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Chelating C4-bound Imidazolylidene Complexes via Oxidative Addition of Imidazolium Salts to Palladium(0)

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Keywords: N-heterocyclic carbene / palladium / abnormal bonding / oxidative addition / chelation

Oxidative addition of donor-functionalised 4-iodoimidazolium salts to palladium(0) provides a selective route for the preparation of chelating abnormal N-heterocylic carbene complexes and enables the introduction of a variety of donor groups. The activation of the C4 position does not necessitate the imidazolium C2 position to be protected, 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, sequential metallation of first the C2 position via transmetallation followed by C4–I oxidative addition afforded a dimetallic complex comprising two palladium centres bridged by a single NHC ligand.

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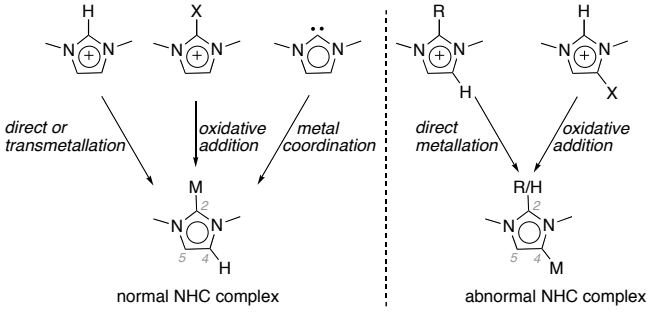
Introduction

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] Transmetallation via a silver carbene complex 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 towards the synthesis of normal NHC complexes.[7] 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 through metallation via C2–H activation. While dimetallic triazol-diylidene complexes have been explored in depth,[8] related 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 comprise two different metals, provide interesting opportunities for catalysing tandem processes.[10]



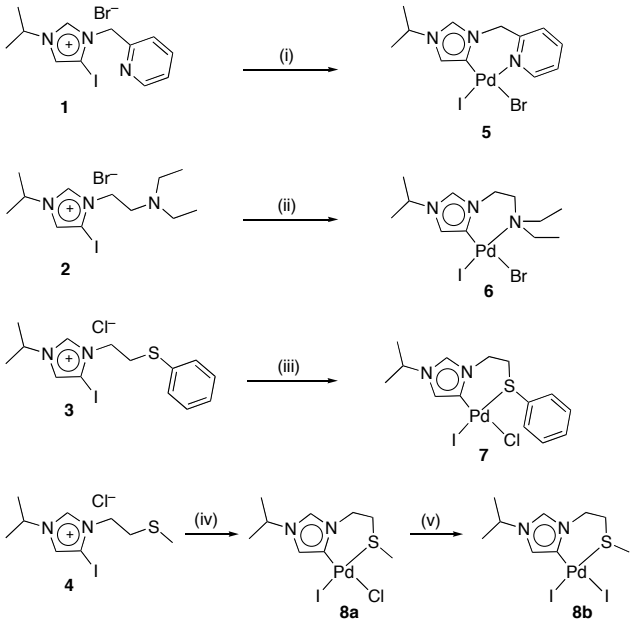
Scheme 1. Typical synthetic pathways to normal and abnormal imidazolylidene complexes.

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 E as wingtip substituents, ranging from 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 heterobimetallic 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 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 conceivable isomers, i.e. 4-iodo- and 5-iodo-*N*-ethylimidazole. 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-quarternisation 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 (RT), 12 h; (ii) $Pd(dba)_2$, CH_2Cl_2 (0 °C to RT), 2 d; (iii) $Pd(dba)_2$, DMSO (RT), 2 d; (iv) $Pd(dba)_2$, DMSO, (RT), 12 h; (v) NaI, acetone (RT), 16 h.

Oxidative addition of the imidazolium salts **1**–**4** to the palladium(0) metal centre in $Pd(dba)_2$ yielded abnormal NHC palladium(II) complexes **5**–**8** in unoptimized 18–60% yield (Scheme 2). The syntheses were carried out under inert conditions at room temperature in CH_2Cl_2 or DMSO as solvent, 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 Fig. 1. In all three structures the palladium centre resides in a slightly distorted square-planar environment comprising the *C,E*-bidentate carbene ligand and two halides. The halides in the structures of **6** and **7** were scrambled and their occupancy 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 features a mutual *trans* arrangement of the NHC and iodide 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* also 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 comprising two sp^3-hybridised carbons. The imidazolylidene ring in **6**, **7**, and **8b** is furthermore twisted out of the metal coordination plane by roughly 30º, 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]

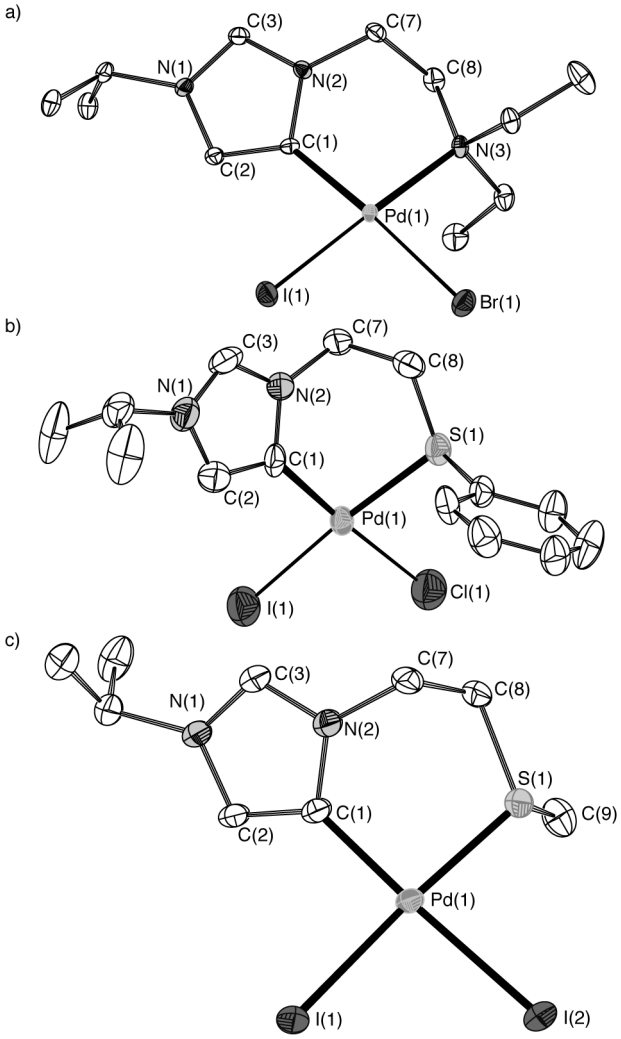


Figure 1. ORTEP representation of **6** (a), **7** (b), and **8b** (c). All thermal ellipsoids drawn at 50% probability level, hydrogen atoms and co-crystallised solvent molecules omitted for clarity.

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)

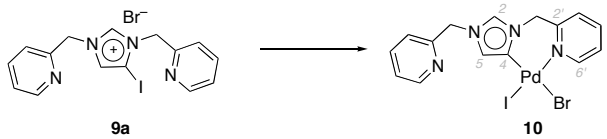
[a] data for complex **5** from reference [11]. [b] E = N(3). [c] E = S(1).

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, while in **8b**, halide scrambling is irrelevant.[17] The Pd–I(1) bond length in **8b** (2.6350(5) Å) is significantly longer than the corresponding bond length in **5** (2.5179 Å), indicating a stronger *trans* influence of the soft S(alkyl) ligand in **8b** compared to the pyridyl ligand in **5**.[18] In addition, the less pronounced puckering of the ligand in **8b** may induce steric repulsion between the *i*Pr group and the iodide 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 does not differ from related complexes featuring a normal C2 bonding mode of the NHC ligand.[15,16,20] The Pd–$C_{carbene}$ bond length 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 a vinyl-type bonding of the C4–bound carbene ligand.[21] In normal NHC complexes the C–C bond 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 *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 *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 in *cis* position in complex **5**.[11] Such short contacts between the pyridyl C6–H and halide in *cis* position have also been reported in related normal NHC complexes.[23]

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. Palladation furthermore induced an upfield shift of the C2–H and C5–H protons (to δ_H ~8.3 and δ_H ~7.2 respectively) in all complexes.[24] In DMSO–D_6 these signals appear broad in both the ^{1}H 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 sulphur 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 a 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 ^{1}H 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 lowfield resonance of the C2-bound proton, which appears at 8.90 for the major species and at 8.84 ppm for the minor one. In the 13C NMR spectrum, all resonances are broadended 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 an 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 a fluxional behaviour of the six-membered metallacycle cannot be excluded, it is worth noting that the sulfide complexes **7** and **8** display a single set of resonances, despite the chirality at sulfur.

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 bromomethylpyridine following a known procedure.[26] Subsequent oxidative addition to $Pd(dba)_2$ afforded complex **10** as an air- and moisture-stable solid in 60% yield.



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

The structure of **10** was unambiguously confirmed by X-ray crystallography (Figure 2), which revealed the expected distorted square-planar coordination geometry around palladium and *C*,*N*-bidentate chelation of the ligand. Similar to **5**, the bicyclic ligand assumed 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 approximate 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.

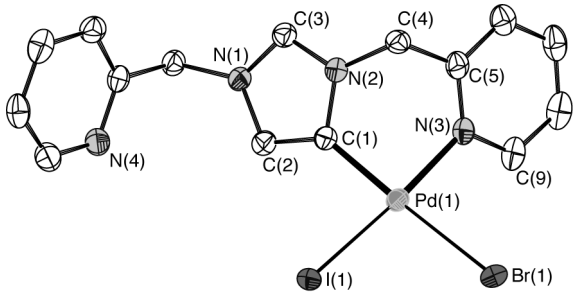
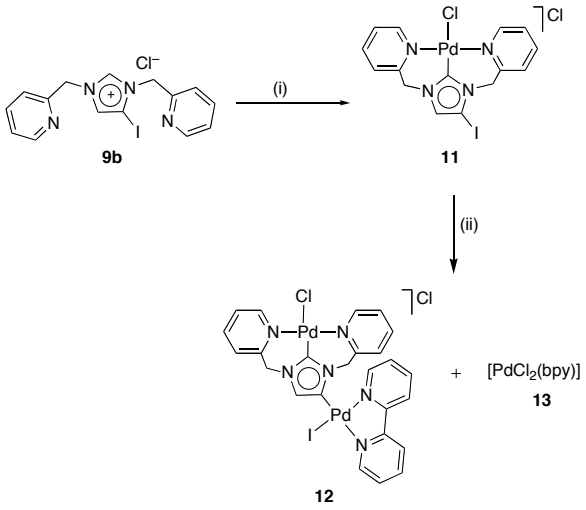


Figure 2. ORTEP representation of **10** (50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angle (°): Pd(1)–C(1) 1.976(4), Pd(1)–N(3) 2.080(3), C(1)–C(2) 1.363(5), C(1)–Pd(1)–N(3) 86.76(14).

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 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 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 δ_H 8.89, which suggests 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 in **7** 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 reaction 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 δ_H 7.82. No broadening of the imidazolylidene signals was observed in the ^{13}C NMR spectrum and the carbene carbon resonance was noted at δ_C 151.3. 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 of the two singlets in the ^1H NMR spectrum.



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

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** has precluded its isolation in pure form thus far, NMR spectra of the crude reaction mixture were instructive. Metallation of the C4 position of **11** led to a upfield shift of the C5-bound hydrogen from δ_H 7.82 to δ_H 7.06. The NCH_2 signals appeared as two sets of AB doublets at δ_H 5.94 and 5.87 ($^2J_{HH}$ = 15.4 Hz) and at δ_H 5.73 and 5.66 ($^2J_{HH}$ = 15.3 Hz). Two-dimensional 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 dissymmetric 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 to the corresponding shifts in **11**.

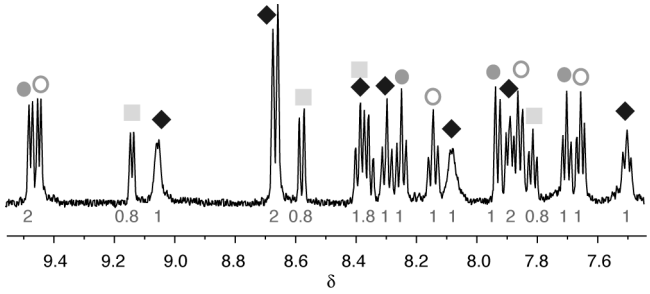


Figure 3. Section of the 500 MHz ^1H NMR spectrum of the crude reaction mixture (DMSO–D_6 solution) showing **12** and **13** in a 1:0.4 ratio (●,○ py signals and ◆ bpy signals of **12,** ■ bpy signals of **13**).

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*-isopropyl)-imidazole, 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 on 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 (δ 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*-isopropyl)imidazole (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 days. The colour of the reaction mixture changed from colourless to yellow. After cooling to r.t. the solvent was removed *in vacuo* and the residue was redissolved in CH_2Cl_2 (100 mL) and filtered over 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). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 9.32 (d, 1H, $^4J_{HH}$ = 1.6 Hz, H_{imi}), 8.13 (d, 1H, $^4J_{HH}$ = 1.6 Hz, H_{imi}), 4.66 (septet, 1H, $^3J_{HH}$ = 6.7 Hz, $CHMe_2$), 4.11 (t, 2H, $^3J_{HH}$ = 6.0 Hz, NCH_2CH_2N), 2.69 (t, 2H, $^3J_{HH}$ = 6.0 Hz, NCH_2CH_2N), 2.45 (q, 4H, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_3), 1.46 (d, 6H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$), 0.83 (t, 6H, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_3). ^{13}C{^{1}H} NMR (DMSO–D_6, 125 MHz): δ 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). Anal. calc. for $C_{12}H_{23}BrIN_3$ × 0.5 H_2O (425.15): 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*-isopropyl)imidazole (0.24 g, 1.0 mmol) and 2-chloroethyl(phenyl) sulphide (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). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 9.45 (d, 1H, $^4J_{HH}$ = 1.6 Hz, H_{imi}), 8.03 (d, 1H, $^4J_{HH}$ = 1.6 Hz, H_{imi}), 7.39–7.33 (m, 4H, H_{aryl}), 7.26–7.21 (m, 1H, H_{aryl}), 4.56 (septet, 1H, $^3J_{HH}$ = 6.7 Hz, $CHMe_2$), 4.32 (t, 2H, $^3J_{HH}$ = 6.6 Hz, NCH_2CH_2N), 3.50 (t, 2H, $^3J_{HH}$ = 6.6 Hz, NCH_2CH_2N), 1.41 (d, 6H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (DMSO–D_6, 125 MHz): δ 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 ($CH(CH_3)_2$). Anal. calc. for $C_{14}H_{18}ClIN_2S$ × H_2O (426.74): 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*-isopropyl)imidazole (0.24 g, 1.0 mmol) and 2-chloroethyl(methyl) sulphide (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 r.t. and Et_2O (5 mL) was added upon which a white precipitate immediately formed. The mixture was stirred for 10 minutes 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). ^{1}H NMR ($CDCl_3$, 360 MHz): δ 10.88 (s, 1H, H_{imi}), 7.44 (s, 1H, H_{imi}), 4.82 (septet, 1H, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 4.58 (t, 2H, $^3J_{HH}$ = 6.4 Hz, NCH_2CH_2N), 2.98 (t, 2H, $^3J_{HH}$ = 6.4 Hz, NCH_2CH_2N), 2.28 (s, 3H, SMe), 1.63 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 90 MHz): δ 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). Anal. calc. for $C_9H_{16}ClIN_2S$ (346.66): 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 r.t. and stirred for 2 days. A yellow precipitate gradually formed. The reaction mixture was concentrated to 7 mL and filtered over Celite. The residue was washed with CH_2Cl_2 and subsequently extracted with MeCN. The combined MeCN fractions were evaporated and the residue was triturated with Et_2O and dried *in vacuo* to yield **6** as a yellow solid (38 mg, 18% yield). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 8.90 (s, 1H, H_{imi}), 7.13 (s, 1H, H_{imi}), 4.49 (septet, 1H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 4.27 (br, 2H, NCH_2), 3.3, 3.0 (br, 4H, NCH_2CH_3), 2.8 (br, 2H, NCH_2), 1.40 (d, 6H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$), 1.4 (br, 6H, NCH_2CH_3). ^{13}C{^{1}H} NMR (DMSO–D_6, 125 MHz): δ 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), carbene carbon not resolved. HR-MS (ESI$^+$): Calc. for $C_{12}H_{23}IN_3Pd$ ([M – Br]$^+$): 441.9971. Found: 441.9990. Anal. calc. for $C_{12}H_{23}BrIN_3Pd$ (522.56) × 0.25 Et_2O: 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 for 2 days at r.t.. The reaction mixture was filtered over Celite and the filtrate was added to a 1:1 mixture of Et_2O and 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). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 8.89 (s, 1H, H_{imi}), 8.1–7.7 (m, 2H, H_{aryl}), 7.55–7.40 (m, 3H, H_{aryl}), 7.3 (br, 1H, H_{imi}), 4.52 (septet, 1H, $^3J_{HH}$ = 6.7 Hz, $CHMe_2$), 4.3 (br, 2H, NCH_2), 3.2 (br, 2H, SCH_2), 1.42 (d, 6H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (DMSO–D_6, 125 MHz): δ 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 ($CH(CH_3)_2$), carbene carbon and quartenary C_{aryl} not resolved. Anal. calc. for $C_{14}H_{18}ClIN_2PdS$ (515.15): 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 r.t. for 1 day. The solution was filtered over 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). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 8.86 (s, 1H, H_{imi}), 7.3 (br, 1H, H_{imi}), 4.51 (septet, 1H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 4.4 (br, 2H, NCH_2), 2.8 (br, 2H, SCH_2), 2.70 (s, 3H, SMe), 1.42 (d, 6H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (DMSO–D_6, 125 MHz): δ 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). Anal. calc. for $C_9H_{16}ClIN_2PdS$ (453.08): 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 r.t. for 16 h. The solvent was removed *in vacuo* and the residue redissolved in hot MeCN (20 mL) and filtered. Cooling the filtrate to –30 °C yielded orange crystals of **8b** (38 mg, 39% yield). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 8.86 (s, 1H, H_{imi}), 7.4 (br, 1H, H_{imi}), 4.50 (septet, 1H, $^3J_{HH}$ = 6.7 Hz, $CHMe_2$), 4.4 (br, 2H, NCH_2), 2.8 (br, 2H, SCH_2), 2.77 (s, 3H, SMe), 1.41 (d, 6H, $^3J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (DMSO–D_6, 125 MHz): δ 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 ($CH(CH_3)_2$, carbene carbon not resolved. Anal. calc. for $C_9H_{16}I_2N_2PdS$ (544.53): 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 refluxed for 3 days. The colour of the reaction mixture turned from colourless to pink within a few minutes. At r.t. the reaction mixture was filtered and washed with EtOH. 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). ^{1}H NMR (DMSO–D_6, 500 MHz): δ 9.59 (d, 1H, $^4J_{HH}$ = 1.4 Hz, H_{imi}), 8.59 (d, 1H, $^3J_{HH}$ = 4.8 Hz, H_{py}), 8.53 (d, 1H, $^3J_{HH}$ = 4.8 Hz, H_{py}), 8.05 (d, 1H, $^4J_{HH}$ = 1.4 Hz, H_{imi}), 7.94–7.87 (m, 2H, H_{py}), 7.53–7.47 (m, 2H, H_{py}), 7.45–7.37 (m, 2H, H_{py}), 5.64 (s, 2H, NCH_2), 5.61 (s, 2H, NCH_2). ^{13}C{^{1}H} NMR (DMSO–D_6, 125 MHz): δ 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). Anal. calc. for $C_{15}H_{14}BrIN_4$ (457.11): 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 over 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). ^{1}H NMR (CD_3OD, 600 MHz): δ 9.54 (d, 1H, $^4J_{HH}$ = 1.3 Hz, H_{imi}), 8.58 (d, 1H, $^3J_{HH}$ = 4.6 Hz, H_{py}), 8.52 (d, 1H, $^3J_{HH}$ = 4.6 Hz, H_{py}), 7.91–7.86 (m, 3H, H_{imi}, H_{py}), 7.59 (d, 1H, $^3J_{HH}$ = 7.8 Hz, H_{py}), 7.52 (d, 1H, $^3J_{HH}$ = 7.8 Hz, H_{py}), 7.45–7.37 (m, 2H, H_{py}), 5.65 (s, 2H, NCH_2), 5.62 (s, 2H, NCH_2). $^{13}C\{^1H\}$ NMR (DMSO–D_6, 125 MHz): δ 154.0, 153.6 (2 × C_{py}), 151.0, 150.9 (2 × C_{py}), 141.4 (t, $^1J_{DC}$ = 32.8, 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_{imi}), 55.7, 55.2 (NCH_2). Anal. calc. for $C_{15}H_{14}ClIN_4$ (412.66): 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) were stirred at r.t. for 5 days. A yellow precipitate gradually formed. The reaction mixture was filtered over 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 (DMSO–D_6, 500 MHz): δ 9.02 (s, 1H, H_{imi}), 8.9 (br, 1H, H_{py}), 8.56–8.50 (m, 1H, H_{py}), 8.20–8.08 (m, 1H, H_{py}) 7.88–7.81 (m, 1H, H_{py}), 7.81–7.74 (m, 1H, H_{py}), 7.66–7.56 (m, 1H, H_{py}), 7.47–7.41 (m, 1H, H_{py}), 7.40–7.33 (m, 1H, H_{py}), 7.13 (s, 1H, H_{imi}), 5.65 (s, 2H, NCH_2), 5.42 (s, 2H, NCH_2). $^{13}C\{^1H\}$ NMR (DMSO–D_6, 125 MHz): δ 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), carbene carbon and pyridyl C6 not resolved. Anal. calc. for $C_{15}H_{14}BrIN_4Pd$ × 0.5 DMSO (602.59): 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 r.t. for 4 days 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 and 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 over Celite and the filtrate was concentrated *in vacuo*. The concentrated solution was added to a 1:1 mixture of Et_2O and 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 (DMSO–D_6, 600 MHz): δ 9.41–9.38 (m, 2H, H_{py}), 8.27–8.22 (m, 2H, H_{py}), 8.14 (d, 1H, $^3J_{HH}$ = 7.6 Hz, H_{py}) 7.89 (d, 1H, $^3J_{HH}$ = 7.0 Hz, H_{py}), 7.82 (s, 1H, H_{imi}), 7.73–7.68 (m, 2H, H_{py}), 5.71 (s, 2H, NCH_2), 5.61 (s, 2H, NCH_2). $^{13}C\{^1H\}$ NMR (DMSO–D_6, 150 MHz): δ 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). HR-MS (ESI^+): Calc. for $C_{15}H_{13}IN_4Pd$ ($[M - Cl]^+$): 516.8908. Found: 516.8906. Anal. calc. for $C_{15}H_{13}Cl_2IN_4Pd$ (553.52) × $CHCl_3$: 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) were stirred in DMSO (2 mL) at r.t. for 1 day. The reaction mixture was filtered over Celite and the filtrate was added to a 1:1 mixture of CH_2Cl_2 and Et_2O (20 mL). The formed precipitate was isolated by centrifugation, dried *in vacuo*. The light yellow crude product contained **12** and **13** in 2.5:1 molar ratio (20 mg). ^{1}H NMR (DMSO–D_6, 600 MHz): δ 9.48 (d, 1H, $^3J_{HH}$ = 5.8 Hz, H_{py}^A), 9.45 (d, 1H, $^3J_{HH}$ = 5.7 Hz H_{py}^B), 9.1 (br, 1H, H_{bpy}), 8.69–8.63 (m, 2H, H_{bpy}), 8.42–8.37 (m, 1H, H_{bpy}), 8.33–8.27 (m, 1H, H_{bpy}), 8.27–8.22 (m, 1H, H_{py}^A), 8.17–8.12 (m, 1H, H_{py}^B), 8.1 (br, 1H, H_{bpy}), 7.93 (d, 1H, $^3J_{HH}$ = 7.6 Hz, H_{py}^A), 7.91–7.87 (m, 1H, H_{bpy}), 7.86 (d, 1H, $^3J_{HH}$ = 7.6 Hz, H_{py}^B), 7.73–7.63 (m, 1H, H_{py}^A), 7.68–7.63 (m, 1H, H_{py}^B), 7.53–7.47 (m, 1H, H_{bpy}), 7.06 (s, 1H, H_{imi}), 5.94 (d, 1H, $^2J_{HH}$ = 15.4 Hz, NC*H*H^A), 5.87 (d, 1H, $^2J_{HH}$ = 15.4 Hz, NCH*H*^{A}), 5.73 (d, 1H, $^2J_{HH}$ = 15.3 Hz, NC*H*H^B), 5.66 (d, 1H, $^2J_{HH}$ = 15.3 Hz, NCH*H*^{B}); A and B denote the two picoline residues in **12**. HR-MS (ESI^+): Calc. 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–Kα radiation, λ = 0.71073 Å), on an Agilent SuperNova A diffractometer (**7** and **10**) with a mirror-monochromator (Cu–Kα radiation, λ = 1.54184 Å), or on a Stoe Mark II-Image Plate Diffraction System (**8b**) with a graphite-monochromator (Mo–Kα radiation, λ = 0.71073 Å). A semi-empirical absorption correction was applied for **6** using SADABS[31] and for **8b** using MULscanABS as implemented in PLATON.[32] An analytical numeric absorption correction 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 using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically.

Crystals of complex **6** contained one DMSO per complex molecule. Crystals of **8b** contained one disordered DMSO 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

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
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	$C_{15}H_{14}BrIN_4Pd$
Fw	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–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)
α	90	90	90	91.309(1)
β	105.135(1)	96.279(4)	105.579(9)	92.488(1)
γ	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_{calc}/g cm^{-3}	2.000	2.057	2.224	2.239
μ /mm^{-1}	4.590	26.146	4.539	26.255
total refl	47788	8851	23384	23746
unique refl	6618	2378	5028	3462
R_{int}	0.0315	0.0415	0.0615	0.0624
transm rng	0.587–0.327	0.461–0.703	0.406–0.201	0.507–0.056
params restr	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] $wR_2 = [\Sigma w(F_O^2 - F_C^2)^2/\Sigma(w(F_O^4))]^{1/2}$.

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. Crystallographic data (excluding structure factors) have been deposited with the CambridgeCrystallographic Centre as supplementary publication nos. CCDC 843008–843012. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see footnote on the first page of this article): CIF files for complexes **6**, **7**, **8a**, **8b**, and **10**.

Acknowledgments

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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. Int. Ed.* **2005**, *44*, 5282–5284; b) M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *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. 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. 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 the supporting information 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 (DMSO–D_6, 500 MHz): δ 9.25 (br, 1H, H_{py}), 8.97 (s, 1H, H_{imi}), 8.14 (m, 1H, H_{py}), 7.79 (m, 1H, H_{py}), 7.61 (m, 1H, H_{py}), 7.15 (s, 1H, H_{imi}), 5.58 (s, 2H, NCH_2), 4.51 (septet, 1H, $^3J_{HH}$ = 6.4 Hz, $CHMe_2$), 1.39 (d, 6H, $^3J_{HH}$ = 6.4 Hz, $CH(CH_3)_2$).

[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 (2001), Program SADABS, Bruker AXS Inc., Madison, Wisconsin, USA.

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

[33] R. C. Clark, J. S. Reid, *Acta Cryst*. **1995**, *A51*, 887–897.

[34] G. M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112–122.

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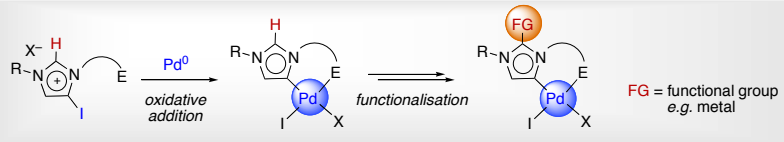
Entry for the Table of Contents



Oxidative addition of 4-iodoimidazolium salts to low-valent palladium(0) provides access to abnormal NHC palladium complexes without requiring the C2 position to be protected. Hence this site is available for further functionalisation, which allows for example dimetallic complexes to be prepared.

Anneke Krüger, Evelyne Kluser, Helge Müller-Bunz, Antonia Neels, Martin Albrecht* ……... Page No. – Page No.

Chelating C4-bound Imidazolylidene Complexes via Oxidative Addition of Imidazolium Salts to Palladium(0)

Keywords: N-heterocyclic carbene / palladium / abnormal bonding / oxidative addition / chelation

Dear Editors,

Many thanks for considering our manuscript favourably for publication in Eur. J. Inorg. Chem. Please find attached a revised version that we have amended according to the useful suggestions of the reviewers as follows:

Reviewer 1:
General: High-resolution MS data have been included for the characterization of complex 12 in the results section and in the experimental part (reviewer 1, general).
1/ The sequence of *trans* influence has been changed (bottom page 2) though we note from a Pd-I bond comparison in complex 8b that the sequence is NHC > SR_2 rather than the suggested SR_2 > NHC. This comparison has been added to reference 18 (reviewer 1.1)
2/ and 3/ We have added a phrase to the NMR spectral discussion on p. 3 to illustrate a potential interplay between conformational rigidity and hydrogen bonding. The discussion has been slightly expanded, treating the two sets of resonances more explicitly and indicating that conformational rigidity of the metallacycle would lead to two diastereomers for complexes 7 and 8, which is not supported.
4/ An atom numbering scheme has been introduced for complex 10 to avoid ambiguities with respect to crystallographic vs chemical atom labeling (Scheme 3).
5/ and 6/ The NMR discussion has been corrected, we thank the reviewer for the careful reading.
7/ We agree with the reviewer and have made the statement in the conlusions less pretentious.
8/ No optimization of yields has been attempted, and we have added this fact when discussing the synthesis of the complexes (below Scheme 2).
9/ Low imidazolium salt yields partially arise from careful purification (some yields are given after crystallization, substantial amounts of product presumably remained in the mother liquor).
10/ Some of the solvents in the microanalyses stem from the hygroscopic nature of the compounds (imidazolium salts), some from recrystallization ($CHCl_3$). As yields of complexes were determined before recrystallization, and further syntheses were carried from the crude material, we have not included the solvents of recrystallization for calculating yields and molar quantities.
11/ Yields in % have been removed from the experiemental section of complex 12, and only overall weight yields together with the observed molar ratio of the compounds are given.
12/ and 13/ Multiplets in ^{1}H NMR spectra are now given consistently as ranges, and weights and molar quantities are given with equal numbers of relevant digits (complexes 6, 10, and 11).
14/ and 15/ The numbers have been corrected, many thanks to the reviewer for the meticulous reading and our apologies for our lack of diligence in the submitted version.
16/ The carbene resonance has been assigned; it is in agreement with that of previous abnormal carbene palladium complexes (refs 2b, 4b).
17/ As we do not discuss the structure of 8a in any depth, we think it would be strange to report 5 structures in the experimental section. Instead, we have expanded footnote 17 to refer also to the supporting information, and we have repeated this footnote at the beginning of the structure determination paragraph in the experimental section.

Reviewer 2: References 1 and 3 have been expanded to include Bertrand's work.

Reviewer 3 is thanked for his encouraging comments.

Editor: Figure 3 is now produced in black/white mode (Editors).

We hope the manuscript with these revisions is now acceptable and we look forward to hearing from you,
With kind regards,

Martin

PS: The manuscript has been submitted for the EuCOMC special issue. If this issue is scheduled to appear in 2012, we wish to dedicate this article to Guy Bertrand (a line has been inserted). Please advise if the issue is scheduled to appear this year.