

[MCl(ligand)]⁺ Complexes (M = Ni, Pd, Pt) with a P,N,N Terdentate Ligand – Solid State and Solution Structures and Catalytic Activity of the Pd^{II} Derivative in the Heck Reaction

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Ni^{II}, Pd^{II} and Pt^{II} cationic complexes of the general formula [MCl(PNN)]PF₆, where PNN is the terdentate ligand *N*-[2-(diphenylphosphanyl)benzylidene][2-(2-pyridyl)ethyl]amine, have been synthesised and fully characterised in solution by NMR spectroscopy. The diamagnetic Ni^{II} complex **1** shows fluxionality, which can be attributed to a conformational rearrangement of the two six-membered chelate rings. On the contrary, the Pd^{II} **2** and Pt^{II} **3** derivatives are stereochemically

rigid on the NMR timescale. The crystal structures of **1** and **2** are reported, which show a planar geometry for both complexes. Complex **2** has been investigated as a precatalyst in the Heck coupling between styrene and bromobenzene. Interestingly, the nature of the solvent has a critical role in determining the yield of the reaction product.

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Introduction

In recent years, transition-metal complexes bearing multidentate ligands that contain significantly different types of hard (N- or O-) and soft (P-) donor functions have been extensively studied because of their potential application in homogeneous catalysis.^[1] These ligands possess weakly coordinating groups that can be reversibly released during the catalytic cycle providing unsaturation at the metal centre. Thus, the less strongly bound moiety of this type of ligand, called hemilabile, can be seen as an intramolecular solvent molecule that is capable of temporarily holding a coordination site on the metal. There are several hemilabile ligands containing a substitutionally inert phosphorus function and a labile oxygen or nitrogen donor. Among the various kinds of P,N hybrid ligands, those showing pyridyl or imine arms have been widely used to prepare complexes of different transition metals,^[1b,1c,1e,1f] some of which have been successfully employed in catalytic reactions. Thus, for example, Ni^{II} complexes have been tested in olefin polymerisation, while Pd^{II} complexes have been found to be very active in asymmetric allylic alkylation and cross-coupling reactions. Also, our group has worked in this field with particular interest in complexes with phosphane–pyridyl bidentate ligands.^[2]

By contrast, few terdentate P,N,N-type ligands showing mixed functionalities such as phosphane-, imine- and pyri-

dyl-donating groups have been reported so far.^[3] The presence of two different sp² N-donors affects the way the ligand binds to the metal, with effects on both reactivity and catalytic activity of the resulting complexes. Effectively, some of these complexes have shown valuable efficiency in different catalysed reactions, such as enantioselective conjugate addition of diethylzinc to enones,^[3e] olefin hydrogenation,^[3f] asymmetric allylic alkylation^[3h] and asymmetric olefin cyclopropanation.^[3i]

Vrieze and co-workers have described the potentially terdentate P,N,N ligand *N*-[2-(diphenylphosphanyl)benzylidene][2-(2-pyridyl)ethyl]amine^[4] (PNN) (Figure 1), which shows the P-sp³, N-sp² (imine), N-sp² (pyridyl) donors sequence. Several different transition-metal complexes bearing PNN have been reported, in particular with group 10 metals,^[4] the ligand acting as both terdentate^[4–6] or bidentate with a dangling pyridyl arm.^[4–6] Among these species, the Pd^{II} η¹-allyl cationic complex has shown good catalytic activity in allylic alkylation^[4b] and 1,3-butadiene telomerisation with methanol.^[7]

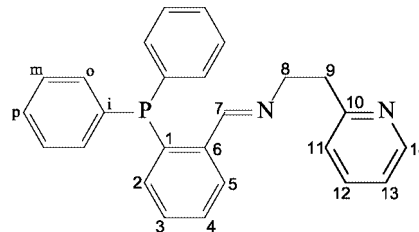


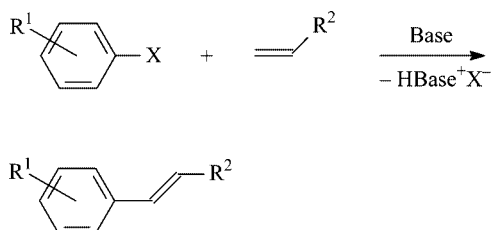
Figure 1. The ligand PNN along with the numbering scheme.

For our part, we decided to investigate the coordination chemistry of PNN towards group 10 metal halides, as the

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first step of a more detailed study on the catalytic properties of PNN-containing late transition-metal complexes. In this paper we present the preparation and characterisation of the cationic complexes $[MCl(PNN)]PF_6$ [$M = Ni$ (**1**), Pd (**2**), Pt (**3**)], also describing preliminary results on the catalytic activity of **2** in the Heck C–C coupling^[8] using aryl bromides as starting material (Scheme 1). The choice for this reaction was stimulated by the fact that PNN is able to stabilise Pd^0 species without the need of additional stabilising ligands^[4b] and that the couple Pd^0/Pd^{II} is thought to be involved in the Pd -catalysed Heck reaction.^[8]



Scheme 1.

Complexes **1–3** have been fully characterised by spectroscopic and analytical methods. In addition, as the NMR investigation has evidenced that, unlike complexes **2** and **3**, the Ni^{II} derivative **1** is fluxional in the whole temperature range 293–183 K, the crystal structure determination of **1** and **2** has been performed to establish whether the different behaviour in solution of the two species could be related to structural modifications due to the nature of the metal ion.

Results and Discussion

The compound PNN was prepared as described in the literature^[4b] and obtained as a cream-coloured powder after double recrystallisation from *n*-hexane. In the original publication,^[4b] besides ^{31}P and ^{15}N NMR spectroscopic data, only selected 1H and ^{13}C values were reported for PNN. Also two later papers dealt with selected 1H NMR values only.^[5,6] Therefore, we decided by means of $^1H\{^{31}P\}$, $^1H-^1H$ COSY, $^1H-^{13}C$ HETCOR, ^{13}C DEPT and ^{13}C PENDANT experiments to assess all 1H (confirmed by computer simulation) and ^{13}C parameters. The 1H and ^{13}C NMR spectroscopic data have been collected in Table 1 and Table 2, respectively, to allow a direct comparison with the data of complexes **1–3**. The numbering scheme of carbon and hydrogen atoms of PNN is reported in Figure 1.

Solution Structure of Complexes 1–3

Complexes $[PdCl(PNN)]PF_6$ (**2**) and $[PtCl(PNN)]PF_6$ (**3**) have been prepared by the room-temperature reaction between the appropriate $[MCl_2(RCN)_2]$ precursor ($M = Pd$, $R = CH_3$; $M = Pt$, $R = C_6H_5$) and the ligand PNN in a 1:1 molar ratio in CH_2Cl_2 solution, followed by addition of an excess of NH_4PF_6 in propan-2-ol and vacuum elimination of CH_2Cl_2 . The complexes were obtained pure as pale yellow crystals by recrystallisation from CH_2Cl_2 /propan-2-ol. For both **2** and **3**, the best fit of the elemental analysis data is obtained for the formula $[MCl(PNN)]PF_6 \cdot 0.5CH_2Cl_2$. The presence of dichloromethane within the crystals has

Table 1. 1H NMR values of the ligand PNN (in $CDCl_3$) and complexes **1–3** (in CD_2Cl_2) at 293 K.^[a,b]

	H ²	H ³	H ⁴	H ⁵	H ⁷	H ⁸	H ⁹	H ¹¹	H ¹²	H ¹³	H ¹⁴	H ^{P^h[c]}
PNN ^[d]	7.93 m	7.37 m	7.24 m	6.87 m ^[e]	8.85 dt	3.88 dt	2.98 t	7.03 m	7.48 m	7.02 m	8.48 m	7.15–7.45 m
1				7.12 br. d	8.04 br. s	3.61 br. t	4.03 br. m		7.85 dt		8.72 br. d	7.30–7.85 m
2 ^[f]	7.81 m			7.16 m	8.51 dt	3.93 m	3.47 m		7.93 m		8.83 m	7.36–7.74 m
3 ^[g]	7.89 m			7.21 m	8.75 dt	4.07 m	3.50 m		8.00 m		8.81 m	7.42–7.72 m

[a] The numbering of the H atoms is shown in Figure 1. [b] The resonances not reported overlap with those of aromatic protons. [c] $H^{P^h} = H^o + H^m + H^p$. [d] Coupling constants in Hz: $J(H^2-H^3) = 7.7$; $J(H^2-H^4) = 1.6$; $J(H^3-H^4) = 7.5$; $J(H^3-H^5) = 1.3$; $J(H^4-H^5) = 7.6$; $J(H^5-H^7) = 4.7$; $J(H^7-H^8) = 1.3$; $J(H^{11}-H^{12}) = 7.7$; $J(H^{11}-H^{13}) = 1.5$; $J(H^{11}-H^{14}) = 0.8$; $J(H^{12}-H^{13}) = 7.5$; $J(H^{12}-H^{14}) = 1.9$; $J(H^{13}-H^{14}) = 4.8$; $J(H^2-^{31}P) = 3.9$; $J(H^3-^{31}P) = 0.5$; $J(H^5-^{31}P) = 4.6$; $J(H^7-^{31}P) = 4.7$; no splitting due to $^1H-^{31}P$ coupling is observed on the signal of H^4 , as previously reported.^[4b] [e] An uncorrected value (7.03) has been previously reported.^[4b] [f] Coupling constants in Hz: $J(H^2-^{31}P) = 2.1$; $J(H^5-^{31}P) = 10.7$; $J(H^7-^{31}P) = 1.7$; $J(H^{14}-^{31}P) = 3.3$. [g] Coupling constants in Hz: $J(H^2-^{31}P) = 2.2$; $J(H^5-^{31}P) = 11.0$; $J(H^7-^{31}P) = 0.5$; $J(H^{14}-^{31}P) = 3.4$; $J(H^7-^{195}Pt) = 115$; $J(H^8-^{195}Pt) = 26$; $J(H^{14}-^{195}Pt) = 25$.

Table 2. $^{13}C\{^1H\}$ NMR values of the ligand PNN (in $CDCl_3$) and complexes **1–3** (in CD_2Cl_2).^[a,b]

	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ⁷	C ⁸	C ⁹	C ¹⁰	C ¹¹	C ¹²	C ¹³	C ¹⁴	C ⁱ	C ^o	C ^m	C ^p
PNN ^[c]	139.5	127.6	128.8	130.1	133.3	137.3	160.3	60.8	39.4	159.8	123.4	136.0	121.1	149.2	136.2	133.9	128.5	128.7
	[17.6]	[4.4]		[1.1]		[19.7]	[21.1]								[10.0]	[20.0]	[7.3]	
1 ^[d]	119.4	135.9	134.0	132.6	133.6	134.7	171.0	52.4	35.0	155.8	123.6	140.0	123.5	150.4	122.7	133.4	128.7	132.3
	[44.0]	[8.2]	[7.0]			[13.5]	[7.6]								[56.9]	[11.6]	[11.7]	
2 ^[e]	120.0	138.1	135.3	134.1	134.6	136.2	168.0	57.1	37.6	158.2	125.1	141.0	124.2	151.7	125.2	134.3	129.6	133.1
	[50.5]	[8.8]	[8.2]	[2.9]	[2.9]	[15.3]	[8.5]				[3.5]		[2.9]	[1.2]	[62.8]	[11.2]	[12.3]	[2.9]
3 ^[e]	120.4	137.7	135.2	133.9	134.0	136.2	166.6	57.5	37.8	158.3	125.1	141.5	124.6	151.5	125.2	134.3	129.3	132.8
	[59.9]	[8.8]	[8.2]	[2.3]	[3.5]	[13.5]	[7.6]				[3.5]		[3.5]	[1.2]	[70.4]	[11.1]	[12.3]	[2.9]

[a] The numbering of the C atoms is shown in Figure 1. [b] $J(^{13}C-^{31}P)$ in Hz are reported in brackets. [c] At 293 K. [d] At 183 K.

been confirmed by ¹H NMR analysis and crystal structure determination of complex **2** (see below).

The ¹H NMR spectra of **2** and **3**, which are very similar, indicate that the structures of the cations are static on the NMR timescale. Meaningful shifts of some resonances can be observed upon coordination of the ligand to the metal centre (Table 1). For example, the signal of the H⁹ proton, which is at δ = 2.98 in the free ligand, is shifted to lower fields in complexes **2** (δ = 3.47) and **3** (δ = 3.50), while that of the H⁸ proton does not show an appreciable shift. Furthermore, both methylene signals of the –CH₂CH₂– chain appear as unsymmetric multiplets whose lines have about the same intensity. This spectral feature is diagnostic of the presence of diastereotopic pairs of protons within each methylene group, arising from the rigidity of the chelate N,N ring. The H⁷ resonance, which is at δ = 8.85 in the free ligand, is shifted to higher fields in complexes **2** (δ = 8.51) and **3** (δ = 8.75). On the contrary, the H¹⁴ resonance, which is at δ = 8.48 in the free ligand, is markedly shifted to lower fields (**1**, δ = 8.83; **2**, δ = 8.81 ppm).

In the free ligand, H², H³, H⁵ and H⁷ protons are coupled to the ³¹P nucleus. In complexes **2** and **3** the ¹H–³¹P coupling constants are not lost but considerably modified. In particular, the ⁴J(H–³¹P) value on H⁷, which is 4.7 Hz in free PNN, is reduced to 1.7 Hz in **2** and 0.5 Hz in **3**. This observation contrasts with the lack of coupling between H⁷ and ³¹P nuclei found in previously reported Pd^{II} and Pt^{II} complexes bearing PNN.^[4b] It is worth noting that also H¹⁴ shows a coupling with phosphorus both in **2** [⁴J(H–³¹P) = 3.3 Hz] and **3** [⁴J(H–³¹P) = 2.9 Hz]. This feature again confirms that the pyridine nitrogen of the ligand is coordinated to the metal centre.

Interestingly, the H⁷, H⁸ and H¹⁴ resonances in the spectrum of **3** show the presence of satellites due to ¹H–¹⁹⁵Pt coupling. While H⁸ and H¹⁴ show similar low ³J values (28 and 26 Hz, respectively), the coupling constant on H⁷ is 115 Hz. As can be seen in Figure 2, these hydrogen atoms are the closest to the metal centre, all others being separated from it by four or more bonds. The ¹H–¹⁹⁵Pt coupling value found for H⁷ is much higher than that reported by Puddephatt and co-workers for the imine proton in other Pt^{II} four-coordinate complexes.^[9]

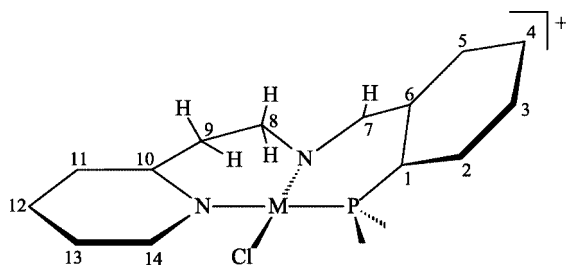


Figure 2. Structure of the cationic complexes (the two phenyl rings bound to phosphorus have been omitted for clarity).

The orange cationic diamagnetic complex [NiCl(PNN)]-PF₆ (**1**) was prepared by reacting equimolar amounts of NiCl₂·6H₂O and PNN in methanol, followed by addition of an excess of NH₄PF₆ dissolved in propan-2-ol and con-

centration of the solution. The ³¹P{¹H} NMR spectrum of **1** recorded at 293 K in CD₂Cl₂ solution shows a broad singlet at δ = 22.4 ($\Delta\nu_{1/2}$ $\approx$ 340 Hz) along with the regular sharp septet at δ = –143.9 [¹J(¹⁹F–³¹P) = 711 Hz], which is typical of the PF₆[–] ion. On lowering the temperature, the width of the broad signal progressively sharpens and at 183 K, the lowest available temperature, $\Delta\nu_{1/2}$ is reduced to 4 Hz (δ = 24.7). The process is completely reversible and also the room-temperature ¹H and ¹³C{¹H} spectra of complex **1** exhibit broad signals and no ³¹P–¹³C coupling constant is shown.

We have examined the possibility that the broadening of the signals may arise from the presence of a paramagnetic Ni^{II} species. In this regard, it should be noted that complexes [NiX₂(P–N)], where P–N is a phosphane-pyridyl^[10] or a phosphane-imine^[10d,11] ligand, are tetrahedral, with magnetic moments in the range 1.82–2.62 μ_B . Furthermore, for a Ni^{II} derivative with a PNNX donor set the possibility for a temperature-dependent equilibrium between diamagnetic square-planar and high-spin tetrahedral structures should be considered.^[12] However, determinations of the magnetic moment in dichloromethane (183–293 K) and 1,2-dichloroethane (293–343 K) solutions show that complex **1** is diamagnetic in agreement with a square-planar structure. This finding fits well with the observation that there is no colour change of the solutions in the whole temperature range 183–343 K. Another Ni^{II} complex with a X(P–N–N) donor set has been found to be diamagnetic.^[13]

In the ¹³C{¹H} spectrum of **1** recorded at 183 K almost all signals are rather sharp and ³¹P–¹³C couplings are shown by C⁷ and several carbon atoms of both phenyl and phenylene rings. Unfortunately, the slow-exchange limit spectrum is not reached and the resonances of C⁸ and C⁹ appear as still broad signals. However, the comparison between the ¹³C{¹H} spectra of **1** (at 183 K) and **2** (at 293 K) allows us to conclude that, as chemical shifts and coupling constants do not exhibit remarkable differences (see Table 2), the “frozen” structure of **1** is analogous to that of **2**. Most probably, the dynamic process observed for complex **1** in solution is due to a conformational flexibility of the chelate ring, which allows both chair and boat conformations. In this regard, several different transition-metal complexes bearing bidentate ligands that form a six-membered chelate ring,^[14] including square-planar species of the type [Ni(P–P)X₂],^[14b] exhibit a fluxional behaviour due to δ -twist-boat– λ -twist-boat rearrangement through a higher-energy chair conformation. It is likely that the dynamic process shown by complex **1** involves a rearrangement of both rings; that formed by the nitrogen donors being more flexible, as suggested by the observation that the most significant modifications of the spectral pattern mainly involve the resonances of the –CH₂CH₂– bridge of the PNN ligand. It should be noted that the other chelate ring exhibits a chain of four sp²-hybridised atoms (–C–C–C–N–), which reduces the conformational flexibility of the cycle. At very low temperatures, the rate of the rearrangement processes is strongly slowed down and the two rings most probably adopt the conformation characteristic of the solid-state

structure of the complex (see below). Another interpretation of the fluxional behaviour of **1** invoking the rupture of the metal–nitrogen bond *trans* to the P atom is less preceded.

Crystal Structure Determination of Complexes **1** and **2**

Structural analysis of complexes **1** and **2** in the solid state was undertaken in order to understand the different dynamic behaviour of the two species observed in solution. Orange-red needles of **1**, as well as pale yellow needles of **2**, suitable for X-ray analysis were obtained by slow diffusion of propan-2-ol into a dichloromethane solution of the complex. The molecular structures of **1** and **2** are presented in Figure 3 and Figure 4, respectively. The metal in both the complexes exhibits the expected square-planar geometry with coordination distances that are slightly shorter

in **1** because of the smaller radius of the Ni^{II} ion. The bond lengths and angles are reported in Table 3, and data of the Pd derivative have values similar to those measured in similar complexes.^[4] In both complexes, the ring formed by the N,N donor set shows a nearly ideal boat conformation, while the other one can be seen as a slightly twisted half-chair (Figure 3). It should be noted that the former is considered to be an unconventional form.^[14c] These conformations cause a twist of the ligand around the metal centre. However, the overall configuration of **1** and **2** is closely comparable and there are no significant geometrical differences. The slight differences in the orientation of pyridine and of the imine moiety C(7)–N(2)–C(8)–C(9) with respect to the coordination plane likely originate in the crystal packing. On the other hand, a detailed examination of the coordination environment shows a slight tetrahedral distortion

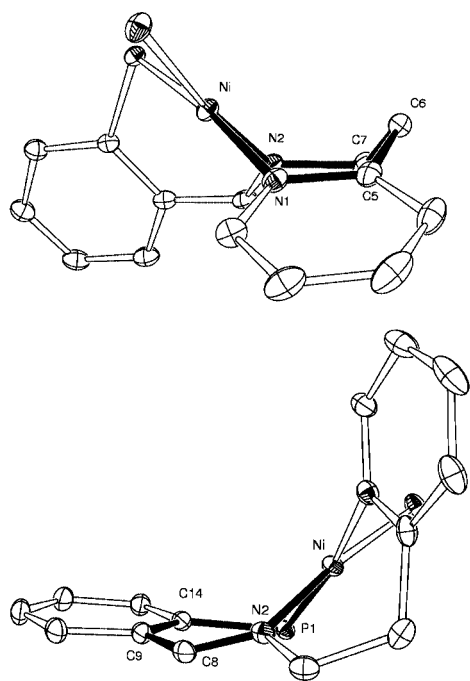
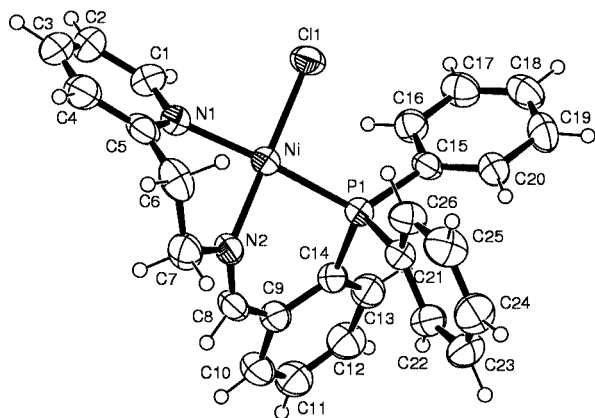


Figure 3. X-ray structure of the cation of complex **1** (ORTEP drawing, thermal ellipsoids at 40% probability level) and a view of the conformations of the two chelate rings.

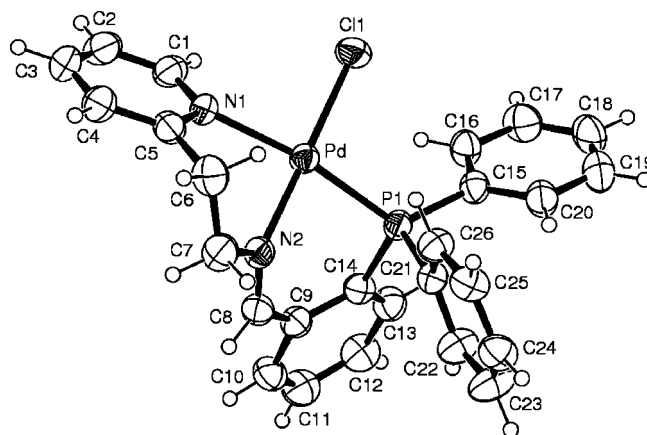


Figure 4. X-ray structure of the cation of complex **2** (ORTEP drawing, thermal ellipsoids at 40% probability level).

Table 3. Coordination bond lengths [Å] and angles [°] and selected geometrical data for **1** and **2**.

	1	2	Δ
M–N(1)	1.944(3)	2.125(4)	0.181
M–N(2)	1.904(3)	2.037(4)	0.133
M–P(1)	2.155(1)	2.226(1)	0.071
M–Cl(1)	2.143(1)	2.282(1)	0.139
N(1)–M–N(2)	89.38(12)	87.12(16)	
N(1)–M–P(1)	172.97(9)	170.28(11)	
N(1)–M–Cl(1)	89.87(9)	91.73(12)	
N(2)–M–P(1)	88.41(9)	85.05(12)	
N(2)–M–Cl(1)	173.05(10)	178.09(11)	
P(1)–M–Cl(1)	93.12(4)	96.25(5)	
N(2)–C(8)	1.283(5)	1.269(7)	
N(2)–C(7)	1.499(5)	1.490(6)	
C(8)–N(2)–C(7)	115.9(3)	117.7(4)	
C(8)–N(2)–Ni	128.5(3)	125.8(3)	
C(7)–N(2)–Ni	115.5(2)	116.4(3)	
C(5)–C(6)–C(7)–N(2)	60.1(4)	59.0(6)	
Py/coord. plane	56.9(1)	50.8(1)	
Imino group/ coord plane	44.7(3)	47.7(2)	
Dev [Å] ^[a]	±0.112(1)	±0.066(2)	

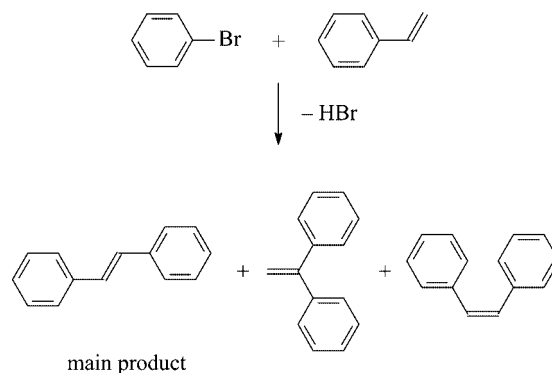
[a] Dev = mean deviation of donors in the square-planar geometry.

tion in the square-planar geometry of the Ni derivative [$\pm 0.112(1)$ Å] in contrast to the more coplanar donors, $\pm 0.066(2)$ Å in the case of Pd. The packing in compound **1** shows a PF_6^- anion located close to the nickel ion with a Ni–F distance of 3.335 Å. This is a feature often encountered in square-planar complexes containing this anion.^[15]

Catalytic Properties of Complexes **1** and **2** in the Heck Reaction

To evaluate the catalytic activity of complex **2** in the Heck reaction, the process of formation of *trans*-stilbene from bromobenzene and styrene has been chosen as a model (Scheme 2). The results of the investigation are collected in Table 4. For all trials, samples of the reaction mixture have been extracted and then analysed by GC after 4, 8 and 20 h. First, we have examined how the nature of the solvent influences yield and selectivity. Thus, the reaction between $\text{C}_6\text{H}_5\text{Br}$ and styrene was performed under argon at 120 °C, using Cs_2CO_3 as the base, in the following solvents: *N*-methylpyrrolidinone (NMP), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), ethylene glycol monomethyl ether (EGME) and 2,2'-thiodiethanol (TDE). NMP, DMF and DMSO are commonly used solvents for the Heck reaction, while the same is not true for the protic solvents EGME and TDE, which have been chosen mainly to ensure a complete dissolution of both the cationic complex and the base. The high final yield (89%) of *trans*-stilbene obtained using EGME (entry 5) with respect to the other solvents (entries 1–4) is rather surprising. Conversely, both regio- and stereoselectivity are rather low, as 9% of a mixture of 1,1-diphenylethene (main byproduct) and *cis*-stilbene is formed. The use of DMF resulted in the immediate formation of an insoluble brown material and only very small amounts of products were detected. The almost negligible activity of complex **2** in DMSO is most probably due to the strong coordinating ability of this solvent, which does not allow substrate activation on the metal centre. Notably, using EGME the yield is very high within a short time (83% after 4 h), despite the formation of palladium black after only a few minutes. We have found that the catalytic activity of complex **2** drastically decreases after the addition of a second batch of reagents. Thus, the *trans*-stilbene yield drops from 83 to 49% after 4 h in the second run. Such a finding agrees with the observed increasing formation of palladium black in the reaction vessel. In this regard, several authors have reported that palladium black is not an active Heck catalyst.^[16] Apparently, the effective catalyst is longer lived, but slightly less active, in TDE, the final yield being good nevertheless (85%). The best base to use in combination with EGME is Cs_2CO_3 , as with dimethylcyclohexylamine, K_2CO_3 and $\text{CsOH}\cdot\text{H}_2\text{O}$ lower yields have been obtained (entries 6–8). In the case of cesium hydroxide the conversion of $\text{C}_6\text{H}_5\text{Br}$ into products is almost complete, but a dramatic lowering of the selectivity is observed. To reduce palladium black formation, the reaction has been performed at lower temperature (80 °C), but in this case the

reaction rate is too low to obtain an acceptable yield (entry 9). Surprisingly, the use of $\text{C}_6\text{H}_5\text{I}$ instead of $\text{C}_6\text{H}_5\text{Br}$ does not correspond to the expected neat increase of the reaction rate^[8g] (entry 10). The mechanism of the reaction is currently under investigation, but some preliminary results can be briefly discussed. ^{31}P NMR measurements indicate that complex **2** is stable at 120 °C in EGME alone and even in the presence of both $\text{C}_6\text{H}_5\text{Br}$ and styrene, but immediately after the introduction of Cs_2CO_3 the pale yellow colour of the solution turns dark orange. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution shows that a singlet at $\delta = 33.0$ has completely replaced the signal at $\delta = 31.1$ because of complex **2**, while no other resonance is detectable. Thus, the starting complex is no longer present in solution under catalytic conditions but is transformed into a new species, most probably the effective catalyst. Attempts to isolate this derivative were unsuccessful. A prolonged warming of the dark orange solution at 120 °C results in the formation of increasing amounts of palladium black.



Scheme 2.

Finally, the Ni^{II} derivative **1** does not show any catalytic property in the reaction between $\text{C}_6\text{H}_5\text{Br}$ and styrene, or in the presence of an excess of zinc dust (entry 11). It is well known that Ni^{II} compounds are less active than Pd^{II} compounds, but the beneficial role of a reductant such as zinc has been demonstrated in several cases.^[17] The complete lack of catalytic activity of **1** is most probably due to the more difficult β -elimination and HBr removal steps for Ni^{II} with respect to Pd^{II} .^[18]

It should be noted that α,β -unsaturated esters, used as starting material in combination with bromobenzene in EGME, undergo a transesterification process, promoted by Cs_2CO_3 , giving the corresponding 2-methoxyethyl ester, which then undergoes the Heck reaction. Thus, for example, a mixture of *cis*- and *trans*-2-methoxyethyl-2-methyl-3-phenylpropenoate (major product) has been obtained from ethyl methacrylate.

In conclusion, complex **2** shows a good catalytic performance in the Heck reaction starting from aryl bromides, and the use of EGME as solvent is crucial to achieve good yields.

Table 4. Catalytic activity of complexes **1** and **2** (1 mol-%) in the Heck reaction.^[a]

Entry	Complex	Aryl halide	Alkene	Solvent ^[b]	Base ^[c]	Temp. (°C)	<i>trans</i> -Stilbene yield (%) ^[d]		
							4 h	8 h	20 h
1	2	C ₆ H ₅ Br	styrene	NMP	Cs ₂ CO ₃	120	42	45	46 (53)
2	2	C ₆ H ₅ Br	styrene	TDE	Cs ₂ CO ₃	120	58	71	83 (89)
3	2	C ₆ H ₅ Br	styrene	DMSO	Cs ₂ CO ₃	120	–	1	2 (5)
4	2	C ₆ H ₅ Br	styrene	DMF	Cs ₂ CO ₃	120	1	2	3 (7)
5	2	C ₆ H ₅ Br	styrene	EGME	Cs ₂ CO ₃	120	83	86	89 (98)
6	2	C ₆ H ₅ Br	styrene	EGME	DMCA	120	13	28	41 (45)
7	2	C ₆ H ₅ Br	styrene	EGME	K ₂ CO ₃	120	64	67	68 (74)
8	2	C ₆ H ₅ Br	styrene	EGME	CsOH·H ₂ O	120	69	74	75 (98)
9	2	C ₆ H ₅ Br	styrene	EGME	Cs ₂ CO ₃	80	11	14	18 (24)
10	2	C ₆ H ₅ I	styrene	EGME	Cs ₂ CO ₃	120	87	88	90 (100)
11	1 ^[e]	C ₆ H ₅ Br	styrene	EGME	Cs ₂ CO ₃	120	–	–	–

[a] Experimental conditions: aryl halide (1.0 equiv.), alkene (1.2 equiv.), base (1.2 equiv.). [b] NMP = 1-methyl-2-pyrrolidinone, DMSO = dimethyl sulfoxide, TDE = 2,2'-thiodiethanol, EGME = ethylene glycol monomethyl ether. [c] DMCA = dimethylcyclohexylamine. [d] GC yield. Aryl halide conversion after 20 h is reported in parenthesis. [e] With 10% Zn (dust) added.

Experimental Section

General Remarks: All reagents were purchased from Aldrich and used without further purification. Commercial solvents were dried according to standard methods^[19] and freshly distilled under argon before use. All syntheses and manipulations were carried out under argon using standard Schlenk techniques. The ligand *N*-[2-(diphenylphosphanyl)benzylidene][2-(2-pyridyl)ethyl]amine (PNN) was prepared as described in the literature^[4b] and was obtained very pure as a cream-coloured powder after double recrystallisation from *n*-hexane.

Instrumentation and Analyses: The ¹H, ¹³C and ³¹P NMR spectra (at 200.13, 50.32 and 81.02 MHz, respectively) were recorded with a Bruker AC 200 F QNP spectrometer equipped with a variable-temperature probe. The ¹H and ¹³C chemical shifts were referenced to SiMe₄, while positive ³¹P chemical shifts were downfield from 85% H₃PO₄ as external standard. The temperature in the range 273–183 K was calibrated with methanol. The simulation of the 293 K ¹H spectrum of PNN was performed with an Aspect 2000 computer using the programme PANIC (Bruker Spectrospin AG). The GC-MS analyses, run to control the identity of the compounds obtained in the catalytic trials, were carried out with a Fisons TRIO 2000 gas chromatograph-mass spectrometer working in the positive ion 70 eV electron impact mode. Injector temperature was kept at 250 °C and the column (Supelco® SE-54, 30 m long, 0.25 mm i.d., coated with a 0.5 µm phenyl methyl silicone film) temperature was programmed from 50 °C to 310 °C with a gradient of 10 °C/min. The GC analyses were run on a Fisons GC 8000 Series gas chromatograph equipped with a Supelco® PTA-5 column [30 m long, 0.53 mm i.d., coated with a 3.0 µm poly(5% diphenyl/95% dimethylsiloxane) film]. Injector and column temperatures were as indicated above. The elemental analyses (C, H, N) were carried out in the Microanalytical Laboratory of our department.

Synthesis of [NiCl(PNN)]PF₆ (1**):** A methanol solution (10 mL) of PNN (158 mg, 0.40 mmol) was added to 15 mL of a methanol solu-

tion of NiCl₂·6H₂O (90 mg, 0.38 mmol). The red solution was stirred for 10 min and then NH₄PF₆ (196 mg, 1.2 mmol) dissolved in propan-2-ol (20 mL) was added. An orange powder immediately formed, which was filtered off, washed with methanol and dried. The product was then recrystallised from dichloromethane/propan-2-ol. Needle-shaped red crystals were obtained by slow diffusion of propan-2-ol into a dichloromethane solution of the complex. Yield: 195 mg, 81%. C₂₆H₂₃ClF₆N₂NiP₂ (633.57): calcd. C 49.29, H 3.66, N 4.42; found C 48.93, H 3.62, N 4.37. ³¹P NMR (CD₂Cl₂, 183 K): δ = 24.7 ppm. ¹H and ¹³C NMR spectroscopic data are reported in Table 1 and Table 2, respectively.

Synthesis of [PdCl(PNN)]PF₆ (2**):** A mixture of [PdCl₂(CH₃CN)₂] (156 mg, 0.60 mmol) and PNN (245 mg, 0.62 mmol) in dichloromethane (20 mL) was stirred for 30 min. NH₄PF₆ (294 mg, 1.8 mmol) dissolved in propan-2-ol (25 mL) was then added to the yellow solution and the dichloromethane was pumped off. The pale yellow precipitate, which was filtered off, washed with propan-2-ol and vacuum dried, was then recrystallised from dichloromethane/propan-2-ol. Needle-shaped pale yellow crystals were obtained by slow diffusion of propan-2-ol into a dichloromethane solution of the complex. The crystals contain half mol of CH₂Cl₂ per mol of complex. Yield: 379 mg, 87%. C₂₆H₂₃ClF₆N₂Pd·0.5CH₂Cl₂ (723.76): calcd. C 43.98, H 3.34, N 3.87; found C 43.72, H 3.37, N 3.81. ³¹P NMR (CD₂Cl₂, 293 K): δ = 31.0 ppm. ¹H and ¹³C NMR spectroscopic data are reported in Table 1 and Table 2, respectively.

Synthesis of [PtCl(PNN)]PF₆ (3**):** A mixture of [PtCl₂(C₆H₅CN)₂] (118 mg, 0.25 mmol) and PNN (103 mg, 0.26 mmol) in dichloromethane (20 mL) was stirred for 30 min. After the addition of NH₄PF₆ (130 mg, 0.8 mmol) dissolved in propan-2-ol (20 mL), the dichloromethane was eliminated in vacuo affording a pale yellow product, which was filtered off, washed with propan-2-ol and vacuum dried. The crude product was recrystallised from dichloromethane/propan-2-ol. Needle-shaped pale yellow crystals were obtained by slow diffusion of propan-2-ol into a dichloromethane solution of the complex. The crystals contain half mol of CH₂Cl₂

per mol of complex. Yield: 186 mg, 91%. $C_{26}H_{23}ClF_6N_2P_2Pt \cdot 0.5CH_2Cl_2$ (812.42): calcd. C 39.18, H 2.98, N 3.45; found C 38.94, H 3.03, N 3.40. ^{31}P NMR (CD_2Cl_2 , 293 K): δ = 1.4; $^1J(^{31}P-^{195}Pt)$ = 3459 Hz. 1H and ^{13}C NMR spectroscopic data are reported in Table 1 and Table 2, respectively.

Magnetic Moment Measurements on Complex 1 in Solution: Measurements were run on CH_2Cl_2 and $ClCH_2-CH_2Cl$ solutions of the complex, at temperatures below and above 293 K, respectively. The method described by Evans^[20] was adopted using a 5-mm NMR tube with a 2-mm coaxial capillary inside containing the pure solvent. The solutions (5×10^{-2} M) were prepared by dissolving 15.8 mg (25 μ mol) of **1** into 0.5 mL of the appropriate solvent. Spectra were recorded at 183, 193, 213, 233, 253, 273, 293, 313, 333 and 343 K.

General Procedure for the Heck Reaction: Under argon, a 10-mL Schlenk flask containing a magnetic stir bar was charged with the catalyst (2.0 mg for each single experiment, 1 mol-%) and appropriate amounts of aryl halide (1.0 equiv.), alkene (1.2 equiv.) and base (1.2 equiv.). After addition of the solvent (2 mL), the flask was capped with a silicon stopper and heated at 120 °C in an oil bath. The reaction mixture was extracted from the flask by syringe after 4, 8 and 20 h. The samples were treated with water, extracted with ethyl ether, dried with Na_2SO_4 and then analysed by GC.

Crystallographic Structure Determination: Diffraction data of the structures reported were carried out on a rotating anode Nonius FR591 (Cu- K_α radiation λ = 1.54178 Å) equipped with a Kappa CCD imaging plate. Cell refinement, indexing and scaling of the data sets were carried out using Denzo^[21] and Scalepack.^[21] Both the structures were solved by Patterson and Fourier analyses^[22] and refined by the full-matrix least-squares method based on F^2 with all observed reflections.^[22] A ΔF map of **2** revealed, besides the PF_6^- anion, a disordered molecule of CH_2Cl_2 (occupancy factor 0.5, based on the electron density peaks). The hydrogen atoms were

located at geometrically calculated positions. All the calculations were performed using the WinGX System, version 1.70.00.^[23] Crystallographic data and details of structure refinements are reported in Table 5.

CCDC-282001 (for **2**) and -282002 (for **1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 5. Crystallographic data and details of structure refinements for **1** and **2**.

	1	2 ·0.5CH ₂ Cl ₂
Formula	C ₂₆ H ₂₃ ClF ₆ N ₂ NiP ₂	C _{26.5} H ₂₄ Cl ₂ F ₆ N ₂ P ₂ Pd
M_r	633.56	723.72
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.125(3)	8.544(2)
b [Å]	12.214(3)	13.097(4)
c [Å]	13.101(4)	13.643(4)
α [°]	103.51(2)	102.97(2)
β [°]	111.03(3)	103.63(2)
γ [°]	106.81(2)	97.57(2)
Volume [Å ³]	1340.5(7)	1418.1(7)
Z	2	2
$D_{\text{calcd.}}$ [g cm ⁻³]	1.570	1.695
μ (Mo- K_α) [mm ⁻¹]	3.647	8.627
$F(000)$	644	722
θ_{max} [°]	64.56	64.70
Reflections collected	15767	20902
Unique reflections	3954	4352
R_{int}	0.0751	0.0438
Observed $I > 2\sigma(I)$	3404	4024
Parameters	343	355
Goodness of fit (F^2)	1.078	1.073
R_1 [$I > 2\sigma(I)$] ^[a]	0.0631	0.0564
wR_2 ^[b]	0.1808	0.1521
$\Delta\rho$ [e/Å ³]	0.364, -0.429	0.885, -0.984

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$.

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