Substituent-dependent structures and catalysis of benzimidazole-tethered N-heterocyclic carbene complexes of Ag(I), Ni(II) and Pd(II)† ‡

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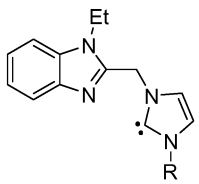
Homoleptic cationic benzimidazole-imidazolin-2-ylidene N-heterocyclic carbene (NHC = L) complexes of Ni^{II} and Pd^{II} have been prepared directly from the ligand precursor in salt form [H.L]Cl and from the transmetallation route *via* Ag^{I}. The N-tether of the imidazolinylidene ring imposes a significant influence on the nuclearity of the intermediate Ag(I)-NHC complexes and the geometric isomer outcome of the d^8 products. Use of a benzyl-substituted NHC gives $[Ag_4(L^{Bn})_2Cl_4]$, **2a** (from $[HL^{Bn}]Cl$, **1a**, and Ag_2O) (Bn = benzyl), which shows an alignment of four silver atoms bridged by the difunctional C–N ligands and chlorides. Its transmetallation with $NiCl_2(PPh_3)_4$ and $PdCl_2(MeCN)_2$ results in double-metal salts $2[M(L^{Bn})_2]^{2+}[Ag_4Cl_8]^{4-}$ (M = Ni (**3a**) and Pd (**4a**)). The nuclearity of the Ag_4 aggregate is maintained in the transmetallation process. Their Ag-free forms $[M(L^{Bn})_2]Cl_2$ (M = Ni (**5**) and Pd (**6**)) were prepared by direct deprotonation of **1a** with $M(OAc)_2$. The two carbenic carbon donor are *cis*- to each other in both **3a** and **4a**, thus imposing the weaker σ-benzimidazole nitrogen donor to be *trans* to them. A sterically demanding mesityl pendant however gives the dinuclear dissymmetic $[Ag_2(L^{Mes})_2Cl_2]$, **2b** (Mes = mesityl) that shows a 12-membered metallomacrocyclic ring with a 2-coordinated $[Ag^{I}(NHC)_2]$ and 4-coordinated $[Ag^{I}(Imd)_2Cl_2]$ (Imd = imidazole). Transmetallation of the latter, or direct metallation from $[HL^{Mes}]Cl$, **1b**, gives $[M(L^{Mes})_2]Cl_2$ (M = Ni (**3b**) and Pd (**4b**)) with the two carbonic carbon *trans* to each other. The catalytic potential of **3b** and **4b**, which are more effective than **5** and **6**, has been demonstrated by their high activities in Ni-catalyzed Kumada at room temperature and Pd-catalyzed Heck couplings of aryl and/or heteroaryl halides, respectively.

Introduction

N-Heterocyclic carbenes (NHCs) have attracted considerable interest for their diverse applications in coordination chemistry and homogeneous catalysis.[1] In recent times, much attention has been turned to the design of carbene hybrid ligands, namely, NHCs that are functionalized with other donor functions.[2] It provides a ready method to tune the electronic and steric characters of the resulting complexes, as well as to raise the ligand hemilability, both of which are essential considerations in catalytic designs. Nitrogen donors of different dissociability such as amine,[3] imine,[4] oxazoline,[5] pyridine,[6] pyrimidine,[7] quinoline[8] and phenanthroline[9] are among the successful examples that can be hybridized with pure NHC. We have recently reported the use of benzimidazole-functionalized imidazolium NHC ligand (Fig. 1, L^{Me}) to support the trinuclear $Ag_3Cl_2(\mu\text{-}Cl)(\mu\text{-}L^{Me})_2$ and its use as a transmetallation agent to give $PdCl_2(\eta\text{-}L^{Me})$, which is a Suzuki-active catalyst with high TON (~11 750).[10a] Other benzimidazole hybrid ligands have also emerged accordingly.[10b,10c] In view of the very unusual structural motif found in the intermediate Ag_3 complex and its synthetic utility for other d^8 carbene-hybrid complexes,[10a,11] we have investigated the coordination of other related ligands and found that the structural assemblies of both the transmetallation intermediates and final products are dependent on the ligand substituents. These variations however do not appear to adversely affect the efficiency of the transmetallation step. The synthesis of two other ligands with bulkier N-substituents (Fig. 1, L^{Bn} **1a** and L^{Mes} **1b**) (Bn = benzyl; Mes = mesityl) and their complexation with Ag(I) (**2a** and **2b**), Ni(II) (**3a**, **3b** and **5**) and Pd(II) (**4a**, **4b** and **6**) as well as the use of **3b** and **4b** as catalysts for the Ni-catalyzed Kumada and Pd-catalyzed Heck couplings of aryl and/or heteroaryl halides are herein reported.



R = CH_3, L^{Me}; CH_2Ph, L^{Bn}; $(CH_3)_3C_6H_5$, L^{Mes}

Fig. 1 A structural representation of benzimidazole-functionalized NHC ligands.

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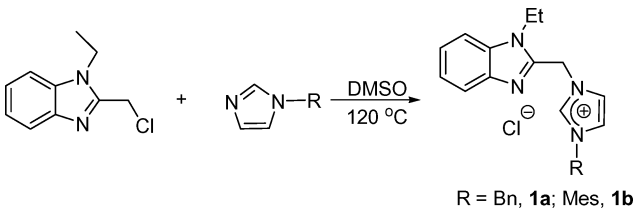
† CCDC reference numbers 760767–760776. For crystallographic data for **1a–4a**, **1b–4b**, **5** and **6** in CIF or other electronic format see DOI: 10.1039/c000722f

‡ This paper is dedicated to the memory of Professor Robert Bau (1944–2008).

Results and discussion

Synthesis of new benzimidazole-functionalized imidazolium salts (1a and 1b)

The imidazolium salts **1a** and **1b** were prepared from the quarternization of N-substituted imidazoles by 2-chloromethyl-1-ethylbenzimidazole in DMSO at 120 °C (Scheme 1). ^{1}H NMR spectra of **1a** and **1b** show characteristic downfield resonances of the NCHN protons at 9.59 and 9.92 ppm (in d_6-DMSO). The ^{13}C NMR spectra display characteristic downfield resonances at 148.15 and 147.71 ppm for the NCN carbons. The positive mode of ESI-MS give base peaks at $m/z = 317$ and 345 which correspond to the cations of **1a** and **1b** respectively. The molecular structures of **1a** and **1b** have been unambiguously identified by single-crystal X-ray diffraction (Fig. 2, depository numbers: CCDC 760767 (**1a**) and CCDC 760768 (**1b**)†), which indeed revealed the expected benzimidazole-functionalized imidazolium cation associated with Cl^- anion.



Scheme 1 Synthesis of ligand precursor $[HL]^+Cl^-$.

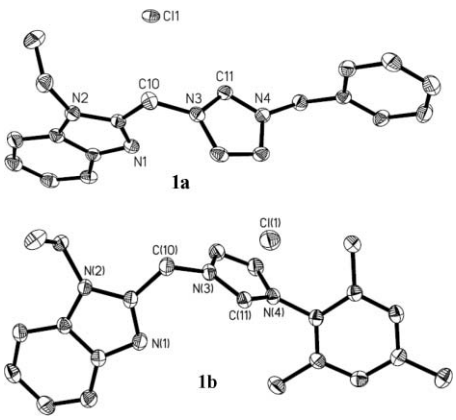
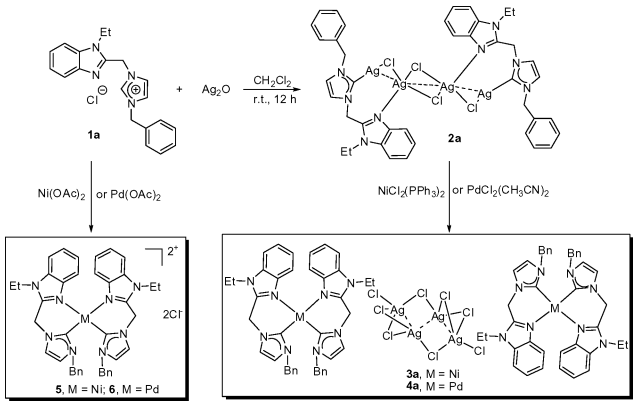


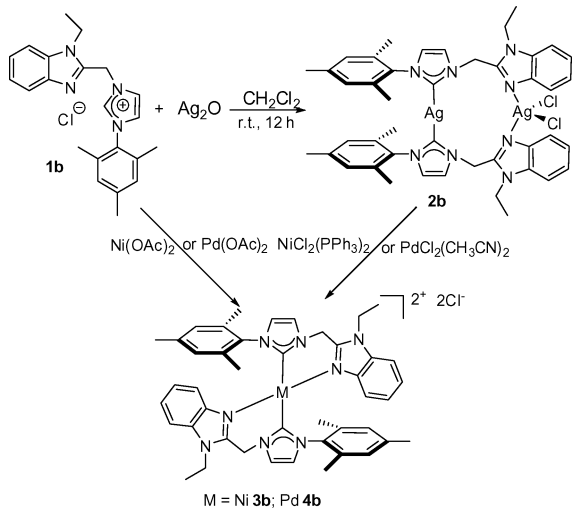
Fig. 2 Molecular structures of benzimidazole-functionalized imidazolium salts $[HL^{Bn}]Cl$ (**1a**) and $[HL^{Mes}]Cl$ (**1b**) with 30% thermal ellipsoids and labeling scheme; hydrogen atoms are omitted for clarity.

Synthesis of Ag^I complexes (2a and 2b)

Reactions of **1a** and **1b** in CH_2Cl_2 at r.t. with Ag_2O yield colorless complexes **2a** $[Ag_4(\mu\text{-}Cl)_4(L^{Bn})_2]$ and **2b** $[Ag_2Cl_2(L^{Mes})_2]$, respectively (Scheme 2 and 3). Their ^{1}H-NMR spectra in d_6-DMSO reveal the complete disappearance of the resonances for the acidic 2H-imidazolium protons, supporting the formation of the silver-carbene moieties. Their ^{13}C NMR spectra also display significant downfield shifted resonances (180.39 and 181.66 ppm) for the NCN carbon, thus pointing to NHC complex formation. Similar to the reported trinuclear $Ag_3Cl_2(\mu\text{-}Cl)(\mu\text{-}L^{Me})_2$,[10a] the two



Scheme 2 Synthesis of NHC complexes of Ag^I (**2a**), Ni^{II} (**3a** and **5**) and Pd^{II} (**4a** and **6**) from the precursor **1a**.



Scheme 3 Synthesis of NHC complexes of Ag^I (**2b**), Ni^{II} (**3b**) and Pd^{II} (**4b**) from **1b**.

protons on the bridgehead carbon (C10/10A, Fig. 3, depository number: CCDC 760769 (**2a**)†) appear as singlets (5.75 and 5.86 ppm respectively) in the ^{1}H-NMR spectra, which probably indicate unhindered rotation about carbon linker in solution. The positive mode of ESI-MS spectra give no further structural information except confirmation of the presence of $[Ag(L)_2]^+$ for both **2a** (m/z 741) and **2b** (m/z 797).

Unlike the known $Ag_3Cl_2(\mu\text{-}Cl)(\mu\text{-}L^{Me})_2$, the X-ray structure of **2a** shows an open alignment of four silver atoms with the carbene-benzimidazole hetero-donating ligand bridging the two external silver atoms, supplemented by alternate singly and doubly bridging chlorides (Scheme 2 and Fig. 3). This assembly could be a result of dimerisation of two dinuclear $[ClAg(\mu\text{-}L^{Bn})AgCl]$ moieties as a means to gain stability. No formal Ag^I–Ag^I bonding is envisaged although Ag1–Ag2 (2.988(2) Å) is within bonding distance and internal Ag(1)–Ag(1A) is confined to a close contact of 3.338(2) Å. The stark contrast between $Ag_3Cl_2(\mu\text{-}Cl)(\mu\text{-}L^{Me})_2$ and $[Ag_4(\mu\text{-}Cl)_4(L^{Bn})_2]$ demonstrates the structural sensitivity of these Ag(I), which are intermediates in the transmetallation process, on the N-substituent of the imidazole ring. The geometric, coordination and nuclearity flexibilities of Ag(I) enables it to adjust and adapt to different electronic and steric demands of different hybrid carbene

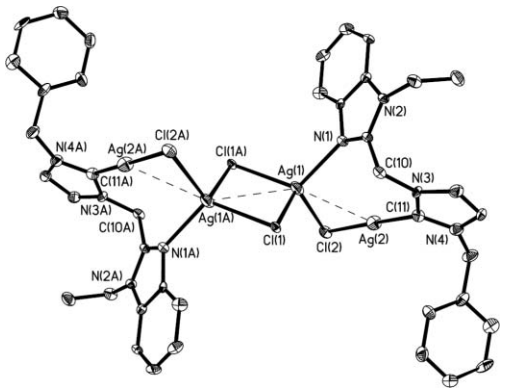


Fig. 3 ORTEP view of $[Ag_4Cl_4(L^{Bn})_2]$ (**2a**) with 30% thermal ellipsoids and labeling scheme. Selected bond lengths (Å) and angles (°): Ag1···Ag2 2.988(2), Ag1···Ag1A 3.338(2), Ag1–N1 2.314(9), Ag1–Cl1 2.664(3), Ag1–Cl1A 2.616(3), Ag1–Cl2 2.805(4), Ag2–C11 2.068(1), Ag2–Cl2 2.337(3), Ag1A–Cl1 2.616(3), N1–Ag1–Ag2 73.4(3), N1–Ag1–Ag1A 126.1(2), N1–Ag1–Cl1 107.1(2), N1–Ag1–Cl2 109.5(3), N1–Ag1–Cl1A 117.0(3), C11–Ag2–Ag1 115.7(4), C11–Ag2–Cl2 176.3(4), Ag2–Ag1–Ag1A 145.6(6), Ag2–Cl2–Ag1 70.4(9), Cl2–Ag1–Ag2 47.5(7), Cl2–Ag1–Ag1A 124.4(8), Cl2–Ag2–Ag1 62.2(9), Ag1–Cl1–Ag1A 78.4(9), Cl1–Ag1–Cl2 116.1(1), Cl1–Ag1–Ag2 99.7(8), Cl1–Ag1–Ag1A 50.2(7), Cl1A–Ag1–Cl1 101.6(9), Cl1A–Ag1–Cl2 105.8(1), Cl1A–Ag1–Ag2 151.8(8), Cl1A–Ag1–Ag1A 51.4(7).

ligands, thus explaining the synthetic utility of the transmetallation methodology in NHC carbene syntheses.

The structural variation of these Ag(I) complexes is further exemplified in the identification of **2b** which crystallizes with the triclinic space group $P\bar{1}$. The bulky mesityl substituent exerts a strong influence on the molecular structure of its Ag^I complex, giving a dissymmetric bridged structure of 2- and 4-coordinated Ag(I) spheres (Scheme 3 and Fig. 4, depository number: CCDC 760770 (**2b**)†). The former comprises a binary NHC moiety with two NHC ligands (Ag2–C11 2.090(6) and Ag2–C33 2.087(6) Å) attached to a Ag(I) that is significantly distorted from linear ((C11–Ag2–C33) 166.4(3)°). The distortion could be a result of the constraint imposed by the twelve-membered metallomacrocyclic ring. The second Ag(I) is tetrahedrally bound to the N-donating-benzimidazoles and two terminal chlorides. The Ag–N bonds (Ag1–N1 2.359(5), Ag1–N5 2.328(5) Å) are longest among this series of Ag-NHC complexes (Ag–N (2.242(2) Å) in $Ag_3Cl_2(\mu\text{-}Cl)(\mu\text{-}L^{Me})_2$ and (2.314(9) Å) in $[Ag_4(\mu\text{-}Cl)_4(L^{Bn})_2]$), probably due to the saturation of Ag(I) here. The Ag1···Ag2 non-bonding separation of 3.739(3) Å is significantly larger than the combined van der Waals radii (3.20 Å) and at the large end of the Ag···Ag distances (3.232(1)–3.852(1) Å) found in other Ag(I) metallomacrocycles.[11f]

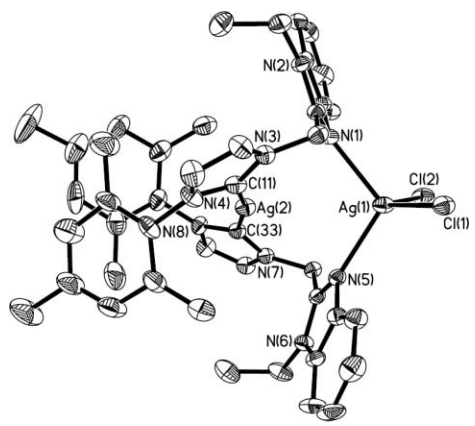


Fig. 4 ORTEP view of $[Ag_2(L^{Mes})_2Cl_2]$ (**2b**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag2–C11 2.092(6), Ag2–C33 2.088(6), Ag1–N1 2.359(5), Ag1–N5 2.330(5), Ag1–Cl1 2.574(2), Ag1–Cl2 2.590(2), Ag1···Ag2 3.739(3), C11–Ag2–C33 166.2(3), N1–Ag1–N5 109.2(2), Cl1–Ag1–Cl2 117.6(7).

Synthesis of Ni^{II} and Pd^{II} from transmetallation of Ag^I-NHC complexes

The significance of silver NHC carbene complexes is evident in its common use as a transmetallation agent in the preparation of NHC complexes of other late transition metals.[11,12] Reaction of **2a** with $NiCl_2(PPh_3)_2$ in CH_2Cl_2 at r.t. gives $[Ni(L^{Bn})_2]_2[Ag_4Cl_8]$ (Scheme 2, **3a**), which is a result of phosphine replacement at Ni^{II} and chloride migration to Ag(I). Its formation is inferred from the disappearance of the ^{1}H-NMR resonance of the acidic imidazolium C_2–H at 9.59 ppm. The bidentate chelate at Ni^{II} shows two doublets for the methylene linkage at 6.32 and 6.23 ppm. Its ^{13}C-NMR spectrum shows the carbenic carbon at 159.94 ppm. The positive mode ESI-MS shows two base peaks of $[Ni(L^{Bn})_2]^{2+}$ at $m/z = 345$ and 690 with isotopic peak difference of 0.5 and 1.0 mass units respectively.

The identity of **3a** was unambiguously verified in an X-ray single-crystal diffraction analysis (Fig. 5, depository number:

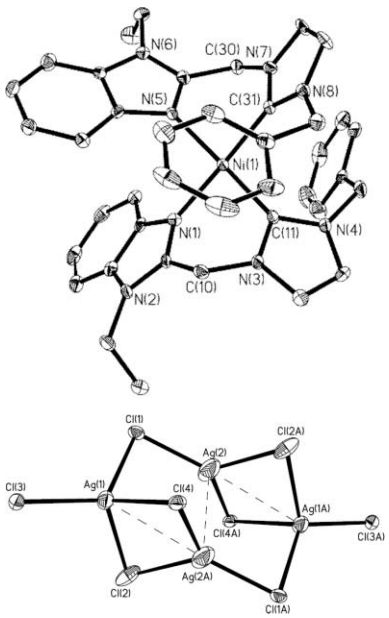


Fig. 5 ORTEP view of one of the two $[Ni(L^{Bn})_2]^{2+}$ cation (up) and its counteranion $[Ag_4Cl_8]^{4-}$ (down) of $[Ni(L^{Bn})_2]_2[Ag_4Cl_8]$ (**3a**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–C11 1.879(2), Ni1–C31 1.884(1), Ni–N1 1.922(1), Ni–N5 1.914(1), C11–Ni1–C31 94.4 (6), C11–Ni1–N5 178.6(6), C31–Ni1–N5 86.6(6), C11–Ni1–N1 88.2(6), C31–Ni1–N1 177.3(6), N1–Ni1–N5 90.8(5); Ag1–Cl1 2.61(4), Ag1–Cl2 2.61(6), Ag1–Cl3 2.53(5), Ag1–Cl4 2.69(5), Ag2–Cl1 2.463(5), Ag1–Ag2A 3.26(3), Ag2–Ag2A 2.83(5).

CCDC 760771 (**3a**)†). It reveals a hydrated ionic dual-metal complex formulated as $[Ni(L^{Bn})_2]_2^{4+}[Ag_4Cl_8]^{4-}\cdot 2H_2O$. The Ni^{II} is completely stripped of its original ligands which are replaced by two C,N-chelate on a square planar sphere (deviation of Ni from N1N5C31C11 coordination plane is 0 Å). As expected, the two *cis*-directing carbon donors avoid a mutually-*trans* configuration. Both Ni–C (1.879(2) and 1.884(1) Å) and Ni–N lengths (1.922(1) and 1.914(1) Å) are comparable with related analogues with pyridyl donors.[13] A similar but *in situ* method was used by Jin *et al.* in the preparation of 3-alkyl-1-picolylimidazolin-2-ylidene Ni(II) through Ag_2O,[13b] which yields the chloride salt instead of the $[Ag_4Cl_8]^{4-}$ complex form. We are not aware of any crystallographic report of this aggregate anion but many iodide aggregates $[Ag_xI_y]^{n-}$ are known.[14] Its congeneric but structurally different $[Ag_4I_8]^{4-}$ has also been reported in the preparation of pyrimidine-functionalized Ni-NHC complex by Chen *et al.*[6d] A closer analogue is found in $[Ag_4I_8]^{4-}$ which occurs as a counter-ion in the synthesis of homoleptic crown Ag-NHC complexes.[14a] This Ag_4 aggregate can also be viewed as zig-zag silver chain with negligible external Ag···Ag interaction (Ag(1)···Ag(2A) 3.26(3) Å) but strong argentophilic contacts for the internal metals (Ag(2)···Ag(2A) 2.83(5) Å).

This convenient transmetallation method to give homoleptic benzimidazole-hybridized carbene cations can also be applied to other d^8 complexes. This is demonstrated by a similar transfer to $PdCl_2(CH_3CN)_2$ to give $[Pd(L^{Bn})_2][Ag_4Cl_8]$ **4a** (Scheme 2). Similar to **3a**, the disappearance of C_2–H in the ^{1}H-NMR spectrum (9.59 ppm) and the doublet at 6.09–5.44 ppm are indicative of successful formation of the carbene-nitrogen chelate. Unlike **3a**, however, **4a** is only sparingly soluble in many deuterated solvents, thus hampering ^{13}C NMR analysis. The positive mode of ESI-MS is dominated by isotopic patterns centered at m/z = 369 and 738 corresponding to $[Pd(L^{Bn})_2]^{2+}$ with peak differences of 0.5 and 1.0 mass units respectively. Its X-ray diffraction analysis shows an isostructural complex as **3a**, *viz.* a square-planar Pd^{II} center (deviation of Pd atom from N1N5C31C11 plane is 0.01 Å) enclaved by two bidentate benzimidazolyl-imidazolilydenes and the C- and N- donors opposite to each other (Fig. 6, depository number: CCDC 760773 (**4a**)†). This is similar to the reported pyridine functionalized imidazolium or benzimidazolium Pd-NHC complexes,[15,6b] but different from the earlier reported $PdCl_2L^{Me}$ which is a neutral mononuclear complex. The Pd–C (1.986(5) and 1.974(4) Å) and Pd–N bond lengths (2.066(4) and 2.054(4) Å) are normal when compared to many of the known Pd-NHC complexes. Like **3a**, **4a** is also balanced by $[Ag_4Cl_8]^{4-}$, suggesting similar mode of formation for these congeneric complexes. Facile formation of $[AgCl_2]^-$ from AgCl and its tetramerisation to give the stable $[Ag_4Cl_8]^{4-}$ would offer a ready driving force for the chloride abstraction from $PdCl_2L$ that leads to the observed $[PdL_2]^{2+}$.

Although the *cis*-disposition of the two carbene donors help to impose the weaker benzimidazole ligand at the *trans*-position, it brings into proximity the two substituents on the N-atom of the NHC ring. To examine if we can use a greater steric effect to overcome the thermodynamically favored product, we have carried out similar experiments by using $[Ag_2Cl_2(L^{Mes})_2]$ **2b** which bears a sterically more demanding mesityl group. The Ni^{II} product *viz.* $[Ni(L^{Mes})_2]Cl_2$ **3b** is isolated as a greenish yellow powder which is highly soluble in common solvents such as CH_2Cl_2, MeOH, DMF and DMSO, *etc.* It is also moderately stable in dry air. Its ^{1}H

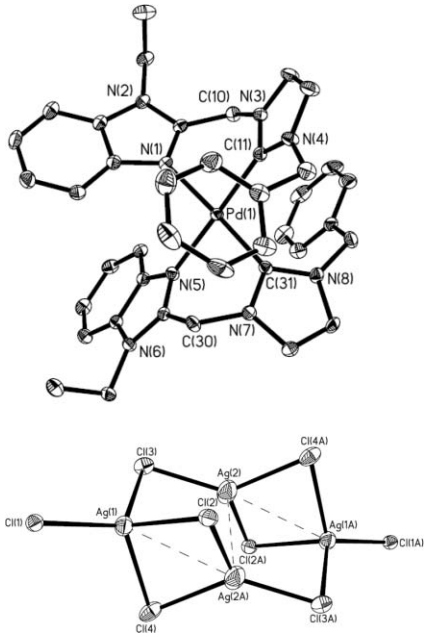


Fig. 6 ORTEP view of one of the two $[Pd(L^{Bn})_2]^{2+}$ cation (up) and its counteranion $[Ag_4Cl_8]^{4-}$ (down) of $[Pd(L^{Bn})_2]_2[Ag_4Cl_8]$ (**4a**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C11 1.986(5), Pd1–C31 1.974 (4), Pd1–N1 2.066(4), Pd1–N5 2.054(4), C11–Pd1–C31 96.7(2), C11–Pd1–N1 86.0(2), C31–Pd1–N1 177.3(2), C11–Pd1–N5 178.4(2), C31–Pd1–N5 84.9 (2), N1–Pd1–N5 92.5(2); Ag1–Ag2A 3.325(2), Ag2–Ag2A 2.838(2).

NMR spectral diagnosis comes from the disappearance of C_2–H at 9.92 ppm in d_6-DMSO and the presence of doublets at 6.28 and 6.17 ppm for the methylene linkage. The downfield carbenic carbon resonance at 176.45 ppm is also characteristic. Its ESI-MS spectrum gives the molecular peaks of $[Ni(L^{Mes})_2]^{2+}$ at m/z 373 and 746, and $[NiCl(L^{Mes})_2]^+$ at 781.

X-Ray single-crystal diffraction of **3b** (Fig. 7, depository number: CCDC 760772 (**3b**)†) reveals a similar homoleptic cationic structure of **3a** except that, as anticipated, the two

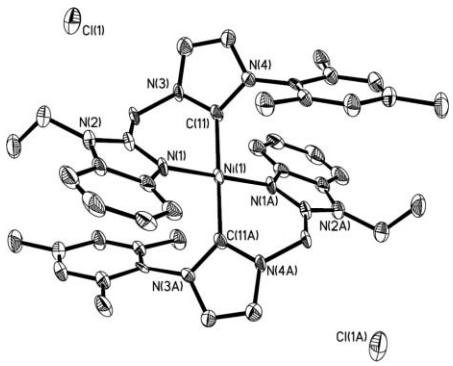


Fig. 7 ORTEP view of $[Ni(L^{Mes})_2][Cl]_2$ (**3b**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–N1 1.891(7), Ni1–C11 1.909(8), N1–Ni1–N1A 179.997(1), N1–Ni1–C11 86.3(3), N1–Ni1–C11A 93.7(3), C11–Ni1–C11A 179.997(1). Symmetry code: A, $-x$, $-y$, $-z$.

mesityl substituents have moved away to avoid conflict, which is achieved by placing the two carbene carbon at a mutually *trans* configuration in a near-perfect square planar geometry (N1–Ni1–N1A 179.999(1) and C11–Ni1–C11A 179.998(1)°, distortion of Ni from the N1C11N1AC11A coordination plane is 0 Å). Such geometric arrangement is also found in similar NHC-phosphine chlelates imposed by a sterically bulky aryl or naphthyl.[16] It is intriguing that, unlike **3a**, **3b** is formed as a chloride salt. It suggests that, upon carbene departure, the residual Ag_2 moieties in **2b** probably picks up the adventitious phosphine and hence less reactive towards the chloride in **3b**. These collectively suggests that the N-substituent of imidazole ring could influence both anionic and cationic structures of the product as well as that of the Ag(I) intermediate.

The analogous Pd-NHC complex **4b** of L^{Mes} is also easily obtained from **2b** and $PdCl_2(CH_3CN)_2$. The X-ray crystal structure reveals that **4b** is isostructural to **3b** with an ideal square planar geometry (N1–Pd1–N1A 180.0 and C11–Pd1–C11A 180.0°, distortion of Pd from the N1C11N1AC11A coordination plane is also 0 Å) (Fig. 8, depository number: CCDC 760774 (**4b**)). It is remarkably consistent that, like **3b**, **4b** is also balanced by chloride instead of the Ag_4 aggregate, thus supporting that the anion of the transmetallation product is influenced by the composition of the Ag(I) precursor. The *trans*-configuration of the cation of **4b** is in contrary to the reported cations of [Pd(N-phenyl-N-(α-pyridyl)imidazolin-2-ylidene)]$_2$[PF_6]$_2$[15] and [Pd(N-alkyl-N-(α-picolyl)benzimidazolin-2-ylidene)]$_2X_2$ (alkyl = methyl, ethyl, propyl, butyl; X = Br, BF_4),[6b] but structurally similar to the cation of [Pd(N-butyl-N-(8-quinolinyl)methyl)imidazolin-2-ylidene)]$_2$[PF_6]$_2$.[8a]

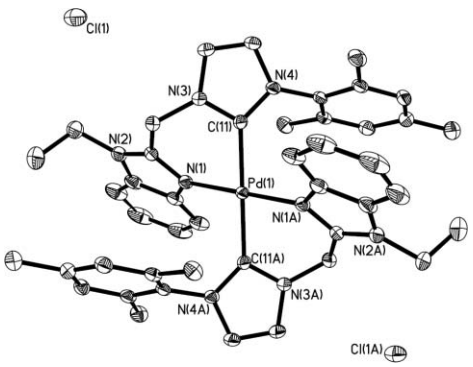


Fig. 8 ORTEP view of the molecule [Pd(L^{Mes})$_2$]Cl_2 (**4b**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–N1 2.009(2), Pd1–N1A 2.009(2), Pd1–C11 2.023(3), Pd1–C11A 2.023(3), N1–Pd1–N1A 180.0, N1–Pd1–C11 84.09(10), N1–Pd1–C11A 95.91(10), N1A–Pd1–C11 95.91(10), N1A–Pd1–C11A 84.09(10), C11–Pd1–C11A 180.0. Symmetry code: A, $-x$, $-y$, $-z$.

Synthesis of Ni^{II} (5 and 3b) and Pd^{II} (6 and 4b) complexes from direct deprotonation of imidazolium salt with $M(OAc)_2$ (M = Ni or Pd)

To obtain the silver-free form of **5** and **6**, we have used the established direct deprotonation method on the imidazolium salt.[17] A mixture of benzimidazolyl imidazolium chloride salts (**1a**, $HL^{Bn}Cl$) with $M(OAc)_2$ (M = Ni, Pd) is heated in DMSO for 12 h to afford the corresponding chloride salts of Ni^{II} (**5**) and Pd^{II} (**6**) (Scheme 2). Replacing the bulky and highly-charged $[Ag_4Cl_8]^{4-}$ in **3a** and **4a** by the more solvating Cl^-, **5** and **6** give highly soluble products in common solvents such as CH_2Cl_2, MeOH, DMF and DMSO. The X-ray crystal structures confirm that the cations of **5** and **6** are isostructural to those of **3a** and **4a** (Fig. 9 and 10, depository numbers: CCDC 760775 (**5**) and CCDC 760776 (**6**)†).

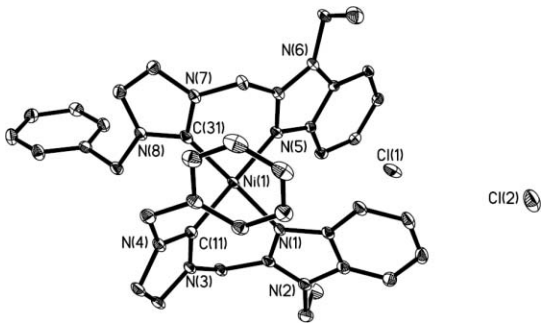


Fig. 9 ORTEP view of [Ni(L^{Bn})$_2$][Cl]$_2$ (**5**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–C11 1.868(2), Ni1–C31 1.876(3), Ni–N1 1.933(2), Ni–N5 1.919(2), C11–Ni1–C31 92.4 (1), C11–Ni1–N5 179.4(1), C31–Ni1–N5 87.9(1), C11–Ni1–N1 86.7(1), C31–Ni1–N1 177.4(1), N1–Ni1–N5 93.1(9).

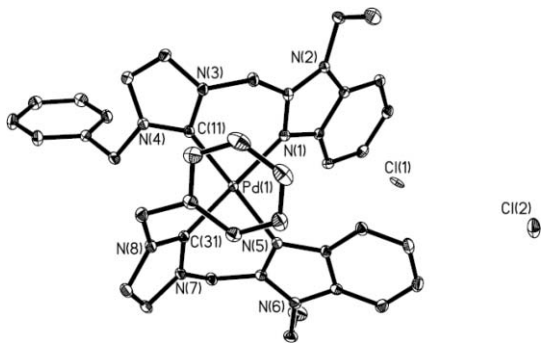


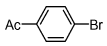
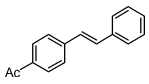
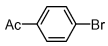
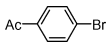
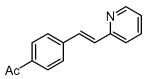
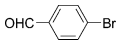
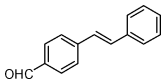
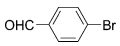
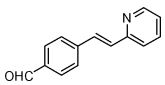
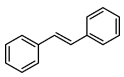
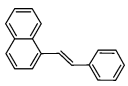
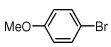
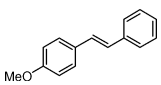
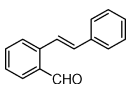
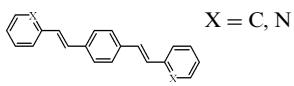
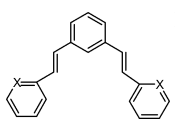
Fig. 10 ORTEP view of [Pd(L^{Bn})$_2$][Cl]$_2$ (**6**) with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C11 1.978(3), Pd1–C31 1.980 (3), Pd1–N1 2.061(3), Pd1–N5 2.070(3), C11–Pd1–C31 94.9(1), C11–Pd1–N1 85.8(1), C31–Pd1–N1 179.1(1), C11–Pd1–N5 177.3(1), C31–Pd1–N5 84.5 (1), N1–Pd1–N5 94.9(1).

Complexes **3b** and **4b** can also be prepared directly from **1b** with $M(OAc)_2$. In general, the yields of these Ni and Pd complexes are higher when prepared by this direct method compared to transmetallation through silver carbenes.

Pd-NHC complex catalyzed Heck coupling reaction

The N-mesityl substituted complex **4b** (*trans*-NHCs) and N-benzyl substituted complex **6** (*cis*-NHCs) were compared in their catalytic activities towards the Heck reaction of 4-acetylphenyl bromide with styrene. Reactions conducted in N,N-dimethyl acetamide (DMAc) in the presence of NaOAc as the base at 130 °C under

Table 1 Mizoroki–Heck reaction of aryl bromides with styrene or 2-vinyl pyridine catalyzed by Pd-NHC complex **4b**[a]

Entry	Ar–Br	Olefin	Time	Product	Conv. (%)[c]
1			24		>99
2[b]			24		87
3			24		96
4			24		>99
5			24		100
6			20		85
7			24		81
8			24		83
9			24		100
10[d]			30	 X = C, N	99
11[d]			30		95
12[d]			30	 X = C, N	96
13[d]			30		95

[a] Reaction conditions: aryl halide 0.5 mmol, olefin 0.75 mmol, 0.25 mol% complex **4b**, DMAc 3 mL, NaOAc 1.0 mmol, temperature 130 °C. [b] Catalyst is complex **6**. [c] Conversion of aryl halide analyzed by GC-MS. [d] NaOAc 2.0 mmol.

a low catalyst load of 0.25% showed that the former gives almost quantitative conversion of the aryl halide whereas the latter returns with 87% (Table 1, entries 1 and 2). Complex **4b** was hence chosen as a model of this series to examine its Heck activities towards other aryl bromides (Table 1). It gives an excellent conversion of 96% in the coupling between 4-acetyl bromobenzene and 2-vinyl pyridine (entry 3), suggesting its potential to be applied to the more demanding Heck reactions using heterocycle-bearing olefins. Reactions of styrene or 2-vinyl pyridine with 4-aldehyde bromobenzene proceed quantitatively (entries 4 and 5). Use of bromobenzene or 1-bromonaphthalene (entries 6 and 7) also give satisfactory outcomes. Use of electronic rich (entry 8) and sterically hindered *ortho*-substituted substrates (entry 9) could also result in 83% and 100% conversions respectively. This method can also be applied to dual-coupling on dihaloarenes. This is exemplified by the efficient Heck reactions between styrene or 2-vinyl pyridine with 1,4-diiodo benzene or 1,3-diiodo benzene (entries 10–13). The di-pyridyl products would be useful ligands for complexation and supramolecular assembly. The catalytic activity of complex **4b** is superior to the pyridine-functionalized benzimidazolium Pd-NHC complex.[6b]

Ni-NHC complex catalyzed Kumada–Corriu coupling reaction

Many boronic acids, stannanes, and organozincs are obtained from Grignard reagents or organolithium compounds, but Suzuki,

Stille, and Negishi coupling routes may be the preferred choices because of the higher functional group tolerance. Kumada coupling, however, offers a more direct access to biaryls when the substrates can tolerate the background reactivity of a Grignard reagent or when sensitive functional groups are absent in the product. For this reason, the Kumada coupling reaction still remains an attractive route to bi- or ter-aryls.[18] N- or S-containing heteroaryls are relatively less used in coupling with Grignard reagent.

The catalytic difference of **3b** (*trans*-NHCs) and **5** (*cis*-NHCs) was compared in the coupling of 3-chloro-6-methoxypyridazine with *p*-Me-C_6H_4MgBr. Both give good conversions (≥ 90%) in THF at r.t. under a low catalyst loading (0.5 mol%) but, like the Pd analogue, the former is slightly better (Table 2, entries 1 and 2). It was hence used as a representative model to examine coupling of selected aryl- and heteroaryl halides with *p*-Me-C_6H_4MgBr at r.t. It is highly effective towards 2-chloropyridine and 2-chloropyrimidine, giving near-quantitative conversions (entries 3 and 4). High efficiency is also observed towards bromoarenes under 1.0 mol% catalyst loading (entries 9 and 10). Coupling of 2-bromopyridine or 8-bromoquinoline is also satisfactory (entries 6 and 7). This system is also effective towards *ortho*- or *meso*-dibromobenzene (entries 11 and 12). Some limitations are experienced when electron-rich 3-methoxyl-2-chloropyridine (entry 5) or other heterocycles like 2-bromothiophene (entry 8) is used. These activities are comparable with the reported imidazolium[9,18h] and benzimidazolium Ni-NHC complexes.[18c]

Conclusions

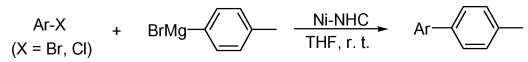
The N-substituent on the imidazolin-2-ylidene ring has a profound effect on the structures on the transmetallation Ag(I) intermediate and the Ni(II) and Pd(II) products. It does not appear however to influence the course or efficiency of the transmetallation process. Its use in the benzimidazol-imidazolin-2-ylidene difunctional C–N ligand enables the isolation of the intermediate Ag(I) complexes of different nuclearities, and both geometric isomers of the homoleptic products. Crystallographic analysis of the latter reveals that the metal is almost completely engulfed by the ligands. This suggests that in the catalytic activation process, some form of ligand dissociation process would be inevitable for the metal to be exposed to substrate approach. This is in contrary to the classical chelating ligands and illustrates the value of using a more labile donor such as the nitrogen-donating benzimidazole. Current experiments are directed at the stoichiometric reactions of these active d^8 dications with key catalytic substrates in an attempt to isolate and identify products that could shed clearer light on the mode of action of catalytically important species.

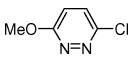
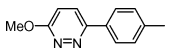
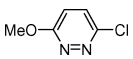
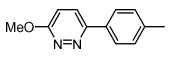
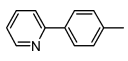
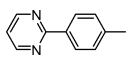
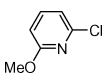
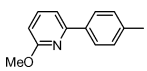
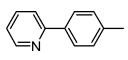
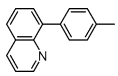
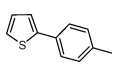
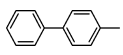
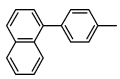
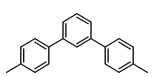
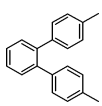
Experimental

General procedures

All operations were carried out without exclusion of air unless otherwise stated. 2-Chloromethyl-1-ethylbenzimidazole was synthesized according to the reported method.[10a] N-substituted imidazole,[19a] $PdCl_2(CH_3CN)_2$[19b] and $NiCl_2(PPh_3)$[19c] were prepared by using published procedures. NMR spectra were measured on Bruker ACF300 300 MHz and AMX500 500 MHz FT NMR spectrometers. Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in house. All Kumada-Corriu reactions were conducted in a glovebox. GC-MS analyses were recorded on Agilent 6890N/5973N system.

Table 2 Ni-NHC complex catalyzed Kumada–Corriu cross-coupling reaction[a]



Entry	Aryl halide	Catalyst	Time	Product	Conv. (%)[b]
1		**5** (0.5%)	12		90
2		**3b** (0.5%)	12		95
3		**3b** (1.0%)	24		99
4		**3b** (0.5%)	24		97
5		**3b** (0.5%)	12		62
6		**3b** (0.5%)	12		81
7		**3b** (1.0%)	24		89
8		**3b** (1.0%)	24		69
9		**3b** (1.0%)	24		97
10		**3b** (1.0%)	24		96
11[c]		**3b** (2.0%)	36		92
12[c]		**3b** (2.0%)	36		84

[a] Reaction conditions: aryl halide 0.5 mmol, *p*-Me-C_6H_4MgBr 0.75 mmol, Ni complex 0.5–2.0 mol%, THF 3 mL, r.t. [b] Conversion of aryl halide analyzed by GC-MS. [c] *p*-Me-C_6H_4MgBr 1.5 mmol.

Preparation of ligand precursors

Synthesis of 1-(1-ethyl-benzimidazol-2-ylmethyl)-3-benzyl-imidazolium chloride (1a). 1-Benzylimidazole (650 mg, 4.11 mmol) was added to a solution of 2-chloromethyl-1-ethylbenzimidazole (779 mg, 4.00 mmol) in DMSO (5 mL), and the mixture was heated at 120 °C for 24 h. The solution was reduced to 2 mL under vacuum and Et_2O (10 mL) was added to precipitate the product. The resultant NHC ligand precursor $[HL^{Bn}]Cl$ **1a** was washed with Et_2O (3 × 10 mL) and collected as

a white solid powder (1.30 g, 92%). Single crystals of **1a** were grown by slow evaporation of its CH_2Cl_2 solution. ^{1}H NMR (500 MHz, d_6-DMSO): 9.59 (s, 1H, NC(H)N), 7.93 (t, J = 1.9 Hz, 2H, Ar–H), 7.65 (d, J = 8.2 Hz, 1H, Ar–H), 7.61 (d, J = 7.6 Hz, 1H, Ar–H), 7.49–7.40 (m, 5H, Ar–H), 7.32–7.29 (t, J = 7.6 Hz, 1H, Ar–H), 7.25–7.22 (t, J = 7.6 Hz, 1H, Ar–H), 5.97 (s, 2H, CH_2), 5.56 (s, 2H, CH_2), 4.40–4.35 (q, 2H, CH_2CH_3), 1.33–1.31 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C(^{1}H) NMR (125.77 MHz, d_6-DMSO): 148.15 (s, NCN), 141.81, 137.30, 134.93, 129.00, 128.78, 128.28, 124.09, 122.76, 122.45, 121.98, 119.09, 110.46 (s, Ar–C), 52.04, 45.27 (s, CH_2), 38.18 (s, CH_2CH_3), 14.96 (s, CH_3). MS (ESI): m/z 317 $[HL^{Bn}]^+$. Crystal data for **1a**: formula $C_{20}H_{21}N_4Cl.\ H_2O$, colorless crystal, monoclinic, space group $P2_1/c$; a = 4.994(5), b = 12.846(1), c = 30.023(3) Å; β = 92.145(3)°; V = 1924.6(3) Å^3; Z = 4; crystal size 0.60 × 0.20 × 0.06 mm^3; GOF = 1.052; reflections collected: 13 565; independent reflections: 4430 [R_{int} = 0.0487]; R_1 = 0.0582; wR_2 = 0.1285. Depository number: CCDC 760767.

Synthesis of 1-(1-ethyl-benzimidazol-2-ylmethyl)-3-mesityl-imidazolium chloride (1b). 1-Mesitylimidazole (391.02 mg, 2.1 mmol) and 2-chloromethyl-1-ethylbenzimidazole (389.40 mg, 2.00 mmol) were heated at 120 °C in DMSO (5 mL) for 24 h. $[HL^{Mes}]Cl$ **1b** was obtained as a white powder (685 mg, 90%) and its single crystals were grown by slow evaporation of its CH_2Cl_2 solution. ^{1}H NMR (300 MHz, d_6-DMSO): 9.92 (s, 1H, NC(H)N), 8.22 (s, 1H, Ar–H), 8.03 (s, 1H, Ar–H), 7.65 (d, J = 7.7 Hz, 1H, Ar–H), 7.57 (d, J = 7.7 Hz, 1H, Ar–H), 7.32–7.17 (m, 4H, Ar–H), 6.15 (s, 2H, CH_2), 4.44–4.41 (q, 2H, CH_2CH_3), 2.34 (s, 3H, CH_3), 2.10 (s, 6H, CH_3), 1.39–1.34 (t, J = 6.7, 3H, CH_2CH_3); ^{13}C(^{1}H) NMR (75.77 MHz, d_6-DMSO): 147.71 (s, NCN), 141.88, 140.23, 138.97, 135.10, 134.27, 131.15, 129.24, 124.33, 123.65, 122.73, 121.93, 119.09, 110.45 (s, Ar–C), 45.54, 38.21 (s, CH_2), 20.55, 16.90, 15.01 (s, CH_3). MS (ESI): m/z 345 $[HL^{Mes}]^+$. Crystal data for **7**: formula $C_{22}H_{25}N_4Cl.\ 2H_2O$, colorless crystal, monoclinic, space group $P2_1/c$; a = 14.227(7), b = 9.707(5), c = 16.060(8) Å; β = 96.868(1)°; V = 2202.1(2) Å^3; Z = 4; crystal size 0.48 × 0.36 × 0.16 mm^3; GOF = 1.028; reflections collected: 15 263; independent reflections: 5046 [R_{int} = 0.0345]; R_1 = 0.0492; wR_2 = 0.1233. Depository number: CCDC 760768.

Preparation of complexes

Synthesis of Ag_4Cl_4(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-benzylimidazolin-2-ylidene)$_2$ (2a). A slurry of $[HL^{Bn}]Cl$ **1a** (500 mg, 1.42 mmol) and Ag_2O (670 mg, 2.90 mmol) in CH_2Cl_2 (50 mL) was stirred for 18 h at r.t. with exclusion of light. Filtration of the reaction mixture through Celite gave a colorless solution, which was then concentrated to about 5 mL. Upon the addition of Et_2O to the crude reaction mixture, $Ag_4Cl_4(L^{Bn})_2$ **2a** was obtained as a white powder. Yield: 727.8 mg (85%). ^{1}H NMR (300 MHz, d_6-DMSO): 7.57–7.54 (m, 4H, Ar–H), 7.29–7.17 (m, 7H, Ar–H), 5.75 (s, 2H, CH_2), 5.33 (s, 2H, CH_2), 4.30 (q, J = 7.2, 2H, CH_2CH_3), 1.10 (t, J = 7.1, 3H, CH_2CH_3); ^{13}C(^{1}H) NMR (75.47 MHz, d_6-DMSO): 180.39 (s, NCN), 149.18, 141.95, 137.06, 134.79, 128.67, 127.97, 127.61, 123.20, 122.62, 122.17, 121.82, 119.18, 110.38 (s, Ar–C), 54.39, 47.17, 38.26 (s, CH_2), 14.84 (s, CH_3). MS (ESI): m/z 741 $[Ag(L^{Bn})_2]^+$. Anal. Calc for $C_{40}H_{40}Cl_4N_8Ag_4$: C, 39.77; H, 3.55; N, 9.28. Found: C, 39.83; H, 3.55; N, 9.33. Single crystals suitable for X-ray crystallography of **2a** were obtained by slow diffusion of Et_2O into its CH_2Cl_2 solution. Crystal data for **2a**: formula $C_{40}H_{40}Cl_4N_8Ag_4$, colorless crystal, monoclinic, space group $P2_1/c$; a = 13.040(4), b = 9.580(3), c = 16.361(6) Å; β = 98.899(7)°; V = 2019.3(1) Å^3; Z = 2; crystal size 0.12 × 0.10 × 0.02 mm^3; GOF = 1.194; reflections collected: 10 445; independent reflections: 3553 [R_{int} = 0.0684]; R_1 = 0.0966; wR_2 = 0.1883. Depository number: CCDC 760769.

Synthesis of Ag_2Cl_2(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-mesitylimidazolin-2-ylidene)$_2$ (2b). Similar procedure to **2a**, a white powder of $Ag_2Cl_2(L^{Mes})_2$ **2b** was isolated from the CH_2Cl_2 solution of $[HL^{Mes}]Cl$ **1b** (570.30 mg, 1.50 mmol) and Ag_2O (693 mg, 2.30 mmol) after stirring at r.t. for 18 h with exclusion of light. Yield 564.5 mg (77%). ^{1}H NMR (300 MHz, d_6-DMSO): 7.77 (d, J = 7.6 Hz, 1H, Ar–C), 7.65–7.59 (m, 2H, Ar–H), 7.49 (d, J = 1.8 Hz, 1H, Ar–H), 7.31–7.18 (m, 2H, Ar–H), 6.96 (s, 2H, CH_2), 5.87 (s, 2H, CH_2), 4.38–4.31 (q, 2H, CH_2CH_3), 2.30 (s, 3H, CH_3), 1.74 (s, 6H, CH_3), 1.17–1.13 (t, J = 7.0, 3H, CH_2CH_3); ^{13}C(^{1}H) NMR (75.77 MHz, $CDCl_3$): 181.66 (s, NCN), 149.29, 142.34, 138.86, 136.04, 135.19, 134.67, 129.23, 123.67, 123.39, 123.15, 122.31, 119.69, 110.88 (s, Ar–C), 47.51 (s, CH_2), 38.71 (s, CH_2CH_3), 20.97, 17.43, 15.37 (s, CH_3). MS (ESI): m/z 797 $[Ag(L^{Mes})_2]^+$. Anal. Calc for $C_{44}H_{50}Cl_2N_8Ag_2$: C, 54.06; H, 5.16; N, 11.46. Found: C, 54.07; H, 5.06; N, 11.27. Crystal data for **2b.1.5CH$_3$CN**: formula $C_{47}H_{52.50}N_{9.50}Ag_2Cl_2$, colorless crystal, triclinic, space group $P\bar{1}$; a = 14.016(1), b = 19.413(2), c = 19.940(2) Å; β = 88.669(2)°; V = 4817.9(8) Å^3; Z = 4; crystal size 0.14 × 0.10 × 0.02 mm^3; GOF = 0.963; reflections collected: 33 829; Independent reflections: 22 017 [R_{int} = 0.0509]; R_1 = 0.0722; wR_2 = 0.1904. Depository number: CCDC 760770.

Synthesis of [Ni(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-benzyl-imidazolin-2-ylidene)$_2$]$_2$[Ag_4Cl_8] (3a). To a solution of $Ag_4Cl_4(L^{Bn})_2$ (121 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added $NiCl_2(PPh_3)_2$ (33 mg, 0.1 mmol). The mixture was stirred overnight at r.t. with the exclusion of light. The resultant suspension was filtered through a short column of Celite and the filtrate was then concentrated to *ca.* 3 mL. Addition of Et_2O to the filtrate afforded a white powder $[Ni(L^{Bn})_2]_2[Ag_4Cl_8]$ **3a**. Yield: 54.6 mg (52%). ^{1}H NMR (500 MHz, d_6-DMSO): 7.79 (s, 1H, Ar–H), 7.65 (d, J = 8.2 Hz, 1H, Ar–H), 7.34–7.29 (m, 6H, Ar–H), 7.12-7.09 (t, J = 85.3 Hz, 1H, Ar–H), 6.71–6.68 (t, J = 7.6 Hz, 1H, Ar–H), 6.35 (s, 1H, Ar–H), 6.32 (d, J = 12.6 Hz, 1H, CH_2), 6.23 (d, J = 16.4 Hz, 1H, CH_2), 5.03 (d, J = 15.2 Hz, 1H, CH_2), 4.59-4.56 (t, J = 6.3 Hz, 2H, CH_2), 4.52 (d, J = 15.1 Hz, 1H, CH_2), 1.47 (t, J = 6.6 Hz, 3H, CH_3); ^{13}C(^{1}H) NMR (75.47 MHz, d_6-DMSO): 159.94 (s, NCN), 150.12, 138.56, 136.33, 129.28, 128.57, 127.71, 125.07, 124.50, 124.03, 123.56, 116, 57, 112. 20 (s, Ar–C), 53.17, 45.62, 40.79 (s, CH_2), 15.85 (s, CH_3). MS (ESI): m/z 345 and 690 $[Ni(L^{Bn})_2]^{2+}$. Crystal data for **3a.2H$_2$O**: formula $C_{80}H_{84}Cl_8N_{16}O_2Ag_4Ni_2$, colorless crystal, triclinic, space group $P\bar{1}$; a = 11.350(1), b = 13.156(1), c = 14.964(2) Å; β = 82.205(3)°; V = 2036.9(4) Å^3; Z = 2; crystal size 0.20 × 0.16 × 0.10 mm^3; GOF = 1.069; reflections collected: 12 105; independent reflections: 7180 [R_{int} = 0.0377]; R_1 = 0.0826; wR_2 = 0.1731. Depository number: CCDC 760771.

Synthesis of [Pd(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-benzyl-imidazolin-2-ylidene)$_2$]$_2$[Ag_4Cl_8] (4a). To a solution of **2a** (121 mg,

0.1 mmol) in 20 mL CH_2Cl_2 was added $PdCl_2(CH_3CN)_2$ (26 mg, 0.1 mmol). Following the similar procedure to **3a**, **4a** was isolated as a white powder. Yield: 60.5 mg (55%). ^{1}H NMR (500 MHz, d_6-DMSO at 353 K): δ 8.17–7.71 (m, 2H, Ar–H), 7.63–7.53 (m, 3H, Ar–H), 7.39–7.30 (m, 6H, Ar–H), 6.06 (d, J = 27.8 Hz, 1H, CH_2), 5.98 (s, 2H, CH_2), 5.44 (d, J = 13.3 Hz, 1H, CH_2), 4.53–4.48 (m, 2H, CH_2), 1.40 (t, J = 6.9 Hz, 3H, CH_3); MS(ESI) : m/z 369 and 738 $[Pd(L^{Bn})_2]^{2+}$. Crystal data for **4a.2H$_2$O**: formula $C_{80}H_{84}Cl_8N_{16}O_2Ag_4Pd_2$, colorless crystal, triclinic, space group $P\bar{1}$; a = 11.284(3), b = 13.141(5), c = 15.104(4) Å; β = 83.08(2)°; V = 2054.5(1) Å^3; Z = 2; crystal size 0.28 × 0.16 × 0.06 mm^3; GOF = 1.057; reflections collected: 26 695; independent reflections: 9403 [R_{int} = 0.0423]; R_1 = 0.0554; wR_2 = 0.1285. Depository number: CCDC 760773.

Synthesis of [Ni(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-mesityl-imidazolin-2-ylidene)$_2$][Cl]$_2$ (3b). Following a similar procedure and scale in the preparation of **3a**, $[Ni(L^{Mes})_2][Cl]_2$ **3b** was obtained as a yellow powder. Yield: 68.1 mg (83%). ^{1}H NMR (300 MHz, d_6-DMSO): 7.85 (s, 1H, Ar–H), 7.70–7.68 (d, J = 7.1 Hz, 1H, Ar–H), 7.42–7.31 (m, 4H, Ar–H), 7.13 (s, 1H, Ar–H), 6.42 (s, 1H, Ar–H), 6.28 (d, J = 16.4, 1H, CH_2), 6.14 (d, J = 17.4, 1H, CH_2), 4.40 (m, 2H, CH_2), 2.64 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.25 (s, 3H, CH_2), 0.94 (t, 3H, CH_3); ^{13}C(^{1}H) NMR (125.77 MHz, $CDCl_3$): 176.45 (s, Ar–C), 158.80, 148.22, 147.33, 142.81, 142.74, 142.43, 142.41, 138.33, 138.28, 134.32, 134.12, 134.06, 133.11, 126.91, 121.80 (s, Ar–C), 53. 99, 40.13, 29.98, 29.20, 25.85, 25.06 (s, CH_3). MS (ESI): m/z = 373 and 746 $[Ni(L^{Mes})_2]^{2+}$, 781 $[NiCl(L^{Mes})_2]^+$. Anal. Calc for $C_{44}H_{50}Cl_2N_8Ni$: C, 64.41; H, 6.14; N, 13.66. Found: C, 64.40; H, 6.02; N, 14.45. Crystal data for **3b.H$_2$O.2CH$_3$OH**: formula $C_{47}H_{62}N_8O_4NiCl_2$, green yellow crystal, monoclinic, space group $C2/c$; a = 16.880(6), b = 13.061(5), c = 22.335(8) Å; β = 109.268(8)°; V = 4648.0(3) Å^3; Z = 4; crystal size 0.24 × 0.12 × 0.08 mm^3; GOF = 1.073; reflections collected: 13 065; independent reflections: 4097 [R_{int} = 0.1254]; R_1 = 0.1165; wR_2 = 0.2595. Depository number: CCDC 760772.

Synthesis of [Pd(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-mesityl-imidazolin-2-ylidene)$_2$][Cl]$_2$ (4b). Following the same procedure and scale in the preparation of **4a**, $[Pd(L^{Mes})_2][Cl]_2$ **4b** was obtained as a yellowish powder. Yield: 74 mg (85%). ^{1}H NMR (300 MHz, d_6-DMSO): 7.93 (d, J = 1.3 Hz, 1H, Ar–H), 7.75 (d, J = 8.9 Hz, 1H, Ar–H), 7.49 (d, J = 1.9 Hz, 1H, Ar–H), 7.45 (t, J = 7.6 Hz, 1H, Ar–H), 7.38–7.31 (m, 2H, Ar–H), 6.92 (s, 1H, Ar–H), 6.27 (s, 1H, Ar–H), 6.18 (d, J = 16.4, 1H, CH_2), 5.91 (d, J = 16.4, 1H, CH_2), 4.57–4.46 (m, 2H, CH_2), 2.14 (s, 6H, CH_3), 1.34 (t, J = 7.6, 3H, CH_3), 1.21 (s, 3H, CH_3); ^{13}C(^{1}H) NMR (125.77 MHz, $CDCl_3$): 167.42 (s, NCN), 148.52, 138.71, 137.71, 133.40, 133.23, 132.99, 132.42, 128.49, 128.14, 124.93, 124.83, 124.07, 123.32, 117.50, 112.08 (s, Ar–C), 44.99, 40.00 (s, CH_2), 20. 42, 18.90, 17.55, 15.73 (s, CH_3). MS (ESI): m/z = 397 and 794 $[Pd(L^{Mes})_2]^{2+}$. Anal. Calc for $C_{44}H_{50}Cl_2N_8Pd$: C, 60.87; H, 5.80; N, 12.91. Found: C, 60.74; H, 5.74; N, 12.75. Crystal data for **4b.4CH$_3$OH**: formula $C_{48}H_{64}N_8O_4PdCl_2$, colorless crystal, Triclinic, space group $P\bar{1}$; a = 10.672(8), b = 10.857(7), c = 11.628(8) Å; β = 84.498(2)°; V = 1210.2(2) Å^3; Z = 1; crystal size 0.20 × 0.14 × 0.06 mm^3; GOF = 1.073; reflections collected: 8644; independent reflections: 5445 [R_{int} = 0.0294]; R_1 = 0.0482; wR_2 = 0.1127. Depository number: CCDC 760774.

Synthesis of [Ni(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-benzyl-imidazolin-2-ylidene)$_2$][Cl]$_2$ (5). $Ni(OAc)_2{\cdot}4H_2O$ (124 mg, 0.5 mmol) and $[HL^{Bn}]Cl$ **1a** (352 mg, 1.0 mmol) were dissolved in DMSO (10 mL) and stirred at r.t. for 2 h and then 80 °C for another 12 h. The solvent was reduced under vacuum to 1 mL. Addition of Et_2O to the concentrated solution resulted in a yellow precipitate, which was collected and washed with Et_2O (3 × 10 mL) to give $[Ni(L^{Bn})_2][Cl]_2$ **5** as a greenish yellow powder. Yield, 342 mg (90%). ^{1}H NMR (500 MHz, MeOD): δ = 7.74 (s, 1H, Ar–H), 7.56 (d, J = 8.2 Hz, 1H, Ar–H), 7.41–7.36 (m, 4H, Ar–H), 7.16–7.13 (m, 3H, Ar–H), 6.73–6.70 (t, J = 7.6 Hz, 1H, Ar–H), 6.13 (d, J = 8.2 Hz, 1H, Ar–H), 6.07 (d, J = 16.4 Hz, 1H, CH_2), 5.58 (d, J = 16.4 Hz, 1H, CH_2), 5.22 (d, J = 16.4 Hz, 1H, CH_2), 4.60–4.58 (q, J = 7.0 Hz, 2H, CH_2), 4.47 (d, J = 16.4 Hz, 1H, CH_2), 1.50 (t, J = 6.6 Hz, 3H, CH_3); ^{13}C(^{1}H) NMR (75.47 MHz, MeOD): δ = 160.54 (s, NCN), 148.83, 138.50, 136.24, 133.34, 128.98, 128.03, 126.39, 124.40, 123.78, 123.51, 115.79, 111.33 (s, Ar–C), 53.32, 39.80 (s, CH_2), 14.44 (s, CH_3). MS (ESI): m/z = 345, $[Ni(L^{Bn})_2]^{2+}$, 725 $[NiCl(L^{Bn})_2]^+$. Anal. Calc for $C_{40}H_{40}Cl_2N_8Ni$: C, 63.02; H, 5.29; N, 14.70. Found: C, 59.61; H, 5.52; N, 13.89. Crystal data for **5.2CH$_3$OH. H$_2$O**: formula $C_{42}H_{50}Cl_2N_8O_3Ni$, colorless crystal, triclinic, space group $P\bar{1}$; a = 12.717(6), b = 13.937(7), c = 14.023(7) Å; β = 66.401(1)°; V = 2052.0(2) Å^3; Z = 2; crystal size 0.30 × 0.20 × 0.10 mm^3; GOF = 1.056; reflections collected: 27 158; independent reflections: 9416 [R_{int} = 0.0456]; R_1 = 0.0526; wR_2 = 0.1323. Depository number: CCDC 760775.

Synthesis of [Pd(1-(1-ethyl-benzimidazol-2-ylmethyl)-3-benzyl-imidazolin-2-ylidene)$_2$][Cl]$_2$ (6). $Pd(OAc)_2$ (112 mg, 0.5 mmol) and $[HL^{Bn}]Cl$ **1a** (352 mg, 1.0 mmol) were dissolved in DMSO (10 mL). Using a similar procedure for the synthesis of **5**, a yellowish white powder of $PdCl_2(L^{Bn})_2$ **6** was obtained. Yield, 372 mg, 92%. ^{1}H NMR (500 MHz, d_6-DMSO): 8.19–8.17 (d, J = 8.2 Hz, 1H, Ar–H), 7.75–7.73 (d, J = 8.2 Hz, 1H, Ar–H), 7.64–7.59 (m, 3H, Ar–H), 7.41–7.26 (m, 6H, Ar–H), 6.11–6.08 (d, J = 14.50, 1H, CH_2), 5.99 (s, 2H, CH_2), 5.46–5.43 (d, J = 14.50, 1H, CH_2), 4.57–4.47 (m, 2H, CH_2), 1.41–1.39 (t, J = 7.25, 3H, CH_3); ^{13}C(^{1}H) NMR (125.77 MHz, d_6-DMSO): 151.57 (s, NCN), 148.48, 139.13, 137.55, 133.30, 129.03, 128.71, 128.47, 124.67, 123.59, 123.44, 122.73, 120.59, 112.00 (s, Ar–C), 55.37, 53.06, 45.70 (s, CH_2), 15.88 (s, CH_3). MS (ESI): m/z = 369 and 738 $[Pd(L^{Bn})_2]^{2+}$. Anal. Calc for $C_{42}H_{50}Cl_2N_8O_3Pd$: C, 56.54; H, 5.65; N, 12.56. Found: C, 55.86; H, 5.16; N, 12.88. Crystal data for **6.2CH$_3$OH.H$_2$O**: formula $C_{42}H_{50}Cl_2N_8O_3Pd$, colorless crystal, triclinic, space group $P\bar{1}$; a = 12.600(1), b = 13.967(1), c = 14.219(1) Å; β = 72.213(2)°; V = 2068.7(3) Å^3; Z = 2; crystal size 0.40 × 0.22 × 0.20 mm^3; GOF = 1.061; reflections collected: 26 609; independent reflections: 9487 [R_{int} = 0.0266]; R_1 = 0.0455; wR_2 = 0.1253. Depository number: CCDC 760776.

Complexes **3b** and **4b** could also be easily prepared from the direct reaction of **1b** and $M(OAc)_2$ (M = Ni and Pd) with a yield of 92% and 90%, respectively.

Catalytic applications

General procedure for the Heck reactions. Complex **4b** or **6** (0.25 mol%), an aryl halide (0.5 mmol), styrene or 2-vinyl pyridine (0.75 mmol), and NaOAc (1.0 or 2.0 mmol) were dissolved in dimethylacetamide (DMAc, 3mL) in a 10 mL tube. The reaction

mixture was stirred at 130 °C for a specified duration. After cooling to r.t., the mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (3 × 5 mL). The organic extract was dried over $MgSO_4$, filtered, and the resultant mixture analyzed by GC-MS.

General procedure for the Kumada reactions. The reaction was done in a glove box. A 10 mL tube was charged with an aryl halide (0.5 mmol), a specified Ni complex and THF (3 mL). To the solution was added a solution of *p*-MeC_6H_4MgBr (0.75 or 1.0 mL, 1.0 M in THF) at r.t. with stirring. After a specified duration, the reaction was taken out from the glove box and quenched by addition of water. The mixture was extracted with ethyl acetate (3 × 5 mL), and the combined organic phase was dried over $MgSO_4$, filtered, and the product mixture analyzed by GC-MS.

Crystallographic analysis

Diffraction measurements were conducted at 100(2)–293(2) K on a Bruker AXS APEX CCD diffractometer using Mo KR radiation ($\gamma = 0.71073$ Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.[20] Structure solutions and refinements were performed by using the programs SHELXS-97[21a] and SHELXL-97.[21b] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. In the structure of **3a** and **4a**, the asymmetric unit contains one complex cation $[M(C_{20}H_{20}N_4)_2]^{2+}$ (M = Ni and Pd), half of the complex anion $[Ag_4Cl_8]^{4-}$ and one water molecule. One of the Ag atoms in $[Ag_4Cl_8]^{4-}$ of **4a** is disordered into two parts with occupancy 75 : 25. In the structure of **2b**, the asymmetric unit contains two independent molecules of the compound $Ag_2Cl_2(L^{Mes})_2$.

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