Direct synthesis of a new class of N,N,N ligands based on 1,2-dihydro-1,10-phenanthroline backbone and their coordination to Pd complexes[†]

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Reactions of acetylpyridine derivatives with 8-aminoquinolines provide a general and simple access to an unexpected class of versatile N,N,N ligands, which offer interesting perspectives in coordination chemistry.

Tridentate N.N.N ligands centered on N-heterocycles, such as bis(imino)pyridines, have been extensively studied in the last few years because they provide interesting and tunable ligands for coordination to transition metals, especially iron, nickel and cobalt, and lead to highly active catalytic systems for olefin polymerization or oligomerization.1-3 In the search for alternative multidentate systems, Sun and Bortoluzzi recently explored ligands containing Schiff bases resulting from the condensation of 8-aminoquinoline with aldehydo- or keto-pyridine derivatives.^{2e,4,5} Whereas they did not succeed in isolating the pure imino ligands, these authors employed a one-pot metal-assisted synthesis to obtain the N-((pyridin-2-yl)methylidene)quinoline-8amine metal complexes in good yields. Herein, we report the first successful direct synthesis and isolation of a pure N-((pyridin-2yl)methylidene)quinoline-8-amine derivative by condensation reaction between 2,2-dimethyl-1-(pyridin-2-yl)-propane-1-one with 8-aminoquinoline (see Scheme 1, path A, 1). Moreover, the reaction of 2-acetylpyridine with 8-aminoquinoline derivatives did not yield the expected Schiff bases but instead an unprecedented class of versatile N,N,N ligands based on a 2,4-bis(pyridin-2-yl)-2methyl-1,2-dihydro-1,10-phenanthroline scaffold (Scheme 1, path B). This new ligand backbone provides not only a favourable environment for the coordination to various metal centres but also a structure which can be fine-tuned by changing the R substituents and thus offers the opportunity to easily control the metal coordination environment and therefore the catalytic behaviour of the resulting complexes.

The reaction in Scheme 1, path A, was carried out in refluxing toluene for 5 days in the presence of an acid catalyst. Such conditions are needed because of the low reactivity of the hindered ketone precursor. Compound 1 was obtained in *ca.* 35 wt% yield. Its IR spectrum shows an absorption at 1644 cm⁻¹, consistent with



Scheme 1 Condensation reaction (path A and B) and complexation to Pd.

a C=N stretching vibration. Ligand 1 was also characterized by GC-MS, NMR and X-ray diffraction (Fig. 1).



Fig. 1 ORTEP plot of the molecular structure of 1 in CH₂Cl₂. Ellipsoids are represented at 50% probability level.

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The N(2)–C(10) distance of 1.276(2) Å is typical for a C=N double bond. The imino-pyridine derivative **1** exists in the solid state as the Z isomer at the C=N bond, a configuration that is clearly unfavourable for tridentate coordination to a metal centre.

The pyridine and 8-quinoline planes are nearly perpendicular to the imine plane, with torsion angles N(2)-C(10)-C(15)-N(3) of 93.70(19)° and C(9)-C(8)-N(2)-C(10) of 92.30(18)°, and the nitrogen atoms are placed on either side of this plane. ¹H NMR analysis of **1** indicates the presence of a single isomer in solution.

The condensation reactions of 2-acetylpyridine derivatives with 8-aminoquinoline were performed in refluxing methanol with formic acid as a catalyst (Scheme 1, path B). The presence of both the enolizable 2-acetylpyridine ketone and the 8-aminoquinoline enables a Mannich-type reaction to take place, followed by a cyclization under mild conditions which involves aromatic C–H activation and C–C bond formation (Scheme 2). This method was readily generalized for the synthesis of various 2,4-bis(pyridin-2-yl)-2-methyl-1,2-dihydro-1,10-phenanthroline derivatives. Only ligand **7** was obtained by a Suzuki coupling of ligand **6** with phenyl boronic acid.

The structural characterization of these new ligands has been achieved by several analytical methods, such as ¹H and ¹³C NMR, mass spectroscopy and IR spectroscopy. The ¹H and ¹³C NMR spectra contain characteristic peaks: a singlet at 2.9 ppm for the methyl group and a doublet around 6.2 ppm for the ethylene proton. A broad signal at 6.9–7.1 ppm shows the presence of the amine proton. In ¹³C NMR, the aliphatic quaternary carbon peak is observed at 60 ppm.

In addition, the IR spectra of all compounds show a band between 3380 cm⁻¹ and 3360 cm⁻¹, consistent with a N–H stretching vibration. Ligands **4** and **6** were further characterized by X-ray diffraction analysis.

Single crystals were obtained by slow evaporation of their dichloromethane solution. The molecular structure of **4**, shown in Fig. 2, unambiguously established the existence of the 2,2,4-substituted 1,2-dihydro-1,10-phenanthroline scaffold. The presence of a quaternary aliphatic carbon leads to a racemic mixture. The pyridine ring at C_{10} forms a dihedral angle of 71.62(5)° with the phenanthroline ring. The crystal structure of **6** is similar (Fig. 3).

These new, bi- or tridentate N,N,N ligands have obvious potential in coordination chemistry and their stereoelectronic environment could be readily modified by varying the substituents in the precursors.



Fig. 2 ORTEP plot of the molecular structure of 4 grown in CH_2Cl_2 . Ellipsoids are represented at 50% probability.



Fig. 3 ORTEP plot of the molecular structure of 6 grown in CH_2Cl_2 . Ellipsoids are represented at 50% probability.

Palladium complexes are of considerable importance in homogeneous catalysis⁶ and Pd(II) diimine systems are, for example, capable of polymerizing ethylene and other α -olefins to form high molecular weight polymers.⁷⁻⁹ Ligand 7 was reacted with



Scheme 2 Proposed mechanism for the formation of 2,4-bis(pyridin-2-yl)-2-methyl-1,2-dihydro-1,10-phenanthroline derivatives.

[PdCl₂(NCPh)₂] in dichloromethane at room temperature and complex **9** was isolated as an air-stable, red solid. The shifts of its ¹H NMR peaks provide evidence for the coordination of the quinoline and amine nitrogen atoms to the palladium centre. Compared with the free ligand **7**, **9** displays a large downfield shift for the aromatic proton attached to the carbon alpha to the quinoline nitrogen. The amine proton shows a similar downfield shift. The molecular structure of **9** was determined by X-ray diffraction (Fig. 4).



Fig. 4 ORTEP plot of the molecular structure of 9. Ellipsoids are represented at 50% probability level. H atoms and solvent molecules omitted for clarity.

The palladium centre is coordinated by two *cis* nitrogen and two chlorine atoms. The average deviation from the mean plane C(12)-N(1)-Pd(1)-N(2) is $8.1(3)^\circ$, which indicates a nearly planar coordination geometry. The Pd–Cl distances (2.291(1) Å) and (2.298(1) Å) are within the usual range for such bonds,^{10,11} and the Pd–N_{amine} bond length (2.111(4) Å) is slightly longer than Pd–N_{phen} (2.028(3) Å). The N(1)–Pd(1)–N(2) bite angle of 82.1(2)° results in a slightly distorted square planar structure, also observed in other palladium complexes ligated by pyridyl-imine or bis(pyridine) ligands.¹²

The coordination of Pd to the amine nitrogen creates a second stereogenic centre on N(2). Only two enantiomers, *RR* and *SS*, are observed in the crystal lattice, although four diastereoisomers, *i.e. RR*, *RS*, *SS* and *SR*, could have been present. We suggest that steric hindrance imposes the bonds N(2)–H and C(10)–C(13)H₃ to be placed on opposite sides of the phenanthroline plane. The configuration of C(10) thus induces that of N(2). This also allows a potential H-bonding with N(3) which improves stabilization

of the palladium complex (H–N(3), 2.16(6) Å). The pyridine ring on C(10) is nearly orthogonal to the phenanthroline ring $(C(9)-C(10)-C(14)-N(3), 88.0(5)^{\circ})$. There is no direct interaction between the palladium centre and the nitrogen pyridine atom with a distance of 3.79(8) Å.

In conclusion, we have discovered a new, versatile class of N,N,N ligands based on the 2,4-bis(pyridin-2-yl)-substituted 1,2-dihydro-1,10-phenanthroline structure. They were readily synthesized by the direct and general reaction of 2-acetylpyridine with 8-aminoquinoline derivatives. These ligands coordinate to Pd(II) in a bidentate mode. We are currently investigating their coordination to iron and nickel and the application of these complexes for the catalytic oligomerization and polymerization of ethylene.

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