

Stable Palladium(0) and Palladium(II) Complexes Containing a New, Multifunctional and Semi-labile Phosphorus–Bisnitrogen Ligand

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The new, multifunctional, semi-labile phosphorus–bisnitrogen ligand *N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine, PNN, stabilises methyl(chloro)-, η^1 -allyl(chloro)-, dichloro- and bis(tetrafluoroborate)-palladium(II) PNN complexes in a terdentate coordination fashion, resulting in ionic palladium complexes, as well as an unprecedented palladium(0) PNN complex as is evidenced from ¹H, ¹³C, ³¹P and ¹⁵N NMR spectra and an X-ray structural analysis of [(PNN)PdMe]⁺[Cl][−].

As part of our ongoing research on palladium complexes in catalytic reactions it was our goal to design a multifunctional, semi-labile ligand that would stabilise both Pd⁰ and Pd^{II} under reaction conditions, without additional stabilising ligands. This may be achieved by a ligand that is able to act as a bidentate as well as a terdentate ligand. We thus designed the multifunctional phosphorus–bisnitrogen ligand *N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine (PNN) **1** (Fig. 1), which may be useful, *e.g.* in the catalytic reductive carbonylation of aromatic nitro compounds¹ and in carbon–carbon bond formation reactions.²

The nitrogen atoms of the ligand are incorporated in a benzylideneamino and a pyridyl group in an effort to enhance the π -accepting capacity of the system. A related PNN ligand has been reported by Rauchfuss as its molybdenum complex.³ Because of its flexible structure **1** can act either as a bidentate P–N or as a terdentate P–N–N ligand. Upon coordination both the P–N and the N–N sets will form six-membered chelate rings. The intrinsic flexibility of the ligand facilitates the adaptation of the bite angles between the metal and the donor atoms, as needed in the different oxidation states of palladium.

The terdentate ligand **1** and its very stable palladium(II) dichloride **2a**, palladium(II) bistetrafluoroborate **2b**, methylpalladium(II) chloride **2c** and η^1 -allylpalladium(II) chloride **2d** complexes have been synthesised, isolated and characterised.† PNN was synthesised in 63% yield from the Schiff's base condensation reaction of 2-(diphenyl)phosphinobenzaldehyde⁴ and 2-(2-aminoethyl)pyridine, according to the method of Lavery and Nelson.⁵ The palladium compounds **2a** and **2c** were prepared from (C₆H₅CN)₂PdCl₂⁶ and (COD)PdMe(Cl),⁷ respectively, in a manner analogous to literature procedures.^{7,8} Compound **2b** precipitated quantitatively after stirring (MeCN)₄Pd(BF₄)₂⁹ and **1** in acetone for 4 h. When **1** was treated with [(C₃H₅)Pd(μ -Cl)]₂ in chloroform, compound **2d** was formed quantitatively after refluxing for 2 h.

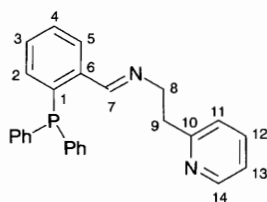


Fig. 1 Structure of **1** and the numbering scheme as used for interpretation of the NMR spectra

In the divalent complexes **1** coordinates in a terdentate fashion as is confirmed by ¹⁵N NMR, an especially powerful tool for these systems. The typical high-field shift of the nitrogen atoms is observed upon coordination of the ligand to palladium.¹⁰ Furthermore, a large phosphorus coupling constant of 45 Hz on the *trans* situated pyridyl nitrogen is observed in the spectra of **2a–c**, which is not the case for the free ligand. Detachment of the flexible ethylpyridyl moiety in **2a–c** was not observed by NMR between -50 and 50 °C.

The strong tendency of **1** towards coordination in a terdentate fashion is exemplified by complex **2d**, in which the allyl fragment is η^1 -coordinated, without a sign of the η^3 -allyl isomer in the temperature range of -50 to 50 °C.

The molecular structure‡ of [(PNN)PdMe]Cl **2c**, presented in Fig. 2, confirms the square planar arrangement of the three donor atoms of PNN and the methyl ligand around the

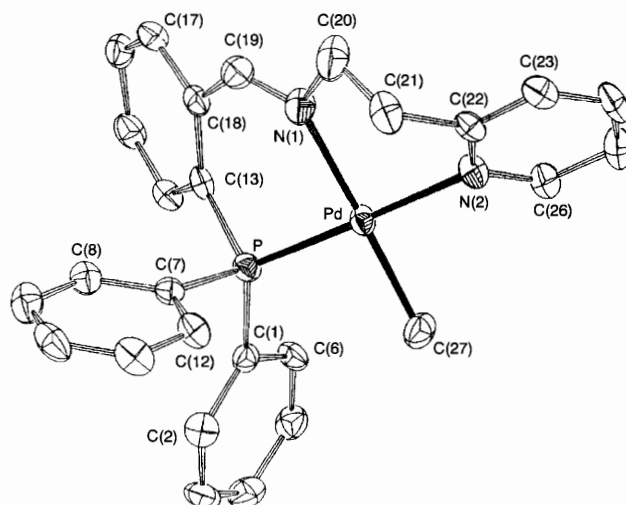
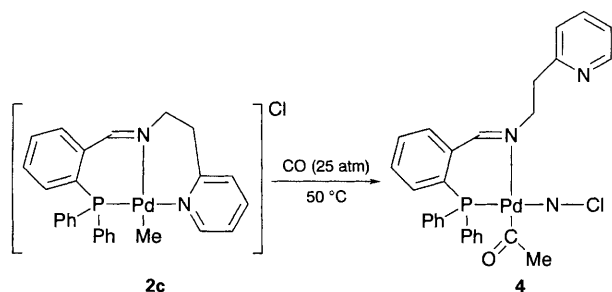


Fig. 2 Structure of the cation of complex **2c**. Ellipsoids drawn at 50% level. The chloride bisolvate anion as well as the hydrogen atoms have been omitted for clarity. Selected geometrical parameters: bond lengths (Å): Pd–P 2.2007(16), Pd–N(1) 2.131(5), Pd–N(2) 2.117(5), P–C(27) 2.036(6), P–C(13) 1.821(5), C(13)–C(18) 1.422(7), C(18)–C(19) 1.470(8), C(19)–N(1) 1.266(8), N(1)–C(20) 1.476(8), C(20)–C(21) 1.523(9), C(21)–C(22) 1.506(8), C(22)–N(2) 1.346(7); bond angles (°): P–Pd–N(1) 88.80(15), N(1)–Pd–N(2) 89.89(19), N(2)–Pd–C(27) 90.9(2), C(27)–Pd–P 90.43(17).



Scheme 1 CO insertion into ionic [(PNN)PdMe]Cl **2c** to give neutral [(PNN)Pd{C(O)Me}(Cl)] **4**

palladium atom. The chloride anion is obviously not within the first coordination sphere (Pd–Cl = 6.649 Å). The bond angles P–Pd–N(1) and N(1)–Pd–N(2) are almost 90°. The ligand–palladium distances are normal for complexes of this type. The double six-membered ring chelate of the PNN ligand causes a twisted conformation of the ligand around the palladium atom. The pyridyl group is rotated by 45.0(2)°, and the imino group by ca. 19.2(4)° with regard to the palladium coordination plane.

When the alkylpalladium complex **2c** is subjected to 25 atm of CO pressure at 50 °C in chloroform, insertion of CO into the Pd–Me bond occurs. Surprisingly, the thus formed acetyl-palladium complex **4** has the ligand coordinating as a bidentate P–N chelate with a pendant ethylpyridyl group¹¹ (Scheme 1). This feature confirms that PNN may indeed act both as a terdentate and as a bidentate ligand.

A stable palladium(0) complex of **1** has been synthesised by reduction of complex **2d** with pyrrolidine in chloroform. This zerovalent compound **3** was characterised by ¹H, ¹³C and ³¹P NMR. Mass spectroscopy, using the very soft plasma desorption ionisation technique, confirmed the presence of Pd⁰PNN **3** at *m/z* = 500.7. To our knowledge, **3** is the first example of a Pd⁰ compound stabilised by a phosphorus–bisnitrogen donor set. The solubility of complex **3** in non-halogenated solvents is too low for ¹⁵N NMR measurements, so the exact arrangement of PNN in **3** remains uncertain.

Interestingly, the Pd⁰ compound **3** does meet the required stability for which we aimed. It is stable in the solid state as well as in solution. The high stability of both the zerovalent and divalent palladium complexes of **1** now opens a way to catalytic applications through a Pd⁰–Pd^{II} cycle, similar to the Pd(PPh₃)₄–Pd(PPh₃)₂Cl₂ system, without additional stabilising ligands.

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Footnotes

† Selected NMR data:

Cpd ^a	³¹ P	¹⁵ N		¹ H					
		N _{imine}	N _{pyridyl}	Pd–R	H ₂	H ₇	H ₈	H ₉	H ₁₄
1	–13.6	–45	–68	—	7.93	8.85	3.89	2.97	8.49
2a	31.1	–162	–134	—	8.53	10.17	4.25	3.49	8.82
2b	30.2	–176	–138	—	obsc.	8.60	4.06	3.87	8.49
2c	37.0	–123	–122	0.36	8.15	9.47	4.22	3.48	8.41
2d	33.0	–119 ^b	–119 ^b	2.19	8.08	9.43	4.03	3.54	8.59
3	30.9	—	—	—	8.49	10.00	4.11	3.56	8.87
4	20.9	—	—	2.19	obsc.	8.51	4.25	3.38	8.45

^a For compounds **1**, **2c–d**, **3** and **4**, all measurements were carried out in CDCl₃ and for compound **2b** in [2H₆]Me₂SO, while for compound **2a** ¹H and ³¹P NMR were measured in CDCl₃ and ¹⁵N NMR (MeNO₂) was measured in [2H₆]Me₂SO. ^b Only one broad signal was observed.

‡ Crystal data for complex **2c**, C₂₇H₂₆ClN₂PPd·2CHCl₃, monoclinic, space group P2₁/c, *a* = 10.6845(7), *b* = 19.330(2), *c* = 16.0434(19) Å, β = 97.906(8)°, *V* = 3282.0(6) Å³, *Z* = 4, *D_c* = 1.599 g cm^{–3}, *F*(000) = 1584, μ(Mo–Kα) = 12 cm^{–1}, 8595 reflections measured, 7509 independent (1.06 < θ < 27.50°, *T* = 150 K, Mo–Kα radiation, graphite monochromator, λ = 0.71073 Å, Enraf Nonius CAD4T diffractometer on rotating anode). Data were corrected for Lorentz polarization and for a linear decay of 4% of the reference reflections; empirical absorption correction applied (DIFABS, correction range 0.828–1.343). The structure was solved with DIRDIF92/PATT. Refinement on *F* by full-matrix least-squares techniques (SHELX76); final *R* value 0.050, *wR* = 0.046, *w* = 1/[σ²(*F*) + 0.000039*F*²], *S* = 2.89, for 365 parameters and 4428 reflections with *I* > 2.5σ(*I*). Hydrogen atoms were included on calculated positions (C–H = 0.98 Å). All non-hydrogen were refined with anisotropic thermal parameters. No residual density outside –0.80 and 0.75 e Å^{–3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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