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FULL PAPER

Bis-carbene complexes from oxidative addition of imidazolium C–H bonds to palladium(0)

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Oxidative addition of the C–H bond at the 2-position of *N*-(2-pyridyl)imidazolium salts takes place to palladium(0) to lead to unexpected final products containing two carbenes. The formation of either *cis* or *trans* bis-carbene complexes, both identified by X-ray crystallography and spectroscopy, apparently is a consequence of the substitution pattern of the imidazolium moiety. A mechanism is suggested based on recent theoretical studies.

Introduction

The success of every organometallic catalyst system strongly depends on its availability and hence on convenient methods for its preparation. Recently, several efficient transition metal catalysts have been developed that were derived from heterocyclic carbenes.[1] These new ligands proved to be competitive with classical phosphines in many respects.[2] For example, the synthesis of the carbene precursors usually involves straightforward nitrogen quaternization to form N,N′-disubstituted imidazolium salts. Methodologies for the metallation of such imidazolium salt precursors is therefore of substantial current interest and a number of methods have been established. In their pioneering work, Lappert and coworkers used electron-rich alkenes (enetetramines) as ligand precursors.[3] The C=C double bond in these alkenes could be activated by various metal salts to give the corresponding metallated carbenes.

By far the most common route to prepare a metal–carbene bond, however, is the 'free carbene route', involving the abstraction of the acidic imidazolium proton with BuLi and trapping of the free carbene, after isolation or *in situ*,[4] with a metal precursor.[5] This method requires the carbene to be at least transiently stable and has tended to limit the method to salts with bulky N-substituents that stabilize the free carbene. More problematic, the precursor must not contain functionality that would react with BuLi or provide a more acidic proton than the intended one. This has prevented use of more elaborate chelating carbene ligands that could significantly expand the utility of carbene ligands in catalysis.

Transmetallation from a suitable precursor, typically *via* a silver carbene is an alternative procedure to form new metal-carbenes. The free carbene is probably never involved, since silver insertion is thought to occur in a base-mediated proton abstraction and the silver-complex may be considered as a heavily protected carbene; transmetallation can occur with a variety of different transition metals.[6] Finally, it has been shown that oxidative addition of a low-valent metal precursor to a carbon–halogen bond is possible.[7] All of these methods either require the extra step of pre-functionalization of the ligand precursor or afford undesired side-products, which have to be removed in separate purification procedures. Oxidative addition to a C–H bond would clearly be the most desired method for the formation of the $M–C_{carbene}$ bond, since no base is used and atom economy is maintained.[8] Recent experimental studies have shown that both oxidative addition and reductive elimination of an imidazolium C–H may occur and that these two reactions are, in principle, in equilibrium.[7b,9] Useful theoretical investigations established the factors that should favor one or the other direction of this reaction. One conclusion was that oxidative addition of 2-H imidazolium salts should favor formation of $M–C_{carbene}$ hydride species. This has been demonstrated for Pt salts.[7b] For Pd, only weak indications are available, however.[10]

Here, we report the oxidative addition of some imidazolium salts to Pd(0) precursors. Unexpectedly, the isolated products were bis-carbene species resulting from apparent double oxidative addition, and not palladium-hydride species. Indeed, the reaction could not be stopped at the mono-carbene stage. A mechanism that may explain the formation of the observed products is proposed.

Results

Reaction of the pyridine-substituted imidazolium salts **1**–**3** with $Pd_2(dba)_3$ in refluxing thf gave, after workup, the Pd bis-carbene complexes **4**–**6** as off-white solids. Remarkably, formation of these products is independent of the stoichiometry of the starting reagents. **4** is obtained as the exclusive organometallic compound from the reaction of 4 : 1 mixtures of imidazolium/$Pd_2(dba)_3$ and also from a 1 : 1 mixture. We were not able to see mono-carbene formation even at lower temperatures. This demonstrates a strong preference for the formation of Pd-bis-carbenes. The second likely product of the reaction, H_2, would be difficult to detect since the reaction is carried out at reflux temperature. At present, we cannot exclude hydrogen transfer to the solvent, or to C=C or C=O of dba.

The solids are stable towards air and moisture and thermally decompose only at temperatures above 200 °C. In view of the doubts sometimes expressed about the stability of carbenes, we looked at their stability to H_2 and protons. The palladium complexes are stable when kept under ambient H_2 atmosphere for 30 minutes. Remarkably, formation of neither the metal-free imidazolium salts nor of any palladium-hydride species has been observed, indicating that reductive elimination does not take place. Also, addition of HOAc (10 eq.) did not induce any Pd–C bond cleavage and even after heating of a $CHCl_3$ solution at 55 °C for 16 h, the corresponding palladium bis-carbene complex was recovered unchanged.

The ^1H NMR spectrum ($CDCl_3$ solution) of **4** is characteristic and displays four different imidazole protons, as expected for two differently bound carbenes. The absence of any acidic

imidazolium proton, normally seen near δ 10.5 in the NMR spectrum, suggests that both ligand sets are bound *via* C-2 (δ_C 158.50, 154.36). Two-dimensional NMR spectroscopy (homo- and hetero-nuclear correlation) revealed two independent ligands were present. For example in **4**, two *ortho*-pyridine protons are observed in 1 : 1 ratio at δ 9.39 and 9.07, suggesting that the bonding mode of the two ligands is different. Furthermore, the two methyl groups of the isopropyl substituents in both ligands are diastereotopic and hence appear as four well-resolved doublets at δ 1.67, 1.53, 1.26, 0.91 ($^3J_{HH}$ = 6.4–6.7 Hz). These data are fully consistent with the proposed structure of **4**. Obviously, nitrogen coordination is rigid at 25 °C on the NMR time scale. In addition, rotation about the Pd–C bond is restricted in both ligand moieties no doubt due to the large alkyl substituents on the two imidazole rings. Orbital and steric considerations suggest that the monodentate carbene should be oriented perpendicular to the palladium square plane, in contrast to the necessarily in-plane carbene of the *C*,*N*-bidentate bound ligand.

Variable temperature ^{1}H NMR measurements in dmso-d_6 show that **4** is fluxional above room temperature. At 135 °C only one set of broad signals is observed for the ligand, which is consistent with a higher molecular symmetry of the compound at this temperature. Such a dynamic process could occur by pyridine exchange at the metal, *i.e.*, coordination of the free pyridine and decoordination of the metal-bound pyridine.

Unequivocal evidence for the structure comes from a single crystal structure determination of **4**. The molecular structure of Fig. 1a shows a palladium(II) center in slightly distorted square-planar geometry, defined by a bromide ligand, pyridine and two mutually *cis* carbenes. The *C*,*N*-bidentate carbene ligand is coplanar with the metal coordination plane (N2–C11–Pd1–C31 2.6(7)°, N3–Pd1–C11–N1 5.1(3)°). As expected, the monodentate carbene is twisted by nearly 90° out of the metal square plane (Br1–Pd1–C31–N4 92.7(4)°). The two Pd–C bond lengths are identical within the errors (Pd1–C11 1.974(5) Å, Pd1–C31 1.970(5) Å, see Table 1). This is unexpected, since the Pd–C11 bond in the chelate ring might be expected to be shorter than the unsupported Pd–C31 bond. Probably, the different *trans* influences of bromide *vs*. pyridine exerts a compensating effect.

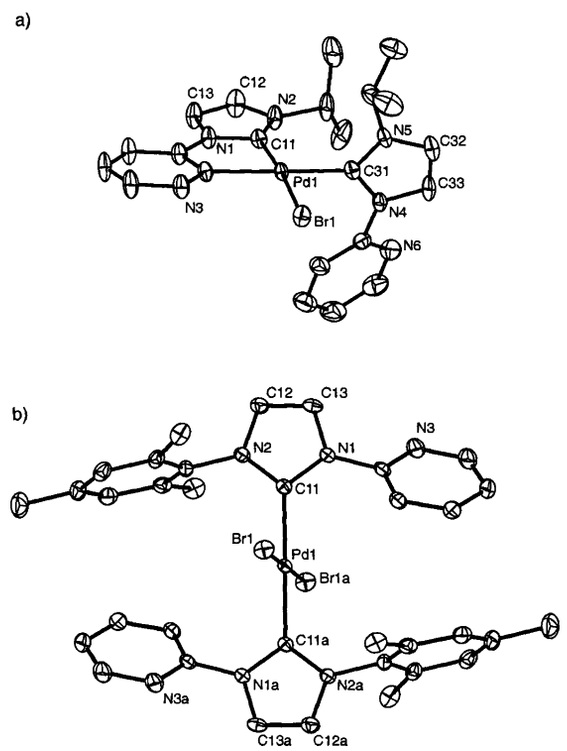


Fig. 1 Thermal ellipsoid plot of the crystal structures of **4** (a) and **6** (b). Hydrogen atoms have been omitted and for **4**, only the cation is shown. The suffix a in **6** denotes symmetry operation $-x$, $-y$, $-z$.

Table 1 Selected bond lengths (Å) and angles (°) for **4** and **6**

	4 (L = C31)	**6** (L = C11a)
Pd1–N3	2.094(4)	
Pd1–Br1	2.4633(6)	2.4338(4)
Pd1–C11	1.974(5)	2.041(4)
Pd1–L	1.970(5)	2.041(4)
N3–Pd1–Br1	95.25(11)	
N3–Pd1–C11	80.1(2)	
N3–Pd1–C21	177.0(2)	
C11–Pd1–L	96.9(2)	180.0
C11–Pd1–Br1	174.76(13)	86.85(11)
Br1–Pd1–L	87.76(13)	93.15(11)

[a] Suffix a denotes symmetry operation $-x$, $-y$, $-z$.

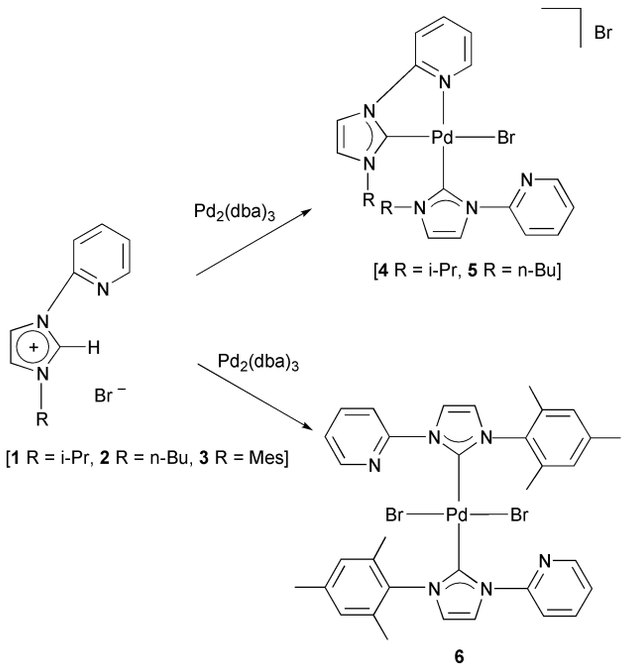
The spectroscopic data for **6** significantly differ from those for **4**. The proton NMR spectrum is relatively simple since it consists of only one set of signals. For example, only one set of pyridine protons and one set of mesitylene protons are observed, which indicates a structure with higher symmetry than **4**. Coordination of the carbene carbons only was suggested from the fact that **6** can be purified by column chromatography on SiO_2, which suggests a neutral rather than a mono- or dicationic palladium complex with one or two *C*,*N*-bidentate carbene ligands.

An X-ray analysis showed (Fig. 1b) a C_2-centrosymmetric palladium complex, comprising two monodentate carbene ligands in mutually *trans* positions. The palladium atom is located on a crystallographic center of symmetry and therefore, the *trans*-orientation of the two carbons is perfect (C11–Pd1–C11a 180.0°, Pd–C11 2.041(4) Å). The Pd–Br bond in **6** (2.4338(4) Å) is slightly shorter than that in **4** (2.4633(6) Å). Consequently, the *trans* influence of the carbene is larger than that of bromide, but smaller than that of hydride or methyl groups.[7b] Obviously, the large steric demand of the mesityl groups prevents the formation of stable *cis* carbene complexes as well as *C*,*N*-bidentate chelation *via* the pyridine nitrogen.

Discussion

Oxidative addition of imidazolium salts to zerovalent platinum group metal precursors has thus far only been reported for Pt(0).[7b] For Pd(0) precursors, *in situ* oxidative addition has been reported,[10] but neither characterization nor isolation of the corresponding Pd(II) carbene products has been possible. Extensive theoretical studies have predicted, however, that thermodynamic and kinetic factors prefer oxidative addition rather than the reverse, reductive elimination, provided that the imidazolium precursor is not alkyl-substituted in the 2-position.[7b] The successful preparation of complexes **4**–**6** confirms these ideas qualitatively (Scheme 1). We therefore propose a mechanism (Scheme 2) for the formation of these complexes that is based on the general conclusions of the theoretical study.

Because reaction mixtures containing substoichiometric amounts of ligand still prefer formation of the bis-carbene products, the second carbene bond formation must be relatively fast and the first oxidative addition is likely to be rate-limiting. Intramolecular nitrogen coordination to the metal center seems to be essential, since no carbene products were detected when the reaction was carried out with imidazolium salts that do not contain chelating donor substituents. This would also explain our observation that carbene formation occurs with *C*,*N*-chelating ligands such as **1**, but not with mixtures of pyridine and a dialkylated imidazolium salt (*N*-butyl-*N*′-methylimidazolium iodide). Apparently, nitrogen coordination directs and keeps the imidazolium C–H bond in close proximity to the palladium center.



Scheme 1 Synthesis of the bis-carbene palladium complexes **4**–**6**.

Our preferred mechanism (Scheme 2) involves binding of the pyridyl group followed by the oxidative addition of the imidazolium C–H bond to the Pd(0) center. Presumably, this leads to a highly reactive Pd(II) hydride species with or without a coordinated bromide ion. The exact nature of such a complex is elusive thus far, since we were not able to detect any hydride signal of an intermediate while monitoring the reaction by *in situ* NMR spectroscopy. Probably, the high reactivity of the hydride prevents the accumulation of such species in detectable concentrations. However, formation of $M–C_{carbene}$ bonds from a metal hydride and imidazolium salts has recently been demonstrated in related iridium chemistry.[11]

Several routes could lead to the final product. For example, a subsequent oxidative addition of a second imidazolium ligand could generate a palladium(IV) dihydride. Elimination of H_2, not yet detected, is assumed to give the final products. The second imidazolium addition might possibly take place after reductive elimination again on a Pd(0) species, in which a pyridine-bound proton may or may not be stabilized by the metal center *via* bidentate *Pd*,*N* bonding.[12] Theoretical considerations may help to distinguish between these and other pathways and such studies are planned. In any case, a perpendicular orientation of the carbenes with respect to the metal coordination plane is probably required. Reorientation into the metal square-plane and chelation *via* pyridine recoordination is likely to be dependent on the steric size of the imidazolium substituents; it seems to be possible for alkyls as in **4** and **5**, but not for aryls (*e.g.* **6**). The presence of very bulky aryls such as in bis-mesitylated imidazoles (IMes) may prevent the second oxidative addition,[10] since in these cases, unstable palladium-hydride species have been observed in solution.

Conclusions

Oxidative addition of an imidazolium C–H bond to Pd(0) is shown to be a viable method of synthesis of Pd(II) carbene complexes, but the rapid trapping of the presumed intermediate hydride leads to final products that contain two bound carbenes. If the bis-carbene is desired, the method is very useful, but further work will be needed to modify the method for the synthesis of mono-carbenes. A mechanism is suggested based on recent theoretical studies.

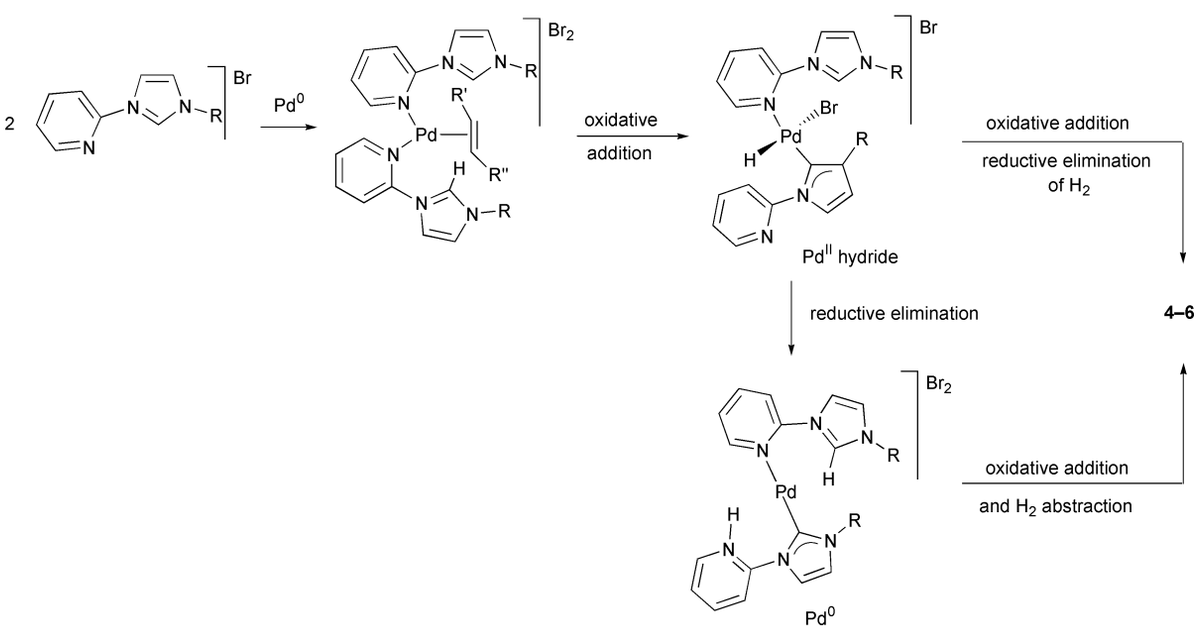
Experimental

General

Isopropylimidazole,[13] mesitylimidazole,[14] and **2** [1j] were prepared according to literature methods, all other reagents are commercially available and were used as received. All NMR spectra were recorded at room temperature on Bruker spectrometers operating at 400 or 500 MHz (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in ppm, J in Hz). Assignments are based on COSY, HMQC and HMBC spectroscopy. Melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc.; residual solvent molecules have been identified by ^{1}H NMR.

Syntheses

***N*-Isopropyl-*N*′-2-pyridylimidazolium bromide (1).** A mixture of 2-bromopyridine (1.58 g, 10.0 mmol) and 1-isopropylimidazole (1.10 g, 10.0 mmol) was kept neat at 170 °C for 22 h. After cooling, the formed solid was purified by repetitive precipitation from CH_2Cl_2–Et_2O mixtures (1 : 10 v/v) and the



Scheme 2 Possible pathways for the formation of the bis-carbene palladium complexes *via* consecutive oxidative addition of two C–H bonds.

off-white solid dried *in vacuo*. An analytically pure sample was obtained from $CHCl_3$–Et_2O. Yield: 2.14 g (80%). ^{1}H NMR ($CHCl_3$, 298 K): δ 11.72 (s, 1H, NC*H*N), 8.73 (d, 1H, $^3J_{HH}$ = 8.1 Hz, py-*H*), 8.51–8.46 (m, 1H, py-H), 8.34 (s, 1H, im-*H*), 8.04 (dt, 1H, $^4J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 7.6 Hz, py-H), 7.58 (s, 1H, im-H), 7.47–7.41 (m, 1H, py-H), 5.21 (septet, 1H, $^3J_{HH}$ = 6.8 Hz, CH), 1.72 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 148.78 (C_{py}), 145.94 (C_{py}), 140.64 (C_{py}), 134.87 (NCN), 125.08 (C_{py}), 119.61 (C_{im}), 118.98 (C_{im}), 115.32 (C_{py}), 54.16 (CH), 23.19 (CH_3); mp = 157–159 °C; Anal. calc. for $C_{11}H_{14}BrN_3$ (268.15)·H_2O: C, 46.17; H, 5.64; N, 14.68. Found: C, 46.56; H, 5.29; N, 14.76%.

***N*-Mesityl-*N*′-2-pyridylimidazolium bromide (3).** A mixture of 2-bromopyridine (1.1 g, 6.9 mmol) and 1-mesitylimidazole (1.3 g, 6.9 mmol) was kept neat at 160 °C for 12 h. After cooling, the formed solid was purified by repetitive precipitation from CH_2Cl_2–Et_2O mixtures and the resulting product dried *in vacuo*. Yield: 2.03 g (85%). ^{1}H NMR ($CHCl_3$, 298 K): δ 11.45 (t, 1H, $^4J_{HH}$ = 1.5 Hz, NCHN), 9.25 (d, 1H, $^3J_{HH}$ = 8.4 Hz, py-H), 8.91 (t, 1H, $^3J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 1.5 Hz, im-H), 8.54–8.51 (m, 1H, py-H), 8.11 (dt, 1H, $^4J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 8.1 Hz, py-H), 7.51–7.47 (m, 1H, py-H), 7.33 (t, 1H, $^3J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 1.5 Hz, im-H), 7.05 (s, 2H, arom-H), 2.35 (s, 3H, CH_3), 2.19 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 148.63 (C_{py}), 145.90 (C_{py}), 141.65 (C_{ar}), 140.98 (C_{py}), 136.29 (2C, C_{ar}), 133.99 (NCN), 130.53 (C_{ar}), 130.07 (2C, C_{ar}), 125.50 (C_{py}), 123.74 (C_{im}), 120.08 (C_{im}), 116.58 (C_{py}), 21.13 (3C, CH_3), 17.85 (6C, CH_3); mp = 280–282 °C (dec.); Anal. calc. for $C_{17}H_{18}BrN_5$ (344.25): C, 59.31; H, 5.27; N, 12.21. Found: C, 58.80; H, 5.21; N, 11.75%.

[Bis(η^1-*C*)(η^2-*C*,*N*)(*N*-isopropyl-*N*′-2-pyridylimidazol-2-ylidene)bromopalladium(II)]bromide (4). A mixture of **1** (150 mg, 0.56 mmol) and $Pd_2(dba)_3$ (151 mg, 0.17 mmol) was refluxed under Ar in 15 mL thf for 3 hours. The thf was evaporated and the remaining solid dissolved in CH_2Cl_2 (10 mL). Residual black Pd was removed *via* filtration through Celite and the clear solution was treated with Et_2O (50 mL). The formed precipitate was collected by filtration and dried in vacuum to give **4** as a white powder. Yield: 100.0 mg (62%). The complex can be recrystallized from $CHCl_3$–pentane. ^{1}H NMR ($CDCl_3$, 298 K): δ 9.47 (s, 1H, im-H), 9.39 (d, 1H, $^3J_{HH}$ = 5.0 Hz, py-H), 9.07 (d, 2H, $^3J_{HH}$ = 8.2 Hz, py-H), 8.49 (s, 1H, py-H), 8.27 (t, 1H, $^3J_{HH}$ = 7.7 Hz, py-H), 8.08 (s, 1H, im-H), 7.90 (t, 1H, $^3J_{HH}$ = 7.7 Hz, py-H), 7.46 (t, 1H, $^3J_{HH}$ = 6.0 Hz, py-H), 7.41 (s, 1H, im-H), 7.38 (t, 1H, $^3J_{HH}$ = 6.0 Hz, py-H), 7.18 (s, 1H, im-H), 5.59–5.47 (m, 1H, CH), 3.02–2.90 (m, 1H, CH), 1.67 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.53 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3), 1.26 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3), 0.91 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 158.50 ($C_{carbene}$), 154.36 ($C_{carbene}$), 151.53 (C_{py}), 149.97 (C_{py}), 149.84 (C_{py}), 148.90 (C_{py}), 143.67 (C_{py}), 139.33 (C_{py}), 124.35 (C_{py}), 123.37 (C_{py}), 123.31 (C_{im}), 121.72 (C_{im}), 118.92 (2C, C_{im}), 117.37 (C_{py}), 114.75 (C_{py}), 54.98 (CH), 52.41 (CH), 23.74 (CH_3), 23.09 (2C, CH_3), 22.86 (CH_3); mp = 208–210 °C (dec.); Anal. calc. for $C_{22}H_{26}Br_2N_6Pd$ (637.96)·0.5 H_2O: C, 40.67; H, 4.19; N, 12.93. Found: C, 40.78; H, 3.93; N, 12.47%.

[Bis(η^1-*C*)(η^2-*C*,*N*)(*N*-butyl-*N*′-2-pyridylimidazol-2-ylidene)-bromopalladium(II)]bromide (5). A mixture of **2** (130 mg, 0.46 mmol) and $Pd_2(dba)_3$ (110 mg, 0.12 mmol) was refluxed under Ar in 5 mL thf for 3 hours. The thf was evaporated and the remaining solid dissolved in CH_2Cl_2 (10 mL). After removal of black Pd by filtration through Celite a solid was precitated by addition of Et_2O (100 mL). After filtration and drying *in vacuo* a white powder was obtained. Yield: 80.5 mg (52%). The complex can be recrystallized from CH_2Cl_2–Et_2O. ^{1}H NMR ($CDCl_3$, 298 K): δ 9.40–9.30 (m, 2H, py-H, im-H), 9.07–8.95 (m, 2H, py-H), 8.50 (d, 1H, py-H), 8.27 (t, 1H, $^3J_{HH}$ = 7.7 Hz, py-H), 8.03 (s, 1H, im-H), 7.53 (t, $^3J_{HH}$ = 7.5 Hz, py-H), 7.46 (t, 1H, $^3J_{HH}$ = 6.5 Hz, py-H), 7.72–7.34 (m, 2H, py-*H*, im-H), 7.25 (s, 1H, im-H), 4.59–4.38 (br m, 2H, CH_2), 4.59–4.38 (br m, 2H, CH_2), 3.25–2.88 (br m, 2H, CH_2), 2.10–1.86 (br m, 2H, CH_2), 1.54–1.42 (br m, 2H, CH_2), 1.41–1.23 (br m, 2H, CH_2), 1.15–1.02 (br m, 2H, CH_2), 0.98 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH_3), 0.80 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 159.25 ($C_{carbene}$), 155.87 ($C_{carbene}$), 151.54 (C_{py}), 149.97 (C_{py}), 149.94 (C_{py}), 149.03 (C_{py}), 143.63 (C_{py}), 139.24 (C_{py}), 124.39 (C_{py}), 123.42 (C_{py}), 122.93 (C_{im}), 122.79 (C_{im}), 122.51 (C_{im}), 120.62 (C_{im}), 117.64 (C_{py}), 114.59 (C_{py}), 52.61 (CH_2), 50.22 (CH_2), 32.65 (CH_2), 31.72 (CH_2), 19.93 (CH_2), 19.90 (CH_2), 13.65 (CH_3), 13.52 (CH_3); mp = 234–236 °C (dec.); Anal. calc. for $C_{24}H_{30}Br_2N_6Pd$ (668.76)·0.5 CH_2Cl_2: C, 41.37; H, 4.39; N, 11.82. Found: C, 41.37; H, 4.32; N, 11.49%.

[Bis-η^1-*C*-(*N*-mesityl-*N*′-2-pyridylimidazol-2-ylidene)dibromopalladium(II)] (6). A mixture of **3** (100 mg, 0.29 mmol) and $Pd_2(dba)_3$ (160 mg, 0.17 mmol) was refluxed under Ar in 10 mL thf for 3 hours. The thf was evaporated and the remaining solid dissolved in CH_2Cl_2 (10 mL) and filtered. The filtrate was purified by column chromatography (SiO_2; eluent first CH_2Cl_2, then CH_2Cl_2–acetone 1 : 1) yielding **6** as an off-white solid (60 mg, 52%). Analytically pure **6** suitable for a single crystal structure determination was obtained by slow diffusion of Et_2O into a solution of **6** in CH_2Cl_2. ^{1}H NMR (acetone-d_6, 298 K): δ 9.69 (d, 1H, $^3J_{HH}$ = 6.0 Hz, py), 8.05 (d, 1H, $^3J_{HH}$ = 2.0 Hz, im-H), 8.42 (dt, 1H, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 7.9 Hz, py-H), 8.20 (d, 1H, $^3J_{HH}$ = 7.9 Hz, py-H), 7.69–7.64 (m, 1H, py-H), 7.42 (d, 1H, $^3J_{HH}$ = 2.0 Hz, im-H), 6.94 (s, 2H, arom-H), 2.32 (s, 3H, CH_3), 2.09 (s, 6H, CH_3); ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ 160.11 ($C_{carbene}$), 152.91 (C_{py}), 152.25 (C_{py}), 143.23 (C_{py}), 139.87 (C_{ar}), 136.89 (C_{ar}), 135.49 (2C, C_{ar}), 129.49 (2C, C_{ar}), 126.24 (C_{im}), 124.16 (C_{py}), 117.91 (C_{im}), 112.94 (C_{py}), 21.18 (CH_3), 18.25 (2C, CH_3); mp (dec.) > 280 °C; Anal. calc. for $C_{34}H_{34}Br_2N_6Pd$ (792.90): C, 51.50; H, 4.32; N, 10.60. Found: C, 51.50; H, 4.39; N, 10.40%.

Crystallography

Structure determination and refinement of 4. Crystals were obtained upon crystallization from $CHCl_3$ and diethyl ether. The crystals rapidly lost pentane of crystallization at room temperature. After removal of solvent the crystal was mounted quickly and cooled to −90 °C. Data for **4** were collected on a Nonius KappaCCD diffractometer (Mo-Kα radiation) and corrected for absorption (SORTAV).[15] The structure was solved by direct methods (SIR92)[16] and refined on *F* for all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, except for the pentane. Hydrogen atoms were included at calculated positions. Two independent molecules of $CHCl_3$ were located in the asymmetric unit and both were disordered. Each was modeled as having chlorine atoms at half occupancy. Pentane was located in the asymmetric unit, but not at full occupancy; it was modeled with isotropic atoms at half-occupancy and hydrogen atoms were not included for it. There also appears to be a disorder in this solvent, but the disorder was accommodated by large thermal parameters rather than attempting to model the disorder. Relevant crystal and data parameters are presented in Table 2.

CCDC reference number 175638.

Structure determination and refinement of 6. Crystals were obtained upon crystallization from CH_2Cl_2 and pentane. Data for **6** were collected on a Nonius KappaCCD diffractometer (Mo-Kα radiation) and corrected for absorption (SORTAV).[15] The structure was solved by direct methods (SIR92)[16] and refined on *F* for all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 2. The

Table 2 Crystallographic data for **4** and **6**

	4	**6**
Color, shape	Colorless, prism	Pale yellow, needles
Empirical formula	$C_{22}H_{26}Br_2N_6Pd\cdot0.5C_5H_{12}\cdot2CHCl_3$	$C_{34}H_{34}Br_2N_6Pd$
Formula weight	914.52	792.89
Radiation/Å	Mo-Kα (monochromatic) 0.71073	Mo-Kα (monochromatic) 0.71073
T/K	183	183
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/n$ (no. 14)	$I4_1/a$ (no. 88)
a/Å	19.4495(5)	26.1740(9)
b/Å	9.6816(3)	26.1740(9)
c/Å	20.3347(5)	9.5139(5)
β/°	104.809(2)	90
V/Å^3	3701.9(2)	6517.8(4)
Z	4	8
μ/mm^{-1} (Mo-Kα)	3.126	3.063
Total, unique reflections	29122, 8927	10939, 3939
R_{int}	0.048	0.051
Parameters, restraints	426, 0	196, 0
R^a, $R_w{}^b$, GOF	0.031, 0.041, 1.15	0.030, 0.033, 0.78

[a] For **4** $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for all $I > 5\sigma(I)$; for **6** for all $I > 3\sigma(I)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

molecule is on a special position in the tetragonal centrosymmetric space group $I4_1/a$ which produces a rigorously centrosymmetric structure.

CCDC reference number 175637.

See http://www.rsc.org/suppdata/dt/b1/b110964b/ for crystallographic data in CIF or other electronic format.

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