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Rotamers of palladium complexes bearing IR active *N*-heterocyclic carbene ligands: Synthesis, structural characterization and catalytic activities

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ABSTRACT

The preparation and properties of mono- versus bis(carbene) Pd(II) complexes bearing unsymmetrical cyano- and ester-functionalized NHC ligands as potential IR probes were studied in detail. Direct reaction of $Pd(OAc)_2$ with functionalized imidazolium salts afforded either bis(carbene) (**3a, c**) or monocarbene complexes (**5, 6**) with a *N*-coordinated imidazole co-ligand. The latter were exclusively obtained with *N*-ethylene substituted salts, which were found to undergo N–C cleavage reaction. The milder Ag-carbene transfer reaction on the other hand was tolerable to the length of the substituents and the nature of the functional groups. All bis(carbene) complexes (**3a–c**, **4a–c**) were obtained as a inseparable mixture of square-planar *trans-anti* and *trans-syn* rotamers. The identity, ratio and dynamic equilibrium of these rotamers have been investigated and the relatively high rotational barrier for rotamers of **3a** was estimated to be about 74 kJ mol^{-1} at 380 K. All eight complexes were fully characterized by NMR and IR spectroscopies, ESI mass spectrometry and X-ray single crystal and powder diffraction. A preliminary catalytic study showed that ester-functionalized complexes **4a** and **4b** gave rise to highly active catalyst in the double Mizoroki–Heck coupling of aryl dibromides, while the in situ ester-hydrolyzed complexes were also active in the coupling of activated aryl chlorides.

1. Introduction

In recent years, *N*-heterocyclic carbenes (NHCs) have attracted increasing attention in organometallic chemistry and catalysis mainly due to their strong donor-abilities surpassing those of classical phosphines and the ease of their preparation [1]. Moreover, additional functionalities can be introduced at the nitrogen atoms of the *N*-heterocyclic ring in a straightforward manner, and accordingly, various donor-functionalized NHCs and their complexes have been explored [2], some of which show hemilabile behaviour [3]. In addition to their extensive use in catalysis, some NHC complexes of Ag, Au and Pd have also been investigated for potential biomedical applications [4–8]. Furthermore, application of NHCs in material science [9] and supramolecular chemistry [10] are just beginning to unfold. In view of these wide applications, we became interested in the introduction of IR active functions in NHC complexes as an additional spectroscopic probe, which may be useful in the characterization of materials and for sensing purposes. Herein, we report the design of six unsymmetrical carbene precursors functionalized with IR active cyano- and ester-groups and an initial study on their coordination chemistry on palladium(II). Furthermore, we describe properties, molecular structures and some catalytic activities of the resulting complexes.

2. Result and discussion

2.1. Ligand precursors

The cyano- and ester-functionalized imidazolium bromide salts (**1a–c** and **2a–c**), were prepared by direct alkylation of *N*-mesitylimidazole with alkyl bromides bearing the desired functional groups as shown in Scheme 1. The alkylating agents methyl-3-bromopropionate and methyl-4-bromobutyrate were prepared by esterification of the respective bromo-substituted carboxylic acids in methanol with catalytic amount of concentrated sulfuric acid.

Formation of imidazolium salts was indicated by the presence of a downfield chemical shift at ~9.50–10.50 ppm in their ^1H NMR spectra for the proton on the C2 carbon of the heterocyclic ring. The yield for most salts was generally quite high. The relatively lower yields for salts **1b** and **2b** may be due to subsequent base-catalyzed *N*-alkyl cleavage of the ß-cyanoethyl and ß-esterethyl group from the heterocycle (vide infra) [11]. Ligand precursors **1** and **2** are all solids due to the *N*-mesityl group. Other known cyano- [12] or ester-functionalized [13] imidazolium salts bearing purely *N*-alkyl substituents are ionic liquids at room temperature. Increasing the chain length of the *N*-alkyl substituent leads to more hygroscopic carbene precursors. In general, imidazolium salts with ester functional groups tend to be more hygroscopic than their cyano counterparts, which we tentatively ascribe to stronger interaction of the salts with water molecules via hydrogen bonds to the oxygen of the ester function.

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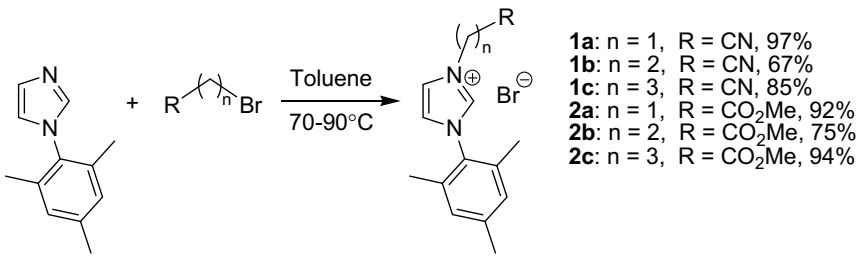


Scheme 1. Preparation of cyano- and ester-functionalized imidazolium salts.

2.2. Synthesis of Pd–NHC complexes

To study the coordination chemistry of proligands **1a–c** and **2a–c**, we opted for palladium(II) as a common and catalytically active metal center in NHC chemistry. The general method for the preparation of dihalo-bis(carbene) Pd(II) complexes by reacting $Pd(OAc)_2$ with 2 equiv. of imidazolium salt works well for cyanomethyl and cyanopropyl derivatives **1a** and **1c** yielding 85% and 94% of the desired products $[PdBr_2(^{meCN}NHC)_2]$ (**3a**) and $[PdBr_2(^{propCN}NHC)_2]$ (**3c**), respectively (Method A, Scheme 2).

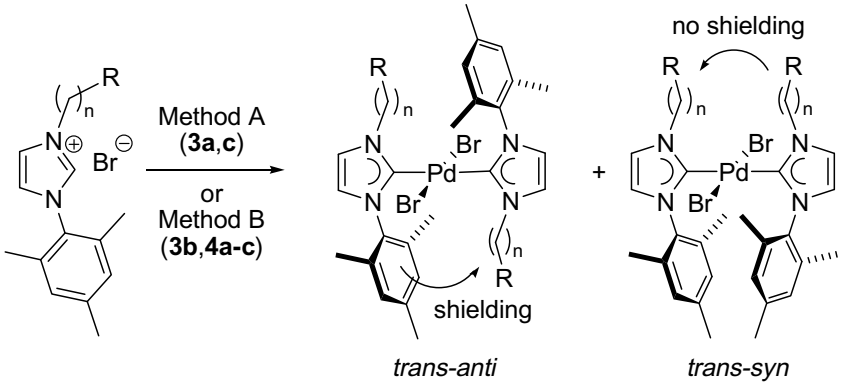
However, reaction of the cyanoethyl substituted imidazolium salt **1b** under similar reaction conditions gave the monocarbene complex $[PdBr_2(^{etCN}NHC)(imd)]$ (**5**) with a *N*-coordinated mesitylimidazole ligand (imd), which presumably resulted from N–C cleavage of the ß-cyanoethyl group under the basic and relatively harsh reaction condition [6]. Similar cleavage was observed in the analogous reaction of the esterethyl substituted imidazolium salt **2b** resulting in complex $[PdBr_2(^{etCO2Me}NHC)(imd)]$ (**6**) (Scheme 3b). The relatively high yields of these two complexes indicate that only 1 equiv. of the precursor salts was successfully deprotonated to give the carbene ligand, whereas the second equivalent underwent base-catalyzed *N*-alkyl cleavage under elimination of HBr and an alkene (Scheme 3a). To prevent this cleavage, the relatively milder Ag-carbene-transfer method was explored (Method B, Scheme 2). Indeed, this method gave the desired bis(carbene) complexes, $[PdBr_2(^{etCN}NHC)_2]$ (**3b**) and $[PdBr_2(^{etCO2Me}NHC)_2]$ (**4b**), as major products in yields of 67 and 75% with only minor amounts of the monocarbene complexes. This method has also been applied for the synthesis of another two ester-functionalized Pd–NHC complexes $[PdBr_2(^{meCO2Me}NHC)_2]$ (**4a**) and $[PdBr_2(^{propCO2Me}NHC)_2]$ (**4c**) to avoid possible hydrolysis of the ester group on the functionalized imidazolium salt.

2.3. Characterization of Pd–NHC complexes

All Pd–NHC complexes (**3–6**), were fully characterized by electrospray ionization (ESI) mass spectrometry, IR, ^1H and ^{13}C NMR spectroscopies. In the ESI mass spectra of the bis(carbene) complexes **3** and **4**, *m/z* values corresponding to both $[M-Br]^+$ and $[M+Na]^+$ ($[M+NH_4]^+$ for **4b**) fragments were observed, with the latter as the base peak. The spectra for the monocarbene complexes **5** and **6**, on the other hand, showed only $[M-Br]^+$ fragments. The isotopic envelopes match with the calculated pattern as illustrated in Fig. 1 using the zoom scan spectra of complex **3c** as an example.

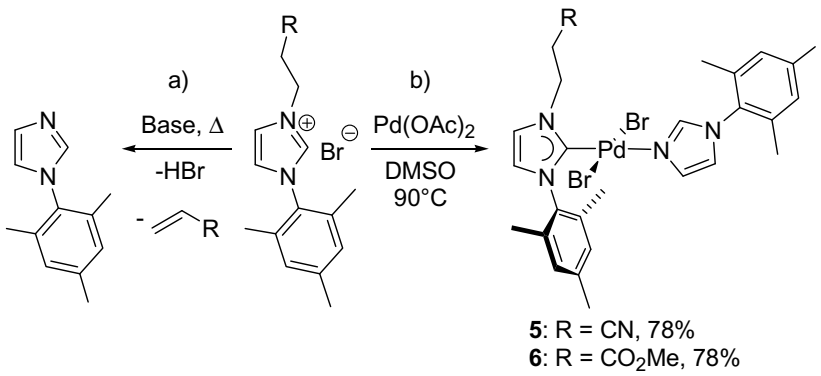
The cyano stretching frequencies of complexes **3** and **5** and carbonyl stretching frequencies of **4** and **6** measured by IR spectroscopy are summarized in Table 1. The intensity of the C=O stretching band is generally strong, while that of C≡N is relatively weak. In complex **3a**, the C≡N stretching is so weak that it could not be distinguished from the baseline. This might be due to the small difference in bond polarity when the C≡N group is in close proximity to the *N*-atom of the heterocycle. As a consequence, a potential application of cyanomethylene-derivatives for IR sensing purposes can be excluded.

In both ^1H NMR and ^{13}C NMR spectra for the bis(carbene) complexes **3** and **4**, two sets of signals were observed. These are



3a: n = 1, R = CN, 85%, anti:syn = 1:4
3b: n = 2, R = CN, 65%, anti:syn = 2:1
3c: n = 3, R = CN, 94%, anti:syn = 3:1
4a: n = 1, R = CO_2Me, 93%, anti:syn = 1:4
4b: n = 2, R = CO_2Me, 89%, anti:syn = 1:1.5
4c: n = 3, R = CO_2Me, 97%, anti:syn = 1.3:1

Scheme 2. Preparation of Pd(II) complexes. Method A (**3a,c**): 0.5 equiv. $Pd(OAc)_2$/DMSO/90 °C. Method B (**3b, 4a–c**): (i) 0.5 equiv. Ag_2O/CH_2Cl_2, (ii) 0.5 equiv. $[PdBr_2(MeCN)_2]$. All *anti-syn* ratios determined by ^1H NMR in $CDCl_3$ solutions.



Scheme 3. Base-catalyzed *N*-alkyl cleavage reaction (a) and preparation of Pd(II) monocarbene complexes (b).

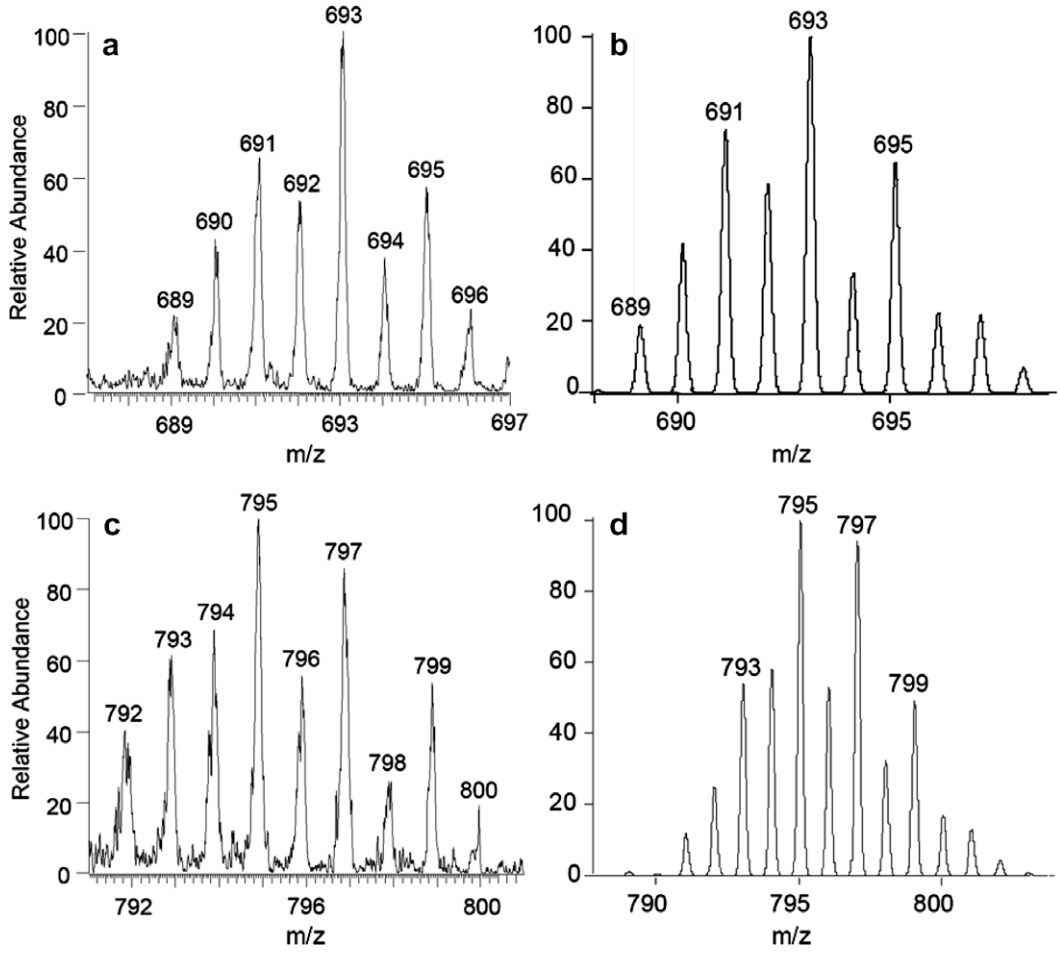


Fig. 1. Experimental isotopic pattern for complex fragments [**3c**−Br]$^+$ (a) and [**3c**+Na]$^+$ (c) obtained by ESI-MS; simulated isotopic pattern for complex fragments [**3c**−Br]$^+$ (b) and [**3c**+Na]$^+$ (d).

Table 1
C≡N or C=O stretching frequencies of complexes **3**–**6** measured as KBr pellets.

Complex	C≡N stretch (cm^{-1})	C=O stretch (cm^{-1})
3a	Too weak to detect	–
3b	2253 (medium)	–
3c	2246 (medium)	–
4a	–	1757 (strong)
4b	–	1725 (strong)
4c	–	1734 (strong)
5	2252 (medium)	–
6	–	1733 (strong)

assigned to *trans-anti* and *trans-syn* isomers, which are due to a hindered rotation of the unsymmetrical ligand around the carbene–palladium bond. Notably, the isomeric ^{1}H NMR resonances for the NCH_2 protons are well separated, which allows an easy assignment and determination of their relative ratios for all rotamers of **3** and **4** (Fig. 2). In the *trans-anti* rotamers, the NCH_2 groups are situated in the shielding region of the aromatic mesityl substituent giving rise to distinctively more highfield shifts as compared to those in the *syn* rotamers, which do not experience shielding by the ring current (Scheme 2). Correspondingly, all bis(carbene) complexes also show two carbene resonances ranging from 168

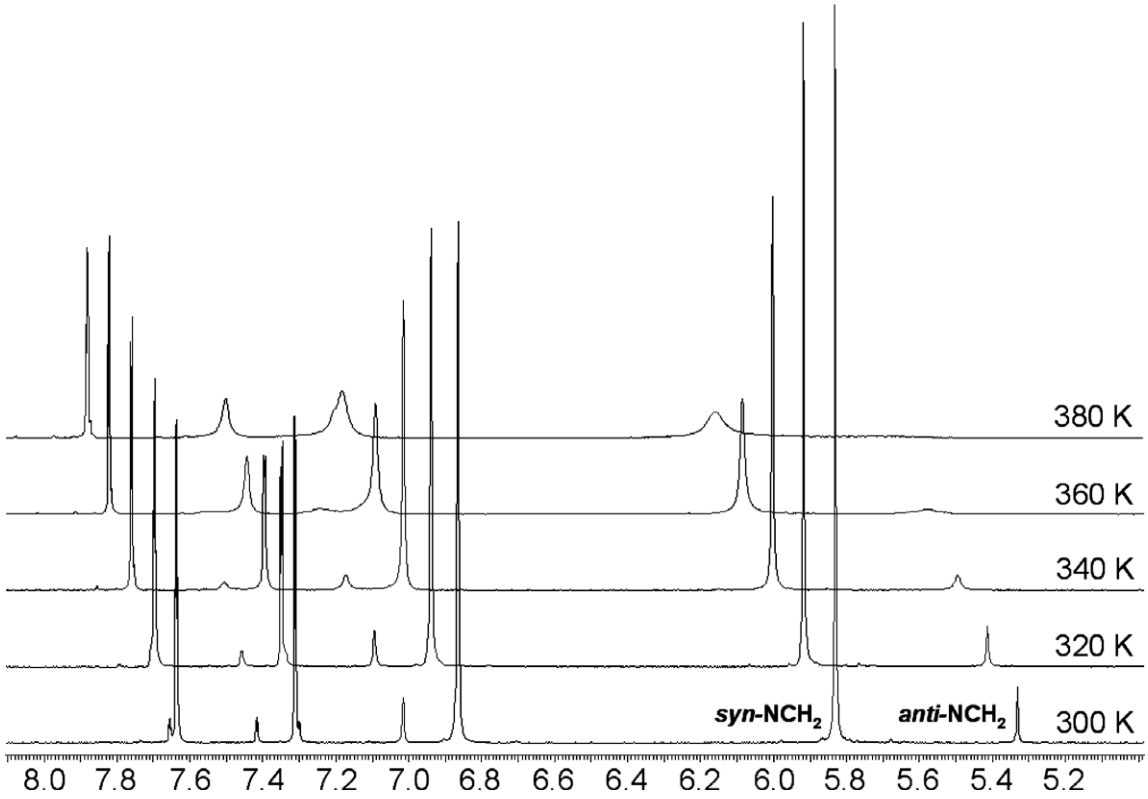


Fig. 2. Variable-temperature ^{1}H NMR spectral plot of complex **3a** in d_6-DMSO.

to 172 ppm, which is indicative of *trans* configured bis(imidazolin-2-ylidene) complexes. The difference between these two carbene signals is less than 0.2 ppm corroborating the presence of rotameric pairs. A separation of these rotamers was unsuccessful, which leads to the assumption of a dynamic equilibrium between them in solution. *cis*-Complexes, on the other hand, would usually give rise to more highfield shifts of ~160–165 ppm that are absent in all spectra. The observed preference for *trans* isomers is most likely due to the bulky *N*-mesityl substituent in all NHC ligands.

In order to study this equilibrium, ^{1}H NMR experiments and X-ray powder diffraction (vide infra) were conducted. It was found that pure single crystals of *trans-anti*-**3c** (vide infra) undergo isomerization upon dissolution in $CDCl_3$ to give a stable *anti:syn* rotamer ratio of 3:1. Similarly, we observed that **3a** gives rise to different rotamer-ratios in different deuterated solvents. For example, the *anti:syn* rotamer ratio amounts to 1:4 in $CDCl_3$, while the ratio is 1:12 in d_6-DMSO. Apparently, the polarity of **3a** rotamers is so different that chloroform and DMSO stabilize them differently. Furthermore, variable-temperature (VT) ^{1}H NMR spectra of **3a** were recorded in d_6-DMSO from 300–380 K (Fig. 2). The ratio of the two different isomers was observed to change slowly with increasing temperatures, which suggests that the activation barrier for this isomerization process is relatively high. At >340 K, the signals broaden and coalescence for the NCH_2 protons occurs at 380 K allowing for an estimate of the rotational barrier as about 74 kJ mol^{-1} [14]. In general, the *trans-anti* configuration is favoured in complexes with longer substituents. The monocarbene complexes **5** and **6** show as expected one set of signals with equivalent *o*-CH_3 group of the *N*-mesityl substituents, which points to a *trans* arrangement of the NHC and the imidazole ligands.

2.4. Molecular structures

Single crystals of complexes **3a** · 0.5($C_6H_5CH_3$), **3b**, **3c**, **4a** · $(CH_3)_2CO$, **4b** · CH_3OH, **4c**, **5** and **6** · 0.25$(CH_3)_2CO$, were obtained by slow evaporation of a chloroform/toluene (**3a**), acetone (**3b**, **4a**/**b**, **6**), acetonitrile (**5**), and methanol solutions (**4b**) or by cooling of a hot saturated dichloromethane solution (**3c**). The molecular structures of *trans-anti*-**3c**, *trans-syn*-**4a** and **5** along with their numbering scheme and selected bond lengths and angles are depicted in Figs. 3–5 as representatives.

All bis(carbene) complexes crystallized in a *trans* configuration with two carbene and two bromo ligands coordinated to the metal center in a nearly perfect square-planar geometry. In complexes **3a, 4a**, and **4b**, the two carbene ligands are orientated in a *trans-syn* manner, while in complexes, **3b, 3c** and **4c**, a *trans-anti* configuration is adopted. In all cases, the configuration found in solid state also represents the major isomer found by ^{1}H NMR in solution. For all 6 bis(carbene) complexes **3** and **4**, the Pd–$C_{carbene}$ bond distances range from 2.015–2.036 Å. The monocarbene complexes **5** and **6**, on the other hand, have slightly shorter Pd–$C_{carbene}$ bond lengths ranging from 1.960–1.976 Å, which is due to the weaker *trans* influence of the *N*-coordinated mesitylimidazole ligand as compared to that of a NHC ligand.

In order to provide concrete evidence that the single crystals used for crystal diffraction, and thus the determined solid-state conformation, is representative of the crystalline bulk, X-ray powder diffraction analysis was performed. Crystalline materials of **3c** were ground into fine powders, which were subjected to X-ray powder diffraction. The experimental powder pattern agrees well with the calculated pattern for *trans-anti*-**3c** (Fig. 6) suggesting that only one isomeric form crystallized and isomerization occurs upon dissolution (vide supra). To find further support for this statement, a solution of initially pure *trans-anti*-**3b** was evaporated under vacuum and the residue thus obtained was analyzed by X-ray powder diffraction. A comparison with the calculated data based on *trans-anti*-**3b** revealed an additional set of peaks in the experimental data attributable to its rotamer *trans-syn*-**3b**, which apparently has formed upon dissolution of *trans-anti*-**3b** (Fig. 7).

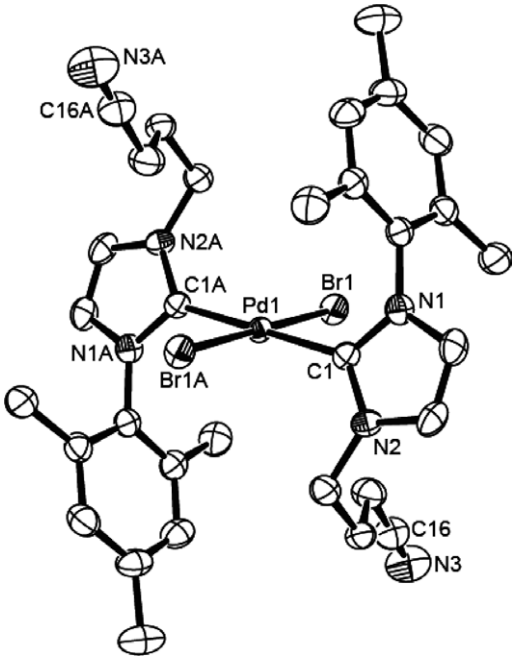


Fig. 3. Molecular structure of *trans-anti*-**3c** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 2.019 (4), Pd1–Br1 2.4365(4), N1–C1 1.362(5), N2–C1 1.369(5), N3–C16 1.141(6); C1–Pd1–Br1 91.08(11), C1–Pd1–Br1A 88.92(11), N1–C1–N2 103.7(4).

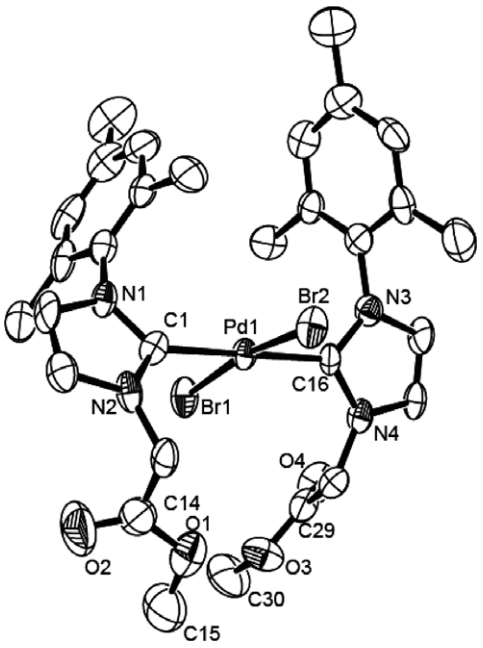


Fig. 4. Molecular structure of *trans-syn*-**4a** · $(CH_3)_2CO$ showing 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 2.036(9), Pd1–C16 2.027(8), Pd1–Br1 2.4339(12), Pd1–Br2 2.4516(11), N1–C1 1.356(10), N2–C1 1.351(11), N3–C16 1.340(11), N4–C16 1.367(11), O2–C14 1.182(13), O4–C29 1.195(11); C1–Pd1–Br1 88.9(2), C1–Pd1–Br2 91.1(2), C16–Pd1–Br1 90.4(2), C16–Pd1–Br2 89.6(2), N1–C1–N2 104.5(8), N3–C16–N4 104.2(7).

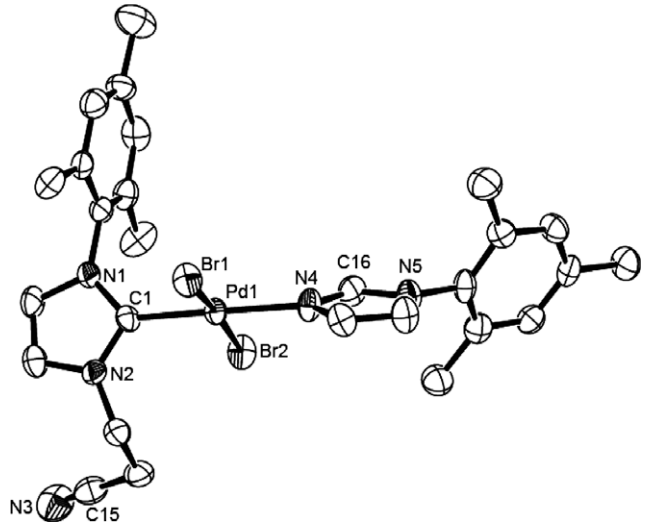


Fig. 5. Molecular structure of **5** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 1.969(5), Pd1–Br1 2.4178(7), Pd1–Br2 2.4361(8), N1–C1 1.358(7), N2–C1 1.395(7), N4–C16 1.335(7), N5–C16 1.340(7), N3–C15 1.122(8); C1–Pd1–Br1 89.59(16), C1–Pd1–Br2 90.75(16), N4–Pd1–Br1 90.49(13), N4–Pd1–Br2 89.07(13), N1–C1–N2 104.9(5), N4–C16–N5 110.7(5).

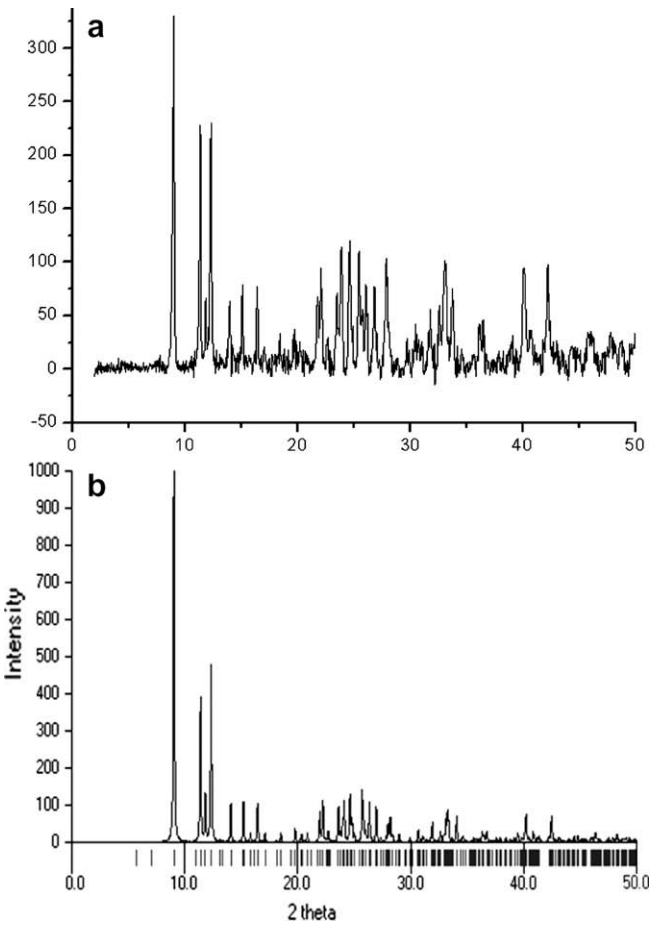


Fig. 6. Experimental (a) and calculated (b) X-ray powder diffraction pattern for *trans-anti*-**3c**.

2.5. Mizoroki–Heck catalysis

Complexes of *N*-heterocyclic carbene ligands have been applied in both homogeneous and heterogeneous catalysis. In particular, Pd–NHC complexes have been widely used in the making of C–C bonds often employing the Mizoroki–Heck and Suzuki–Miyaura coupling reactions. A preliminary study was carried out in this work to investigate the catalytic activities of the ester-functionalized

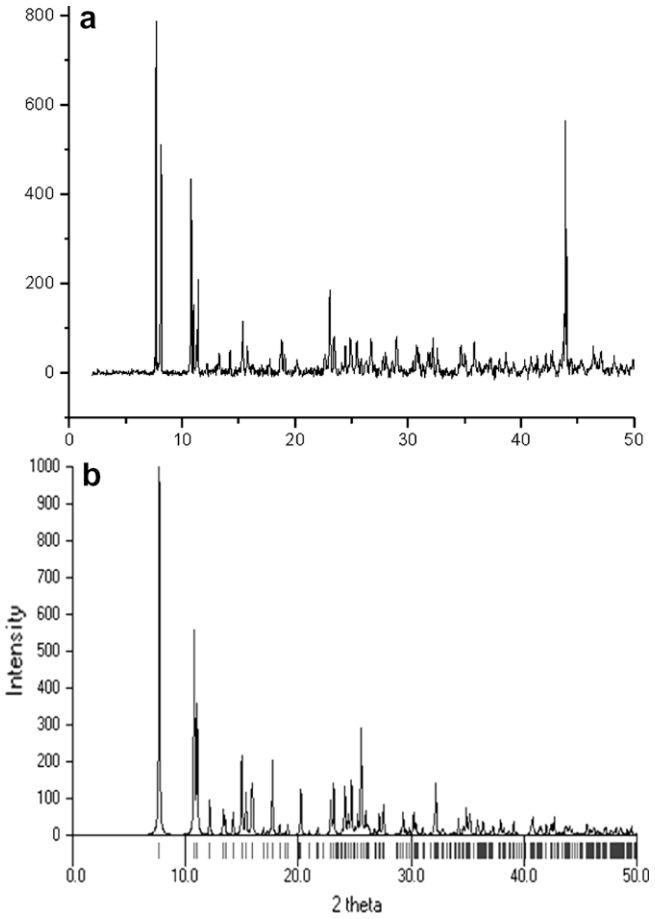
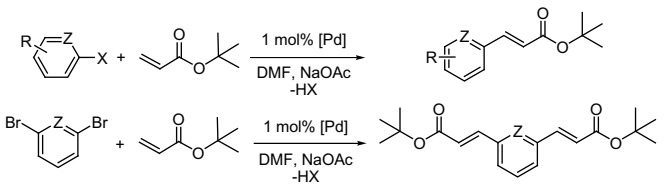


Fig. 7. Experimental X-ray powder diffraction pattern for precipitated **3b** (a) and calculated pattern for *trans-anti*-**3b** (b).

complexes **4a** and **4b** in the Mizoroki–Heck reaction. The coupling of aryl bromides and chlorides with *tert*-butyl acrylate at 120 °C in DMF with 1 mol% catalyst loading and a reaction time of 18 h was chosen as a standard test reaction.

The results summarized in Table 2 showed that both complexes are highly efficient in the coupling of the activated aryl bromides achieving >90% yield (Entries 1–6). Double Mizoroki–Heck reactions have also been investigated with our catalysts, as shown in Entries 3–6. Notably, all double Mizoroki–Heck reactions proceeded smoothly even though the introduction of a vinylic substituent would deactivate the substrate for the second coupling step. A similar coupling reaction of 1,3–dibromobenzene with *tert*-butyl acrylate to give (*E,E*′)-di-*tert*-butyl-3,3′-(1,3-phenylene)diacrylate has been reported with 2 mol% $Pd(OAc)_2$/tri-*o*-tolylphosphine and higher temperature giving a lower yield of 80% [15]. In our work, very high yields of >90% were obtained with 1 mol% of our pre-catalysts as shown in Entries 3 and 4. The extension of this double coupling protocol to the heterocyclic substrate 2,6-dibromopyridine, which has been rarely studied, also led to a high yields for the doubly-coupled product (*E,E*′)-di-*tert*-butyl-3,3′-(pyridine-2,6-diyl)diacrylate of 91% and 93%, respectively, which to the best of our knowledge has not been reported so far. The coupling of aryl chlorides was less successful and afforded only moderate yields for 4-chlorobenzaldehyde (Entries 7/8) and even lower yields for 2-chloropyridine (Entries 9/10). Recently, we reported that mixed dicarboxylato-bis(carbene)palladium(II) complexes could activate aryl chlorides readily [16]. In an attempt to generate chelating mixed carbene-carboxylato ligands in situ for catalysis, 1 mol% of NaOH was added. The yield for the coupling of 4-chlorobenzaldehyde could thus be efficiently improved from 58% to 86% in the case for **4b** (Entry 8 versus Entry 12). The yield improvement for complex **4a** on the other hand was less substantial, which may be due to the short methylene-spacer restricting an efficient coordination of the carboxylato group (Entry 7 versus Entry 11). The coupling of 2-chloropyridine, on the other hand, could not be improved. Overall, the imidazolium-based NHC complexes **4a** and **4b** are less active than some benzimidazolium-derived NHC Pd complexes reported by us earlier [17,18].

Table 2
Mizoroki–Heck Coupling reactions catalyzed by complexes **4a** and **4b**.[a]



Z = C, N; X = Br, Cl; R = CHO, H

Entry	Catalyst	Aryl halide	Yield (%)[b]
1	**4a**	4-Bromobenzaldehyde	>99
2	**4b**	4-Bromobenzaldehyde	>99
3	**4a**	1,3-Dibromobenzene	90[c]
4	**4b**	1,3-Dibromobenzene	9 [c]
5	**4a**	2,6-Dibromopyridine	91[c]
6	**4b**	2,6-Dibromopyridine	93[c]
7	**4a**	4-Chlorobenzaldehyde	51[c]
8	**4b**	4-Chlorobenzaldehyde	58[c]
9	**4a**	2-Chloropyridine	5[c]
10	**4b**	2-Chloropyridine	3[c]
11	**4a**	4-Chlorobenzaldehyde	71[c,d]
12	**4b**	4-Chlorobenzaldehyde	86[c,d]
13	**4a**	2-Chloropyridine	9[c,d]
14	**4b**	2-Chloropyridine	8[c,d]

[a] Reaction conditions generally not optimized.
[b] Yields were determined by ^1H NMR spectroscopy and calculated based on average of two independent runs.
[c] With addition of 1.5 equiv. of $[N(n\text{-}C_4H_9)_4]Br$.
[d] With addition of 0.01 mmol of NaOH.

3. Conclusion

A series of palladium(II) mono- and bis(carbene) complexes bearing IR active cyano (**3a–c, 5**) or ester-groups (**4a–c, 6**) have been prepared. It was found that *N*-ethylene substituents undergo C–N bond cleavage reactions under basic/harsh conditions giving rise to formation of monocarbene complexes. Apart from **3a**, all complexes show medium to strong IR bands, which render them potentially useful for IR sensing purposes. Furthermore, the *trans-anti* and *trans-syn* rotamers of all bis(carbene) complexes have been studied in detail. A preliminary study showed that complexes **4a** and **4b** have good catalytic activities in double Mizoroki–Heck coupling reactions with aryl dibromides yielding diacrylates. Further studies are underway to explore the potential of these complexes as IR sensing probes in bio-related areas and for the elucidation of reaction mechanism.

4. Experimental

4.1. General considerations

Unless otherwise noted all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. 1-Mesitylimidazole was prepared according

to a previously reported method [19]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 spectrometer or AMX 500 spectrophotometer and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C). ESI Mass spectra were measured using a Finnigan MAT LCQ spectrometer. Infrared spectra were measured with a Varian 3100 FT-IR spectrophotometer as KBr pellets. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

4.2. Synthesis of 1-mesityl-3-cyanomethylimidazolium bromide (**1a**)

A mixture of mesitylimidazole (373 mg, 2.0 mmol) and bromoacetonitrile (0.139 mL, 2.0 mmol) was dissolved in toluene (5 mL) and stirred at 90 °C for 36 h. The off-white precipitate formed on heating was then collected via filtration and washed with diethyl ether (597 mg, 1.95 mmol, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.22 (s, 1H, NCHN), 8.43 (s, 1H, CH_{imid}), 7.27 (s, 1H, CH_{imid}), 7.00 (s, 2H, Ar-H), 6.47 (s, 2H, NCH_2), 2.34 (s, 3H, *p*-CH_3), 2.09 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 142.3 (NCN), 138.9, 134.9, 131.1, 130.6, 124.8, 124.3 (Ar-C), 114.3 (CN), 39.3 (NCH_2), 21.8 (*p*-CH_3), 18.5 (*o*-CH_3). ESI-MS: *m/z* 226 $[M-Br]^+$.

4.3. Synthesis of 1-mesityl-3-(2-cyanoethyl)imidazolium bromide (**1b**)

A mixture of mesitylimidazole (373 mg, 2.0 mmol) and 3-bromopropionitrile (0.167 mL, 2.0 mmol) was heated in toluene (5 mL) at 75 °C for 6 h. The off-white product was collected via filtration and then purified by column chromatography (429 mg, 1.34 mmol, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.05 (s, 1H, NCHN), 8.36 (s, 1H, CH_{imid}), 7.21 (s, 1H, CH_{imid}), 7.01 (s, 2H, Ar-H), 5.14 (t, ^3J(H,H) = 6.2 Hz, 2H, NCH_2), 3.48 (t, ^3J(H,H) = 6.2 Hz, 2H, CH_2CN), 2.36 (s, 3H, *p*-CH_3), 2.06 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): 142.3 (NCN), 138.6, 135.0, 131.2, 130.6, 124.8, 124.1 (Ar-C), 117.4 (CN), 46.7 (NCH_2), 21.8 (CH_2CN), 21.2 (*p*-CH_3), 18.3 (*o*-CH_3). ESI-MS: *m/z* 240 $[M-Br]^+$.

4.4. Synthesis of 1-mesityl-3-(3-cyanopropyl)imidazolium bromide (**1c**)

A mixture of mesitylimidazole (373 mg, 2.0 mmol) and 4-bromobutyronitrile (0.200 mL, 2.0 mmol) was heated in toluene (5 mL) at 90 °C for 48 h. After removing toluene under vacuum, the sticky oil remained was stirred in THF overnight to give a hygroscopic white powder (569 mg, 1.7 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.19 (s, 1H, NCHN), 8.17 (s, 1H, CH_{imid}), 7.18 (s, 1H, CH_{imid}), 6.99 (s, 2H, Ar-H), 4.93 (t, ^3J(H,H) = 7.0 Hz, 2H, NCH_2), 2.75 (t, ^3J(H,H) = 6.8 Hz, 2H, CH_2CN), 2.48 (m, 2H, $CH_2CH_2CH_2$), 2.32 (s, 3H, *p*-CH_3), 2.07 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 141.7 (NCN), 138.1, 134.7, 131.1, 130.4, 124.7, 123.9 (Ar-C), 119.3 (CN), 49.1 (NCH_2), 27.0 (CH_2CN), 21.6 ($CH_2CH_2CH_2$), 18.2 (*o*-CH_3), 14.9 (*p*-CH_3). ESI-MS: *m/z* 254 $[M-Br]^+$.

4.5. Synthesis of 1-mesityl-3-(methylacetyl)imidazolium bromide (**2a**)

A mixture of mesitylimidazole (373 mg, 2.0 mmol) and methylbromoacetate (0.139 mL, 2.0 mmol) were dissolved in toluene (5 mL) and stirred at 90° C for 18 h. The off-white precipitate formed was filtered, washed with diethyl ether and dried under vacuum (0.627 g, 1.85 mmol, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H, NCHN), 8.06 (s, 1H, CH_{imid}), 7.17 (s, 1H, CH_{imid}), 7.00 (s, 2H, Ar-H), 5.94 (s, 2H, NCH_2), 3.82 (s, 3H, OCH_3), 2.33 (s, 3H, *p*-CH_3), 2.09 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 167.7 (C=O), 142.1 (NCN) 139.7, 135.0, 131.3, 130.5, 125.5, 123.1 (Ar-C), 54.1 (NCH_2), 51.4 (OCH_3), 21.8 (*p*-CH_3), 18.2 (*o*-CH_3). ESI-MS: *m/z* 259 $[M-Br]^+$.

4.6. Synthesis of 1-mesityl-3-(3-methylpropionate)imidazolium bromide (**2b**)

A solution of mesitylimidazole (373 mg, 2.0 mmol) and methyl-3-bromopropionate (0.218 mL, 2.0 mmol) was heated in THF (20 mL) at 75° C for 36 h. The solvent was removed under vacuum and the residue was dissolved in dichloromethane and extracted with dilute $NaHCO_3$ solution. The aqueous layer was collected and evaporated to dryness. The white solid obtained was then dissolved in chloroform and filtered over celite. The filtrate was dried under vacuum to obtain the desired product (529 mg, 1.50 mmol, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.05 (s, 1H, NCHN), 8.15 (s, 1H, CH_{imid}), 7.13 (s, 1H, CH_{imid}), 6.99 (s, 2H, Ar-H), 5.00 (t, ^3J(H,H) = 5.8 Hz, 2H, NCH_2), 3.67 (s, 3H, OCH_3), 3.20 (t, ^3J(H,H) = 5.7 Hz, 2H, CH_2C=O), 2.32 (s, 3H, *p*-CH_3), 2.05 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 172.1 (C=O), 142.0 (NCN), 138.9, 134.9, 131.3, 130.5, 124.9, 123.4 (Ar-C), 52.9 (OCH_3), 46.7 (NCH_2), 35.4 (CH_2C=O), 21.7 (*p*-CH_3), 18.2 (*o*-CH_3). ESI-MS: *m/z*: 273 $[M-Br]^+$.

4.7. Synthesis of 1-mesityl-3-(4-methylbutyrate)imidazolium bromide (**2c**)

A solution of mesitylimidazole (373 mg, 2.0 mmol) and methyl-4-bromobutyrate (0.252 mL, 2.0 mmol) was heated in THF (20 mL) at 75 °C for 36 h. The solvent was removed under vacuum and the residue was stirred in diethyl ether for 4 h. The diethyl ether was decanted and the insoluble product was dried under vacuum to afford a hygroscopic solid (682 mg, 1.87 mmol, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.17 (s, 1H, NCHN), 8.07 (s, 1H, CH_{imid}), 7.21 (s, 1H, CH_{imid}), 6.91 (s, 2H, Ar-H), 4.73 (t, ^3J(H,H) = 5.8 Hz, 2H, NCH_2), 3,57 (s, 3H, OCH_3), 2.45 (t, ^3J(H,H) = 5.7 Hz, 2H, CH_2C=O), 2.27 (m, 2H, $CH_2CH_2CH_2$), 2.26 (s, 3H, *p*-CH_3), 1.99 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 173.2 (C=O), 141.7 (NCN), 138.2, 134.7, 131.2, 130.3, 124.2, 123.9 (Ar-C), 52.4 (OCH_3), 49.7 (NCH_2), 30.9 (CH_2C=O), 26.4 ($CH_2CH_2CH_2$), 21.6 (*p*-CH_3), 18.1 (*o*-CH_3). ESI-MS: *m/z*: 287 $[M-Br]^+$.

4.8. Method A: synthesis of bis(carbene) complexes **3a**, **3c** and monocarbene complexes **5** and **6**

A mixture of $Pd(OAc)_2$ (68 mg, 0.3 mmol) and appropriate amount of imidazolium salt (0.6 mmol) were heated at 90 °C for 12 h in DMSO (5 mL). The reaction mixture was filtered over celite and the DMSO of the filtrate was removed via vacuum distillation. The residue was then dissolved in dichloromethane (25 mL) and extracted with water (3 × 25 mL). The organic layer was collected, dried over Na_2SO_4 and the solvent was removed under vacuum to give a pale yellow solid.

4.9. Method B: synthesis of bis(carbene) complexes **3b** and **4a–c**

Appropriate amount of imidazolium salt (0.6 mmol) and silver oxide (70 mg, 0.3 mmol) were suspended in dichloromethane and stirred at ambient temperature for 12 h shielded from light. The mixture was then filtered into an acetonitrile solution of $[PdBr_2(CH_3CN)_2]$. After stirring at ambient temperature for 12 h, the reaction mixture was filtered over celite and the solvent was removed under vacuum to give pale yellow powders.

4.10. trans-Dibromo-bis(1-mesityl-3-cyanomethylimidazolin-2-ylidene)palladium(II) (**3a**)

Yield for both rotamers: 183 mg (0.255 mmol, 85%). *trans-syn*-**3a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, ^3J(H,H) = 1.9 Hz, 2H, CH_{imid}), 6.87 (s, 4H, Ar-H), 6.82 (d, ^3J(H,H) = 1.9 Hz, 2H, CH_{imid}), 5.71 (s, 4H, NCH_2), 2.47 (s, 6H, *p*-CH_3), 1.92 (s, 12H, *o*-CH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.1 (NCN), 138.9, 136.4, 135.4, 129.8, 125.1, 121.5 (Ar-C), 115.1 (CN), 40.2 (NCH_2), 21.9 (*p*-CH_3), 19.9 (*o*-CH_3). *trans-anti*-**3a**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 7.03 (s, 4H, Ar-H), 6.90 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 5.18 (s, 4H, NCH_2), 2.39 (s, 6H, *p*-CH_3), 2.23 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.2 (NCN), 140.1, 136.9, 135.6, 129.8, 125.3, 121.0 (Ar-C), 114.4 (CN), 39.4 (NCH_2), 21.8 (*p*-CH_3), 20.3 (*o*-CH_3). Anal. Calc. for $C_{28}H_{30}Br_2N_6Pd$: C, 46.92; H, 4.22; N, 11.72. Found: C, 47.20; H, 4.27; N, 11.73%. ESI-MS: *m/z* = 637 $[M-Br]^+$, 739 $[M+Na]^+$.

4.11. trans-Dibromo-bis[1-mesityl-3-(2-cyanoethyl)imidazolin-2-ylidene]palladium(II) (**3b**)

Yield for both rotamers: 146 mg (0.196 mmol, 65%). *trans-anti*-**3b**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 7.01 (s, 4H, Ar-H), 6.81 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.47 (t, $^3J(H,H)$ = 7.0 Hz, 4H, NCH_2), 2.90 (t, $^3J(H,H)$ = 7.0 Hz, 4H, CH_2CN), 2.37 (s, 6H, *p*-CH_3), 2.21 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 171.3 (NCN), 139.8, 137.1, 136.0, 129.7, 124.2, 122.4 (Ar-C) 118.0 (CN), 47.4 (NCH_2), 21.8 (*p*-CH_3), 20.4 (CH_2CN), 19.8 (*o*-CH_3). *trans-syn*-**3b**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 6.83 (s, 4H, Ar-H), 6.74 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.92 (t, $^3J(H,H)$ = 7.0 Hz, 4H, NCH_2), 3.44 (t, $^3J(H,H)$ = 7.0 Hz, 4H, CH_2CN), 2.47 (s, 6H, *p*-CH_3), 1.92 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 171.1 (NCN), 138.7, 136.4, 135.5, 129.8, 124.7, 122.0 (Ar-C), 118.3 (CN), 47.6 (NCH_2), 22.0 (*p*-CH_3), 20.6 (CH_2CN), 20.0 (*o*-CH_3). Anal. Calc. for $C_{32}H_{40}Br_2N_4O_4Pd$: C, 47.40; H, 4.97; N, 6.91. Found: C, 45.80; H, 5.07; N, 6.85% (the unsuccessful attempts to obtain better values were attributed to the general lower thermal stability of *N*-ethylene substituents.). ESI-MS: *m/z* = 665 $[M-Br]^+$, 767 $[M+Na]^+$. FT-IR (KBr pellet): $\tilde{\nu}$ (CN) 2253 cm^{-1} (m).

4.12. trans-Dibromo-bis[1-mesityl-3-(3-cyanopropyl)imidazolin-2-ylidene]palladium(II) (**3c**)

Yield for both rotamers: 217 mg (0.280 mmol, 94%). *trans-anti*-3c: 1H NMR (500 MHz, CDCl3): δ 7.00 (s, 4H, Ar-H), 6.99 (d, $^3J(H,H)$ = 2.5 Hz, 2H, CH_{imid}), 6.79 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.36 (t, $^3J(H,H)$ = 7.0 Hz, 4H, NCH_2), 2.39 (s, 6H, *p*-CH_3), 2.22 (s, 12H, *o*-CH_3), 2.22 (m, 4H, $CH_2CH_2CH_2$), 2.08 (t, $^3J(H,H)$ = 7.0 Hz, 4H, CH_2CN). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 170.4 (NCN), 139.6, 137.4, 136.4, 129.5, 124.0, 122.5 (Ar-C), 119.8 (CN), 50.0 (NCH_2), 26.6 (CH_2CN), 21.9 (*p*-CH_3), 20.4 (*o*-CH_3), 15.2 ($CH_2CH_2CH_2$). *trans-syn*-**3c**: ^1H NMR (500 MHz, $CDCl_3$): 7.02 (d, $^3J(H,H)$ = 2.5 Hz, 2H, CH_{imid}), 6.83 (s, 4H, Ar-C), 6.72 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.77 (t, $^3J(H,H)$ = 7.0 Hz, 4H, NCH_2), 2.62 (m, 4H, $CH_2CH_2CH_2$), 2.50 (t, $^3J(H,H)$ = 7.0 Hz, 4H, CH_2CN), 2.47 (s, 6H, *p*-CH_3), 1.90 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 170.2 (NCN), 138.4, 137.4, 136.0, 129.8, 124.5, 121.9 (Ar-C), 119.8 (CN), 50.0 (NCH_2), 26.9 (CH_2CN), 21.8 (*p*-CH_3), 19.9 (*o*-CH_3), 15.0 ($CH_2CH_2CH_2$). Anal. Calc. for $C_{32}H_{38}Br_2N_6Pd$: C, 49.73; H, 4.96; N, 10.87. Found: C, 49.48; H, 4.97; N, 10.68%. ESI-MS: *m/z* = 693 $[M-Br]^+$, 795 $[M+Na]^+$. FT-IR (KBr pellet): $\tilde{\nu}$ (CN) 2246 cm^{-1} (m).

4.13. trans-Dibromo-bis[1-mesityl-3-(methylacetyl)imidazolin-2-ylidene]palladium(II) (**4a**)

Yield for both rotamers: 218 mg (0.278 mmol, 93%). *trans-syn*-**4a**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 6.84 (s, 4H, Ar-H), 6.74 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 5.45 (s, 4H, NCH_2), 3.84 (s, 6H, OCH_3), 2.45 (s, 6H, *p*-CH_3), 1.93 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 171.8 (C=O), 169.2 (NCN), 138.4, 136.6, 135.8, 129.6, 124.1, 122.9 (Ar-C), 53.4 (OCH_3), 53.1 (NCH_2), 21.9 (*p*-CH_3), 19.9 (*o*-CH_3). *trans-anti*-**4a**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 6.98 (s, 4H, Ar-H), 6.80 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 5.07 (s, 4H, NCH_2), 3.73 (s, 6H, OCH_3), 2.37 (s, 6H, *p*-CH_3), 2.24 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 171.9 (C=O), 169.1 (NCN), 139.2, 137.0, 136.1, 129.5, 124.1, 122.8 (Ar-C), 53.2 (OCH_3), 52.5 (NCH_2), 21.8 (*p*-CH_3), 20.4 (*o*-CH_3). Anal. Calc. for $C_{30}H_{36}Br_2N_4O_4Pd$: C, 46.03; H, 4.64; N, 7.16. Found: C, 45.75; H, 4.71; N, 6.99%. ESI-MS: *m/z* = 703 $[M-Br]^+$, 805 $[M+Na]^+$. FT-IR (KBr pellet): $\tilde{\nu}$ (C=O) 1757 cm^{-1} (s).

4.14. trans-Dibromo-bis[1-mesityl-3-(3-methylpropionate) imidazolin-2-ylidene]palladium(II) (**4b**)

Yield for both rotamers: 217 mg (0.268 mmol, 89%). *trans-syn*-**4b**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 6.82 (s, 4H, Ar-H), 6.65 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.93 (t, $^3J(H,H)$ = 7.0 Hz, 4H, NCH_2), 3.72 (s, 6H, OCH_3), 3.33 (t, $^3J(H,H)$ = 7.0 Hz, 4H, $CH_2C{=}O$), 2.45 (s, 6H, *p*-CH_3), 1.92 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.8 (C=O), 170.7 (NCN) 138.3, 136.6, 136.0, 129.6, 123.7, 122.4 (Ar-C), 52.6 (OCH_3), 47.4 (NCH_2), 36.2 ($CH_2C{=}O$), 21.9 (*p*-CH_3), 20.0 (*o*-CH_3). *trans-anti*-**4b**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 6.96 (s, 4H, Ar-H), 6.70 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.50 (t, $^3J(H,H)$ = 7.0 Hz, 4H, NCH_2), 3.69 (s, 6H, OCH_3), 2.86 (t, $^3J(H,H)$ = 7.0 Hz, 4H, $CH_2C{=}O$), 2.34 (s, 6H, *p*-CH_3), 2.22 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 173.1 (C=O), 170.7 (NCN), 139.2, 137.2, 136.4, 129.4, 123.2, 123.0 (Ar-C), 52.4 (OCH_3), 47.0 (NCH_2), 35.6 ($CH_2C{=}O$), 21.7 (*p*-CH_3), 20.4 (*o*-CH_3). Anal. Calc. for $C_{30}H_{34}Br_2N_6Pd$: C, 48.38; H, 4.60; N, 11.28. Found: C, 49.14; H, 5.31; N, 11.42% (the unsuccessful attempts to obtain better values were attributed to the general lower thermal stability of *N*-ethylene substituents.). ESI-MS: *m/z* = 731 $[M-Br]^+$, 828 $[M+NH_4]^+$. FT-IR (KBr pellet): $\tilde{\nu}$ (C=O) 1725 cm^{-1} (s).

4.15. trans-Dibromo-bis[1-mesityl-3-(4-methylbutyrate)imidazolin-2-ylidene]palladium(II) (**4c**)

Yield for both rotamers: 217 mg (0.290 mmol, 97%). *trans-anti*-**4c**: ^1H NMR (500 MHz, $CDCl_3$): δ 6.97 (s, 4H, Ar-H), 6.95 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 6.74 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.27 (t, $^3J(H,H)$ = 6.9 Hz, 4H, NCH_2), 3.71 (s, 6H, OCH_3), 2.49 (t, $^3J(H,H)$ = 6.9 Hz, 4H, CH_2CO), 2.35 (s, 6H, *p*-CH_3), 2.23 (s, 12H, *o*-CH_3), 2.15 (m, 4H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 174.2 (C=O), 170.4 (NCN), 139.2, 137.3, 136.5, 129.5, 123.7, 121.8 (Ar-C), 52.3 (OCH_3), 50.7 (NCH_2), 31.4 ($CH_2C{=}O$), 26.3 ($CH_2CH_2CH_2$), 21.9 (*p*-CH_3), 20.4 (*o*-CH_3). *trans-syn*-**4c**: ^1H NMR (500 MHz, $CDCl_3$): δ 6.98 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 6.83 (s, 4H, Ar-H), 6.68 (d, $^3J(H,H)$ = 1.9 Hz, 2H, CH_{imid}), 4.69 (t, $^3J(H,H)$ = 6.9 Hz, 4H, NCH_2), 3.71 (s, 6H, OCH_3), 2.50 (t, $^3J(H,H)$ = 6.9 Hz, 4H, CH_2CO), 2.46 (s, 6H, *p*-CH_3), 2.16 (m, 4H, $CH_2CH_2CH_2$), 1.92 (s, 12H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 174.1 (C=O), 170.3 (NCN), 138.2, 136.6, 136.1, 129.6, 123.9, 121.6 (Ar-C), 52.4 (OCH_3), 50.9 (NCH_2), 31.3 ($CH_2C{=}O$), 26.5 ($CH_2CH_2CH_2$), 21.7 (*p*-CH_3), 20.0 (*o*-CH_3). Anal. Calc. for $C_{34}H_{44}Br_2N_4O_4Pd$: C, 48.68; H, 5.29; N, 6.68. Found: C, 48.80; H, 5.07; N, 6.85%. ESI-MS: *m/z* = 759 $[M-Br]^+$, 862 $[M+Na]^+$. FT-IR (KBr pellet): $\tilde{\nu}$ (C=O) 1734 cm^{-1} (s).

4.16. trans-Dibromo-(mesitylimidazole)(1-mesityl-3-cyanoethylimidazolin-2-ylidene)palladium(II) (**5**)

Yield: 0.162 mg (0.234 mmol, 78%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.02 (s, 1H, CH_{imid}), 7.66 (s, 1H, CH_{imid}), 7.33 (s, 1H, CH_{imid}), 6.99 (s, 2H, Ar-H), 6.92 (s, 2H, Ar-H), 6.90 (s, 1H, CH_{imid}), 6.70 (s, 1H,

CH_{imid}), 5.06 (t, ^3J(H,H) = 7.0 Hz, 2H, NCH_2), 3.46 (t, ^3J(H,H) = 7.0 Hz, 2H, CH_2CN), 2.34 (s, 3H, *p*-CH_3), 2.30 (s, 3H, *p*-CH_3), 2.28 (s, 6H, *o*-CH_3), 1.94 (s, 6H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 153.1 (NCN), 141.2, 140.0, 139.9, 136.9, 135.6, 135.2, 133.2, 130.7, 130.0, 129.8, 125.8, 123.0, 120.2 (Ar-C) 118.4 (CN), 47.9 (NCH_2), 21.8 (*p*-CH_3), 21.6 (*p*-CH_3), 20.5 (*o*-CH_3), 20.3 (CH_2CN), 18.2 (*o*-CH_3). Anal. Calc. for $C_{27}H_{31}Br_2N_5Pd$: C, 46.88; H, 4.52; N, 10.12. Found: C, 46.93; H, 4.62; N, 10.34%. ESI-MS: *m/z* = 612 $[M-Br]^+$. FT-IR (KBr pellet): $\tilde{\nu}$ (CN) 2252 cm^{-1} (m).

4.17. trans-Dibromo-(mesitylimidazole)[1-mesityl-3-(3-methylpropionate)imidazolin-2-ylidene]palladium(II) (**6**)

Yield: 0.162 mg (0.234 mmol, 78%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.04 (s, 1H, CH_{imid}), 7.68 (s, 1H, CH_{imid}), 7.29 (s, 1H, CH_{imid}), 6.98 (s, 2H, Ar-H), 6.91 (s, 2H, Ar-H), 6.81 (s, 1H, CH_{imid}), 6.68 (s, 1H, CH_{imid}), 5.06 (t, ^3J(H,H) = 7.0 Hz, 2H, NCH_2), 3.73 (s, 3H, OCH_3), 3.37 (t, ^3J(H,H) = 7.0 Hz, 2H, $CH_2C{=}O$), 2.33 (s, 3H, *p*-CH_3), 2.30 (s, 3H, *p*-CH_{3a}), 2.27 (s, 6H, *o*-CH_3), 1.95 (s, 6H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 173.0 (C=O), 151.7 (NCN), 141.3, 140.0, 139.6, 137.1, 135.7, 133.4, 130.8, 130.6, 130.0, 129.8, 125.1, 123.5, 120.1 (Ar-C), 52.6 (OCH_3), 47.7 (NCH_2), 35.7 ($CH_2C{=}O$), 21.8 (*p*-CH_3), 21.7 (*p*-CH_3), 20.6 (*o*-CH_3), 18.3 (*o*-CH_3). Anal. Calc. for $C_{28}H_{34}Br_2N_4O_2Pd$: C, 46.40; H, 4.73; N, 7.73. Found: C, 45.98; H, 4.69; N, 7.54%. ESI-MS: *m/z* = 645 $[M-Br]^+$. FT-IR (KBr pellet): $\tilde{\nu}$ (C=O) 1733 cm^{-1} (s).

4.18. General procedure for the Mizoroki–Heck coupling

In a typical run, a reaction tube was charged with a mixture of aryl halide (1.0 mmol for monohalides, 0.5 mmol for dihalides), anhydrous sodium acetate (1.5 mmol), *tert*-butyl acrylate (1.4 mmol), catalyst (0.01 mmol) and DMF (3 mL). The reaction was stirred and heated at 120 °C for 18 h. After the mixture was cooled to the ambient temperature, dichloromethane (10 mL) was added. The organic layer was then extracted with water (6 × 8 mL) and dried over $NaSO_4$. The solvent was allowed to evaporate and the residue was analyzed by ^1H NMR spectroscopy.

4.19. X-ray diffraction studies

Diffraction data for complexes **3**–**6** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using SHELXL-97 [20] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in the Supplementary material.

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Appendix A. Supplementary material

CCDC 699197, 699198, 699199, 699200, 699201, 699202, 699203 and 699204 contain the supplementary crystallographic data for **5**, **6** · 0.25$(CH_3)_2CO$, **3b**, **3c**, **4c**, **3a** · 0.5$(C_6H_5CH_3)$, **4a** · $(CH_3)_2CO$, and **4b** · CH_3OH. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data (Synthesis and analytical data of bromo-esters; analytical data for double Mizoroki-Heck coupling products; ORTEP plots with selected bond lengths and angles of complexes *trans-syn*-**3a**, *trans-anti*-**3b**, *trans-syn*-**4b**, *trans-anti*-**4c** and **6**; selected crystallographic data for all complexes) associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.044.

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