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Pyridine functionalised N-heterocyclic carbene complexes of palladium

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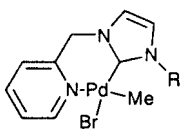
The pyridine functionalised N-heterocyclic carbene complexes (C–N)PdMeBr, C–N = 3-R-1-(2-picolyl)imidazolin-2-ylidene, (R = Bu^t 1a, R = mes 1b, mes = mesityl) are described; they are excellent catalysts for the Heck arylation; 1b is monomeric with a chelating C–N ligand; the product obtained by interaction of 1a with AgO_2CCF_3 shows a $[Pd(C–N)]_4$ framework with bridging C–N ligands.

N-heterocyclic carbenes have recently emerged as a new family of ligands with electronic characteristics similar to those of the phosphines.[1] The great interest in their complexes with transition metals has been stimulated by the realisation that they can act as catalysts or catalyst precursors to important transformations, such as Pd-catalysed Heck and Suzuki couplings, CO–ethylene copolymerisations, Ru-catalysed olefin metathesis and Rh catalysed hydrosilylations.[2] Furthermore, electronic and steric optimisation of the catalytic site should be achievable *via* ligand design. Recent reports on the synthesis of functionalised hemilabile N-heterocyclic carbene complexes[3,4] and their use as catalyst precursors prompted us to communicate our results describing the full characterisation of three novel pyridine functionalised N-heterocyclic carbene complexes of palladium, including two crystal structures and preliminary studies on their catalytic activities in Heck coupling and amination reactions.

The complexes (C–N)PdMeBr, C–N = 3-R-1-(2-picolyl)-imidazolin-2-ylidene, (R = Bu^t **1a**, R = mes **1b**, Scheme 1) were prepared in good yields by careful deprotonation at low temperatures of 3-R-1-(2-picolyl)imidazolium bromide, [H(C–N)] Br, (R = Bu^t, mes), with $LiNPr^i_2$ in THF, followed by trapping of the *in situ* formed carbene with (cod)PdMeBr. Complexes **1a**,**b** are air-stable solids and **1b** can be crystallised from CH_2Cl_2 by slow evaporation.† The structure of **1b** was determined by X-ray crystallography and is shown in Fig. 1.‡ The chelating ligand is coordinated to the square planar palladium centre with the carbene end disposed *trans* to the bromide. The carbene plane forms an angle of 64.2° with the square plane of the palladium. The resulting six-membered ring is puckered to release conformational strain.



R=Bu^t, **1a**; R=mes, **1b**

Scheme 1

Abstraction of the halide from **1a** by $Ag(O_2CCF_3)$ in acetonitrile results in isolation of complex **2**† the structure of which is shown in Fig. 2.‡ In this case the C–N ligand is bridging with carbene and pyridine ends occupying mutually *trans* positions. The four Pd atoms occupy the corners of a distorted tetrahedron and the ligands bridge four of the six sides in a way which leaves two opposite sites free.

Compounds analogous to **1** (R = Me) have recently been reported by McGuinness and Cavell,[4] however, they could not obtain crystallographic data. In the absence of such data for comparison, we note with interest that there are several other aspects of their paper, which point towards important differences between their complexes and the ones reported herein. Mention is made of the unselective reaction of bases with the precursor imidazolium salts, which precludes the use of the simple synthetic technique employed by us to synthesise the palladium complexes. They also note that their complexes once formed are unstable towards strong bases,which limits their use in amination catalysis. Both problems are believed to arise from

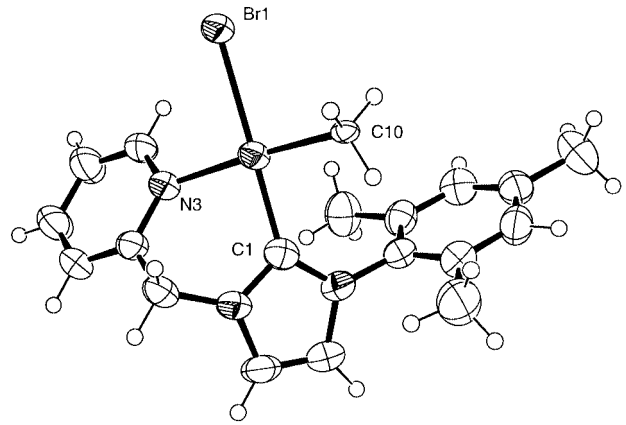


Fig. 1 Molecular structure of **1b**. Selected bond lengths (Å) and angles (°): Pd1–C1 1.964(4), Pd1–C10, 2.147(3), Pd11–N3 2.183(3), Pd1–Br1 2.4969(6); Br1–Pd1–C1 177.5(1), Br1–Pd1–C10 90.51(8), Br1–Pd1–N3 92.59(8).

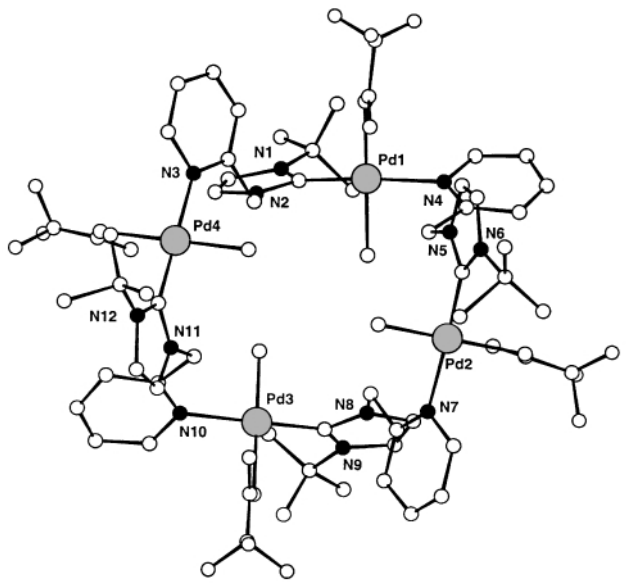


Fig. 2 Molecular structure of **2**. Selected bond lengths (Å): Pd–N 1.99(2)–2.11(2), Pd–O 2.145(15)–2.170(15), Pd–C_{methyl} 1.94(2)–2.10(2), Pd–$C_{carbene}$ 1.89(3)–1.96(3).

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Table 1 Selected results of Heck reactions catalysed by **1a**

Aryl halide[a]	Alkene[b]/amine	*t*/h	*T*/°C	Catalyst (mol %)	Base	Yield (%)[d]	TON
PhI	mac	3	130	7×10^{-3}	Na_2CO_3	90	12 900
PhI	mac	1	130	7×10^{-4}	NEt_3	85	121 400
PhI	mac	2	130	7×10^{-4}	NEt_3	95	135 700
PhI	mac	3	130	7×10^{-4}	NEt_3	100	142 900
PhI	mac	6	130	3.5×10^{-4}	NEt_3	100	285 800
PhI	mac	18	140	7×10^{-5}	NEt_3	98	1400 000
PhI	mac	38	140	3.5×10^{-5}	NEt_3	100	2858 000
4-$NO_2C_6H_4Br$	bac	18	140	0.5	NaOAc	95	190
4-$MeCOC_6H_4Br$	bac	18	140	0.5	NaOAc	100	200
PhBr[c]	PhNHMe	24	65	7×10^{-4}	NEt_3	10	14 300
PhBr	mac	75	130	7×10^{-3}	NEt_3	10	1 400
PhBr	mac	152	130	7×10^{-3}	NEt_3	20	2 900

[a] ArX, 5 mmol; alkene/amine, 6 mmol; NEt_3, 7 mmol; NaOAc, 7 mmol; Na_2CO_3, 3.5 mmol; *N*-methylpyrrolidone used as solvent. [b] mac = Methyl acrylate; bac = *n*-butyl acrylate. [c] Determined by GC, based on the aryl halide. [d] THF used as solvent.

undesired deprotonation of the methylene protons linking the carbene to the heterocyclic donor, or even the methyl substituent of the carbene. We believe these initial observations may presage structure–property relationships in similar catalysts.

Complexes **1a** and **1b** are excellent precatalysts for the Heck coupling and show good activity for amination reactions (see Table 1). The activity of **1a** does not seem to decrease with time, implying high thermal stability under the reaction conditions. It is highest in *N*-methylpyrrolidone and *N*,*N*′-dimethylacetamide but is dependent on reaction temperature. The highest turnover frequencies are observed when triethylamine is used as base; other bases such as Na_2CO_3 or NaO_2CMe have also been used successfully but require longer reaction times. The results for the coupling of aryl iodides with acrylates are comparable to the best systems known.[5] Although the mechanism and the nature of the active species in the Heck reaction is far from clear,[6] our results show that (i) highly active palladium catalysts are obtained by using hemilabile carbene complexes, (ii) the presence of other labile ligands in the coordination sphere of the metal makes predictions of the nature of the catalytic species difficult and (iii) higher nuclearity complexes such as **2** may be precursors to the active catalyst which could be obtained by dissociation of the labile end of the ligand. Catalysis by higher nuclearity complexes, especially under Heck conditions, is less likely.

Studies on the reactivity of the new complexes, extension of the methodology to other transition metals and the synthesis of other functionalised N-heterocyclic carbene ligands with a variety of other donor functionalities is under way.

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Notes and references

† *Spectroscopic data*: **1a**: MS (ES): *m/z* 377, $[Pd(C–N)Me(MeCN)]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ 9.14 (d, 1H, α-*N*-pyridyl H), 7.70 (dt, 1H, γ-*N*-pyridyl H), 7.33 (t, 1H, β-*N*-pyridyl H), 7.24 (d, 1H, *H*CCH), 7.14 (d, 1H, HCC*H*), 6.66 (m, 1H, β-*N*-pyridyl H), 5.23 (m, 1H,NCH*H*), 5.92 (m, 1H, NC*H*H), 1.95 [s, 9H, $C(CH_3)_3$], 0.56 (s, 3H, $PdCH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 175.2 (NCN), 159.7, 152.7, 137.9 (pyridyl C), 123.6, 122.2, 120.4, 119.1 (pyridyl C, NCCN), 59.3 (NCH_2), 54.3 [$C(CH_3)_3$], 30.2 [$C(CH_3)_3$], −7.5 ($PdCH_3$).

1b: MS (ES): *m/z* 439, $[Pd(C–N)Me(MeCN)]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ 9.33 (d, 1H, α-*N*-pyridyl H), 7.76 (dt, 1H, γ-*N*-pyridyl H), 7.50 (d, 1H, β-*N*-pyridyl H), 7.34 (m, 1H, β-*N*-pyridyl H), 7.27 (d, 1H, HCCH), 6.93 (s, 2H, mes CH), 6.78 (d, 1H, *H*CCH), 5.50 (br, 2H, CH_2), 2.31 (s, 3H, mes CH_3), 2.08 (s, 6H, mes CH_3), 0.22 (s, 3H, $PdCH_3$). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 174.4 (NCN), 153.3, 152.8, 138.7 (pyridyl C), 135.6, 134.9 (mes C), 129.2, 128.8 (mes CH), 124.5, 124.2, 122.2, 121.7 (pyridyl C, NCCN), 55.5 (NCH_2), 21.2, 18.5 (mes CH_3), −13.9 ($PdCH_3$).

2: MS (ES): *m/z* 377, $[Pd(C–N)Me(MeCN)]^+$. ^1H NMR (300 MHz, CD_3CN): δ 8.8 (d, 1H, α-*N*-pyridyl H), 7.5 (dt, 1H, γ-*N*-pyridyl H), 7.2 (m, 1H, β-*N*-pyridyl H), 7.1 (d, 1H, β-*N*-pyridyl H), 7.0 (d, 1H, *H*CCH), 6.4 (d, 1H, HCC*H*), 5.3 (br, CH_2), 0.56 (s, 3H, $PdCH_3$), 1.7 [s, 9H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ 174.0 (NCN), 158.5 (pyridyl C), 151.5 ($PdCO_2CF_3$), 150.5, 138.2 (pyridyl C), 123.3, 122.8, 121.4, 120.3 (pyridyl C, NCCN), 97.6 (CF_3), 58.4 (NCH_2), 56.1 [$C(CH_3)_3$], 31.8 [$C(CH_3)_3$], −9.2 ($PdCH_3$).

‡ *Crystal data*: for **1b**: $C_{19}H_{22}BrN_3Pd$, M = 478.71, rhombohedral, space group $R\bar{3}h$ (no. 148), a = 24.521(4), c = 20.201(4) Å, U = 10519(3) Å^3, T = 150 K, Z = 18, μ(Mo-Kα) = 2.507 mm^{-1}, 25874 reflections measured, 4782 unique (R_{int} = 0.047) which were used in all calculations. The final $wR(F^2)$ was 0.1142 (all data) and R = 0.0439 [$F > 2\sigma(F)$]. The structure contains highly disordered solvent CH_2Cl_2 which is located in channels along the c axis (1035 e cell^{-1}) and was treated in the manner described by Sluis and Spek.[7]

For **2**: crystals were obtained by layering of CH_2Cl_2 solution of **2** with ether: $C_{60}H_{80}F_{12}N_{12}O_8Pd_4 \cdot (x$ THF ($x \approx 4$), M_r = 1749.04, triclinic, space group $P\bar{1}$ (no. 2), a = 9.852(2), b = 20.026(4), c = 21.056(4) Å, α = 89.95(3), β = 90.19(3), γ = 90.04(3) °, U = 4154.2(14) Å^3, Z = 2, T = 150 K, μ = 0.935, 34221 reflections measured, 10208 reflections observed, R = 0.1095, R_w = 0.2539. The crystals were of particularly poor quality, and the data reported is the best of four data collections and refinements tried. Recognising the approximate C_2 symmetry of the molecule and orthorhombic cell geometry, we have explored the possibility of higher symmetry structure. Whilst strong data merge reasonably well for orthorhombic (R_{int} = 0.13), monoclinic (R_{int} = 0.062; *cf.* R_{int} = 0.056 for triclinic) we were not able to solve or refine in the higher symmetries.

CCDC 182/1666. See http://www.rsc.org/suppdata/cc/b0/b002645j/ for crystallographic files in .cif format.

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