the transition metal of neighboring molecules were not present in these complexes.

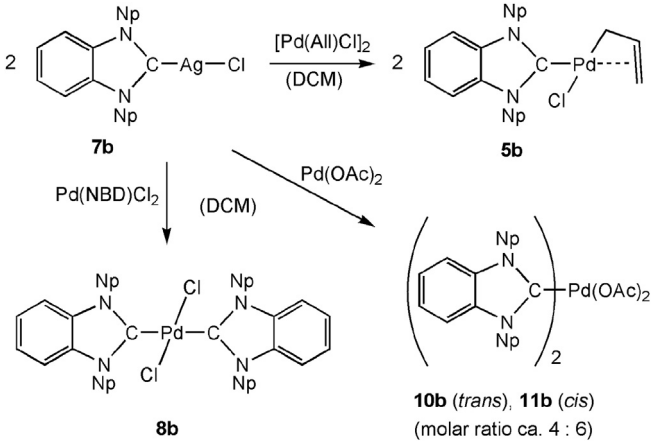
The cationic silver complex **3pb** contains two formula units and one molecule of DCM in the asymmetric unit. Both cations display linear coordination at the metal (176.85(18), 178.33(17) °), typical for more spatially demanding ligands, but differ in their structural parameters and adopt different ligand interplanar angles of ca. 61° and 6° (Fig. 1, left and right respectively). The Ag-C(II) bonds (2.106(5)-2.118(5) Å) are slightly longer than in the cationic $[(IMes_2)_2Ag]CF_3SO_3$ complex (2.067, 2.078 (4) Å) [19] and in the carbocyclically annulated LAgCl complexes **7b** (2.0845(14) Å, [8b]) and **7n** (2.079(3) Å [8a]) (see below), but comparable with those of the pyrido-annulated AgCl complexes **7pb** and **7bc**. The N-C^{II} bonds of **3pb** are on average slightly longer (1.364(6)) than in the annulated LAgCl complexes of type **7** (average ca. 1.355 Å [8a,b]). Crystals of the complex **3pc** were also studied; an analogous structure was confirmed qualitatively but disorder, particularly of the anion, did not allow a detailed analysis.

The Rh-Cl and Rh-C^{II} bonds of **4pb** are slightly longer than those of **4pc** and also of the analogous quinoxalino-annulated complex **4q**, whereas the bond lengths and angles within the ligands alter only slightly for the different complexes, even with other metals (Table 1). Within the five-membered ring the N-C^{II} bonds are shorter than the N-C bonds to the bridging carbon atoms, indicating an increased N-C double bond character in the diaminocarbene substructure, though less than that of C-N-C in the pyridine ring. The N-C^{II}-N and other angles in the five-membered ring are controlled by the ring size and thus considerably smaller than typical values for sp^2 hybridization in acyclic or six-membered ring structures. The rhodium atom in the complexes **4pb** and **4pc** exhibits the typical slightly distorted square-planar coordination, involving the centers of the two C=C bonds of 1,5-COD, chloride

Table 1
Selected bond lengths (Å), angles and torsion angles (°) for **3pb**, **4pb**, **4pc**, **7pb** and **7pc** and comparison with related carbo- or heterocyclically annulated imidazolin-2-ylidene complexes.[a]

Compd.	M-Cl; M-C^{II}; C^{II}-M-Cl	C^{II}-N; N-C^{II}-N	C_{bridge}-N; C-$N_{pyr(average)}$	C^{II}-M-C_{trans}; C^{II}-M-*Cent*;abs. N1-C^{II}-M-Cl
3pb	-; 2.106(5), 2.118(5), 2.106(5), 2.116(5); –	1.350(6) - 1.377(6); 105.5(5) – 107.0(4)	1.383(6) – 1.398(6); 1.332(6) – 1.345(8)	176.85(18), 178.33(17); –
4pb	2.4042(6); 2.032(2); 86.17(6)	1.375(3), 1.374(3); 105.77(18)	1.394(3), 1.389(3); 1.340(3)	156.69(9), 167.19(9); 91.5; 105.2(2)
4pc	2.3773(5); 2.0269(18); 96.22(5)	1.372(2), 1.383(2); 106.06(15)	1.383(2) 1.393(2); 1.346(3)	159.66(8), 162.91(8); 89.0; 106.74(14)
4q [9a]	2.3756(9); 1.998(3); 91.08(8)	1.395(3), 1.381(3); 107.2(2)	1.375(3), 1.393(3); 1.344	158.36(12), 164.97(11); 90.3; 99.8
7pb	2.3863(14);[b] 2.106(5); 164.69(14), Cl#1 106.88(14)	1.361(6), 1.349(6); 106.2(4)	1.388(6), 1.395(6); 1.339(7)	-; -;
7pc	2.3770(7);[c] 2.107(3); 166.94(8), Cl#1 100.75(8)	1.358(4), 1.351(4); 106.3(3)	1.391(4), 1.395(4); 1.346(4)	-; -;
7b [8b]	2.3356(4); 2.0845(14); 175.88(4)	1.3572(18), 1.3586(17); 106.21(12)	1.3921(18), 1.3956(18); –	-; –
7n [8a]	2.3178(7); 2.079(3); 176.56(7)	1.351(3), 1.355(3); 107.1(2)	1.403(3), 1.401(3); –	-; –

[a] C^{II} is C2; C_{bridge} is C3A or C7A; N_{pyr} is N4 or N5; N without suffix are the carbenic nitrogens N1 and N3; *Cent* is the midpoint of the coordinated double bond *cis* to the chlorine.
[b] Cl-bridged dimer: Ag-Cl#1 2.9729(15) Å, Cl-Ag-Cl#1 88.05(4), Ag-Cl-Ag#1 91.95(4)°.
[c] Cl-bridged dimer: Ag-Cl#1 3.0180(7) Å, Cl-Ag-Cl#1 92.06(2), Ag-Cl-Ag#1 87.94(2)°.



Scheme 4. Transmetalation of **7b** [8b] to **5b**, **8b** and **10b/11b**.

and C^{II} of the carbene; the coordination plane is approximately perpendicular to the NHC ring plane (Figs. 2 and 3; interplanar angles 70° for **4 pb** and 83° for **4pc**). The asymmetry within the ligand (position of the pyridine-N) and the coordination planes (*cis*-Cl/COD) might imply the presence of two isomers. The fact that only one is observed in the solid state is probably associated with a low barrier to rotation around the C2-Rh axis and crystallization of the more stable form. Also the orientation of the CMe_3 termini of the neopentyl groups (CH_2 lies in the ring plane) could be different, allowing two rotamers. **4 pb** displays the rotamer with one CMe_3 above, the other below the ring plane, whereas in **4pc** both CMe_3 groups are on the same side, thus conveying (very) approximate mirror symmetry on the molecule.

The NHC ligands affect the coordination geometry of the 1,5-COD ligand. The C=C bond *trans* to C(II) (1.365(3), 1.367(3) Å) is significantly shorter than *cis*-C=C (1.399(3), 1.401(4) Å) and indicates, together with longer *trans*-C=C/Rh distances (2.198(2), 2.202(2) for **4 pb** and 2.214(2), 2.242(2) Å for **4pc**) than *cis*-C=C/Rh (2.108(2), 2.123(2) and 2.1056(19), 2.1184(18) Å), a strong *trans*-influence of the pyrido-imy ligands. The more electron-withdrawing and π-acidic cationic pyridine-*N*-methylated $[Ir(NMe\text{-}\mathbf{4pb})(COD)Cl]^+$ complex [1f] exhibits similar values for the *trans*-C=C and *trans*-C=C/Rh bond lengths, whereas the *cis*-C=C (1.416(6) Å) and *cis*-C=C/Rh bonds (2.118(4), 2.149(4) Å) are slightly lengthened. This trend for the C=C/Rh bonds is observed also in the quinoxaline-annulated LRh(COD)Cl complex **4q** (*trans* 2.206(3), 2.253(3); *cis* 2.125(3), 2.155(3) Å) [9a]. The largely unchanged *trans*-influence but weakening of the *cis*-C=C/Rh and the C(II)-N bonds with π-bonding contributions might be accounted for in terms of Rh-C^{II} (d-π^*)π-back bonding and repulsion of π-density from the C^{II}-N bonds towards the pyridine ring. Unfortunately, no crystallographic data could be obtained for the analogous non-annulated rhodium complex **4i**.

The silver chloride complexes **7pb** and **7pc** differ from the strictly monomeric and almost linear benzo- and naphtho-annulated complexes **7b** and **7n** (C-Ag-Cl 175.88(4), [8b] 176.56(7)° [8a]) by formation of weakly associated dimers, at least in the crystal (Figs. 4 and 5). The polarity of the π-density within

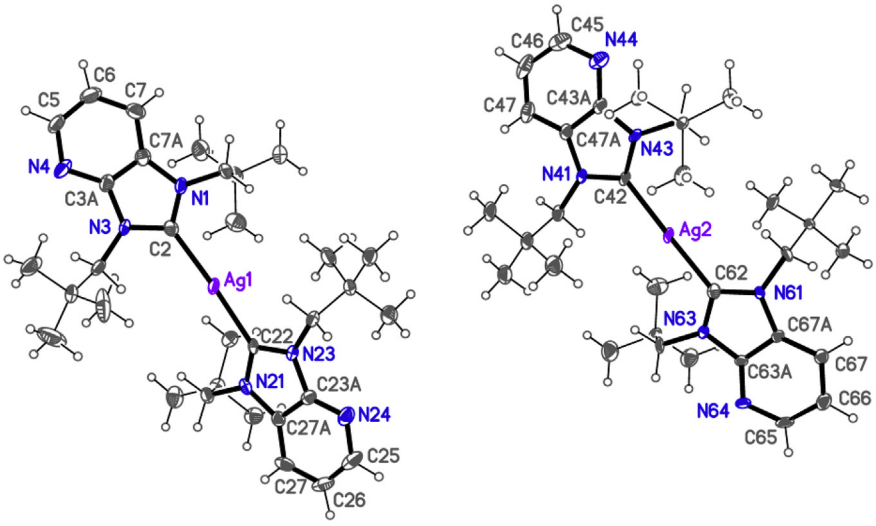


Fig. 1. The two independent cations of **3pb** in the crystal (ellipsoids with 50% probability).

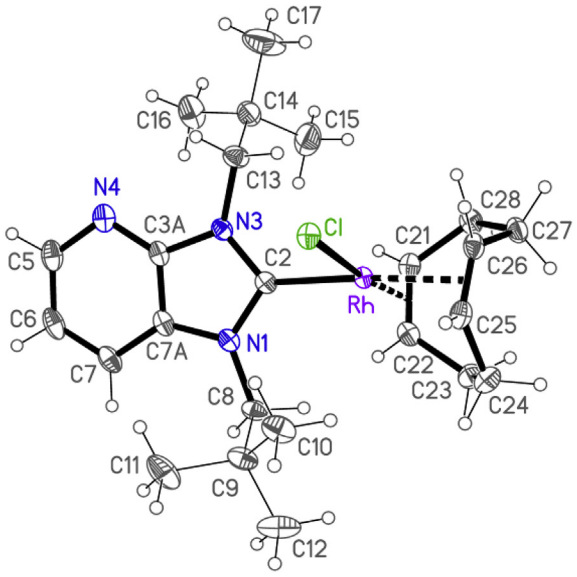


Fig. 2. Molecular structure of **4pb** in the crystal (ellipsoids with 50% probability).

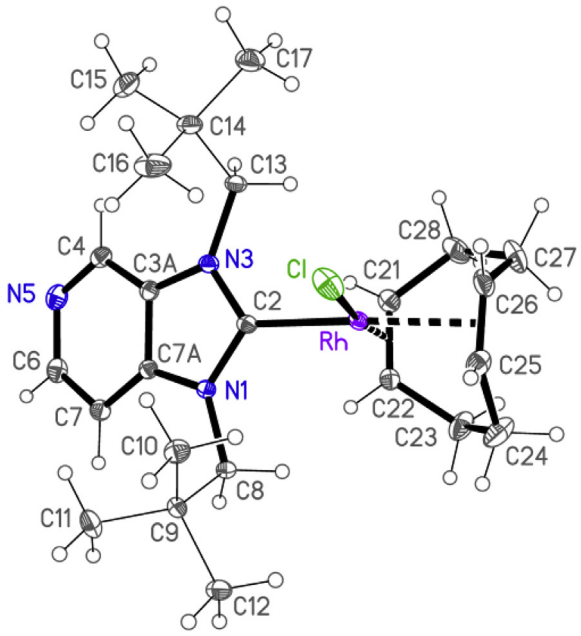


Fig. 3. Molecular structure of **4pc** in the crystal (ellipsoids with 30% probability).

the ring plane, caused by the pyridine-N atom, seems to favor a slight bending of Cl away from the C(II)-Ag axis and dimerization to an Ag_2Cl_2 rhombus with a slightly lengthened polar covalent and a greatly lengthened coordinative Ag-Cl contact (bond lengths and angles see Table 1). The planar five-membered ring of **7pb**, average deviation 0.01 Å, adopts in the crystal an interplanar angle of 57° towards the Ag_2Cl_2 plane (58° in **7pc**) The packing of **7pc** also involves the short intermolecular contacts H7LCl 2.71 and H4LN5 2.57 Å. The benzanellated **7b** under the same conditions involves stabilization of the monomer by a weak ClLH hydrogen bond to CH_2Cl_2 and displays a completely different packing involving single molecules [8b]. The naphtho-anellated complex **7n** shows in the packing a pairwise π-stacking arrangement with the AgCl groups at opposite ends [8a]. It is well known that NHC-AgCl complexes, depending on the substituents, adopt various structure types [20], also structures with $(NHC)_2Ag^+$ and $AgCl_2^-$ units, whose ^{13}C NMR spectra display a broad singlet instead of doublets of doublets. In this context it should be mentioned that **7pc** shows a broadened

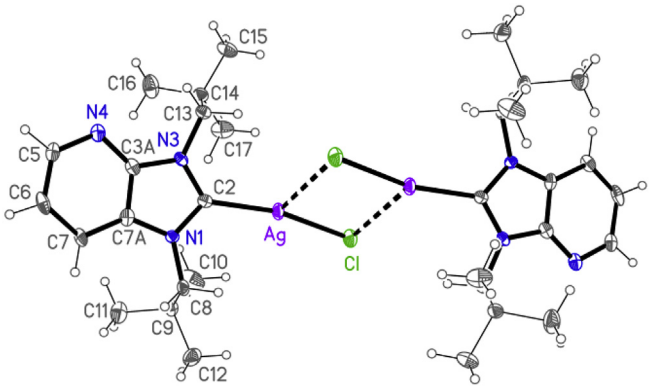


Fig. 4. An inversion-symmetric dimer in the structure of **7pb** in the crystal (ellipsoids with 50% probability).

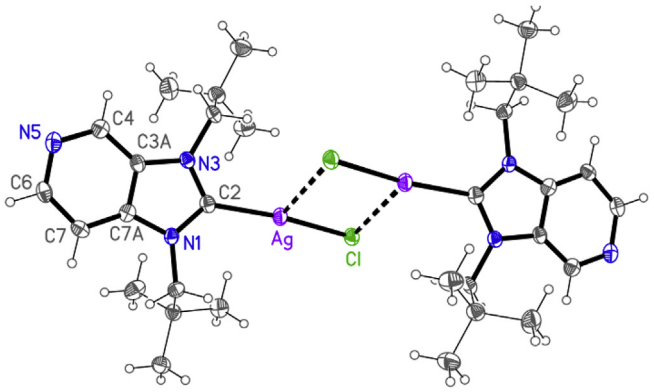


Fig. 5. An inversion-symmetric dimer in the structure of **7pc** in the crystal (ellipsoids with 50% probability).

doublet of doublets for C(II) with a markedly decreased Ag-C coupling constant, which hints at stronger intermolecular interactions in **7pc** than in **7pb**.

2.2.2. Solution NMR characterization

The molecular structures of the pyridoimidazolium salts, the pyridoimidazolin-2-ylidenes and their complexes in solution were confirmed by conclusive $^{13}C\{^1H\}$ and proton solution NMR data. The most typical feature of the "free" carbenes **1 pb** and **1pc** is their strong C^{II} downfield shift [21]. This increases within the series of related carbenes **1i** < **1ph** < **1b** < **1pb** < **1pc** < **1n** much more strongly than $\delta^{13}C(H)$-2 of their azolium precursors (*cf.* Table 2), particularly with linear extension of the annulated π-system and inclusion of electron-withdrawing σ^2N-atoms, whereas the effect of phenanthrene-annulation [8d,22], with a Y-shaped π-system, is much smaller. This may be attributed to a push-pull polarization of π-density diminishing at the $N_2C(II)$-end in favor of the annulated heterocycle at the opposite end. Driving forces are σ/π-electron repulsion at C(II) and electron withdrawal by the annulated N-deficient-aromatic heterocycle. The result is increased π-acidity and destabilization of the NHC, preventing isolation of the quinoxalino-annulated **1q** [9a] at room temperature. An indication of the N-C(II)-N double bond character and cyclodelocalization (ring current effect) is provided by the strong downfield shifts of the NCH_2 protons of **1pb** and **1b** (Table 2) compared to the NCH_2 signals of the C2-hydrogenated derivatives (**1pb**H_2 $\delta^1H = 2.77$, 3.06 ppm [8a], **1b**H_2 $\delta^1H = 2.53$ ppm [12]).

Sharing of the C^{II} lone pair with a transition metal extinguishes or diminishes the σ-π electron repulsion in the complexes and causes significant upfield shifts of the $^{13}C^{II}$ signal. For the pyrido- and some related non-, carbo- or quinoxalino-annulated imidazolin-2-ylidene Rh(I), Ag(I) and Pd(II) complexes, these values and the $^{13}C^{II}$-coordination chemical shifts ($\Delta\delta^{13}C^{II}_{complex\text{-}ligand}$) are compiled for comparison in Table 3. The $\Delta\delta^{13}C^{II}$ values range from −30 to −51 ppm and depend mainly on the metal and its substituents, but to a minor extent also on the type of annulation. Within comparable complex/ligand pairs with identical *N*-substituents (**3i**, **3pb**, **3pc** / **4i**, **4pb**, **4pc**, **4n** / **5pb**, **5pc**, **5b** / **7pb**, **7pc**, **7b**, **7n** / **8pb**, **8b**, **8n**), the upfield coordination chemical shifts increase in most cases slightly in the order imy < bimy ≈ pcimy < pbimy ≈ nimy. Replacement of the *N*-neopentyl by isopropyl or mesityl groups has a low impact on $\Delta\delta^{13}C^{II}$. For complexes of the more electron-withdrawing 4-Mepbimy$^+$ [1f] and qimy [9a] ligands the $\delta^{13}C^{II}$ signals were observed further downfield, but low stability of these ligands prevented evaluation of the coordination shift values $\Delta\delta^{13}C$ of C^{II}.

Further aspects worth mentioning for the structures of the complexes in solution are the hindered rotation of the ligand around the C^{II}-metal axis and the impact of the asymmetry within the pyrido-imidazolin-2-ylidene plane. Even for identical *N1*- and *N3*-substituents and for free rotation around the N-CH_2R axes, two isomers or diastereoisomers could be possible for the linear L_2Ag^+ and $L_2Pd(0)$ or the square planar Rh(I) and Pd(II) complexes in solution. However, as for the LAgCl complexes **7pb** and **7pc**, only one data set was found in the ^{13}C and ^1H NMR spectra of the cationic silver complexes **3pb** and **3pc** and in the Pd(0) complex **6pc**. Also, the square-planar LRh(COD)Cl complexes each display only one data set for **4pb** and **4pc**. In contrast to **7pb**, **7pc** and **6pc**, each with two (in the latter case broad) singlets for $N(1)CH_2$ and $N(3)CH_2$, the Rh-complexes exhibit four AB-doublets for the four NCH_2 protons. In the case of the allylpalladium chloride complexes **5pb** and **5pc** two very broad signal ranges were observed for the four NCH_2 protons. This and the occurrence of major and minor *a*- and *c*-allyl proton signals hint at dynamic processes in solutions of **5pb** and **5pc**. The observation of four sharp singlets for the NCH_2 protons of the L_2PdCl_2 complex **8pb**, each two close together, suggest *trans*-configuration, free rotation of the neopentyl groups around the N-CH_2 axes but two obviously non-averaged populations with N1/N3 of the two **1pb** ligands in the same and the opposite orientation.

Table 2
$^{13}C^{II}/^{13}CH$-2 and $^1H(NCH_2)$ NMR data of non-, carbo- or heterocyclically annulated imidazolin-2-ylidenes **1** and their precursors $\mathbf{2_X}$ (δ in ppm).

Compd.	**1** $\delta^{13}C^{II}$, $\Delta\delta C^{II}_{(ann\text{-}np2imy)}$	δ^1H (NCH_2)	$\mathbf{2_X}$ $\delta^{13}CH$-2, $\Delta\delta CH\text{-}2_{(ann\text{-}np2imy)}$	δ^1H (NCH_2)
1i, $\mathbf{2i_{BF4}}$ [9a]	217 (br)	3.72	136.8	4.03
1b [12], $\mathbf{2b_{PF6}}$ [8b]	231.5, 14.5	3.98	143.6, 6.8	4.40
1pb, $\mathbf{2pb_{PF6}}$	235.2, 18.2	3.86, 4.43	148.4, 11.6	4.39, 4.42
1pc, $\mathbf{2pc_{PF6}}$	235.8, 18.8	3.86, 3.91	145.8, 9.0	4.38, 4.47
1n, **3n** [8a]	239.9, 22.9	4.06	147.6, 10.8	4.48
1q, $\mathbf{3q_{PF6}}$ [9a,8b]	–	–	153.2 ($^1J_{CH}$ 221 Hz), 16.4	4.49
1ph, $\mathbf{3ph_{PF6}}$ [8d]	224.5, 224.9, 7.5, 7.9	–	141.5, 141.8, 4.7, 5.0	–
nBu$_2$phimy, [nBu$_2$phimy]BF_4 [22]	225.1, 8.1	4.70	141.6, (4.8)	4.93

Table 3
^{13}C(II) and $^{1}H(NCH_2)$ NMR data of **3**–**9** and some related non-, carbo- or heterocyclically annulated imidazolin-2-ylidene complexes (δ [ppm], *J* [Hz]).

Metal/Complex	$\delta^{13}C$(II)	$\Delta\delta_{(complex-L)}$	$^{1}J_{CRh}$ or $^{1}J_{CAg}$	$\delta^{1}H$ (NCH_2)
Rh(I)/				
4i	184.0	−33	52.2	4.60, 5.01[b]
4pb	202.9	−32.3	52.7	4.51, 5.21, 4.73, 5.15[c]
4pc	205.2	−30.5	51.9	4.43, 4.46, 5.32, 5.37[c]
[3,4-Me_2-1-Np-pbimy-Rh(COD)Cl]PF_6 [1f]	212.95	–	53.5	4.64, 5.23,[c] (3-Me: 5.01, 5.14, 2 s)
4n [8a]	208.1	−31.8	52.8	4.43, 5.49[b]
4q [9a]	219.5	–	52	4.86, 5.25[b]
Ag(I)/				
3i [9a]	181.9	−35.1	213.8, 185.8	3.94 (s)
3pb	192.2	−41.5	218.8, 189.4	4.34, 4.46 (2 s)
3pc	193.9	−39.9	219.7, 190.5	
[($i$$Pr_2$qimy)$_2$Ag]$PF_6$ [9a]	197.4	–	214.9, 185.8	CH: 5.41 (sep)
7pb	193.7	−43.1	270.6, 234.7	4.29, 4.41 (2 s)
7pc	195.8	−41.8	273.1, 236.1	4.31, 4.38 (2 s)
7b [8b]	193.2	−38.3	271.0, 234.9	4.27 (s)
7b [8a]	197.5	−42.4	269.1, 233.1	4.37 (s)
Pd(0)/				
6pc	202.3	−33.5	–	4.26 (br), 4.31 (br)
Pd(II)/				
[($i$$Pr_2$imy)Pd(Allyl)Cl] [23]	177.2($i$$Pr_2$imy 211.9 [24])	−34.7	–	CH: 4.98 (br)
5pb	197.9	−37.3	–	4.04.3 (vbr), 4.5–4.9 (vbr)
5pc	200.0	−35.8	–	4.14.4 (vbr), 4.5–4.9 (vbr)
5b	194.4	−37.1	–	4.0–4.9 (vbr)
8pb	185.6	−49.6	–	4.90, 4.91, 5.00, 5.01[d]
8b	182.6	−48.9	–	4.91 (s)
8n [8a]	188.7	−51.2	–	5.06 (br)
9pc	188.7	−47.1	–	4.94 (br), 5.05,5.15 (br)

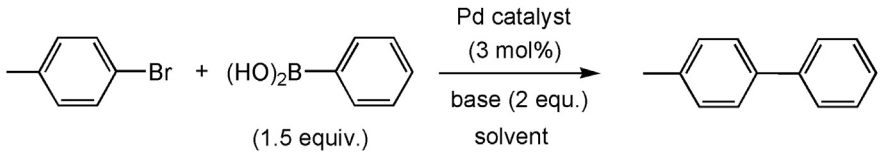
[a] $^{2}J_{PC(II)}$.
[b] Two doublets, $^{2}J = 13.5–13.8$ Hz.
[c] Four doublets, $^{2}J = 13.5–14.0$ Hz).
[d] Four singlets.

2.3. Catalytic ligand screening

Countless reports on the use of NHC ligands in a wide variety of transition-metal-catalyzed conversions have been published in the last three decades, usually with the aim of optimizing a certain transformation with respect to suitable metals, NHC ligand types, reaction conditions, applicability of less reactive but cheaper substrates, of water as solvent, etc. [2–5]. Electronic annulation effects were demonstrated by Organ and coworkers [25] for the Suzuki-Miyaura coupling of *p*-tolylboronic acid with *p*-methoxy-chlorobenzene by 5,6-difluoro- (−M), 5,6-non- and 5,6-dimethoxy-substituted (+M) 1,3-diadamantyl-benzimidazolin-2-ylidene ligands. The increasing yields (53, 72, 83%) with increasing π-density at the bimy ligand/Pd catalyst might be explained by increasing rates of the oxidative additions of the Pd(bimy)-catalysts at the aryl halide as the rate determining step. Similar electronic annulation effects were observed in Heck coupling reactions catalyzed by 5,6-difluoro-, -non- and -dibutoxy-substituted $n$$Bu_2$bimy/Pd catalysts (L/Pd 2:1) [26] and in Suzuki-Miyaura and Mizoroki-Heck couplings catalyzed by *o*-xylylene-*N*,*N*-bridged bis(*N*′-Mebimy)Pd-catalysts with 5,6-dibutoxy-substituents on the benzene ring [27]. In this context we were interested to examine whether annulation of the imidazolin-2-ylidene ligands by the pyridine ring or related carbocyclic aromatic rings, previously studied in our group, effects the Suzuki-Miyaura cross-coupling of *p*-bromotoluene with phenyl boronic acid (Scheme 5), chosen as model reaction.

Most tests were performed with *in-situ* generated catalysts. Pre-investigations with the easily available **2b$_{PF6}$** showed that K_3PO_4 and dry 1,4-dioxane are suitable as base and solvent, respectively. Cs_2CO_3 gave lower yields of *p*-methylbiphenyl (*p*TolPh); KH, applied in the synthesis of **1 pb**, **1pc** and the non- or carbocyclic annulated dineopentyl-imidazolin-2-ylidenes [8], was found to be unsuitable for catalyst generation because of competing reduction reactions, e.g. of *p*-bromotoluene and $PhB(OH)_2$ to toluene and benzene, respectively. Moisture in DMF, dioxane or the base lowered the coupling yields (Table 4, entries 1–5). A 2:1 M ratio of the ligand precursor and $Pd(OAc)_2$ led (in comparison to a 1:1 M ratio) to increased cross-coupling yields with the benzo- and naphtho-annulated catalysts, whereas **1pc**/Pd catalysts generated with these precursor ratios gave almost the same results (entries 3, 6, 7 and 10, 12, 13). Within the 1:1 ligand precursor/Pd series (entries 9–17), the yields of *p*TolPh are similar with non-, benzo- and pyrido [c]-annulated catalysts (74–76%) and markedly higher than with naphtho- and pyrido[b]-annulation (62, 59%). With catalysts generated from $Pd(OAc)_2$ and **2q$_{PF6}$** (1:2 or 1:1), the yields are comparable to the yields in blind tests without a ligand precursor. The low stability of **1q**, not isolable at r.t. [9a], may have prevented formation of the corresponding Pd complex in this case. The lower coupling yields with the di-*o*- and di-*p*-tolyl-phenanthreno-annulated catalysts may be attributable both to different *N*-substituents and annulation types.

Since NMR spectra of CD_2Cl_2-soluble components, formed during heating of **2b$_{PF6}$** with $Pd(OAc)_2$ (2:1) with dry K_3PO_4 in 1.4-dioxane (the first step of the catalytic protocol), displayed roughly



Scheme 5. Suzuki-Miyaura cross-coupling of *p*-bromotoluene with phenyl boronic acid.

Table 4
Suzuki-Miyaura reaction catalysed by annulated imy/Pd catalysts.[a]

entry	Lig. precursor, L/Pd (mol%) or PdL complex (mol%); solvent, (reaction time unless 16 h)	*p*TolBr (mmol), $PhB(OH)_2$ (mmol); Base (mmol)	*p*TolPh (%)[b]
In situ catalyst, L/Pd ratio 2:1			
1	**2b$_{PF6}$**, 6/3; DMF/5%H_2O	1, 1.5; K_3PO_4 2	2[d]
2	**2b$_{PF6}$**, 6/3; DMF/5%H_2O	1, 1.5; Cs_2CO_3 2	29
3	**2b$_{PF6}$**, 6/3; 1.4-dioxane	1, 1.5; K_3PO_4 2	86
4	**2b$_{PF6}$**, 6/3; 1.4-dioxane	1, 1.5; Cs_2CO_3 2	68[d]
5	**2b$_{PF6}$**, 6/3; 1.4-dioxane	1, 1.5; KH 2	1–8[c]
6	**2pc$_{PF6}$**, 6/3; 1.4-dioxane	1, 1.5; K_3PO_4 2	74
7	**2n$_{PF6}$**, 6/3; 1.4-dioxane	1, 1.5; K_3PO_4 2	92
8	**2q$_{PF6}$**, 6/3; 1.4-dioxane	1, 1.5; K_3PO_4 2	12
In situ catalyst, L/Pd ratio 1:1			
9	**2i$_{BF4}$**, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	74
10	**2b$_{PF6}$**, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	75
11	**2pb$_{PF6}$**, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	59
12	**2pc$_{PF6}$**, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	76
13	**2n$_{PF6}$**, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	62
14	**2ph$_{PF6}$**, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	42
15	*p*Tol_2phimyHPF_6, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	38
16	**2q$_{PF6}$**, 3/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	10–18
17	-, 0/3; 1,4-dioxane	1, 1.5; K_3PO_4 2	14–18
One-component precatalyst			
18	**5pb**, 3; 1,4-dioxane	1, 1.5; K_2CO_3 2	65
19	**5pb**, 3; 1,4-dioxane, (2 h)	1, 1.5; K_2CO_3 2	60
20	**5pc**, 3; 1,4-dioxane, (2 h)	1, 1.5; K_2CO_3 2	69
21	**5b**, 3; 1,4-dioxane, (2 h)	1, 1.5; K_2CO_3 2	89
22	**5ph** [8d], 3; 1,4-dioxane, (2 h)	1, 1.5; K_2CO_3 2	52
23	**8b**, 3; 1,4-dioxane	1, 1.5; K_3PO_4 2	26[d]

[a] Reaction conditions: 1. Precatalyst formation from the respective annulated imyH$^+$X$^-$ precursor, $Pd(OAc)_2$ and base in the given solvent (5 mL) by heating for 30 min at 80 °C; 2. heating the *in-situ* formed or one-component precatalyst with *p*-bromotoluene and $PhB(OH)_2$ for ca. 16 h (or 2h) at 80 °C; 3. quenching with aqueous NH_4Cl solution, addition of external standard and GC analysis (for more details see exp. part).
[b] Average of two experiments.
[c] Reduction products 15% toluene and 14% benzene.
[d] Single experiment.

equally intense signals of unconverted **2b$_{PF6}$** and the *cis*- and *trans*-$(bimyPd)_2Pd(OAc)_2$ complexes **10b** and **11b**, supplementary experiments with the LPd(Allyl)Cl complexes **5pb**, **5pc**, **5b** and **5ph** were performed. The weak π-coordination of the σ- and π-bound bidentate allyl group makes them suitable as single-component catalyst precursors and gave rise to comparable or somewhat higher cross-coupling yields compared to the respective *in-situ* reactions. In contrast, the L_2PdCl_2 complex **8b** is too stable and unsuitable for catalysis. It led to only slightly more cross-coupling product *p*TolPh than the blind tests. The amounts of the homo-coupling product diphenyl were generally low (<10%). In sum, the conversions decrease somewhat from non- and benzo-to pyrido[c]- and pyrido[b]-annulated Np_2imy Pd catalysts, and stronger for the phenanthrene- and quinoxaline-annulated imy Pd catalysts and don't reach the high performance of current state of art catalysts with bulkier N-substituents and higher carbene basicity [2,5].

3. Conclusions

Pyrido[b]- and pyrido[c]-annulated imidazol-2-ylidenes are accessible by deprotonation of the corresponding azolium salts, are stable for **1pb** and **1pc** under inert gas at room temperature and can be vacuum-distilled. The C^{II} resonances of **1pb** and **1pc** are downfield shifted compared to **1i** and **1b** but upfield towards **1n** and hint at repulsion of π-electrons by the C^{II} electron lone pair, increasing with the linear extension of the π-system and the number of electron-withdrawing σ^2N-atoms in the annulated rings. This effect is strongly reduced by coordination of Lewis-acidic transition metals, which causes strong upfield C^{II}-coordination chemical shifts. The $\Delta\delta C^{II}$ values of the Rh(I) complexes **4pb** and **4pc** were almost the same as in the analogous non- or naphtho-annulated imy-complexes, whereas for Ag(I) and Pd(II) complexes with annulated imy-ligands the $\Delta\delta C^{II}$ values were slightly larger than for non-annulated analogues. The crystal structure analyses of **7pb** and **7pc** display noticeable bending of the C^{II}-Ag-Cl angle and crystallization as dimer aggregates, reflecting changes of the π-density distribution within the ligand (σ/π-electron repulsion) compared to the linear monomer benzanalogue **7b**, lacking the N-atom in the annulated ring. The C^{II}-Ag bond is then slightly lengthened (weakened) compared to **7b** (and also **7n**) and correlates with the slight decrease of the HOMO energies (C^{II} lone pair) in the order **1b** > **1 pb** > **1pc**. The decrease of the C^{II}-Rh bond lengths in the order **4pb** > **4pc** > **4q** hints at back bonding effects, confirmed also by the influence on the *cis*-C=C/Rh and C^{II}-N bond lengths. The

orbital energy for the pyridine-N electron lone-pair is only slightly influenced by the annulation with the imy-ring and even somewhat raised for the ligand **1pc**, but much lower compared to the C^{II} lone pair. This disfavors coordination of transition metals at the N-atom, which has not yet been observed in the crystallographically characterized complexes.o However, interactions between the N-atom and the metal might play a role in the sparingly soluble Pd(pcimy)Cl_2 complex **9pc**. This suggests an investigation whether **1pc** is able to form mixed C^{II},N-coordinated transition metal complexes or MOF-materials. In the tested Suzuki-Miyaura coupling of *p*-bromotoluene and phenylboronic acid in dioxane the yields of the cross-coupling product were similar for non-, benzo- and pyrido [c]-imy and slightly lower for pyrido[b]-imy 1:1-Pd-catalysts. For 2:1 bimy/Pd and nimy/Pd catalysts and the **5b** precatalyst complex the conversion was noticeably higher than for the 2:1 pcimy/Pd catalyst and the precatalysts **5pc** and **5pb**. The better performance of the pcimy than the pbimy catalysts might hint at stabilizing interactions of the pyridine N atoms of the pcimy ligand and possibly (over)compensate a slightly weaker C^{II}-Pd coordination.

4. Experimental

4.1. General

All syntheses were carried out in carefully dried, freshly distilled solvents under an argon atmosphere using Schlenk techniques. Glyoxal bis(neopentylimine) [15], 2,3- and 3,4- di(neopentylamino) pyridine were prepared as reported earlier [11b], other chemicals were purchased. Potassium hydride (in oil) was repeatedly washed with dry THF and dried under vacuum before use. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. δ-Values are given in ppm. Shift references are tetramethylsilane for ^{1}H and ^{13}C and H_3PO_4 (85%) for ^{31}P or calibrated solvent signals. Assignment numbers for NMR data follow ring-atom numbering and are illustrated for **5pb/5pc** in Scheme 2. Coupling constants refer to J_{HH} unless stated otherwise. For small ^{107}Ag^{13}C and ^{105}Ag^{13}C coupling constants the two doublets are unresolved and are referred to as J_{AgC}. EI(+) Mass spectra were measured on a single focusing sector-field spectrometer AMD40, FAB (NBA) spectra on a Finnigan MAT-95XP (Thermo). High-resolution mass spectra were recorded on double-focussing sector field mass spectrometers Finnigan MAT 8200 or MAT-95XP (Thermo) with EI (70 eV) or ESI. Assignments L in mass spectra of NHC complexes or in NHC metal catalysts mean the respective ligand. Melting points (uncorrected) were determined with a Sanyo Gallenkamp melting point apparatus, elemental analysis with a CHNS-932 analyzer (in some cases calibration problems). Chloride was determined by potentiometrically controlled titration. GC analyses were carried out using a gas chromatograph Hewlett Packard 5890, column HP-5(30 m) (crosslinked 5%PhMe silicone), 30 °C 5 min, 10 °C/min or 20°/min, 250 °C 5 min, external reference *n*-nonane or tridecane.

4.2. Preparation of 1,3-dineopentyl-imidazol-2-ylidene (*1i*)

a) Glyoxal bis(neopentylimine) (1.10 g, 5.60 mmol), $AgCF_3SO_3$ (1.73 g,6.73 mmol) and then chloromethyl pivalate (1.13 mL, 7.84 mmol) were added to DCM (10 mL). The pressure tube was sealed and stirred in the dark at 50 °C for ca. 24 h. After cooling to r.t. the mixture was filtered, the solvent evaporated under vacuum and the resulting oil washed several times with ether to give 1.45 g (72%) of ionic liquid 1,3-dineopentyl-imidazolium triflate (**2i$_{OTf}$**). ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 18 H, CMe_3), 4.02 (s, 4 H, NCH_2), 7.32 (br s, 2 H, H-4, H-5), 8.87 (br s, 1 H, H-2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 26.79 (*C*Me_3), 32.31 (*C*Me_3), 61.02 (NCH_2), 123.28 (CH-4, CH-5), 137.23 (CH-2).

b) A suspension of KH in THF was prepared from 30% KH (105 mg, 0.79 mmol) in mineral oil by repeated washing/filtration with THF to remove the oil. Then **2i$_{OTf}$** (175 mg, 0.488 mmol) was added at −78 °C, the mixture allowed to come to room temperature and stirred overnight. After filtration the solvent was removed under vacuum. The residue was extracted with diethyl ether and the ether evaporated to give 56 mg (55%) of NMR spectroscopically almost pure oily **1i**. ^{1}H NMR (C_6D_6): δ = 0.90 (s, 18 H, CMe_3), 3.72 (s, 4 H, NCH_2), 6.48 (s, 2 H, H-4, H-5). ^{13}C{^{1}H} NMR (C_6D_6): δ = 28.62 (*C*Me_3), 33.37 (*C*Me_3), 63.06 (NCH_2), 120.48 (CH-4, CH-5), 217 (br, C_q-2). The compound is highly sensitive to moisture and air.

4.3. Preparation of bis(1,3-dineopentyl-imidazol-2-ylidene) silver tetrafluoroborate (*3i$_{BF4}$*)

a) Reaction of glyoxal bis(neopentylimine) (435 mg, 2.22 mmol), $AgBF_4$ (519 mg, 2.67 mmol) and chloromethyl pivalate (0.45 mL, 3.12 mmol) in DCM (10 mL) as described for **2i$_{OTf}$** furnished 464 mg (71%) of the ionic liquid **2i$_{BF4}$**. ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 18 H, CMe_3), 4.03 (s, 4 H, NCH_2), 7.38 (br s, 2 H, H-4, H-5), 8.69 (br s, 1 H, H-2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 26.69 (*C*Me_3), 32.19 (*C*Me_3), 60.69 (NCH_2), 123.35 (CH-4, CH-5), 136.78 (CH-2).

b) Ag_2O (133 mg, 0.574 mmol) was added to a solution of **2i$_{BF4}$** (170 mg, 0.574 mmol) in DCM (10 mL). The suspension was stirred for 24 h at r.t., filtered and washed with DCM. The filtrate was concentrated under vacuum (to 1–2 mL) and hexane (4 mL) was added. The resulting white precipitate was separated and crystallized from a small amount of DCM to give 224 mg (63%) white crystals of **3i$_{BF4}$**. ^{1}H NMR (CD_2Cl_2): δ = 1.01 (s, 18 H, CMe_3), 3.94 (s, 4 H, NCH_2), 7.11 (d br, $^4J(^{107/109}Ag^1H)$ = 1.8 Hz, 2 H, H-4, H-5). ^{13}C{^{1}H} and 135-DEPT NMR (CD_2Cl_2): δ = 28.10 (*C*Me_3), 32.97 (*C*Me_3), 63.71 (NCH_2), 122.99 (d, $^3J(^{107/109}Ag^1H)$ = 5.9 Hz, CH-4, CH-5), 181.93 (dd, $^1J(^{13}C\text{-}^{107/109}Ag)$ = 185.8, 213.8 Hz, C_q-2). Elemental analysis calcd. for $C_{26}H_{48}AgBF_4N_4$ (611.38): C, 51.02, H, 7.91, N, 9.17; found: C, 50.77, H, 8.25, N, 9.19.

4.4. Preparation of (1,3-dineopentylimidazole-2-ylidene) rhodium(cyclooctadiene-1,5) chloride (*4i*)

The suspension of 1,3-dineopentylimidazolium tetrafluoroborate (184 mg, 0.620 mmol) and $[Rh(1,5\text{-}COD)Cl]_2$ (153 mg, 0.310 mmol) in THF was added at −78 °C to a suspension of 30% KH in mineral oil (19 mg, 0.992 mmol). The mixture was allowed to come to room temperature and stirred overnight. The solvent was removed in vacuum, the residue was subjected to chromatography on silica gel (hexane, elution with DCM ($[Rh(1,5\text{-}COD)Cl]_2$, 1% MeOH/DCM) to give the pure substance, yield 35 mg (23%). ^{1}H NMR ($CDCl_3$): δ = 1.45 (s, 18 H, CH_3), 2.24 (m, 4 H, CH_2), 2.70 (m, 4 H, CH_2), 3.55 (br q, 2 H, =CH), 4.60 (d, $^4J(^{103}Rh^1H)$ = 13.7 Hz, 2 H, CH_2), 5.01 (d, $^4J(^{103}Rh^1H)$ = 13.7 Hz, 2 H, CH_2), 5.33 (br m, 2 H, =CH), 7.59 (s, 2 H, CHCH) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.83 (CH_2), 28.89 (*C*Me_3), 32.55 (CH_2), 32.78 (*C*Me_3), 62.24 (NCH_2), 68.12 (d, $J(^{103}Rh^{13}C)$ = 14.6 Hz, CH =), 97.47 (d, $J(^{103}Rh^{13}C)$ = 7 Hz, CH =), 121.10 (4,5-CH), 183.97 (d, $^1J(^{103}Rh^{13}C)$ = 52 Hz, C_q-2) ppm. $C_{21}H_{36}ClN_2Rh$ (454.88), HRMS (ESI in MeCN): calc. for $[M-Cl]^+$ 419.1928; found: 419.1926.

4.5. Preparation of 1,3-dineopentyl-imidazolinium[4,5-b]pyridine hexafluorophosphate (*2pb$_{PF6}$*)

2,3-Diaminopyridine (3.0 g, 12.03 mmol) and NH_4PF_6 (1.960 mg, 12.02 mmol) in triethyl orthoformate (20 mL) were heated in a rectification apparatus for 7 h at 140 °C (oil-bath) to remove ethanol formed in the reaction. The precipitate was filtered off at r.t., washed with Et_2O and dissolved in CH_3CN. Insoluble

contamination was separated and volatiles were removed under vacuum to give 4.46 g (91%) crystalline **2pb$_{PF6}$**. ^{1}H NMR (DMSO-d_6): δ = 1.00 (br s, 18 H, 2 CMe$_3$), 4.39, 4.42 (2 s, 4 H, NCH$_2$), 7.78 (dd, ^3J = 8.2, ^3J = 4.4 Hz, 1 H, H6), 8.66 (d, ^3J = 8.2 Hz, 1H, H7), 8.79 (d, ^3J = 4.2 Hz, 1 H, H5), 9.97 (s, 1 H, H2). ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 26.94 (C*Me*$_3$), 27.22 (C*Me*$_3$), 32.89, 33.15 (2 *C*Me$_3$), 55.55 (1-NCH$_2$), 57.64 (3-NCH$_2$), 122.33 (CH6), 124.03 (CH7), 125.33 (C$_q$7a), 143.30 (CH5), 145.10 (C$_q$3a), 148.35 (C2). ^{31}P{^{1}H} NMR (DMSO-d_6): δ = −143.20 (sept, $^1J_{PF}$ = 711.2 Hz). MS (EI, 70 eV, 345 °C): *m/z* (%) = 260 (17) [M − PF$_6$]$^+$, 259 (24), 244 (16), 204 (14), 203 (100) [M-PF$_6$-C$_4$H$_9$]$^+$, 202 (26), 174 (29), 133 (79), 132 (54), 85 (65), 43 (35). Elemental analysis calcd. for C$_{16}$H$_{26}$F$_6$N$_3$P (405.36): C, 47.41, H, 6.46, N, 10.37; found: C, 47.81, H, 6.78, N, 10.34.

4.6. Preparation of 1,3-dineopentyl-imidazolinium[4,5-c]pyridine hexafluorophosphate (**2pc$_{PF6}$**)

Reaction of 3,4-diaminopyridine (1.5 g, 6.01 mmol) andNH_4PF_6 (979 mg, 6.01 mmol) with triethyl orthoformate (20 mL) and work-up as described for **2pb$_{PF6}$** gave 2.2 g (90%) of white crystalline **2pc$_{PF6}$**. ^{1}H NMR (DMSO-d_6): δ = 0.99 (s, 9 H, CMe$_3$), 1.02 (s, 9 H, CMe$_3$), 4.38, 4.47 (2 s, 4 H, NCH$_2$), 8.20 (d, ^3J = 5.8 Hz, 1 H, H7), 8.77 (d, ^3J = 5.8 Hz, 1 H, H6), 9.50 (s, 1 H, H4), 9.85 (s, 1 H, H2). ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 26.91 (2 C*Me*$_3$), 33.10 (*C*Me$_3$), 33.21 (*C*Me$_3$), 57.31 (3-NCH$_2$), 57.70 (1-NCH$_2$), 108.95 (CH7), 129.58 (C$_q$3a), 137.56 (CH6), 137.96 (CH4), 145.16 (C$_q$7a), 145.82 (C-2). ^{31}P{^{1}H} NMR (DMSO-d_6): δ = −143.2 (sept, $^1J_{PF}$ = 711.4 Hz). MS (EI, 70 eV, 200 °C): *m/z* (%) = 260 (29) [M − PF$_6$]$^+$, 259 (24), 203 (100) [M-PF$_6$-C$_4$H$_9$]$^+$, 174 (20), 133 (57), 132 (33), 120 (18), 106 (48), 92 (41), 91 (57), 85 (65), 43 (44). Elemental analysis calcd. for C$_{16}$H$_{26}$F$_6$N$_3$P (405.36): C, 47.41, H, 6.46, N, 10.37; found: C, 47.63, H, 6.56, N, 10.34.

4.7. Preparation of 1,3-dineopentyl-imidazolinium[4,5-b]pyridine chloride (**2pb$_{Cl}$**)

Reaction of 2,3-diaminopyridine (1.5 g, 6.01 mmol) and NH$_4$Cl (322 mg, 6.01 mmol) with triethyl orthoformate (15 mL) and work-up as described for **2pb$_{PF6}$** gave 1.6 g (90%) white solid of **2pb$_{Cl}$**. ^{1}H NMR (CD$_3$OD): δ = 1.09 (s, 9 H, CMe$_3$), 1.10 (s, 9 H, CMe$_3$), 4.48, 4.51 (2 s, 4 H, NCH$_2$), 7.78 (dd, ^3J = 8.5, 4.7 Hz, 1 H, H6), 8.57 (dd, ^3J = 7.9, ^4J = 1.3 Hz, 1 H, H7), 8.81 (dd, ^3J = 4.5, ^4J = 1.3 Hz, 1 H, H5). ^{13}C{^{1}H} NMR (CD$_3$OD): δ = 27.66 (C*Me*$_3$), 27.81 (C*Me*$_3$), 34.08, 34.36 (2 *C*Me$_3$), 57.28 (1-NCH$_2$), 59.62 (3-NCH$_2$), 123.78 (CH6), 124.98 (CH7), 126.82 (C$_q$7a), 144.97 (C$_q$3a), 150.08 (CH5); CD-2 at noise level. MS (EI, 70 eV, 345 °C): *m/z* (%) = 261 (18), 260 (61) [M − Cl]$^+$, 259 (28), 258 (9), 244 (18), 204 (20), 203 (100) [[M-Cl-C$_4$H$_9$]$^+$, 202 (22), 174 (25), 145 (10), 134 (20), 133 (79), 132 (46), 120 (26), 43 (29). Elemental analysis: calcd. for C$_{16}$H$_{26}$N$_3$Cl (295.86): H 8.85, N 14.20, Cl 11.98; found: H 8.51, N 14.39, Cl 11.7.

4.8. Preparation of 1,3-dineopentyl-imidazolinium[4,5-c]pyridine chloride (**2pc$_{Cl}$**)

Reaction of 3,4-diaminopyridine (1.5 g, 6.01 mmol) and NH$_4$Cl (322 mg, 6.01 mmol) with triethyl orthoformate (15 mL) and work-up as described for **2pb$_{PF6}$** gave 1.72 g (96%) white solid of **2pc$_{Cl}$**. ^{1}H NMR (CD$_3$OD): δ = 1.10 (s, 9 H, CMe$_3$), 1.12 (s, 9 H, CMe$_3$), 4.46, 4.55 (2 s, 4 H, NCH$_2$), 8.15 (dd, ^3J = 5.9, ^5J = 0.7 Hz, 1 H, H7), 8.80 (d, ^3J = 5.9 Hz, 1 H, H6), 9.43 (br, 1 H, H4). ^{13}C{^{1}H} NMR (CD$_3$OD): δ = 27.59 (2 C*Me*$_3$), 34.29 (*C*Me$_3$), 34.42 (*C*Me$_3$), 59.31, 59.72 (2 NCH$_2$), 110.26 (CH7), 131.22 (C$_q$3a), 138.98 (CH6), 139.44 (C$_q$7a), 146.56 (CH4); CD-2 in noise. MS (EI, 70 eV, 345 °C): *m/z* (%) = 260 (5) [M − Cl]$^+$, 259 (22), 258 (13), 244 (16), 204 (15), 203 (100) [M-Cl-C$_4$H$_9$]$^+$, 202 (20), 174 (24), 146 (12), 133 (72), 132 (37), 120 (10), 43 (35). Elemental analysis calcd for C$_{16}$H$_{26}$N$_3$Cl (295.86): H 8.85, N 14.20, Cl 11.98; found: H 8.41, N 13.79, Cl 11.5.

4.9. Preparation of 1,3-dineopentyl-imidazolino[4,5-b]pyridin-2-ylidene (**1pb**)

A suspension of **2pb$_{PF6}$** (300 mg, 0.74 mmol) in THF (25 mL) was added at room temperature to a suspension of excess KH (74 mg, 1.85 mmol). Evolution of hydrogen took place, and the color of the solution became red-brown after stirring for 2 h. The mixture was stirred overnight at room temperature and then filtered. The solvent was removed from the filtrate under vacuum, and the residue was extracted with benzene for separation from salts soluble in THF. Evaporation of the solvent afforded 170 mg (88%) of crude **1pb**, colored red-brown by trace impurities. Distillation at 10^{-4} torr/105 °C (bath) provided almost colorless viscous oily **1 pb**. ^{1}H NMR (C$_6$D$_6$): δ = 0.90 (s, 9 H, CMe$_3$), 1.10 (s, 9 H, CMe$_3$), 3.86 (s, 2 H, 1-NCH$_2$), 4.43 (s, 2 H, 3-NCH$_2$), 6.65 (dd, ^3J = 8.0, 4.8 Hz, 1 H, H6), 6.99 (dd, ^3J = 8.0, ^4J = 1.4 Hz, 1 H, H7), 8.20 (dd, ^3J = 4.8, ^4J = 1.4 Hz, 1 H, H5). ^{13}C{^{1}H} and DEPT-135 NMR (C$_6$D$_6$): δ = 29.02 (C*Me*$_3$), 29.13 (C*Me*$_3$), 34.28/34.42 (2 *C*Me$_3$), 57.30 (1-NCH$_2$), 60.06 (3-NCH$_2$), 116.67 (CH6), 117.84 (CH7), 128.3 (C$_q$7a), 142.39 (CH5), 149.72 (C$_q$3a), 235.23 (C2). MS of moisture (H$_2$O) adduct (EI, 70 eV, 100 °C): *m/z* (%) = 277 (24) [M + H$_2$O]$^+$, 275 (28), 261 (28), 260 (49) [M+H]$^+$, 220 (100) [M + H$_2$O-C$_4$H$_9$]$^+$, 219 (33), 204 (24), 192 (98) [M − C$_5$H$_{11}$]$^+$, 134 (36), 120 (26), 43 (48). HRMS (EI 70 eV): C$_{16}$H$_{25}$N$_3$, calcd. for [M+H]$^+$ 260.2121; found 260.2110 (100%).

4.10. Preparation of 1,3-dineopentyl-imidazolino[4,5-c]pyridin-2-ylidene (**1pc**)

Reaction of a suspension of **2pc$_{PF6}$** (500 mg, 1.23 mmol) and KH (123 mg, 3.07 mmol) in THF and work-up as described above for the preparation of **1pb** furnished 268 mg (84%) of red-brown oil. Colorless **1pc** was separated from trace impurities by vacuum distillation at 10^{-4} torr/100 °C bath temperature. ^{1}H NMR (C$_6$D$_6$): δ = 0.88 (s, 9 H, CMe$_3$), 0.90 (s, 9 H, CMe$_3$), 3.86 (s, 2 H, 3-NCH$_2$), 3.91 (s, 2 H, 1-NCH$_2$), 6.78 (dd, ^3J = 5.5, ^5J = 0.9 Hz, 1 H, H7), 8.41 (d, ^3J = 5.5 Hz, 1 H, H6), 8.71 (d, ^5J = 0.9 Hz, 1 H, H4). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 28.95 (2 C*Me*$_3$), 34.22 (*C*Me$_3$), 34.43 (*C*Me$_3$), 59.43, 59.81 (2 NCH$_2$), 106.30 (CH7), 134.28, 134.39 (C$_q$3a, C$_q$7a), 141.48 (CH6), 142.27 (CH4), 235.76 (C2). MS (EI, 70 eV, 165 °C): *m/z* (%) = 259 (18) [M]$^+$, 257 (15), 220 (41), [M − C$_3$H$_9$]$^+$, 210 (18), 204 (13), 203 (99) [M − C$_4$H$_8$]$^+$, 192 (38), 174 (20), 152 (100), 133 (77), 121 (92), 120 (22), 92 (14), 43 (83). HRMS (EI 70 eV): C$_{16}$H$_{25}$N$_3$, calcd. for [M+H]$^+$ 260.2121; found 260.2110 (100%); calcd. for [M$^+$] 259.2043; found 259.2032 (71%).

4.11. Preparation of rhodium(1,5-cyclooctadiene)(1,3-dineopentyl-imidazolino[4,5-b]pyridin-2-ylidene)chloride (**4pb**)

a) [Rh(1,5-COD)Cl]$_2$ (146 mg, 0.295 mmol) was added to a filtered solution of free carbene **1pb** in THF, generated from **2pb$_{PF6}$** (300 mg, 0.74 mmol), and KH (60 mg, 1.50 mmol) at room temperature. The mixture was stirred for 12 h, filtered, and the solvent was removed in vacuum. The residue was washed thoroughly with hexane and recrystallized from a small amount of DCM to give 187 mg (63%) of yellow crystals of **4pb**. Selected bond lengths and angles are compiled in Table 1, crystal data in Table 5. ^{1}H NMR (CDCl$_3$): δ = 1.23 (s, 9 H, CMe$_3$), 1.24 (s, 9 H, CMe$_3$), 1.88−2.03 (m, 4 H, CH$_2$), 2.35−2.51 (m, 4 H, CH$_2$), 2.98−3.10 (m, 2 H, =CH), 4.51 (d, ^2J = 14.0 Hz, 1 H, NCH$_2$), 4.73 (d, ^2J = 13.5 Hz, 1 H, NCH$_2$), 5.15 (d, ^2J = 13.5 Hz, 1 H, NCH$_2$), 5.21 (d, ^2J = 14.0 Hz, 1 H, NCH$_2$), 5.22 (br m, 2 H, =CH), 7.12 (dd, ^3J = 8.1, ^3J = 4.8 Hz, 1 H, H6), 7.64 (dd, ^3J = 8.1, ^4J = 1.3 Hz, 1 H, H7), 8.25 (dd, ^3J = 4.8, ^4J = 1.3 Hz, 1 H, H5). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 28.70, 28.80 (2 CH$_2$), 29.86 (C*Me*$_3$), 29.94 (C*Me*$_3$),

Table 5
a) Crystal data and structure refinement of **3pb**, **4 pb** and **4pc**.

Compound number	**3p**b	**4pb** [9b]	**4pc** [9b]
CCDC number	1880308	617669	617670
Empirical formula	$C_{33.5}H_{51}AgClF_3N_6O_3S$	$C_{24}H_{37}ClN_3Rh$	$C_{24}H_{37}ClN_3Rh$
Formula weight	818.18	505.93	505.93
Temperature	100(2) K	133(2) K	133(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Unit cell dimensions:			
a	11.9279(5) Å	15.3603(14) Å	14.4491(12) Å
b	14.3530(10) Å	12.8518(12) Å	10.6453(8) Å
c	22.6918(15) Å	12.0112(12) Å	16.2096(12) Å
α	88.315(5)°	90°	90°
β	89.393(5)°	92.731(3)°	104.126(4)°
γ	77.965(5)°	90°	90°
Volume	3797.8(4) Å^3	2368.4(4) Å^3	2417.9(3) Å^3
Z	4	4	4
Density (calculated)	1.431 Mg/m^3	1.419 Mg/m^3	1.390 Mg/m^3
Absorption coefficient	0.71 mm^{-1}	0.85 mm^{-1}	0.83 mm^{-1}
F(000)	1700	1056	1056
Crystal size	0.25 × 0.10 × 0.10 mm^3	0.20 × 0.15 × 0.05 mm^3	0.35 × 0.25 × 0.15 mm^3
$2\theta_{max}$	52.7°	61°	61°
Reflections collected	66948	45163	44785
Independent reflections	15106 [R_{int} = 0.067]	7225 [R_{int} = 0.055]	7358 [R_{int} = 0.031]
Completeness to theta	(26.37°) 97.3%	(30°) 100.0%	(30°) 99.8%
Abs. correction	multi-scan	multi-scan	multi-scan
Transmissions	1.00 and 0.92	0.96 and 0.86	0.89 and 0.78
Data/restraints/parameters	15106/49/898	7225/6/284	7358/35/286
Goodness-of-fit on F^2	0.93	1.06	1.09
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.056$, $wR2 = 0.131$	$R1 = 0.032$,$wR2 = 0.065$	$R1 = 0.027$, $wR2 = 0.059$
R indices (all data)	$R1 = 0.098$, $wR2 = 0.139$	$R1 = 0.032$, $wR2 = 0.065$	$R1 = 0.039$, $wR2 = 0.066$
Largest diff. peak and hole	2.20 and −0.77 e·Å^{-3}	1.02 and −0.46 e·Å^{-3}	0.61 and −0.33 e·Å^{-3}
Identification code	**7pb**	**7pc**	**2b$_{PF6}$·H$_2$O**
CCDC number	617671	1880310	1880311
Empirical formula	$C_{16}H_{25}AgClN_3$	$C_{16}H_{25}AgClN_3$	$C_{17}H_{29}ClN_2O$
Formula weight	402.71	402.71	312.87
Temperature	133(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54184 Å	0.71073 Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions:			
a	12.249(2) Å	12.8550(5)	12.1550(2)
b	9.439(2)	9.9307(4)	8.7127(2)
c	15.201(3)	13.7454(6)	16.6474(3)
α	90°	90°	90°
β	90.897(6)°	92.458(4)	93.369(2)°
γ	90°	90°	90°
Volume	1757.2(6) Å^3	1753.11(12) Å^3	1759.95(6) Å^3
Z	4	4	4
Density (calculated)	1.522 Mg/m^3	1.526 Mg/m^3	1.181 Mg/m^3
Absorption coefficient	1.30 mm^{-1}	10.6 mm^{-1}	0.22 mm^{-1}
F(000)	824	824	680
Crystal size	0.12 × 0.12 × 0.06 mm^3	0.15 × 0.10 × 0.01 mm^3	0.45 × 0.25 × 0.15 mm^3
$2\theta_{max}$	56.6°	140.6°	61°
Reflections collected	16929	26233	67596
Independent reflections	4350 [R_{int} = 0.134]	3072 [R_{int} = 0.047]	5278 [R_{int} = 0.027]
Completeness to theta	(28) 99.8%	(67.5°) 95.6%	(30.5°) 98.0%
Absorption correction	none	Numerical	multi-scan
Transmissions		0.88 and 0.40	0.97 and 0.91
Data/restraints/parameters	4350/0/196	3072/0/196	5278/1/208
Goodness-of-fit on F^2	1.08	1.05	1.04
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.076$, $wR2 = 0.099$	$R1 = 0.031$,$wR2 = 0.075$	$R1 = 0.031$,$wR2 = 0.080$
R indices (all data)	$R1 = 0.117$,$wR2 = 0.106$	$R1 = 0.038$, $wR2 = 0.078$	$R1 = 0.036$, $wR2 = 0.083$
Largest diff. peak and hole	1.68 and −1.57 e·Å^{-3}	1.17 and −0.41 e·Å^{-3}	0.42 and −0.24 e·Å^{-3}

32.71 (br, 2 CH_2), 33.30, 33.73 (2 CMe_3), 58.51 (1-NCH_2), 60.89 (3-NCH_2), 69.66, 69.92 (2 d, J_{RhC} = 14.4, 14.5 Hz, 2 CH), 99.92, 100.01 (2 d, J_{RhC} = 1.7 Hz, 2 CH), 117.05 (CH6), 118.20 (CH7), 128.06 (C_q7a), 142.25 (CH5), 148.05 (C_q3a), 202.94 (d, J_{RhC} = 52.7 Hz, C_q2). HRMS (EI 70 eV, 200 °C), M^+ calcd for $C_{24}H_{37}ClN_3Rh$: 505.1731 (100), 506.1765 (27), 507.1702 (32); found: m/e = 505.1694 (100), 506.17248 (23), 507.1642 (33).

b) The silver complex **7pb** (300 mg, 0.74 mmol) was dissolved in DCM (20 mL) and $[Rh(1,5\text{-}COD)Cl]_2$ (183 mg, 0.37 mmol) was added. The mixture was stirred in the dark at room temperature for 24 h and filtered to give a clear yellow solution. The solvent was partly removed, and the saturated solution was layered with hexane. Storage at −20 °C for 24 h gave yellow crystals of **4pb**, contaminated by a small amount of residual silver complex, which

was removed by chromatography using DCM; yield 355 mg (94%). The NMR data correspond to those given above.

4.12. Preparation of rhodium(1,5-cyclooctadiene)(1,3-dineopentyl-imidazolino[4,5-c]pyridin-2-ylidene) chloride (**4pc**)

a) Compound **4pc** was prepared as described for **4pb** from $[Rh(1,5\text{-}COD)Cl]_2$ (121 mg, 0.24 mmol) and crude **1pc** in THF, generated from $\mathbf{2pc_{PF6}}$ (250 mg, 0.62 mmol) and KH (50 mg, 1.25 mmol) at room temperature. The yield of the yellow crystals was 149 mg (60%). Selected bond lengths and angles are listed in Table 1, crystal data in Table 5. ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 9 H, CMe_3), 1.25 (s, 9 H, CMe_3, 1.91–2.05 (m, 4 H, CH_2), 2.37–2.53 (m, 4 H, CH_2), 2.93 (br, 2 H, =CH), 4.43, 4.46 (2 d, ^2J = 14.0, 13.9 Hz, 2 H, NCH_2), 5.24 (br m, 2 H, =CH), 5.32, 5.37 (2 d, ^2J = 14.0, 14.0 Hz, 2 H, NCH_2), 7.32 (d br, ^3J = 5.7 Hz, 1 H, H7), 8.37 (d, ^3J = 5.7 Hz, 1 H, H6), 8.79 (d, ^3J = 0.6 Hz, 1 H, H4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 29.75, 28.83 (2 CH_2), 29.88, 29.93 (2 CMe_3), 32.68, 32.77 (2 CMe_3), 33.71, 33.86 (2 CH_2), 60.26, 60.53 (2 NCH_2), 70.13, 70.32 (2 d, J_{RhC} = 14.1, 14.1 Hz, =CH), 100.54, 100.58 (2 d, J_{RhC} = 6.7, 6.8 Hz, =CH), 106.24 (CH7), 133.42 (C_q3a), 133.67 (CH6), 140.87 (C_q7a), 142.04 (CH4), 205.22 (d, J_{RhC} = 51.9 Hz, C_q2). MS (EI, 70 eV, 370 °C): *m/z* (%) = 507 (6) [M^+], 506 (3), 505 (24) [M^+], 361 (55) [M^+–COD–HCl], 260 (100) [M^+–Rh(COD)Cl], 203 (64), 172 (25), 133 (50), 132 (28), 43 (45). HRMS, M^+ calcd for $C_{24}H_{37}ClN_3Rh$: 505.1731 (100), 506.1765 (27), 507.1702 (32); found (70 eV, 200 °C): m/e = 505.16868 (100), 506.1726 (17), 507.17305 (32).

b) Compound **4pc** was also obtained in analogy to **4pb** from the silver complex **7pc** (250 mg, 0.62 mmol) and $[Rh(1,5\text{-}COD)Cl]_2$ (153 mg, 0.31 mmol) in DCM (20 mL). The mixture was stirred in the dark at room temperature for 12 h and filtered to give a clear yellow solution. Removal of solvent under vacuum gave 300 mg (96%) crude product. A small amount of residual **7b** was removed by column chromatography on silica gel using DCM. The NMR data correspond to those given above.

4.13. Preparation of (η^3-Allyl)(1,3-dineopentyl-imidazolino[4,5-b]pyridin-2-ylidene) palladium(II) chloride (**5pb**)

Potassium hydride (78 mg, 1.94 mmol) was added at room temperature to a suspension of $\mathbf{2pb_{PF6}}$ (400 mg, 0.99 mmol) in THF (25 mL). The mixture was stirred for 3 h, filtered to remove potassium salts, and $[Pd(Allyl)Cl]_2$ (161 mg, 0.44 mmol) was then added as a solid at 0 °C. After stirring overnight at room temperature and filtration the solvent was removed under vacuum. The residue was washed several times with hexane and then crystallized from a concentrated solution in THF by overlayering with hexane yielding 334 mg (86%) of orange-red solid **5pb** ^{1}H NMR (CD_2Cl_2, ref. solvent 5.32 ppm): δ = 1.08 (s br, 2 CMe_3), 2.56 (d br, ^3J = 11.6 Hz, $^8/_9$ H, $CH_{trans\text{-}a}$), 3.06 (d br, ^3J = 13.2 Hz, $^1/_9$ H, $CH_{trans\text{-}a}$), 3.31 (d, ^3J = 13.6 Hz, 1 H, $CH_{trans\text{-}c}$), 3.57 (d br, ^3J = 5.3 Hz, ca. 1H, $CH_{cis\text{-}a}$), 4.23 (dd, ^3J = 7.5, J = 2.0 Hz, ca. 1H, $CH_{cis\text{-}c}$), 4.45 (d br, $^3J \approx 6$ Hz, minor signal, CH_{cis})), 4.0–4.3, 4.5–4.9 (2 superimposed vbr s, 2 NCH_2), 4.36, 4.47 (2 s, minor signals, NCH_2), 5.37 (m, 1 H, CH_b), 7.23 (dd, ^3J = 7.9, 4.9 Hz, $^8/_9$ H, 6-H), 7.24 (superimposed dd, ^3J = 8.1, 4.7 Hz, $^1/_9$ H, 6-H), 7.76 (dd br, ^3J = 7.9, ^4J = 1 Hz, 1 H, 7-H), 8.32 (dd, ^3J = 4.7, ^4J = 1.3 Hz, $^1/_9$ H, 5-H), 8.35 (dd, ^3J = 4.9, ^4J = 1.5 Hz, $^8/_9$ H, 5-H); assignment of allyl protons in analogy to ref. [28]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ref. solvent 53.8 ppm): δ = 29.35 (2 CMe_3), 33.98, 34.38 (2 CMe_3), 51.21 (CH_2-a), 57.68 (br, 1-NCH_2), 59.98 (vbr, 3-NCH_2), 72.23 (CH_2-c), 115.01 (CH-b), 118.16 (CH-6), 119.64 (CH-7), 128.07 (C_q-7a), 143.56 (CH-5), 147.94 (C_q-3a), 197.94 (C_q-2). MS (EI, 70 eV, 165 °C): *m/z* (%) = 446 (4) [M(^{110}Pd)+H]$^+$, 444 (8) [M(^{108}Pd)+H]$^+$, 442 (8) [M(^{106}Pd)+H]$^+$, 441 (5) [M(^{105}Pd)+H]$^+$, 370 (30), 369 (14), 368 (61), 366 (70), 365 (56), 364 (27), 260 (24), 259 (100) [M–allylPdCl)]$^+$, 204 (52), 189 (64). HRMS (EI, 70 eV): $C_{19}H_{30}ClN_3Pd$, calcd. for strongest peak of $[M]^+$ 441.1157; found: 411.1165; the observed isotopic pattern fits with the calculated pattern.

4.14. Preparation of (η^3-Allyl)(1,3-dineopentyl-imidazolino[4,5-c]pyridin-2-ylidene) palladium(II) chloride (**5pc**)

Potassium hydride (98 mg, 2.44 mmol) was added at room temperature to a suspension of $\mathbf{2pc_{PF6}}$ (500 mg, 1.23 mmol) in THF (25 mL). The crude NHC was converted with $[Pd(Allyl)Cl]_2$ (203 mg, 0.55 mmol, calcd. for 90% NHC generation) and worked up as described above for **5pb** affording 430 mg (88%) of red-brown solid **5pc**. ^{1}H NMR (CD_2Cl_2, ref. solvent 5.32 ppm): δ = 1.08 (br s, 2 CMe_3), 2.57 (d br, ^3J = 11.7 Hz, ca. 1H, $CH_{trans\text{-}a}$), 3.17 (d, ^3J = 12.1 Hz, minor, $CH_{trans\text{-}a}$), 3.31 (d, ^3J = 13.4 Hz, 1 H, $CH_{trans\text{-}c}$), 3.60 (d br, ^3J = 5.7 Hz, ca. 1H, $CH_{cis\ \text{-}a}$), 4.02 (d br, ^3J = 6.8 Hz, minor, $CH_{cis\text{-}c}$), 4.25 (d br, ^3J = 7.4 Hz, ca. 1H, $CH_{cis\text{-}c}$), 4.1–4.4, 4.5–4.9 (vbr, 2 NCH_2), 5.37 (m, 1 H, CH_b), 7.44 (d br, ^3J = 5.5 Hz, 1 H, H-7), 8.44 (d br, ^3J = 5.5 Hz, 1 H, H-6), 8.94 (s br, 1 H, H-4); assignment of allyl protons in analogy to ref. [28]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ref. solvent 53.8 ppm): δ = 29.33 (2 CM-e_3), 34.20 (CMe_3), 34.41 (CMe_3), 51.74 (s br, CH_2-a), 59.60, 60.00 (2 NCH_2), 72.45 (CH_2-c), 107.20 (CH-7), 115.18, (CH-b), 133.32 (C_q-3a), 135.10 (CH-6), 140.90 (C_q-7a), 143.01 (CH-4), 199.96 (C_q-2). MS (EI, 70 eV, 165 °C): *m/z* (%) = 446 (5) [M(^{110}Pd)+H]$^+$, 444 (9) [M(^{108}Pd)+H]$^+$, 442 (8) [M(^{106}Pd)+H]$^+$, 441 (6) [M(^{105}Pd)+H]$^+$, 370 (32), 368 (65), 367 (17), 366 (79), 365 (62), 364 (29), 259 (100) [M^+-AllylPdCl)], 204 (52), 189 (64). HRMS (EI): $C_{19}H_{30}ClN_3Pd$, calcd. for strongest peak of $[M]^+$ 441.1157; found: 441.1163; the observed isotopic pattern fits with the calculated pattern.

4.15. Preparation of bis(1,3-dineopentyl-imidazolino[4,5-c]pyridin-2-ylidene)palladium(0) (**6pc**)

A solution of bis(tetramethyldivinyldisiloxane)palladium(0) (8–10% Pd(0)) (0.4 mL, 0.52 mmol) was added to a solution of **1pc** (280 mg, 1.03 mmol) in hexane at room temperature. Hexane was partially removed in vacuum and the concentrated solution was stored at −20 °C for 3 days. The resulting crystals were filtered off and washed several times with hexane to give 205 mg (64%) of brown crystals of **6pc**. ^{1}H NMR (D_8-THF, ref. solvent 1.72 ppm): δ = 1.06 (br s, 18 H, CMe_3), 1.08 (br s, 18 H, CMe_3), 4.26 (br s, 4 H, NCH_2), 4.31 (br s, 4 H, NCH_2), 7.50 (d, ^3J = 5.7, 2 H, H7), 8.31 (d, ^3J = 5.7 Hz 2 H, H6), 8.80 (s, 2 H, H4). $^{13}C\{^1H\}$ NMR (D_8-THF, ref. solvent 25.2 ppm): δ = 29.01, 29.06 (2 CMe_3), 34.69 (CMe_3), 34.92 (CMe_3), 59.11, 59.49 (2 NCH_2), 107.30 (CH-7), 133.69 (C_q-3a), 135.01 (CH-6), 141.02 (C_q-7a), 142.96 (CH-4), 202.26 (C_q-2). Elemental analysis: Calcd. for $C_{32}H_{50}N_6Pd$ (625.20): C 61.48, H 8.06; found: C, 61.51, H, 8.43.

4.16. Preparation of bis(1,3-dineopentyl-imidazolino[4,5-b]pyridin-2-ylidene)silver triflate (**3pb**)

Silver triflate (198 mg, 0.77 mmol) was added to a THF solution of carbene **1pb** (400 mg, 1.54 mmol) at room temperature. The mixture was stirred for 14 h and filtered. After removal of the solvent from the filtrate under vacuum the residue was washed several times with hexane. It was soluble in DCM and crystallized from a concentrated solution by cooling (−5 °C), with slow addition of hexane; yield 480 mg (80%) colorless crystals of **3pb**. Selected bond lengths and angles are compiled in Table 1, crystal data in Table 5. ^{1}H NMR (CD_2Cl_2): δ = 1.12 (s, 18 H, CMe_3), 1.13 (s, 18 H, CMe_3), 4.34 (s, 4 H, NCH_2), 4.46 (s, 4 H, NCH_2), 7.46 (dd, ^3J = 8.3, 4.7 Hz, 2 H, H6), 8.03 (dd, ^3J = 8.3, ^4J = 1.3 Hz, 2 H, H7), 8.55 (dd, ^3J = 4.7, ^4J = 1.3 Hz, 2 H, H5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 28.86 (2 CMe_3), 33.96, 34.27 (2 CMe_3), 58.75 (d, $^3J_{AgC}$ = 1.1 Hz, 1-NCH_2), 61.65

(d, $^3J_{AgC}$ = 1.4 Hz, 3-NCH_2), 120.05 (CH6), 121.61 (CH7), 121.33 (q, $^1J_{FC}$ = 321.2 Hz, $CF_3SO_3^-$), 127.16 (d, $^3J_{AgC}$ = 5.4 Hz, C_q7a), 145.93 (CH5), 146.83 (d, $^3J_{AgC}$ = 7.3 Hz, C_q3a), 192.15 (2 d, $^1J_{AgC}$ = 189.4, 218.8 Hz, C-2). MS (EI, 70 eV, 345 °C): *m/z* (%) = 368 (3) $[L^{109}Ag]^+$, 366 (3) $[L^{107}Ag]^+$, 260 (100) $[L + H]^+$, 259 (17), 258 (12), 244 (23), 203 (78), 174 (22), 133 (65), 132 (39), 120 (30), 43 (49). Elemental analysis: calcd. for $C_{33}H_{51}AgF_3N_6O_3S$ (776.73): C 51.03, H 6.62; found: C 51.06, H 6.68.

4.17. Preparation of bis(1,3-dineopentyl-imidazolino[4,5-c]pyridin-2-ylidene)silver triflate (**3pc**)

Silver triflate (218 mg, 0.84 mmol) was added to a THF solution of carbene **1pc** (440 mg, 1.70 mmol) at room temperature and stirred overnight. Workup as described for **3pb** gave 535 mg (81%) colorless solid **3pc**, soluble in DCM. XRD analysis (Cu K_α) of a small crystal, obtained from DCM/diethyl ether, displayed considerable disorder but confirmed the structure qualitatively. ^{1}H NMR (CD_2Cl_2): δ = 1.12 (s, 18 H, CMe_3), 1.15 (s, 18 H, CMe_3), 4.36 (s, 4 H, NCH_2), 4.42 (s, 4 H, NCH_2), 7.63 (dd, ^3J = 5.7, ^5J = 0.8 Hz, 2 H, H7), 8.59 (d, ^3J = 5.7 Hz, 2 H, H6), 9.02 (br, 2 H, H4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 28.78 (*CMe*$_3$), 28.82 (*CMe*$_3$), 34.07 (*C*Me_3), 34.26 (*C*Me_3), 60.71 (3-NCH_2), 61.21 (1-NCH_2), 107.95 (CH7), 121.24 (q, $^1J_{FC}$ = 321.4 Hz, $CF_3SO_3^-$), 132.24 (d, $^1J_{AgC}$ = 6.3 Hz, C_q3a), 136.13 (CH6), 140.07 (d, $^1J_{AgC}$ = 6.3 Hz, C_q7a), 143.98 (CH4), 193.94 (2d, $^1J_{AgC}$ = 190.5, 219.7 Hz, C2). MS (EI, 70 eV, 345 °C): *m/z* (%) = 368 (5) $[L^{109}Ag]^+$, 366 (5) $[L^{107}Ag]^+$, 260 (94) $[L + H]^+$, 259 (25), 258 (12), 203 (100), 174 (25), 133 (74), 132 (42), 120 (37), 43 (60). Elemental analysis: calcd. for $C_{33}H_{51}AgF_3N_6O_3S$ (776.73): C 51.03, H 6.62; found: C 51.14, H 7.08.

4.18. Preparation of (1,3-dineopentyl-imidazolino[4,5-b]pyridin-2-ylidene)silver chloride (**7pb**)

Ag_2O (392 mg, 1.71 mmol) and freshly activated molecular sieve (3 Å) was added to a suspension of **2pb$_{Cl}$** (500 mg, 1.69 mmol) in DCM (20 mL). The suspension was stirred for 24 h at room temperature and then filtered. Concentration of the filtrate under vacuum (to ca. 4 mL) and addition of hexane (5 mL) led to a white precipitate. This was separated and recrystallized from DCM to give 570 mg (84%) of **7pb**. Selected bond lengths and angles are compiled in Table 1, crystal data in Table 5. ^{1}H NMR (CD_2Cl_2): δ = 1.08 (s, 9 H, CMe_3), 1.09 (s, 9 H, *C*Me_3), 4.29, 4.41 (2 s, 4 H, NCH_2), 7.36 (dd, ^3J = 8.2, 4.8 Hz, 1 H, H6), 7.88 (dd, ^3J = 8.2, ^4J = 1.3 Hz 1 H, H7), 8.47 (dd, ^3J = 4.8, ^4J = 1.3 Hz, 1 H, H5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 28.84 (*CMe*$_3$), 28.88 (*CMe*$_3$), 33.94, 34.28 (2 *C*Me_3), 58.47 (1-NCH_2), 61.37 (3-NCH_2), 119.30 (CH6), 120.88 (CH7), 127.03 (C_q7a), 145.16 (CH5), 146.97 (d, $^3J_{AgC}$ = 6.2 Hz, C_q3a), 193.70 (2 d, $^1J_{AgC}$ = 270.6, 234.7 Hz, C-2). MS (EI, 70 eV, 200 °C): *m/z* (%) = 363 (0.2), 261 (8), 260 (43) [M^+-AgCl], 259 (15), 203 (70), [M^+-*t*Bu-AgCl], 174 (19), 135 (21), 133 (59), 132 (35), 120 (27), 43 (100). Elemental analysis: calcd. for $C_{16}H_{26}AgClN_3$ (403.72): C, 47.60, H, 6.49, N, 10.41; found: C, 47.59, H, 6.50, N, 10.57.

4.19. Preparation of (1,3-dineopentyl-imidazolino[4,5-c]pyridin-2-ylidene)silver chloride (**7pc**)

Complex **7pc** was prepared in analogy to **7pb** from Ag_2O (392 mg, 1.71 mmol) and **2pc$_{Cl}$** (500 mg, 1.69 mmol). Recrystallization from DCM/hexane gave 520 mg (76%) colorless crystals. Selected bond lengths and angles are compiled in Table 1, crystal data in Table 5. ^{1}H NMR (CD_2Cl_2): δ = 1.09 (s, 9 H, CMe_3), 1.11 (s, 9 H, CMe_3), 4.31, 4.38 (2 s, 4 H, NCH_2), 7.50 (dd, ^3J = 5.7, ^5J = 0.9 Hz, 1 H, H7), 8.51 (d, ^3J = 5.7 Hz 1 H, H6), 8.93 (d, ^5J = 0.8 Hz, 1 H, H4). $^{13}C\{^1H\}$ and DEPT-135 NMR (CD_2Cl_2): δ = 28.82 (2 *CMe*$_3$), 34.09 (*C*Me_3), 34.30 (*C*Me_3), 60.46, 60.92 (2 NCH_2), 107.61 (CH7), 132.23 (C_q3a), 135.78 (CH6), 139.94 C_q7a), 143.46 (CH4), 195.82 (dd, $^1J_{AgC}$ = 273.1, 236.1 Hz, C2). MS (EI, 70 eV, 345 °C): *m/z* (%) = 376 (3), 363 (7). 361 (5), 261 (6), 260 (17) [M^+-AgCl], 241 (11), 229 (16), 203 (27) [M^+-*t*Bu-AgCl], 199 (10), 185 (12), 135 (100), 133 (2), 120 (12), 77 (18), 43 (23). Elemental analysis: calcd. for $C_{16}H_{26}AgClN_3$ (403.72): C, 47.60, H, 6.49, N, 10.41; found: C, 47.79, H, 6.42, N, 10.34.

4.20. Preparation of bis(1,3-dineopentyl-imidazolino[4,5-b]pyridin-2-ylidene)palladium dichloride (**8pb**)

The silver complex **7pb** (260 mg, 0.64 mmol) was dissolved in DCM (15 mL), and $Pd(CH_3CN)_2Cl_2$ (84 mg, 0.32 mmol) was added. The mixture was stirred in the dark at room temperature for 12 h, then filtered to give a clear yellow solution. The solvent was partly removed, and the saturated solution was stored at −20 °C for 24 h yielding 164 mg (73%) yellow crystals of **8pb** ^{1}H NMR (CD_2Cl_2): δ = 1.26 (s, 36 H, 4 CMe_3), 4.905, 4.913 (2 s, each 4 H, NCH_2), 5.006, 5.013 (2 s, each 4 H, NCH_2), 7.22 (dd, ^3J = 8.2, 4.8 Hz, 2 H, H6), 7.80 (dd, ^3J = 8.2, ^4J = 1.2 Hz, 2 H, H7), 8.34 (dd, ^3J = 4.8, ^4J = 1.0 Hz, 2 H, H5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 29.83, 29.84, 29.84, 29.87 (3 s, 4 *CMe*$_3$), 34.16, 34.18, 34.60, 34.61 (4 s, *C*Me_3), 57.87, 57.90 (2 s, 3-NCH_2), 60.03 (br, 2 1-NCH_2), 118.14 (br, 2 CH6), 120.17, 120.21 (2 s, 2 CH7), 127.93 (2 C_q7a), 143.64 (2 CH5), 147.81 (2 C_q3a), 185.61 (2C2). Calcd (%) for $C_{32}H_{51}Cl_2N_6Pd$: 695.26 (100), 697.26 (98). MS (FAB pos., NBA): *m/z* (%) = 697 (70), 695 (70), 662 (60), 660 (100), 658 (95), 626 (60), 624 (95), 622 (45).

4.21. Preparation of (1,3-dineopentyl-imidazolino[4,5-c]pyridin-2-ylidene)palladium chloride (**9pc**)

$Pd(CH_3CN)_2Cl_2$ (193 mg, 0.74 mmol) was added to the silver complex **7pc** (300 mg, 0.74 mmol), dissolved in DCM (15 mL). The mixture was stirred in the dark at room temperature for 12 h, then filtered to give a clear yellow solution. The solvent was partly removed and the saturated solution was stored at −20 °C for 24 h. Rapid filtration and drying of the precipitate under vacuum gave 250 mg (77%) **9pc** as yellow powder. The product was insoluble in CD_2Cl_2 and in d_8-THF and sparingly soluble in moist DMSO-d_6. The latter solution displayed NMR signals of two closely related complexes (ca. 4:6) with most of their signals broad and superimposed. ^{1}H NMR (DMSO-d_6, ref. solv. 2.50): δ = 1.19 (br s, 0.4 × 9 H, CMe_3), 1.30 (br s, 0.6 × 9 H, *C*Me_3), 4.94 (superimposed br, NCH_2), 5.05, 5.15 (superimp. br m, NCH_2), 8.06, 8.13 (2 vbr unresolved d, H7), ca. 8.6, 8.69 (2 vbr unres. m, H6), 9.23 (vbr, ca. 0.5 H, H4), 9.35, 9.45 (vbr, 0.5 H, H4); 5.75 (s, 0.25 CH_2Cl_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, ref. solv. 39.5): δ = 28.95 (*CMe*$_3$), 29.16 (st, *CMe*$_3$), 29.40 (*CMe*$_3$), 33.43 (*C*Me_3), 33.66 (*C*Me_3), 33.90 (*C*Me_3), 34.02 (*C*Me_3), 58.0–59.2 (br, NCH_2), 108.5 (br, CH7), 131.45, 131.56, 136.67, 137.23, 140.5 (br), 143.62, 143.93, 188.7 (br, C2); 54.87 (CH_2Cl_2). MS (EI, 70 eV, 370 °C): *m/z* (%) = 401 (4) $[LPdCl]^+$, 243 (27), 242 (23), 178 (70), 169 (49), 113 (36), 105 (35), 43 (100). Elemental analysis: calcd. for $C_{16}H_{25}N_3PdCl_2$ (436.72): C, 44.00, H, 5.77; found: C, 43.02 (incomplete C combustion), H 6.05.

4.22. Preparation of (η^3-allyl)(1,3-dineopentyl-benzimidazolin-2-ylidene)palladium chloride (**5b**)

Allylpalladium chloride dimer (53 mg, 0.145 mmol) was added to a solution of **7b** (115 mg, 0.286 mmol) in DCM (5 mL) and stirred for 4 h at room temperature. Then the mixture was filtered; the residue was washed with the same solvent and the filtrate concentrated to give 62 mg (ca. 98%) **5b**. ^{1}H NMR (CD_3OD): δ = 1.10 (18 H, 2 CMe_3), 2.67 (d br, ^3J = 12.1 Hz, ca. $^2/_3$ H, $H_{trans\text{-}a}$), 3.30 (d,

^3J = 12.1 Hz, ca. $^1/_3$ H, $H_{trans\text{-}a}$), 3.34 (d, superimposed by solvent, $^3J \approx$ 13 Hz, $H_{trans\text{-}c}$), 3.68 (d br, $^3J \approx$ Hz, ca. $^2/_3$ H, $H_{cis\ \text{-}a}$), 3.68 (d br, ^3J = 6.8 Hz, ca. $^1/_3$ H, $H_{cis\ \text{-}a}$), 4.23 (dd, ^3J = 7.6, J = 1.0 Hz, 1 H, $H_{cis\text{-}c}$), 4.0–4.9 (superimposed vbr s, 2 NCH_2), 5.49 (m, 1 H, CH_b), 7.31 ($m_{AA'}$, 2 H, H-4/7), 7.64 ($m_{BB'}$, 2 H, H-5/6). ^{13}C NMR ($CDCl_3$): δ = 29.82 (2 *C*Me_3), 35.02 (2 *C*Me_3), 52.06 (CH_2a), 59.84 (2 NCH_2), 73.38 (CH_2c), 116.40 (CHb), 113.37 (CH4, CH7), 123.69 (CH5, CH6), 136.79 (C_q3a, C_q7a), 194.44 (C2). Elemental analysis: Calculated for $C_{20}H_{31}ClN_2Pd$ (441.35): C 54.43, H 7.08; found: C 54.12, H 6.85.

4.23. Preparation of trans-Bis(1,3-dineopentyl-benzimidazolin-2-yliden)palladium(II) chloride (**8b**)

a) (2,5-Norbornadiene)palladium chloride (167 mg, 0.62 mmol) and two equivalents of **7b** (498.2 mg, 1.24 mmol) were dissolved in DCM (10 mL) and stirred overnight at room temperature. The mixture was then filtered, the precipitate washed with DCM (2 x 5 mL) and the solvent and volatile components removed from the filtrate under vacuum to give 422 mg (98%) pale yellow solid. ^{1}H NMR (CD_2Cl_2): δ = 1.26 (s, 36 H, CMe_3), 4.91 (s, 8 H, NCH_2), 7.25 (m, 4 H, H5/H6), 7.51 (m, 4 H, H4/H7). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ = 29.99 (C*Me*$_3$), 34.62 (*C*Me_3), 59.18 (NCH_2), 112.70 (CH4/7), 122.42 (CH5/6), 135.82 (C_q3a/7a), 182.57 (C2).

b) ^{1}H and ^{13}C NMR spectra of the product, obtained with a 1:1 M ratio of [Pd(NBD)Cl_2] and **7b** (each 0.12 mmol) under the same conditions, displayed identical NMR spectra. HRMS (ESI in MeOH): $C_{34}H_{52}ClN_4Pd$ (694.13), strongest peaks calcd. for $[M-Cl]^+$ 657.2921, 659.2912; found: 657.2892, 659.2903; isotopic pattern in accordance with calcd. pattern.

4.24. Detection of cis- and trans-bis(1,3-dineopentyl-benzimidazolin-2-ylidene)palladium(II) acetates (**10b** and **11b**)

a) Reaction of palladium(II) acetate (108.9 mg, 0.49 mmol) with **7b** (389.7 mg, 0.97 mmol) in DCM (10 mL) and workup as described for **8b** provided a solid mixture of **10b** and **11b**, slightly contaminated by two other Pd complexes of this ligand (integral ratio of *t*Bu ^{1}H NMR signals ca. 5:3:1:1). Attempts to obtain single crystals or to separate the complexes failed. HRMS (ESI in MeCN): $L_2Pd(OAc)_2$ - $C_{38}H_{58}N_4O_4Pd$ (741.31), calcd. for strongest peak of $[M - OAc]^+$ 681.3360; found: 681.3356; good accordance of the isotopic pattern with calc. values; LPd^+ peaks were also observed. **10b** (*cis*) - ^{1}H NMR (CD_2Cl_2): δ = 1.26 (s, 4 CMe_3), 1.8–1.9 (vbr, MeCOO), 4.86, 4.94 (2 d, ^2J = 14.4 Hz, 4 NCH_AH_B); 7.26 (superimposed m, H-4/7), 7.53 (superimposed m, H-5/6). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 22.84 (CH_3CO), 29.50 (C*Me*$_3$), 34.37 (*C*Me_3), 59.20 (NCH_2), 112.93 (CH4/7), 122.70 (CH5/6), 135.50 (C_q3a/7a), 175.73 (Me*C*OO), 181.58 (C2). **11b** (*trans*) - ^{1}H NMR (CD_2Cl_2): δ = 1.25 (s, 4 CMe_3), 1.47 (s, MeCOO, assignment uncertain), 4.95 (br s, NCH_2), CH_3COO and aryl-H signals superimposed. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 22.89 (*Me*COO), 29.78 (C*Me*$_3$), 34.04 (*C*Me_3), 59.25 (NCH_2), 112.40 (CH4/7), 122.26 (C-5/6), 135.43 (C_q3a/7a), 175.80 (Me*C*OO), 183.75 (C2). Side products (anion unidentified) - ^{1}H NMR (CD_2Cl_2): δ = 1.28, 1.29 (2 s, CMe_3), 4.84, 5.05 (2 d, ^2J = 14.4 Hz, NCH_AH_B), 4.91, 4.99 (2 d, ^2J = 14.7 Hz, NCH_AH_B); aryl-H signals superimposed. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 29.92, 30.08 (C*Me*$_3$), 34.41, 34.57, 34.64 (*C*Me_3), 59.04, 59.39 (NCH_2), 112.59, 113.02 (CH-4/7), 122.33, 122.79 (CH-5/6), 135.15, 135.61 (C_q-3a/7a), 180.92, 182.71 (C2).

b) *Formation under conditions of in-situ catalyst generation*: A mixture of **2b$_{PF6}$** (161.7 mg, 0.4 mmol), $Pd(OAc)_2$ (44.9 mg, 0.2 mmol) and K_3PO_4 (191.6 mg, 0.9 mmol) in 1,4-dioxane (10 mL) was heated for 30 min at 80 °C, filtered and the residue washed with dioxane (2 x 5 mL). After removal of the solvent from the dark red filtrate the residue was dissolved in CD_2Cl_2 for NMR analysis. The ^{1}H and ^{13}C NMR spectra displayed roughly equally intense signals of unconverted **2b$_{PF6}$** and the complexes **10b** and **11b**.

4.25. Procedures for Suzuki-Miyaura coupling of p-bromotoluene with $PhB(OH)_2$

a) Procedure with in-situ catalyst generation. A Schlenk flask equipped with magnetic stirrer was charged with $Pd(OAc)_2$ (7 mg, 30 μmol), the respective annulated imidazolium salt (30 or 60 μmol, *cf.* Table 4) and dry K_3PO_4 (425 mg, 2 mmol), Cs_2CO_3 (652 mg, 2 mmol) or KH (80 mg, 2 mmol). After repeated evacuation and refilling with argon, 1,4-dioxane (5 mL) was added and the mixture heated with stirring for 30 min at 80 °C. Then the flask was cooled to r.t., a solution of *p*-bromotoluene (171 mg, 1 mmol) and $PhB(OH)_2$ (183 mg, 1.5 mmol) in 1,4-dioxane (5 mL) was added, and heating with stirring continued for 16 h at 80 °C. After cooling to r.t., the reaction was quenched with aq. NH_4Cl, the product extracted with 3 x 10 mL diethyl ether, the extract concentrated under slightly reduced pressure and analyzed by GC against nonane or tridecane (1 mmol) as internal standards. The results are compiled in Table 4.
b) *Procedure with complexes as precatalyst*. Aliquots of a solution of **5 pb**, **5pc**, **5b**, **5ph** or **8b** corresponding to 30 μmol (3 mol%) in 1,4-dioxane were added to a mixture of K_2CO_3 (277 mg, 2 mmol) or K_3PO_4 (425 mg, 2 mmol) with *p*-bromotoluene (171 mg, 1 mmol) and $PhB(OH)_2$ (183 mg, 1.5 mmol) in 1,4-dioxane (5 mL), heated for 2 or 16 h at 80 °C, and worked up and analyzed as described above; results see Table 4.

c) GC analysis. Tridecane was added after quenching, nonane after concentration of the ethereal extract. Sensitivity factors relative to the internal standard were determined for *p*-bromotoluene, *p*-methyldiphenyl, diphenyl, benzene and toluene and repeated for each measuring series.

4.26. Crystal structure analysis of **4pb**, **4pc** [9b], **3pb**, **7pb**, **7pc** and **2b$_{PF6}$**·H_2O

Data were recorded on a Bruker SMART 1000 CCD (**4pb**, **4pc**, **7pb**) or an Oxford Diffraction Xcalibur S diffractometer (**3pb**), both using Mo *Kα* radiation (λ = 0.71073 Å), or an Oxford Diffraction Nova O diffractometer (**7pc**, **2b$_{PF6}$**·H_2O) using Cu *Kα* radiation (λ = 1.54184 Å). Absorption corrections were applied by face indexing (**10pc**) or multi-scans. Structures were refined anisotropically on F^2 using the program SHELXL-97 [29]. Hydrogen atoms of coordinated double bonds, carbenium H, NH and OH groups were refined freely but with C-H or O-H distances restrained equal (where applicable); methyl groups were refined as rigid groups allowed to rotate but not tip; other H were included using a riding model. *Special details*: For compound **4pb**, the atoms C24, C27 and C28 of the COD ring are disordered over two positions, but the minor position is occupied only to the extent of 8%.

It is important to assign correctly the C and N atoms in the pyridinic rings. We are reasonably confident that our assignments are correct: H atoms of the CH groups are all found in difference syntheses, whereas there is no residual electron density near the N atoms; ellipsoids are of normal dimensions; pyridinic bond lengths at N are significantly and consistently shorter; in some cases the CH group acts as a weak H bond donor and the N atom as an acceptor, and an H atom added artificially at N makes unusually short H···H contacts. However, the assignments of light atoms in heavy-atom structures is always challenging, and a limited amount of disorder can never be completely ruled out by crystallographic methods alone.

For crystal data see Table 5. Complete crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 617669 (**4pb**), 617670 **(4pc)**, 617671 **(7pb),** 1880308 **(3pb)**, 1880310 **(7pc)**, 1080311 **(2b$_{PF6}$**·H_2O**)**.

Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

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Appendix A. Supplementary data

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