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Chiral 2,6-lutidinyl-biscarbene complexes of palladium†

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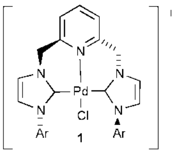
Chiral complexes of palladium, 1, with the new tridentate 'pincer' ligand 2,6-lutidinyl-biscarbene (C^N^C), have been prepared; in the solid state they exhibit helical C_2 symmetrical structures which are persistent in solution at least up to 80 °C; the chiral nature of 1 has been established by NMR methods using Pirkle's acid as a chiral discriminating agent; racemic mixtures of 1 are highly active catalysts in Heck coupling reactions.

The use of *N*-heterocyclic carbene transition metal complexes in catalysis is an area of intense current research activity.[1] This has been stimulated by a number of attractive ligand characteristics, including electronic similarity to the alkyl phosphines,[2] formation of strong and inert metal–ligand bonds and ease of electronic and steric tuning. Compared with the electronically similar phosphine ligands, carbenes appear not to dissociate easily from the metal centre and are less prone to metal assisted decomposition leading to catalyst deactivation. Considerable effort has also been directed to the development of new chiral ligands due to the growing importance of transition metal catalysed asymmetric synthesis.[3] Diphosphines, especially those with C_2 symmetry, have proven to be especially useful, resulting in good enantioselective control of the catalytic reactions, although the potential of chiral auxilliary ligands which bind to the metal through nitrogen and carbon atoms is now being evaluated.[4] In sharp contrast, chiral carbene complexes are very rare and have only recently attracted interest, with current examples of ligands including (i) chiral imidazolin-2-ylidenes and imidazol-2-ylidenes [stereogenic centre(s) on the alkyl substituents of the rings],[5] (ii) chiral imidazolin-2-ylidenes (stereogenic centres integrated in the imidazoline ring),[6] (iii) *N*-functionalised imidazol-2-ylidenes and precursors thereof (stereogenic centres on the functional group)[7] and (iv) binaphthyl bridged dicarbenes (stereogenic axis of the binaphthyl framework).[8] Herein we communicate our results on the isolation and full characterisation of the first racemic carbene complexes of palladium as a result of two carbene moieties being linked by a lutidine backbone, together with a preliminary study of their catalytic activity.

As a logical extension of our own work and that of McGuiness and Cavell on the use of pyridine- and picoline-functionalised carbene complexes of palladium[9] we decided to explore the use of tridentate 'pincer' architectures bearing carbene ligands. Toward this end the complexes [(C^N^C)PdCl]X [C^N^C = α,α′-bis-(3-arylimidazol-2-ylidene)-2,6-picoline, **1a**: Ar = 2,6-$\mathrm{Pr^i_2C_6H_3}$, **1b**: Ar = mes (2,4,6-$\mathrm{Me_3C_6H_2}$); X = $\mathrm{Cl^-}$, $\mathrm{AgCl_2^-}$] were prepared by interaction of the analogous silver complexes[10] with (COD)$\mathrm{PdCl_2}$ in dichloromethane.

Complexes **1a**, **b** are air stable, colourless high-melting solids (ESI).† The structure of **1a** was determined by X-ray crystallography, and the cationic component is shown in Fig 1.‡ The 'pincer' ligand is coordinated to the square planar palladium centre with the carbene ends disposed *trans* to each other and the lutidine nitrogen *trans* to the chloride. The observed geometrical parameters are similar to those previously reported for analogous complexes.[9] However, as a direct result of the combination of the puckering of the two six-membered chelate rings and the bulk of the aromatic substituents around the carbene moieties a beautiful helical structure is generated with a C_2 proper axis coinciding with the N–Pd–Cl vector. The conformation of the cation is best described by the orientation of the ligand ring systems with respect to each other and to the palladium square plane. Thus, the lutidine ring forms a dihedral angle of 40.04(10)° with the square plane, the N1 and N5 carbene rings form dihedral angles of 42.50(13) and −39.70(11)°, respectively, with the square plane and the carbene rings form dihedrals of 81.93(17) and –79.85(14)°, respectively, with the C1 and C26 Ar moieties. As a consequence of the centrosymmetric nature of the space group ($P2_1/c$), the second enantiomer is generated through the inversion centre leading to a racemic mixture in the crystal lattice.



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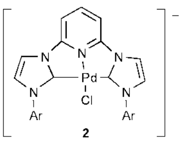

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It is interesting that 'pincer' complexes [(CNC)PdCl]X [CNC = 2,6-bis(3-arylimidazol-2-ylidene)pyridine; **2a**: Ar = 2,6-$\mathrm{Pr^i_2C_6H_3}$, **2b**: Ar = mes; X = $\mathrm{Cl^-}$, $\mathrm{AgCl_2^-}$] have also been obtained following similar synthetic methods (ESI).† The structure of **2a** was also determined by X-ray crystallography and is shown in Fig.2.‡ The coordination sphere of the metal is

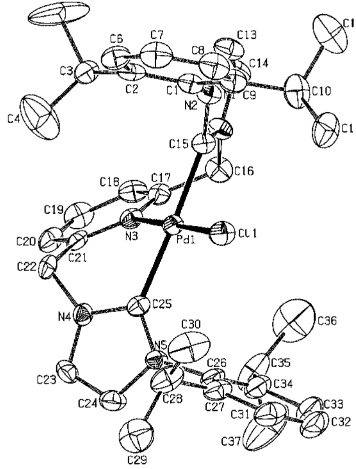

Fig. 1 Molecular structure of the cation in **1a** (view along the N–Pd–Cl vector). Selected bond lengths (Å) and angles (°): Pd1–C15 2.025(4), Pd1–C25 2.029(4), Pd1–N3 2.074(3); N3–Pd1–C15 87.41(14), N3–Pd1–C25 87.67(14).

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† Electronic supplementary information (ESI) available: spectroscopic data for **1a**, **1b**, **2a** and **2b**; Table S1: representative results of the Heck reaction. See http://www.rsc.org/suppdata/cc/b1/b103330c/

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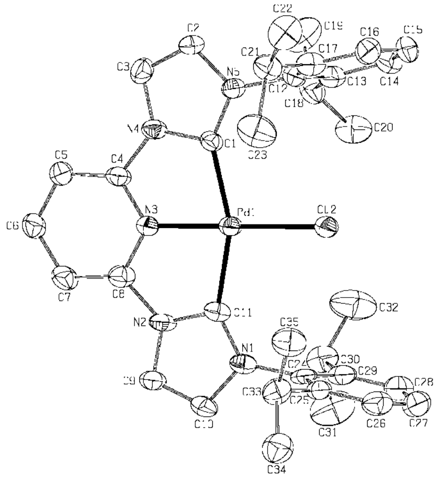

Fig. 2 Molecular structure of the cation in **2a**. Selected bond lengths (Å) and angles (°): Pd1–N3 1.977(16), Pd1–C13 2.02(2), Pd1–C21 2.03(2); N3–Pd1–C13 79.1(8), N3–Pd1–C21 79.0(8).

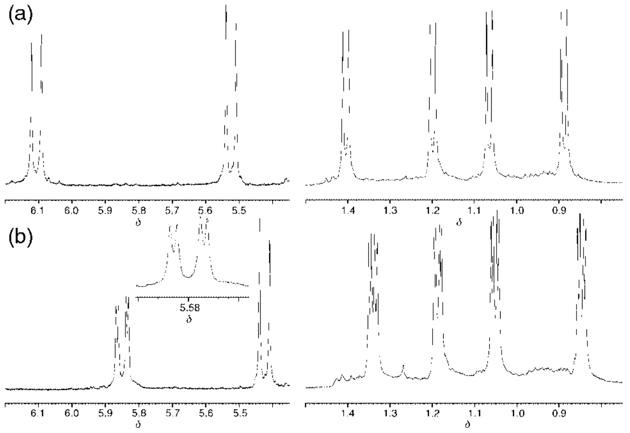

Fig. 3 The isopropyl methyl- and bridging methylene-regions of the ^{1}H NMR spectrum of **1a** before (a) and after (b) the addition of Pirkle's acid.

similar to **1a**. However, the whole molecule is virtually planar, with the Ar groups twisted 76.68(11) and 89.63(22)° out of the plane for rings C12 and C24, respectively. All other geometrical data are very similar to **1a**. It is instructive to view the generation of **1** by desymmetrisation of **2** through a twist deformation around the C_2 axis. The direction of the twist determines the chirality generated. A compound related to **2a** with methyl substituted carbene functionalities has also recently been reported.[11]

The structures of **1a** and **2a** observed in the solid state are persistent in solution. The ^{1}H NMR (CD_2Cl_2) spectrum of **1a** (ESI†) shows four anisochronous doublets which can be assigned to the isopropyl methyl protons. Furthermore, the methylene-bridge protons appear as an AB pattern in the range δ 5.5–6.3 [Fig. 3(a)]. In order to demonstrate the chiral nature of **1a** in solution Pirkle's acid. [TFAE, *S*-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol] was used as a chiral discriminating agent.[12] The isopropyl methyl groups and the bridging methylene regions of the spectrum obtained after addition of 3.4 equivalents of TFAE in CD_2Cl_2 solution of **1a** are shown in Fig 3(b). The doubling of the four anisochronous doublets and one of the doublets due to the methylene linkers originates from the strong interaction of the chiral discriminating agent with one of the two enantiomers of **1a** (degree of non-equivalence $\Delta\delta$ *ca.* 0.2 ppm). The conformation of **1a** is rigid at least up to 80 °C as evidenced by variable temperature ^{1}H NMR spectroscopy (C_6D_5Cl). This supports the contention that a high activation barrier exists for enantiomer interconversion, thus leading to the realistic possibility of resolving the racemic mixture by chemical or chromatographic means.

In contrast to **1a,** the spectrum of the planar **2a** contains only two diastereotopic isopropyl methyl protons and remains also unchanged over the temperature range studied.

Preliminary data show that **1** and **2** are active catalysts in Heck coupling reactions (Table S1, ESI†).[9] The catalysts show excellent long term stability at high temperatures. Furthermore, the activity is sensitive to the steric congestion at the reactive site (**1b** is more active than **1a**). It is interesting that aryl chlorides can also be used as substrates. The mechanism and the nature of the active species in these reactions is far from clear. Heck reaction catalysed by 'pincer' phosphine ligated palladium complexes have been reported.[13]

Isolation of the enantiomerically pure complexes and extension of this methodology to other transition metals and their catalytic reactions are currently under way.

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Notes and references

‡ *Crystal data*: for **1a**: crystals were obtained by layering a CH_2Cl_2 solution of **1a** with light petroleum (bp = 40–60 °C); $C_{40}H_{45}AgCl_9N_5Pd$, M = 1129.13, monoclinic, space group $P2_1/c$, a = 11.559(2), b = 42.043(8), c = 10.631(2) Å, β = 112.51(3)°, U = 4772.6(16) Å^3, T = 150(2) K, Z = 4, μ(Mo-Kα) = 1.325 mm^{-1}, 28393 reflections collected, 10436 unique reflections, R_{int} = 0.0867), Final R indices: wR_2 = 0.1185 and R_1 = 0.0514 [$F^2 > 2\sigma(F^2)$] and 0.1340 and 0.0897 for all data.

For **2a**: crystals were obtained by layering a CH_2Cl_2 solution of **2a** with light petroleum (bp = 40–60 °C), $C_{36}H_{41}Cl_{4.5}N_5Pd$, M = 809.66, triclinic, space group $P\bar{1}$, a = 8.4782(4), b = 11.8790(6), c = 20.8146(11) Å, α = 75.077(3), β = 83.364(3), γ = 71.322°, U = 1917.65 (17) Å^3, T = 150(2) K, Z = 2, μ(Mo-Kα) = 0.829 mm^{-1}, 14147 reflections collected, 6524 unique reflections, R_{int} = 0.0839), Final R indices: wR_2 = 0.2213 and R_1 = 0.0838 [$F^2 > 2\sigma(F^2)$] and 0.2562 and 0.1316 for all data.

The refinement of both structures was hampered by severe disorder of dichloromethane solvent molecules, and, not unrelated, limited quality data from poor crystals, especially for compound **2a**. At the present stage, the modelling of the disorder is not complete, but the definition of the cation is reliable in each case, with reasonable positional esds and good displacement parameters for all component atoms. CCDC reference numbers 162457 and 162458.

See http://www.rsc.org/suppdata/cc/b1/b103330c/ for crystallographic data in CIF or other electronic format.

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