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# Chelating C4-Bound Imidazolylidene Complexes through Oxidative Addition of Imidazolium Salts to Palladium(0)

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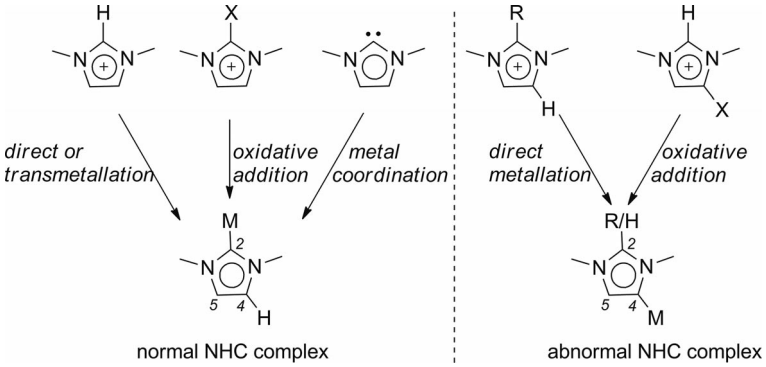
**Keywords:** N-Heterocyclic carbenes / Palladium / N ligands / Abnormal bonding / Oxidative addition / Chelates

Oxidative addition of donor-functionalised 4-iodoimidazolium salts to palladium(0) provides a selective route for the preparation of abnormal chelating N-heterocyclic carbene complexes and enables the introduction of a variety of donor groups. The activation of the C4 position does not necessitate protection of the imidazolium C2 position, thereby leaving this site available for further modification. While metallation of the unsubstituted C2 position of the N-heterocyclic carbene ligand was unsuccessful when palladium was bound to the C4 carbon atom, sequential metallation of first the C2 position, by means of transmetallation, followed by C4–I oxidative addition, afforded a dimetallic complex comprised of two palladium centres bridged by a single NHC ligand.

## Introduction

Abnormal N-heterocyclic carbenes (NHCs) have remarkably different electronic properties from their normal NHC analogues,[1] which has led to distinct reactivity patterns and in some cases enhanced catalytic activity.[2] The features responsible for the special properties of abnormal NHCs, i.e. the enhanced donor capacity due to decreased heteroatom stabilisation, also implies that the free abnormal carbene is far less stable than its normal counterpart.[3] Abnormal imidazolylidene complexes are therefore mostly synthesised through direct or base-assisted C–H activation.[1,4] Formation of a silver carbene complex for transmetallation has proven problematic.[5] In order to ensure the exclusive formation of C4-bound carbenes, the C2 position generally needs to be substituted by an alkyl or aryl group.[6] An alternative to the protection of the C2 position is the activation of the C4 position by a halide substituent, which enables metallation by C–X oxidative addition to a low-valent metal centre (Scheme 1). Oxidative addition of imidazolium salts to transition metal centres is a well-established route for the synthesis of normal NHC complexes.[7]




Scheme 1. Typical synthetic pathways to normal and abnormal imidazolylidene complexes.

Apart from rendering metallation chemoselective, this protocol principally also allows the C2 position to be kept unprotected and available for further functionalisation. For example, dimetallic systems may become accessible by metallation through C2–H activation. While dimetallic triazoldiylidene complexes have been explored in depth,[8] related

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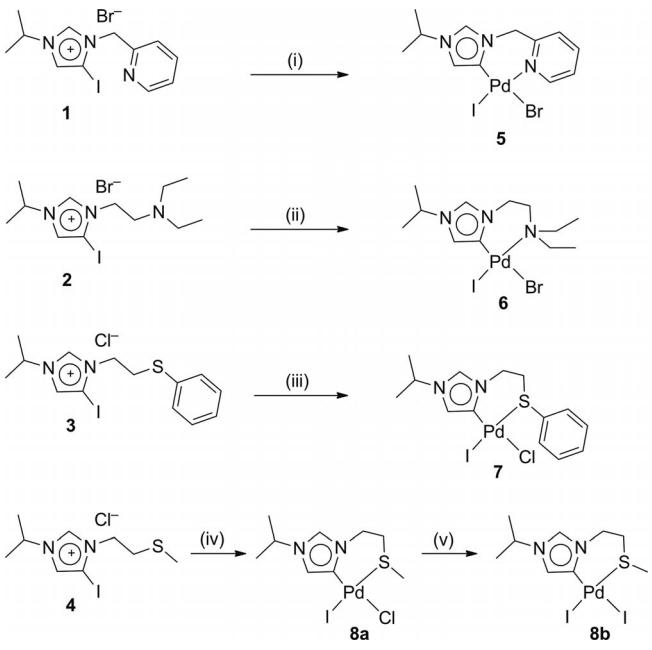
dimetallic carbene/alkenyl complexes derived from imidazolium salts are far less known, though they have received increasing attention recently.[9] Dimetallic complexes, especially when they are comprised of two different metals, provide interesting opportunities for catalysing tandem processes.[10]

Expanding on our initial work,[11] we have used C4-iodinated imidazolium salts as NHC precursors for oxidative addition to palladium(0) and explored the potential of incorporating different chelating donor groups (denoted as "E") as wingtip substituents, ranging from the relatively hard $–NEt_2$ to a comparably soft –SPh group. Preliminary results also indicate that this approach may be useful for the synthesis of a variety of homo- and heterodimetallic systems.

## Results and Discussion

### Synthesis

4/5-Iodoimidazole, which is readily accessible through iodination of imidazole,[12] was used as precursor to the abnormal NHC ligands. Selective alkylation of the remote nitrogen atom was achieved by using 2-iodopropane,[13] thus yielding 4-iodo-*N*-isopropylimidazole. Exclusive alkylation at N1 was demonstrated by NOESY experiments, which unambiguously confirmed the proximity of the *i*Pr group to both residual imidazole protons. In contrast, alkylation with EtI gave an approximate 3:1 mixture of the two possible isomers, i.e. *N*-ethyl-4- and -5-iodoimidazole. The minor isomer exhibited nuclear Overhauser effects with a single imidazole proton only. Apparently, the size of the iodide nucleus in combination with the bulk of the *i*Pr group provides sufficient steric congestion to induce regioselective alkylation. Potentially chelating, functionalised wingtip groups were introduced by N2-quaternisation of the N1-substituted 4-iodoimidazole derivative with appropriately functionalised alkyl halides, thus yielding the ligand precursors **1**–**4** (Scheme 2).[14]




Scheme 2. Synthesis of abnormal carbene complexes by oxidative addition of imidazolium salts. Reagents and conditions: (i) $Pd(dba)_2$, $CH_2Cl_2$, r.t., 12 h; (ii) $Pd(dba)_2$, $CH_2Cl_2$, 0 °C to r.t., 2 d; (iii) $Pd(dba)_2$, DMSO, r.t., 2 d; (iv) $Pd(dba)_2$, DMSO, r.t., 12 h; (v) NaI, acetone, r.t., 16 h.

Oxidative addition of the imidazolium salts **1**–**4** to the palladium(0) centre in $Pd(dba)_2$ yielded abnormal NHC–palladium(II) complexes **5**–**8** in unoptimised yields of 18–60% (Scheme 2). The syntheses were carried out under inert conditions at room temperature in $CH_2Cl_2$ or DMSO, but all the complexes are air- and moisture-stable. Complex **8b** was obtained by treatment of **8a** with NaI at room temperature.

### X-ray Crystallographic Analyses

The chelating nature of the ligands in complexes **5**–**8** was unambiguously confirmed by single-crystal X-ray diffraction analyses. The molecular structure of **5** has been reported previously,[11] and the structures of complexes **6**, **7** and **8b** are depicted in Figure 1. In all three structures the palladium centre resides in a slightly distorted square-planar environment comprised of the *C*,*E*-bidentate carbene ligand and two halides. The halides in the structures of **6** and **7** were scrambled and their occupancies refined to a ratio of 7:3 in **6** and 11:9 in **7**.[15] In both cases the major isomer contains the iodide *cis* to the NHC ligand, and the minor isomer has a mutual *trans* arrangement of the NHC group and iodido ligand. The major isomer represents the kinetic product and is also expected to be thermodynamically most stable when considering the relative *trans* influence (NHC > $SR_2$ > $NR_3$ and iodide > bromide). However, the differences between $I^–$ and $Br^–$ may be sufficiently small to account for the observed solid-state distribution (cf. solution studies below).

The $C_{carbene}$–Pd–E bite angle in the ethylene-linked chelates **6** [93.14(13)°], **7** [93.4(3)°] and **8b** [93.34(12)°] is slightly larger than the corresponding bite angle in **5** [86.7 (3)°], reflecting the larger flexibility of the palladacycle comprised of two $sp^3$-hybridised carbon atoms. The imidazolylidene ring in **6**, **7** and **8b** is furthermore twisted out of the metal coordination plane by roughly 30°, while in **5** the imidazolylidene and pyridyl rings both form a dihedral angle of ca. 40° with the metal coordination plane and assume a puckered conformation.[16]

Because of the halide disorder in complexes **6** and **7**, a sensible bond-length comparison is limited to complexes **5** and **8b**. The structure of **5** contained only one isomer, despite the presence of two different halides, whereas halide scrambling in **8b** is irrelevant.[17] The Pd–I(1) bond in **8b** [2.6350(5) Å] is significantly longer than the corresponding bond in **5** (2.5179 Å) indicating a stronger *trans* influence of the soft S(alkyl) ligand in **8b** compared with the pyridyl ligand in **5**.[18] In addition, the less pronounced puckering

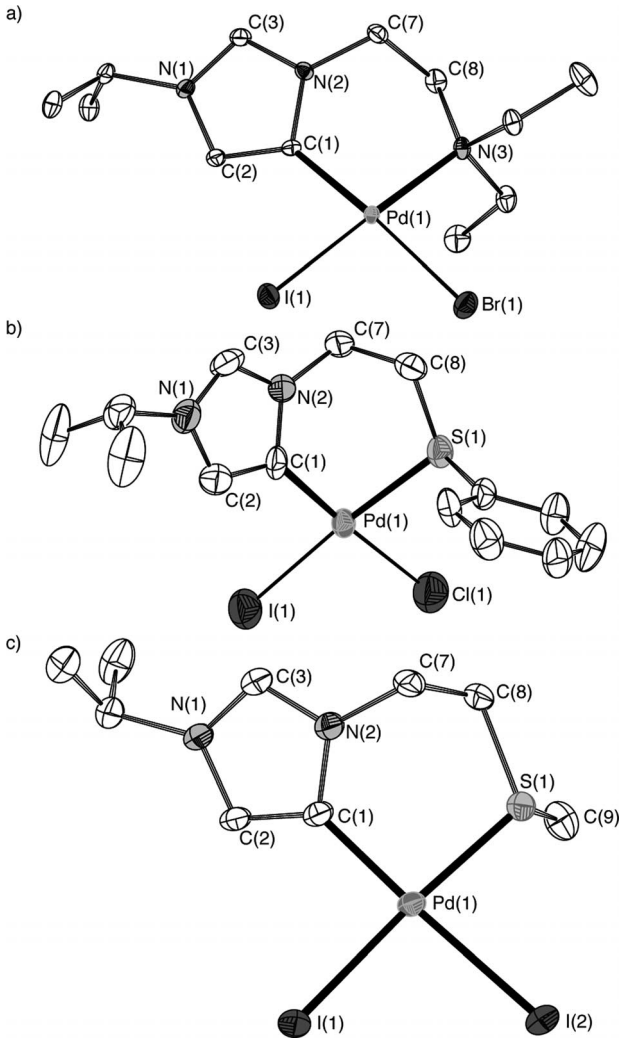



Figure 1. ORTEP representation of **6** (a), **7** (b) and **8b** (c). All thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and cocrystallised solvent molecules omitted for clarity.

of the ligand in **8b** may induce steric repulsion between the *i*Pr group and the iodido ligand. The Pd–$C_{carbene}$ bond lengths in all the complexes fall within the range typically observed for abnormal NHC–palladium complexes [1.99(3) Å][2,4,19] and do not differ from related complexes featuring a normal C2 bonding mode of the NHC ligand.[15,16,20] The Pd–$C_{carbene}$ bond in **8b** [2.013(4) Å] is slightly longer than in **5** [1.961(7) Å], which presumably reflects the different flexibility in the six-membered metallacycle (cf. bite angles). The average heterocyclic C(1)–C(2) bond length in complexes **5**–**8** is 1.37(3) Å, which points to a predominantly π-conjugated system and suggests vinyl-type bonding of the C4-bound carbene ligand.[21] In normal NHC complexes the C–C bond length is typically around 1.33 Å, consistent with a rather localised double bond. In addition, complexes **6** and **7** feature hydrogen bonds between the imidazolylidene C5–H, crystallographically labelled C(2), and the halide in the *cis* position [C(2)–H···X 2.86 and 2.91 Å, respectively].[22] Furthermore, one of the methylene protons of each NEt group in **6** is in close proximity to the metal-bound halide in the *cis* position (C–H···X 2.86 and 2.69 Å, respectively). A hydrogen bond has previously been noted between the pyridyl C6–H and the bromide atom in the *cis* position in complex **5**.[11] Such short contacts between the pyridyl C6–H and halide in the *cis* position have also been identified in related normal NHC complexes.[23] Selected bond lengths and angles for complexes **5**, **6**, **7** and **8b** are shown in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **5**, **6**, **7** and **8b**.[a]

| | **5**[b] | **6**[b] | **7**[c] | **8b**[c] |
|---|---|---|---|---|
| Pd(1)–C(1) | 1.961(7) | 1.989(3) | 1.977(9) | 2.013(4) |
| Pd(1)–E | 2.098(6) | 2.160(3) | 2.281(2) | 2.2865(11) |
| C(1)–C(2) | 1.393(10) | 1.370(5) | 1.376(13) | 1.355(6) |
| C(1)–Pd(1)–E | 86.7(3) | 93.14(13) | 93.4(3) | 93.34(12) |

[a] Data for complex **5** from ref.[11] [b] E = N(3). [c] E = S(1).

## NMR Spectroscopic Studies

Palladium complex formation was evidenced in solution by the shift of the high-field C–I carbon signal in the $^{13}C$ NMR spectrum. Furthermore, palladation induced an upfield shift of the signals of the C2–H and C5–H protons (to $\delta_H \approx 8.3$ and 7.2 ppm, respectively) in all complexes.[24] In [$D_6$]DMSO these signals appear broad in both the $^1H$ NMR and in particular in the $^{13}C$ NMR spectra. The proton and carbon signals due to the ethylene linker and also the signals of the chelating SPh and $NEt_2$ groups in **6**–**8** were broad, in contrast to the *i*Pr proton signals, which were sharp. While this may indicate a degree of fluxionality in the coordination of the nitrogen and sulfur atoms to the palladium centre in solution (hemilability), variable-temperature experiments indicated that the signals remained broad up to 80 °C. Such natural broadening of the signals may originate from reduced flexibility of the ligand due to conformationally stabilised hydrogen bonding to halides (cf. X-ray crystallographic section). This hypothesis is further supported by a 0.73 ppm downfield shift and substantial broadening of the pyridyl C6–H proton signal in complex **5**.

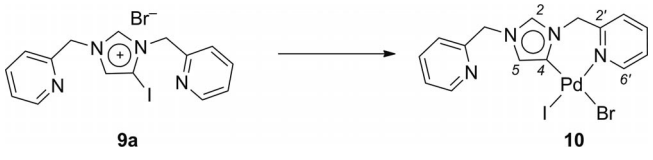
In complex **6**, two sets of imidazolylidene $^1H$ NMR signals are visible in an approximate 5:1 ratio. The minor set is broad and overlaps with the resonances of the major component, except for the low-field resonance of the C2-bound proton, which appears at $\delta = 8.90$ ppm for the major species and at $\delta = 8.84$ ppm for the minor one. In the $^{13}C$ NMR spectrum, all resonances are broadened, and the minor isomer was not detected. The presence of two compounds may be rationalised by halide scrambling (cf. X-ray discussion) or by partial dissociation of the halide *trans* to the NHC ligand.[21b,25] In support of the latter, a single compound with sharp signals was observed when the spectrum was recorded in $CD_3CN$ solution, indicating that the coordinating ability of the solvent is relevant. The $NCH_2CH_3$ signals are diastereotopic and resonate as two well-resolved multiplets. Halide substitution by a solvent

molecule thus induces enhanced flexibility of the *C*,*E*-bidentate ligand, presumably because of the absence of hydrogen bonding between the ligand and a metal-bound halide. While fluxional behaviour of the six-membered metallacycle cannot be excluded, it is worth noting that the sulfido complexes **7** and **8** display a single set of resonances, despite the chirality at the sulfur atom.

### Metallation of the Imidazolium C2 Position

The availability of a C2–H unit in complexes **5**–**8** and the relatively acidic character of this proton, as deduced from NMR spectroscopy, prompted us to explore the possibility of constructing dimetallic complexes by metallation of the C2 position. In order to further stabilise a potentially C2-bound palladium centre, a second donor group was introduced onto the NHC precursor. The imidazolium salt **9a** (Scheme 3) was prepared directly from 4/5-iodoimidazole and (bromomethyl)pyridine according to a known procedure.[26] Subsequent oxidative addition to $Pd(dba)_2$ afforded complex **10** as an air- and moisture-stable solid in 60% yield.




**9a** **10**

Scheme 3. Metallation of **9**. Reagents and conditions: $Pd(dba)_2$, $CH_2Cl_2$, r.t., 5 d.

The structure of **10** was unambiguously confirmed by X-ray crystallography (Figure 2), which revealed the expected distorted square-planar coordination geometry around the palladium atom and *C*,*N*-bidentate chelation of the ligand. Similar to **5**, the bicyclic ligand assumes a puckered conformation with the imidazolylidene and pyridyl rings twisted out of the metal coordination plane by about 40°, and the bite-angle is slightly more acute than 90°. The structure contains two isomers in an approximately 8:2 ratio due to halide scrambling. The major isomer contains the iodide ligand *cis* with respect to the NHC ligand and reveals close C–H···X contacts for the imidazolylidene and the pyridyl heterocycle through C(2)–H···I(1) and C(9)–H···Br(1) interactions, respectively.

In agreement with the NMR analyses of complexes **5**–**8**, palladation of the precursor **9b** to form **10** brings about an upfield shift of the imidazolylidene C2–H and C5–H proton signals and a shift of the resonance due to the carbon atom originally bound to iodide. The chemical shift difference of the inequivalent methylene groups increased from 0.03 ppm to 0.23 ppm upon palladation, indicative of a change in chemical environment due to metal coordination of one picolyl group only. Similarly, the difference in chemical shift of the two sets of pyridyl protons became more pronounced and, notably, one set of signals was less sharp. This broadening was also observed in the $^{13}C$ NMR spectrum and

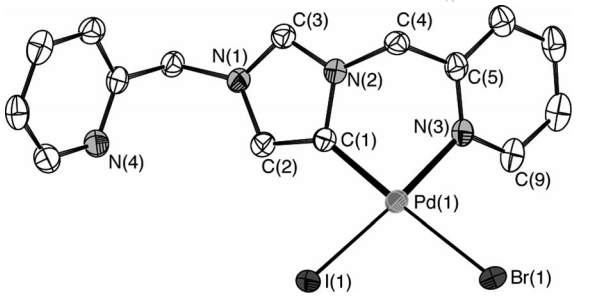


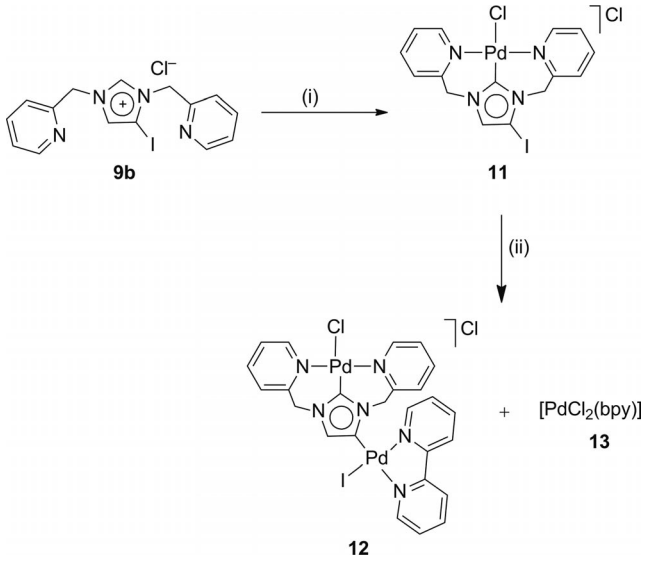

Figure 2. ORTEP representation of **10** (50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angle [°]: Pd(1)–C(1) 1.976(4), Pd(1)–N(3) 2.080(3), C(1)–C(2) 1.363(5), C(1)–Pd(1)–N(3) 86.76(14).

suggests limited flexibility of one picolyl unit in solution akin to complex **5**. The resonance of the C6′–H proton of the coordinated pyridyl ring is broad and shifted downfield to $\delta_H$ = 8.89 ppm suggesting that the crystallographically identified C(9)–H···Br–Pd hydrogen bonding motif persists in solution as was observed for complex **5**.

Reaction of complex **10** or any of the complexes **5**–**8** with $Ag_2O$ did not produce the desired C2-bound silver–carbene complexes for use in transmetallation reactions.[27] Direct metallation with $Pd(OAc)_2$ also proved unsuccessful.[28] After 16 h in DMSO at 60 °C, the complexes apparently decomposed. Attempts to deuterate the C2-bound hydrogen atom in **7** by using $D_2O$ similarly failed, even in the presence of KOH.[29] Inversion of the metallation sequence was more successful. Thus, palladation of the C2 position of the imidazolium chloride **9b**, obtained from **9a** by halide exchange, was accomplished by treatment with $Ag_2O$ and subsequent transmetallation using $[PdCl_2(MeCN)_2]$. This procedure cleanly afforded the pincer complex **11** in 60% yield (Scheme 4). The formation of **11** was confirmed by the disappearance of the C2–H proton signal in the $^1H$ NMR spectrum, as well as by an upfield shift of the C5–H proton signal to $\delta$ = 7.82 ppm. No broadening of the imidazolylidene signals was observed in the $^{13}C$ NMR spectrum, and the carbene carbon resonance was noted at $\delta_C$ = 151.3 ppm. The proton and carbon signals due to the picolyl moieties were also sharp, and chelation therefore seems to be rigid. The inequivalence of the picolyl $NCH_2$ signals is reflected by a 0.1 ppm shift difference between the two singlets in the $^1H$ NMR spectrum.

Subsequent exposure of **11** to $Pd(dba)_2$ in the presence of bipyridine (bpy) under reaction conditions similar to those used previously resulted in the formation of **12** and $[PdCl_2(bpy)]$ (**13**) in a 1:0.4 ratio (Scheme 4). This ratio did not change upon prolonged stirring. Crystallisation attempts yielded a pure fraction of **13** yet induced significant decomposition of **12**. The identity of **13** was confirmed unambiguously by $^1H$ NMR spectroscopy and X-ray crystallography.[30] Formation of the dinuclear complex **12** is supported by ESI mass spectrometry, especially through the characteristic isotope distribution pattern that correlates well with a dipalladium species. While the instability of complex **12** precluded its isolation in pure form thus far,




Scheme 4. Sequential metallation at C2 and C4 to form the dimetallic complex **12**. Reagents and conditions: (i) $Ag_2O$, DMSO/$CH_2Cl_2$, r.t., 4 d, then [$PdCl_2(MeCN)_2$], DMSO/$CH_2Cl_2$/MeCN, 2.5 h; (ii) $Pd(dba)_2$, 2,2-bipyridine, DMSO/MeCN, r.t., 2 d.

NMR spectra of the crude reaction mixture were informative. Metallation of the C4 position of **11** led to an upfield shift of the signal of the C5-bound hydrogen atom from $\delta_H$ = 7.82 to $\delta_H$ = 7.06 ppm. The $NCH_2$ signals appeared as two sets of AB doublets at $\delta_H$ = 5.94 and 5.87 ppm ($^2J_{H,H}$ = 15.4 Hz) and at $\delta_H$ = 5.73 and 5.66 ppm ($^2J_{H,H}$ = 15.3 Hz). 2D shift-correlation experiments revealed the presence of five sets of pyridyl signals, one of which was assigned to the bpy ligand in **13**.[30] The remaining four sets were attributed to the asymmetric bpy ligand and the two picolyl groups of **12** (Figure 3). The two sets of picolyl signals remained sharp, suggesting coordination to the C2-bound rather than to the C4-bound palladium centre. In agreement with this notion, the change in chemical environment upon formation of the dimetallic complex induced only a slight increase in chemical shift difference compared with the corresponding shifts in **11**.

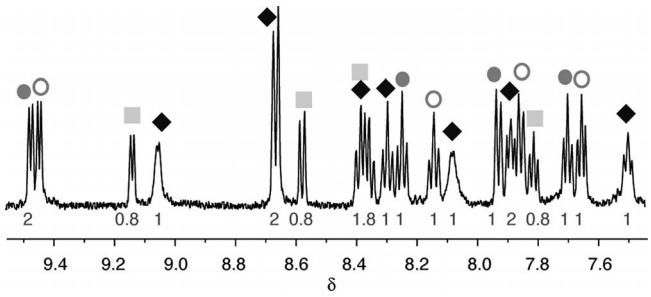



Figure 3. Section of the 500 MHz $^1H$ NMR spectrum of the crude reaction mixture ([$D_6$]DMSO solution) showing **12** and **13** in a 1:0.4 ratio (grey filled circles, grey open circles: py signals; black filled diamonds: bpy signals of **12**; grey filled squares: bpy signals of **13**).

## Conclusions

Abnormal imidazolylidene–palladium(II) complexes were successfully synthesised by oxidative addition of iodo-functionalised imidazolium salts to $Pd(dba)_2$. The complexes are air- and moisture-stable and were fully characterised by NMR spectroscopy and X-ray crystallography. Different functionalised wingtip groups, ranging from hard –$NEt_2$ to soft –SPh, were tolerated, and X-ray crystallography and NMR spectroscopy provided evidence for chelation in the solid state and also in solution. The asymmetry of the bidentate ligand renders the *trans* positions on the complex electronically inequivalent and may lead to interesting reactivity of the complex. Since the oxidative addition protocol does not require the protection of the C2 position, a route to dimetallic complexes has been devised. The generality of the C2 metallation provides vast opportunities for incorporating a range of different transition metals into the dimetallic complex, which may be particularly attractive for redox processes and for exploring synergistic potentials, e.g. for inducing catalytic tandem transformations.

## Experimental Section

**General Comments:** 4-Iodoimidazole, 4-iodo-*N*-isopropylimidazole, the imidazolium salt **1** and complex **5** were synthesised as reported previously.[11–13] All other reagents are commercially available and were used as received. Standard Schlenk techniques were used in the synthesis of compounds **5**–**8** and **10**–**13**. Unless otherwise stated, NMR spectra were recorded at 30 °C with Bruker and Varian spectrometers operating at 400, 500 or 600 MHz ($^1H$ NMR) and 100, 125 or 150 MHz [$^{13}C\{^1H\}$ NMR], respectively. Chemical shifts ($\delta$ in ppm, coupling constants $J$ in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift-correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory at the Federal Institute of Technology in Zurich, Switzerland and at the University College Dublin, Ireland.

**Synthesis of 2:** 4-Iodo-*N*-isopropylimidazole (2.2 g, 9.5 mmol), 2-bromo-*N*,*N*-diethylamine hydrobromide (2.5 g, 9.5 mmol) and $NaHCO_3$ (1.2 g, 14 mmol) were stirred in refluxing EtOH (30 mL) for 4 d. The colour of the reaction mixture changed from colourless to yellow. After cooling to room temp., the solvent was removed in vacuo, and the residue was dissolved in $CH_2Cl_2$ (100 mL) and filtered through Celite. The solution was concentrated to 10 mL and added to $Et_2O$ (100 mL) to precipitate the crude product. Trituration with acetone yielded **2** as a white hygroscopic solid (1.1 g, 26% yield). $^1H$ NMR ([$D_6$]DMSO, 500 MHz): $\delta$ = 9.32 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H, $H_{imi}$), 8.13 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H, $H_{imi}$), 4.66 (septet, $^3J_{H,H}$ = 6.7 Hz, 1 H, $CHMe_2$), 4.11 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, $NCH_2CH_2N$), 2.69 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, $NCH_2CH_2N$), 2.45 (q, $^3J_{H,H}$ = 7.0 Hz, 4 H, $NCH_2CH_3$), 1.46 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, $CH(CH_3)_2$], 0.83 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, $NCH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR ([$D_6$]DMSO, 125 MHz): $\delta$ = 137.6, 126.4 (2× $C_{imi}$), 80.7 ($C_{imi}$-I), 52.7 ($CHMe_2$) 51.1 ($NCH_2CH_2N$), 48.6 ($NCH_2CH_2N$), 46.6 ($NCH_2CH_3$), 22.2 [$CH(CH_3)_2$], 12.0 ($NCH_2CH_3$) ppm. $C_{12}H_{23}BrIN_3 \cdot 0.5H_2O$ (425.15): calcd. C 33.90, H 5.69, N 9.88; found C 34.63, H 5.69, N 9.88.

**Synthesis of 3:** 4-Iodo-*N*-isopropylimidazole (0.24 g, 1.0 mmol) and 2-chloroethyl phenyl sulfide (0.3 mL, 2 mmol) were stirred at

120 °C for 16 h. During this period, the reaction mixture changed colour form light yellow to red. $Et_2O$ was added, and the formed precipitate was isolated by decantation. The crude product was purified by recrystallisation from MeCN and $Et_2O$ to yield **3** as a light yellow hygroscopic solid (0.36 g, 88% yield). $^1H$ NMR ([D$_6$]DMSO, 500 MHz): $\delta$ = 9.45 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H, $H_{imi}$), 8.03 (d, $^4J_{H,H}$ = 1.6 Hz, 1 H, $H_{imi}$), 7.39–7.33 (m, 4 H, $H_{aryl}$), 7.26–7.21 (m, 1 H, $H_{aryl}$), 4.56 (septet, $^3J_{H,H}$ = 6.7 Hz, 1 H, $CHMe_2$), 4.32 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, $NCH_2CH_2N$), 3.50 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, $NCH_2CH_2N$), 1.41 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 137.7 ($C_{imi}$), 133.9, 129.2, 128.7 (3× $C_{aryl}$), 126.5 ($C_{imi}$), 126.5 ($C_{aryl}$), 82.2 ($C_{imi}$-I), 52.8 ($CHMe_2$) 49.7 ($NCH_2CH_2S$), 31.7 ($NCH_2CH_2S$), 22.1 [$CH(CH_3)_2$] ppm. $C_{14}H_{18}ClIN_2S{\cdot}H_2O$ (426.74): calcd. C 39.40, H 4.72, N 6.56; found C 39.39, H 4.36, N 6.27.

**Synthesis of 4:** 4-Iodo-*N*-isopropylimidazole (0.24 g, 1.0 mmol) and 2-chloroethyl methyl sulfide (0.2 mL, 2 mmol) were stirred at 60 °C for 2 h and then at 80 °C for 16 h. The yellowish reaction mixture was cooled to room temp., and $Et_2O$ (5 mL) was added upon which a white precipitate immediately formed. The mixture was stirred for 10 min and then left to settle. The formed precipitate was isolated by decantation. The crude product was purified by recrystallisation from warm MeCN to yield **4** as an off-white solid (81 mg, 23% yield). $^1H$ NMR ($CDCl_3$, 360 MHz): $\delta$ = 10.88 (s, 1 H, $H_{imi}$), 7.44 (s, 1 H, $H_{imi}$), 4.82 (sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, $CHMe_2$), 4.58 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, $NCH_2CH_2N$), 2.98 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, $NCH_2CH_2N$), 2.28 (s, 3 H, SMe), 1.63 [d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 90 MHz): $\delta$ = 139.3, 125.7 (2× $C_{imi}$), 80.3 ($C_{imi}$-I), 54.0 ($CHMe_2$) 49.3 ($NCH_2CH_2S$), 33.8 ($NCH_2CH_2S$), 23.1 [$CH(CH_3)_2$], 15.8 (SMe) ppm. $C_9H_{16}ClIN_2S$ (346.66): calcd. C 31.18, H 4.65, N 8.08; found C 31.31, H 4.73, N 8.01.

**Synthesis of 6:** A suspension of **2** (0.18 g, 0.39 mmol) in dry $CH_2Cl_2$ (15 mL) was cooled to 0 °C and added to $Pd(dba)_2$ (0.23 g, 0.40 mmol). The reaction mixture, which immediately changed colour from colourless to deep red, was allowed to reach room temp. and stirred for 2 d. A yellow precipitate gradually formed. The reaction mixture was concentrated to 7 mL and filtered through Celite. The residue was washed with $CH_2Cl_2$ and subsequently extracted with MeCN. The combined MeCN fractions were concentrated, and the residue was triturated with $Et_2O$ and dried in vacuo to yield **6** as a yellow solid (38 mg, 18% yield). $^1H$ NMR ([D$_6$]-DMSO, 500 MHz): $\delta$ = 8.90 (s, 1 H, $H_{imi}$), 7.13 (s, 1 H, $H_{imi}$), 4.49 (sept, $^3J_{H,H}$ = 6.6 Hz, 1 H, $CHMe_2$), 4.27 (br., 2 H, $NCH_2$), 3.3, 3.0 (br., 4 H, $NCH_2CH_3$), 2.8 (br., 2 H, $NCH_2$), 1.40 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.4 (br., 6 H, $NCH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 132.4, 124.6 (br., 2× $C_{imi}$), 53.2 ($NCH_2CH_3$), 51.9 ($NCH_2$), 51.6 ($CHMe_2$), 46.4 ($NCH_2$), 22.5 [$CH(CH_3)_2$], 11.7 ($NCH_2CH_3$) ppm; carbene C signal not resolved. HR-MS (ESI$^+$): calcd. for $C_{12}H_{23}IN_3Pd$ [M – Br]$^+$ 441.9971; found 441.9990. $C_{12}H_{23}BrIN_3Pd{\cdot}0.25Et_2O$ (541.09): calcd. C 28.86, H 4.75, N 7.77; found C 28.77, H 4.55, N 7.82.

**Synthesis of 7:** A solution of **3** (0.31 g, 0.76 mmol) in dry DMSO (10 mL) was added to $Pd(dba)_2$ (0.44 g, 0.76 mmol) and stirred at room temp. for 2 d. The reaction mixture was filtered through Celite, and the filtrate was added to a 1:1 mixture of $Et_2O/CH_2Cl_2$. The formed precipitate was isolated by centrifugation, washed with $CH_2Cl_2$ and dried in vacuo, thus affording **7** as a yellow solid (0.12 g, 31% yield). $^1H$ NMR ([D$_6$]DMSO, 500 MHz): $\delta$ = 8.89 (s, 1 H, $H_{imi}$), 8.1–7.7 (m, 2 H, $H_{aryl}$), 7.55–7.40 (m, 3 H, $H_{aryl}$), 7.3 (br., 1 H, $H_{imi}$), 4.52 (sept, $^3J_{H,H}$ = 6.7 Hz, 1 H, $CHMe_2$), 4.3 (br., 2 H, $NCH_2$), 3.2 (br., 2 H, $SCH_2$), 1.42 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 133.2 (br., $C_{imi}$), 129.7 (br., $C_{aryl}$), 129.3, 128.8 (2× $C_{aryl}$), 124.7 (br., $C_{imi}$), 51.0 ($CHMe_2$), 47.9 (br., $NCH_2$), 36.5 (br., $SCH_2$), 22.5 [$CH(CH_3)_2$] ppm; carbene C and quaternary $C_{aryl}$ signals not resolved. $C_{14}H_{18}ClIN_2PdS$ (515.15): calcd. C 32.64, H 3.52, N 5.44; found C 32.48, H 3.38, N 5.15.

**Synthesis of 8a:** A suspension of **4** (0.30 g, 0.87 mmol) and $Pd(dba)_2$ (0.50 g, 0.87 mmol) in DMSO (10 mL) were stirred at room temp. for 1 d. The solution was filtered through Celite and added to EtOH (10 mL). The crude product was precipitated from the solution by the addition of $Et_2O$ (100 mL) and isolated by centrifugation. Recrystallisation from hot MeCN (30 mL) yielded **8a** as a yellow solid (120 mg, 30% yield). $^1H$ NMR ([D$_6$]DMSO, 500 MHz): $\delta$ = 8.86 (s, 1 H, $H_{imi}$), 7.3 (br., 1 H, $H_{imi}$), 4.51 (sept, $^3J_{H,H}$ = 6.6 Hz, 1 H, $CHMe_2$), 4.4 (br., 2 H, $NCH_2$), 2.8 (br., 2 H, $SCH_2$), 2.70 (s, 3 H, SMe), 1.42 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 132.6 ($C_{imi}$), 129.2 (br., $C_{imi}$), 123.0 (br., $C_{imi}$-Pd), 50.8 ($CHMe_2$), 47.9 ($NCH_2$), 32.4 ($SCH_2$), 22.4 [$CH(CH_3)_2$], 22.0 (SMe) ppm. $C_9H_{16}ClIN_2PdS$ (453.08): calcd. C 23.86, H 3.56, N 6.18; found C 23.91, H 3.71, N 6.16.

**Synthesis of 8b:** Complex **8a** (80 mg, 0.18 mmol) and an excess of NaI (0.75 g) were stirred in acetone (100 mL) at room temp. for 16 h. The solvent was removed in vacuo and the residue redissolved in hot MeCN (20 mL) and filtered. Cooling of the filtrate to –30 °C yielded orange crystals of **8b** (38 mg, 39% yield). $^1H$ NMR ([D$_6$]-DMSO, 500 MHz): $\delta$ = 8.86 (s, 1 H, $H_{imi}$), 7.4 (br., 1 H, $H_{imi}$), 4.50 (sept, $^3J_{H,H}$ = 6.7 Hz, 1 H, $CHMe_2$), 4.4 (br., 2 H, $NCH_2$), 2.8 (br., 2 H, $SCH_2$), 2.77 (s, 3 H, SMe), 1.41 [d, $^3J_{H,H}$ = 6.7 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 133.2 ($C_{imi}$), 129.2 ($C_{imi}$), 51.4 ($CHMe_2$), 48.5 ($NCH_2$), 33.2 ($SCH_2$), 25.1 (SMe), 23.0 [$CH(CH_3)_2$] ppm; carbene C signal not resolved. $C_9H_{16}I_2N_2PdS$ (544.53): calcd. C 19.85, H 2.96, N 5.14; found C 19.4, H 2.82, N 5.00.

**Synthesis of 9a:** 4-Iodoimidazole (2.9 g, 15 mmol), 2-(bromomethyl)pyridine hydrobromide (7.6 g, 30 mmol) and $NaHCO_3$ (3.8 g, 45 mmol) were suspended in EtOH (80 mL) and heated to reflux for 3 d. The colour of the reaction mixture turned from colourless to pink within a few minutes. At room temp. the reaction mixture was filtered and washed with EtOH, and the red solution was concentrated in vacuo. A precipitate formed, which was isolated by filtration and repeatedly washed with $CH_2Cl_2$ and acetone to yield **9a** as an off-white solid (1.7 g, 25% yield). $^1H$ NMR ([D$_6$]DMSO, 500 MHz): $\delta$ = 9.59 (d, $^4J_{H,H}$ = 1.4 Hz, 1 H, $H_{imi}$), 8.59 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, $H_{py}$), 8.53 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, $H_{py}$), 8.05 (d, $^4J_{H,H}$ = 1.4 Hz, 1 H, $H_{imi}$), 7.94–7.87 (m, 2 H, $H_{py}$), 7.53–7.47 (m, 2 H, $H_{py}$), 7.45–7.37 (m, 2 H, $H_{py}$), 5.64 (s, 2 H, $NCH_2$), 5.61 (s, 2 H, $NCH_2$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 153.2, 152.8 (2× $C_{py}$), 149.6, 149.5 (2× $C_{py}$), 140.4 ($C_{imi}$), 137.5, 137.3 (2× $C_{py}$), 129.4 ($C_{imi}$), 123.7, 123.5 (2× $C_{py}$), 122.5, 122.4 (2× $C_{py}$), 81.0 (C–I), 53.9, 53.4 (2× $NCH_2$) ppm. $C_{15}H_{14}BrIN_4$ (457.11): calcd. C 39.41, H 3.09, N 12.26; found C 39.16, H 3.13, N 12.02.

**Synthesis of 9b:** Compound **9a** (1.7 g, 3.6 mmol) was dissolved in MeOH and filtered through a Dowex ion-exchange resin (1×4 chloride form, 100–200 mesh). After removal of the solvent in vacuo, **9b** was obtained as a light yellow solid (1.1 g, 72% yield). $^1H$ NMR ($CD_3OD$, 600 MHz): $\delta$ = 9.54 (d, $^4J_{H,H}$ = 1.3 Hz, 1 H, $H_{imi}$), 8.58 (d, $^3J_{H,H}$ = 4.6 Hz, 1 H, $H_{py}$), 8.52 (d, $^3J_{H,H}$ = 4.6 Hz, 1 H, $H_{py}$), 7.91–7.86 (m, 3 H, $H_{imi}$, $H_{py}$), 7.59 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, $H_{py}$), 7.52 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, $H_{py}$), 7.45–7.37 (m, 2 H, $H_{py}$), 5.65 (s, 2 H, $NCH_2$), 5.62 (s, 2 H, $NCH_2$) ppm. $^{13}C\{^1H\}$

NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 154.0, 153.6 (2× $C_{py}$), 151.0, 150.9 (2× $C_{py}$), 141.4 (t, $^1J_{D,C}$ = 32.8 Hz, $C_{imi}$), 139.2, 138.9 (2× $C_{py}$), 131.1 ($C_{imi}$), 125.3, 125.0 (2× $C_{py}$), 124.3, 124.0 (2× $C_{py}$), 79.6 (C–I), 55.7, 55.2 ($NCH_2$) ppm. $C_{15}H_{14}ClIN_4$ (412.66): calcd. C 43.66, H 3.42, N 13.58; found C 43.36, H 3.35, N 13.29.

**Synthesis of 10:** A suspension of **9a** (0.23 g, 0.50 mmol) and Pd(dba)$_2$ (0.29 g, 0.50 mmol) in dry $CH_2Cl_2$ (15 mL) was stirred at room temp. for 5 d. A yellow precipitate gradually formed. The reaction mixture was filtered through Celite, and the residue was washed with $CH_2Cl_2$ and cold MeCN. The product was then extracted from the residue with warm DMSO and added to a 5:1 mixture of $Et_2O$ and $CH_2Cl_2$. The formed precipitate was isolated by centrifugation and dried in vacuo as a yellowish solid (168 mg, 60% yield). $^1$H NMR ([D$_6$]DMSO, 500 MHz): $\delta$ = 9.02 (s, 1 H, $H_{imi}$), 8.9 (br., 1 H, $H_{py}$), 8.56–8.50 (m, 1 H, $H_{py}$), 8.20–8.08 (m, 1 H, $H_{py}$) 7.88–7.81 (m, 1 H, $H_{py}$), 7.81–7.74 (m, 1 H, $H_{py}$), 7.66–7.56 (m, 1 H, $H_{py}$), 7.47–7.41 (m, 1 H, $H_{py}$), 7.40–7.33 (m, 1 H, $H_{py}$), 7.13 (s, 1 H, $H_{imi}$), 5.65 (s, 2 H, $NCH_2$), 5.42 (s, 2 H, $NCH_2$) ppm. $^{13}$C{$^1$H} NMR ([D$_6$]DMSO, 125 MHz): $\delta$ = 154.0, 151.8, 149.6, 140.4 (br), 137.5 (5× $C_{py}$), 134.6, 128.5 (2× $C_{imi}$), 125.2, 125.0 (br., 2× $C_{py}$), 123.6, 122.7 (2× $C_{py}$), 53.9 (br., $NCH_2$), 53.4 ($NCH_2$) ppm; carbene C and pyridyl C6 signals not resolved. $C_{15}H_{14}BrIN_4Pd·0.5DMSO$ (602.59): calcd. C 31.89, H 2.84, N 9.30; found C 31.65, H 2.49, N 9.42.

**Synthesis of 11:** A solution of **9b** (0.41 g, 1.0 mmol) in a mixture of dry $CH_2Cl_2$ (35 mL) and DMSO (15 mL) was added to $Ag_2O$ (0.14 g, 0.60 mmol). The reaction mixture was stirred at room temp. for 4 d protected from light, after which it was filtered and transferred to a suspension of [$PdCl_2(MeCN)_2$] (0.26 g, 1.0 mmol) in a 1:1 mixture of $CH_3CN/CH_2Cl_2$ (20 mL). The reaction mixture immediately became clear and orange, and a white precipitate started to form slowly, while the solution became yellow. The reaction mixture was stirred for 2.5 h, filtered through Celite, and the filtrate was concentrated in vacuo. The concentrated solution was added to a 1:1 mixture of $Et_2O/CH_2Cl_2$ (50 mL). The product precipitated as a yellow solid, which was isolated by filtration and dried in vacuo (330 mg, 60% yield). An analytically pure sample was obtained by recrystallisation of **11** from $CHCl_3$ and $Et_2O$. $^1$H NMR ([D$_6$]DMSO, 600 MHz): $\delta$ = 9.41–9.38 (m, 2 H, $H_{py}$), 8.27–8.22 (m, 2 H, $H_{py}$), 8.14 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, $H_{py}$) 7.89 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, $H_{py}$), 7.82 (s, 1 H, $H_{imi}$), 7.73–7.68 (m, 2 H, $H_{py}$), 5.71 (s, 2 H, $NCH_2$), 5.61 (s, 2 H, $NCH_2$) ppm. $^{13}$C{$^1$H} NMR ([D$_6$]DMSO, 150 MHz): $\delta$ = 155.8, 155.7, 152.5, 152.3 (4× $C_{py}$), 151.3 ($C_{carbene}$), 141.4, 141.3 ($C_{py}$), 127.9 ($C_{imi}$), 126.9, 126.6, 125.5, 125.3 (4× $C_{py}$), 75.9 ($C_{imi}$-I), 54.6, 53.9 (2× $NCH_2$) ppm. HR-MS (ESI$^+$): calcd. for $C_{15}H_{13}IN_4Pd$ [M – Cl]$^+$ 516.8908; found 516.8906. $C_{15}H_{13}Cl_2IN_4Pd·CHCl_3$ (672.90): calcd. C 28.56, H 2.10, N 8.33; found C 28.59, H 1.92, N 8.47.

**Synthesis of 12:** A suspension of **11** (19 mg, 0.035 mmol), Pd(dba)$_2$ (20 mg, 0.035 mmol) and 2,2′-bipyridine (5.5 mg, 0.035 mmol) was stirred in DMSO (2 mL) at room temp. for 1 d. The reaction mixture was filtered through Celite, and the filtrate was added to a 1:1 mixture of $CH_2Cl_2/Et_2O$ (20 mL). The formed precipitate was isolated by centrifugation and dried in vacuo. The light yellow crude product contained **12** and **13** in 2.5:1 molar ratio (20 mg). $^1$H NMR ([D$_6$]DMSO, 600 MHz): $\delta$ = 9.48 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, $H_{py}^A$), 9.45 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H $H_{py}^B$), 9.1 (br., 1 H, $H_{bpy}$), 8.69–8.63 (m, 2 H, $H_{bpy}$), 8.42–8.37 (m, 1 H, $H_{bpy}$), 8.33–8.27 (m, 1 H, $H_{bpy}$), 8.27–8.22 (m, 1 H, $H_{py}^A$), 8.17–8.12 (m, 1 H, $H_{py}^B$), 8.1 (br., 1 H, $H_{bpy}$), 7.93 (d, 1 H, $^3J_{H,H}$ = 7.6 Hz, $H_{py}^A$), 7.91–7.87 (m, 1 H, $H_{bpy}$), 7.86 (d, 1 H, $^3J_{H,H}$ = 7.6 Hz, $H_{py}^B$), 7.73–7.63 (m, 1 H, $H_{py}^A$), 7.68–7.63 (m, 1 H, $H_{py}^B$), 7.53–7.47 (m, 1 H, $H_{bpy}$), 7.06 (s, 1 H, $H_{imi}$), 5.94 (d, 1 H, $^2J_{H,H}$ = 15.4 Hz, NC*H,H*$^A$), 5.87 (d, 1 H, $^2J_{H,H}$ = 15.4 Hz, NCH,H$^A$), 5.73 (d, 1 H, $^2J_{H,H}$ = 15.3 Hz,

Table 2. Crystallographic data for complexes **6**, **7**, **8b** and **10**.

| | **6** | **7** | **8b** | **10** |
|---|---|---|---|---|
| Colour | orange | yellow | yellow, | yellow |
| Shape | rod | plate | plate | plate |
| Crystal size [mm] | 0.38×0.18×0.13 | 0.05×0.03×0.01 | 0.20×0.20×0.03 | 0.17×0.14×0.03 |
| Empirical formula | $C_{12}H_{32}BrIN_3Pd·C_2H_6OS$ | $C_{14}H_{18}ClIN_2PdS$ | $C_9H_{16}I_2N_2Pd·C_2H_6OS$ | $C_{15}H_{14}BrIN_4Pd$ |
| Formula mass | 600.67 | 515.11 | 622.63 | 563.51 |
| $T$ [K] | 100(2) | 100(2) | 173(2) | 100(2) |
| Crystal system | monoclinic | monoclinic | monoclinic | triclinic |
| Space group | $P2_1/c$ (# 14) | $P2_1/c$ (# 14) | $P2_1/c$ (# 14) | $P\bar{1}$ (# 2) |
| Unit cell | | | | |
| $a$ [Å] | 12.8889(9) | 10.0971(5) | 13.1246(16) | 8.8721(1) |
| $b$ [Å] | 18.4942(12) | 8.5516(4) | 8.3281(6) | 8.9579(2) |
| $c$ [Å] | 8.6701(6) | 19.3799(9) | 17.658(2) | 10.5343(2) |
| $\alpha$ [°] | 90 | 90 | 90 | 91.309(1) |
| $\beta$ [°] | 105.135(1) | 96.279(4) | 105.579(9) | 92.488(1) |
| $\gamma$ [°] | 90 | 90 | 90 | 91.114(1) |
| $V$ [Å$^3$] | 1995.0(2) | 1663.35(14) | 1859.1(3) | 836.04(3) |
| $Z$ | 4 | 4 | 4 | 2 |
| $D_{calcd.}$ [g cm$^{-3}$] | 2.000 | 2.057 | 2.224 | 2.239 |
| $\mu$ [mm$^{-1}$] | 4.590 | 26.146 | 4.539 | 26.255 |
| Total reflections | 47788 | 8851 | 23384 | 23746 |
| Unique reflections | 6618 | 2378 | 5028 | 3462 |
| $R_{int}$ | 0.0315 | 0.0415 | 0.0615 | 0.0624 |
| Transmittance range | 0.587–0.327 | 0.461–0.703 | 0.406–0.201 | 0.507–0.056 |
| Parameters, restraints | 206, 0 | 184, 0 | 185, 0 | 200, 0 |
| $R$,[a] $R_w$[b] | 0.0375, 0.1032 | 0.0479, 0.1287 | 0.0340, 0.0782 | 0.0287, 0.0808 |
| GOF | 1.067 | 1.044 | 0.977 | 1.067 |
| Largest hole, peak [e Å$^{-3}$] | –1.606, 2.855 | –1.316, 0.823 | –1.800, 0.805 | –1.269, 1.690 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for all $I > 2\sigma(I)$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^4)]\}^{1/2}$.

NC*H*,*H*$^{B}$), 5.66 (d, 1 H, $^{2}J_{H,H}$ = 15.3 Hz, NCH,H$^{B}$) ppm. A and B denote the two picoline residues in **12**. HR-MS (ESI$^{+}$): calcd. for $C_{25}H_{21}Cl_2N_6Pd_2$ [M – I]$^{+}$ 688.9323; found 688.9357.

**Structure Determination and Refinement of 6, 7, 8b and 10:**[17] Suitable single crystals were mounted on a Bruker SMART APEX CCD diffractometer (**6**) with a D8 goniometer and a graphite-monochromator (Mo-$K_\alpha$ radiation, $\lambda$ = 0.71073 Å), on an Agilent SuperNova A diffractometer (**7** and **10**) with a mirror-monochromator (Cu-$K_\alpha$ radiation, $\lambda$ = 1.54184 Å), or on a Stoe Mark II-Image Plate Diffraction System (**8b**) with a graphite-monochromator (Mo-$K_\alpha$ radiation, $\lambda$ = 0.71073 Å). A semi-empirical absorption correction was applied for **6** by using SADABS[31] and for **8b** by using MULscanABS as implemented in PLATON.[32] An analytical numeric absorption correction by using a multifaceted crystal model was applied for **7** and **10**.[33] The structures were solved by direct methods using the program SHELXS-97[34] and refined by full-matrix least squares on $F^2$ with SHELXL-97. The hydrogen atoms were included in calculated positions and treated as riding atoms by using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. Crystals of complex **6** contained one DMSO molecule per complex molecule. Crystals of **8b** contained one disordered DMSO molecule per asymmetric unit, which was refined with occupancies of 0.5 for all participating atoms. In **6**, **7** and **10** the iodide and bromide (**7** and **10**) and the iodide and chloride (**6**) were partially occupied. The major component contained the iodide ligand *cis* to the carbene with a site occupation factor of 0.708(3) in **6**, 0.556(3) in **7** and 0.778(3) in **10**. The minor component contained the iodide *trans* to the carbene with a site occupation factor of 0.292(3) in **6**, 0.444(3) in **7** and 0.222(3) in **10**. The sum of the site occupation factors of the major and minor components were constrained to be 1. Further details on data collection and refinement are summarised in Table 2. CCDC-843008, -843009, -843010, -843011, and -843012 for complexes **6**, **7**, **8a**, **8b**, and **10**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596–609; b) M. Albrecht, *Chem. Commun.* **2008**, 3601–3610; c) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; d) M. Melami, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.

[2] a) D. Bacciu, K. J. Cavell, I. A. Fallis, L. Ooi, *Angew. Chem.* **2005**, *117*, 5416; *Angew. Chem. Int. Ed.* **2005**, *44*, 5282–5284; b) M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Angew. Chem.* **2007**, *119*, 6409; *Angew. Chem. Int. Ed.* **2007**, *46*, 6293–6296; c) A. Krüger, M. Albrecht, in *N-heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools* (Ed.: S. Diez-Gonzalez), RSC, Cambridge, UK, **2011**, pp. 134–165.

[3] a) G. Sini, O. Eisenstein, R. H. Crabtree, *Inorg. Chem.* **2002**, *41*, 602–604; b) R. Tonner, G. Heydenrych, G. Frenking, *Chem. Asian J.* **2007**, *2*, 1555–1567; c) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556–559; d) G. Ung, G. Bertrand, *Chem. Eur. J.* **2011**, *17*, 8269.

[4] a) P. Mathew, A. Neels, M. Albrecht, *J. Am. Chem. Soc.* **2008**, *130*, 13534–13535; b) M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Dalton Trans.* **2008**, 6242–6249.

[5] a) A. R. Chianese, B. M. Zeglis, R. H. Crabtree, *Chem. Commun.* **2004**, 2176–2177; b) A. Prades, M. Viciano, M. Sanau, E. Peris, *Organometallics* **2008**, *27*, 4354–4259.

[6] In some cases, steric constraints enforce an abnormal coordination mode of imidazolylidenes; for examples, see: a) X. Hu, I. Castro-Rodriguez, K. Meyer, *Organometallics* **2003**, *22*, 3016–3018; b) A. A. Danopoulos, N. Tsoureas, J. A. Wright, M. E. Light, *Organometallics* **2004**, *23*, 166–168; c) N. Stylianides, A. A. Danopoulos, N. Tsoureas, *J. Organomet. Chem.* **2005**, *690*, 5948–5958; d) C. E. Ellul, M. F. Mahon, O. Saker, M. K. Whittlesey, *Angew. Chem.* **2007**, *119*, 6459; *Angew. Chem. Int. Ed.* **2007**, *46*, 6343–6345; e) C. E. Cooke, M. C. Jennings, R. K. Pomeroy, J. A. Clyburne, *Organometallics* **2007**, *26*, 6059–6062.

[7] P. J. Fraser, W. R. Roper, R. G. A. Stone, A. Gordon, *J. Chem. Soc., Dalton Trans.* **1974**, 760–764.

[8] a) O. Guerret, S. Sole, H. Gornitzka, M. Teichert, G. Trinquier, G. Bertrand, *J. Am. Chem. Soc.* **1997**, *119*, 6668–6669; b) O. Guerret, S. Sole, H. Gornitzka, G. Trinquier, G. Bertrand, *J. Organomet. Chem.* **2000**, *600*, 112–117; c) E. Mas-Marza, J. A. Mata, E. Peris, *Angew. Chem.* **2007**, *119*, 3803; *Angew. Chem. Int. Ed.* **2007**, *46*, 3729–3731; d) A. Zanardi, R. Coberan, J. A. Mata, E. Peris, *Organometallics* **2008**, *27*, 3570–3576; e) A. Zanardi, J. A. Mata, E. Peris, *Organometallics* **2009**, *28*, 4335–4339.

[9] a) P. L. Arnold, S. T. Liddle, *Organometallics* **2006**, *25*, 1485–1491; b) U. J. Scheele, S. Dechert, F. Meyer, *Chem. Eur. J.* **2008**, *14*, 5112–5115; c) D. Mendoza-Espinosa, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2010**, *132*, 7264–7265; d) R. S. Ghadwal, H. W. Roesky, M. Granitzka, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 10018–10020; e) Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2010**, *132*, 14370–14372.

[10] A. Zanardi, J. A. Mata, E. Peris, *J. Am. Chem. Soc.* **2009**, *131*, 14531–14537.

[11] E. Kluser, A. Neels, M. Albrecht, *Chem. Commun.* **2006**, 4495–4497.

[12] a) H. Pauly, E. Arauner, *J. Prakt. Chem.* **1928**, *118*, 33–47; b) H. B. Bensusan, M. S. R. Naidu, *Biochemistry* **1967**, *6*, 12–15; c) K. J. Brunings, *J. Am. Chem. Soc.* **1947**, *69*, 205–208.

[13] A. A. Gridnev, I. M. Mihaltseva, *Synth. Commun.* **1994**, *24*, 1547–1555.

[14] A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz, G. Eastham, *J. Chem. Soc., Dalton Trans.* **2000**, 4499–4506.

[15] Halide scrambling in carbene–metal complexes has precedents; see, for example: C.-C. Ho, S. Chatterjee, T.-L. Wu, K.-T. Chan, Y.-W. Chang, T.-H. Hsiao, H. M. Lee, *Organometallics* **2009**, *28*, 2837–2847.

[16] a) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, *Chem. Commun.* **2000**, 1247–1248; b) A. A. D. Tulloch, S. Winston, A. A. Danopoulos, G. Eastham, M. B. Hursthouse, *Dalton Trans.* **2003**, 699–708.

[17] A crystal structure determination of **8a** revealed a 100% occupancy of the iodide position, yet the site of the chloride is partially occupied by iodide (34%), presumably due to partial halide metathesis with unreacted ligand precursor imidazolium salt. See CCDC-843010 for crystal structure determination, refinement and further crystallographic details.

[18] a) R. F. Hartley, *Chem. Soc. Rev.* **1973**, *2*, 163–179; b) the stronger *trans* influence of the NHC vs. $SR_2$ is demonstrated by the different Pd–I bond lengths in **8b**: Pd–I1 2.6350(5) Å *trans* to $SR_2$, and Pd–I2 2.6962(5) Å *trans* to NHC.

[19] a) A. Poulain, M. Iglesias, M. Albrecht, *Curr. Org. Chem.* **2011**, *15*, 3325–3336; b) M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers, M. Albrecht, *Chem. Eur. J.* **2009**, *15*, 9375–9386.

[20] a) V. J. Catalano, A. O. Etogo, *Inorg. Chem.* **2007**, *46*, 5608–5615; b) P. L. Chiu, C. L. Lai, C. F. Chang, C. H. Hu, H. M. Lee, *Organometallics* **2005**, *24*, 6169–6178; c) S. Ahrens, A. Zeller, M. Taige, T. Strassner, *Organometallics* **2006**, *25*, 5409–

  

5415; d) T. Scherg, S. K. Schneider, G. D. Frey, J. Schwarz, E. Herdtweck, W. A. Herrmann, *Synlett* **2006**, 2894–2907; e) H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Lin, P. L. Chiu, P. Y. Chen, *Tetrahedron* **2004**, *60*, 5807–5825.

[21] The abnormal NHC ligand may formally be divided into a positively charged amidinium component and an anionic vinylic unit: a) A. Krüger, M. Albrecht, *Aust. J. Chem.* **2011**, *64*, 1113–1117; b) A. Krüger, L. J. L. Häller, H. Müller-Bunz, O. Serada, A. Neels, S. A. Macgregor, M. Albrecht, *Dalton Trans.* **2011**, *40*, 9911–9920.

[22] The site occupancy factor of the atoms has been taken into account in the calculation of the sum of the van der Waals radii.

[23] S.-T. Liu, C.-I. Lee, C.-F. Fu, C.-H. Chen, Y.-H. Liu, C. Elsevier, S.-M. Peng, J.-T. Chen, *Organometallics* **2009**, *28*, 6957–6962.

[24] Assignment of the $^1$H NMR signals of **5** has been revised: $^1$H NMR ([D$_6$]DMSO, 500 MHz): $\delta$ = 9.25 (br., 1 H, H$_{py}$), 8.97 (s, 1 H, H$_{imi}$), 8.14 (m, 1 H, H$_{py}$), 7.79 (m, 1 H, H$_{py}$), 7.61 (m, 1 H, H$_{py}$), 7.15 (s, 1 H, H$_{imi}$), 5.58 (s, 2 H, NCH$_2$), 4.51 (sept, $^3J_{H,H}$ = 6.4 Hz, 1 H, CHMe$_2$), 1.39 [d, $^3J_{H,H}$ = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm.

[25] a) L. Yang, A. Krüger, A. Neels, M. Albrecht, *Organometallics* **2008**, *27*, 3161–6171; b) A. Krüger, A. Neels, M. Albrecht, *Chem. Commun.* **2010**, *46*, 315–317; c) G. Buscemi, M. Basato, A. Biffis, A. Gennaro, A. A. Isse, M. M. Natile, C. Tubaro, *J. Organomet. Chem.* **2010**, *695*, 2359–2365.

[26] A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617–618*, 546–560.

[27] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975.

[28] W. A. Herrmann, C.-P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93–96.

[29] S. T. Handy, M. Okello, *J. Org. Chem.* **2005**, *70*, 1915–1918.

[30] H. S. Sahoo, D. K. Chand, S. Mahalakshmi, H. Mir, R. Raghunathan, *Tetrahedron Lett.* **2007**, *48*, 761–765.

[31] *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

[32] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

[33] R. C. Clark, J. S. Reid, *Acta Crystallogr., Sect. A* **1995**, *51*, 887–897.

[34] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

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