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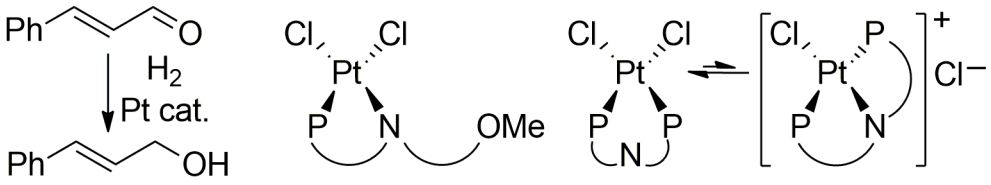

selectivity up to 67% *cis*-Pt(*P*,*N*) *cis*-Pt(*P*,*P*) *trans*-Pt(*P*,*N*,*P*)

Platinum Complexes with a Methoxy-Amino Phosphine or a Nitrogen-Containing Bis(phosphine) Ligand. Synthesis, Characterization and Application to Hydrogenation of *trans*-Cinnamaldehyde

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Abstract

Platinum complexes with a methoxy-amino phosphine or an ethylene-linked nitrogen-containing bis(phosphine) ligand have been synthesized and fully characterized by spectroscopic as well as crystallographic studies. The first ligand is bound to the metal in a *P*,*N*-bidentate coordination mode and with *cis* geometry, independently of the reaction temperature. Synthesis of a platinum complex with the second ligand at room temperature, afforded a mixture comprising 86% of a neutral *cis* complex, in which the ligand is bound to the metal only *via* the two P-donors, and 14% of a *P*,*N*,*P*-terdentate ionic complex where the two P atoms are *trans* to each other. On the other hand, synthesis of the complex at 100 ºC, led almost exclusively to the formation of the *cis*-Pt complex in a *P*,*P*-bidentate coordination mode. The complexes were tested as catalysts without any promoting additive for the hydrogenation of *trans*-cinnamaldehyde under mild reaction conditions and displayed selectivity for the formation of cinnamyl alcohol of up to 67%.

Keywords: Platinum complex; PN Ligand; PNP Ligand; Hydrogenation; Cinnamaldehyde; Homogeneous catalysis

1. Introduction

Hydrogenation of α,β-unsaturated aldehydes such as cinnamaldehyde (CALD), is a subject of a much academic and industrial interest for the synthesis of specialty chemicals. Hydrogenation of the C=C bond of CALD leads to hydrocinnamaldehyde (HCALD) used in the flavouring industry [1] and in the synthesis of pharmaceuticals [2], while hydrogenation of the C=O bond produces cinnamyl alcohol (CALH) used in the manufacture of perfumes [3]. Selective synthesis of CALH is always difficult to achieve because thermodynamics favor the hydrogenation of C=C over C=O by about 35 kJ mol^{-1}, and also the kinetics of the ethylenic double-bond hydrogenation are faster than for the carbonyl group [4]. In addition, further hydrogenation of CALH to hydrocinnamyl alcohol (HCALH) is much faster than the hydrogenation of CALD to CALH [5]. Selective hydrogenation of the C=O bond in

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unsaturated aldehydes is therefore a challenging research topic and in this area we have previously reported the first studies concerning the evaluation of porphyrin–metal complexes [6] as well as Pt/TDPC nanoparticles [7] (TDPC = 3,3´-thiodipropionic acid) as catalysts for hydrogenation of *trans*-cinnamaldehyde. Several unsupported transition metal (e.g. Co, Ru, Ir) complexes have been used as homogeneous catalysts in organic or aqueous medium for the hydrogenation of unsaturated aldehydes, providing an excellent selectivity for the formation of unsaturated alcohols [8]. Metal colloidal nanocatalysts are also known to improve C=O hydrogenation in a homogeneous catalytic system [9]. Heterogeneous platinum catalysts have been widely used in this reaction and an excellent selectivity of over 90% for C=O hydrogenation has been reported for Pt-supported catalysts, Pt-nanoparticles or Pt-nanoclusters [10], as well as for monometallic or bimetallic Pt-nanoparticles on carbon nanotubes [11]. According to a review by Gallezot and Richard, selective C=O hydrogenation of CALD by unpromoted noble metals as heterogeneous catalysts follows the order Os > Ir > Pt > Ru > Rh > Pd, and electronic and steric effects play a crucial role on this selectivity [5]. As is evident from the literature, platinum is the most studied of the above metals for this heterogeneous hydrogenation since it is both an active and selective catalyst. On the other hand, for homogeneous hydrogenation of α,β-unsaturated aldehydes by unsupported metal complexes, metals such as Co, Ru, Ir were found to be beneficial for C=O hydrogenation, and the role of these metals and of the ligands on selectivity has also been investigated [8]. To our knowledge, however, unsupported platinum complexes as homogeneous catalysts for the hydrogenation of α,β-unsaturated aldehydes have rarely been reported and those that have been reported show very low selectivity for the hydrogenation of the C=O bond [12]. Thus, additional studies are required regarding the use of platinum complexes in this reaction.

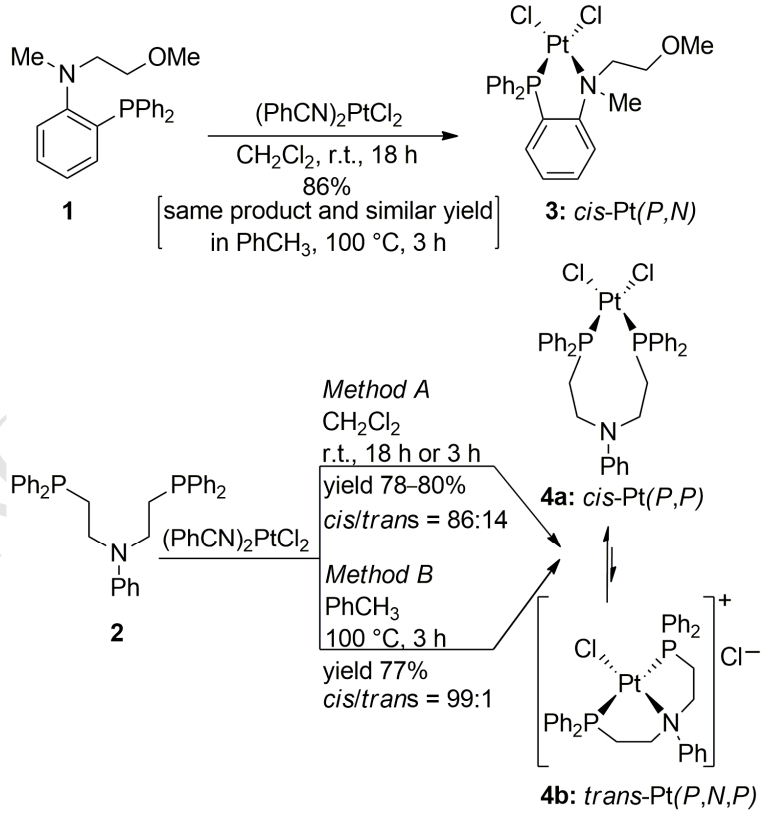
Hybrid chelating ligands which contain at least two different chemical functionalities and, more specifically, hemilabile hybrid ligands with soft and hard donor atoms (e.g. P, N, O, S), have received much attention in transition metal homogeneous catalysis [13]. Ligands which bear phosphorus and nitrogen donors are amongst the most important and widely used heterodentate ligands for homogeneous catalysis (asymmetric or otherwise) and can stabilize intermediate oxidation states or geometries during a catalytic cycle [13,14]. As a part of our efforts in this area [15], we have previously reported the synthesis of the methoxy-amino phosphine **1** [16] and the nitrogen-containing bis(phosphine) **2** [17] (Scheme 1) as efficient ligands for the Rh-catalyzed hydroformylation of styrene. We have shown that ligand **1** is *P*,*N*-bound to rhodium and that coordination of the methoxy oxygen to the metal is not observed [16]. A *P*,*N*-bidentate coordination mode for the analogous phosphino-amino alcohol towards rhodium was also found by us [16], as well as recently by Kollár towards platinum after a reaction time of more than 2 h [18]. In contrast to NP2 ligands that contain a methylene linker between the N- and the P-atoms, which disfavour simultaneous coordination of the three donors, with the N-atom remaining unbound [19], ethylene-linked NP2 ligands such as **2** that impart a structural flexibility commonly coordinate to metal centres in a *P*,*N*,*P*-terdentate fashion. Examples of metal complexes with ethylene-linked NP2 ligands and a brief discussion of their coordination chemistry are given below. The *P*,*N*,*P*-terdentate coordination mode has been reported in iron complexes by Beller [20], Fairweather and Guan [21], and Hazari and Neidig [22]. Gray and colleagues found dual coordination modes in Co^{II} and Ni^{II} iodides, in which coordination to nickel is achieved *via* the three donors, in contrast to cobalt complexes, where the central N-donor generally remains unbound, with only one exception where a Co–N interaction was also observed [23]. Hanson reported a terdentate mode in $Co^{II}(CH_2SiMe_3)$ complexes [24]. Terdentate coordination was also observed in ruthenium complexes by Beller [25], Holthausen and Schneider [26], and Gusev [27], in osmium complexes by Gusev [27], in rhenium complexes by Schneider [28], and in iridium di(or tri)hydride complexes by Holthausen and Schneider [29] and Bianchini [30], while in

monohydride iridium complexes, the ligand is bound to the metal only *via* the two phosphorus atoms [30]. Hii (Mimi) found the formation of *P*,*N*,*P*-bound complexes with Pd^{II} salts, as opposed to a *P*,*P*-bidentate mode with Pd^0 [31]. Kollár reported a *P*,*P*-bidentate coordination mode in a platinum complex with an ethylene-linked NP2 ligand, while nitrogen is also bound to the metal in DMSO-d_6 or by addition of $SnCl_2$ or of KI or KCN in the presence of $SnCl_2$ to the platinum complex [32]. Platinum and other metal complexes with analogous NP2 ligands have been reported by Taqui Khan *et al.*, including examples of bi- and more often terdentate coordination modes [33]. We have also shown a *P*,*P*-bidentate coordination mode in a Rh^I complex with ligand **2** at room temperature, while at low temperatures a Rh–N interaction is also possible [17]. In the present work, we report the synthesis and characterization of platinum complexes with the above-mentioned ligands **1** and **2**. The catalytic activity of these complexes towards the hydrogenation of *trans*-cinnamaldehyde was also investigated.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of platinum complexes

The synthesis of platinum complexes **3** and **4** was achieved by treatment of $(PhCN)_2PtCl_2$ with one equivalent of ligand **1** or **2**, respectively (Scheme 1). All synthetic procedures described below were performed 2–4 times to ensure repeatability and to establish the coordination mode in the complexes, which was determined by spectroscopic techniques as well as by X-ray studies. The $^1J(^{195}Pt,^{31}P)$ coupling constants in the ^{31}P NMR spectra of platinum complexes are diagnostic and it is known that the *trans* P–Cl arrangement gives $^1J_{PtP}$ higher than 3500 Hz, while the *trans* P–P arrangement displays $^1J_{PtP}$ in the range of 2500–3000 Hz [34].



Scheme 1. Synthesis of platinum complexes.
[Scheme to be reproduced in a single column]

Complex **3** was prepared in an overnight experiment (18 h) at room temperature using dichloromethane as a solvent. The same product was also obtained in toluene at 100 ºC for 3 h. ^{1}H and ^{13}C NMR spectra of **3** in $CDCl_3$ showed that the NMe resonance is shifted considerably downfield compared to the corresponding resonance in the free ligand ($\Delta\delta$ = 1.09 ppm in the ^{1}H NMR; $\Delta\delta$ = 15.35 ppm in the ^{13}C NMR) providing clear evidence for Pt–N coordination. On the other hand, the OMe resonance is shifted slightly upfield in the ^{1}H NMR spectrum and is at the same position in the ^{13}C NMR spectrum compared to the free ligand, indicating the absence of a Pt–O interaction. Analogous chemical shifts for the NMe and OMe moieties in the ^{1}H and ^{13}C NMR spectra of **3** were also observed in acetone-d_6. Upon complexation, the four NCH_2CH_2O protons become chemically and magnetically nonequivalent. Indeed, in the ^{1}H NMR spectrum of **3** in $CDCl_3$, the signals for these protons are centered at δ 4.78 (1H, NCH_A), 3.94 (1H, OCH_X), 3.77 (1H, OCH_Z) and 3.64 (1H, NCH_M) corresponding to an AMXZ spin system with a $\Delta\nu_{AM} = 54J_{AM}$ and $\Delta\nu_{XZ} = 10J_{XZ}$ (see spectra in SI). The NCH_2 *gem* coupling constant is $^{2}J_{AM}$ = 12.7 Hz and the OCH_2 *gem* coupling constant is $^{2}J_{XZ}$ = 10.7 Hz. In acetone-d_6, these protons appear at δ 4.68 (1H, NCH_A), 3.85 (1H, NCH_M), 3.80 (1H, OCH_X) and 3.72 (1H, OCH_Y) with a $\Delta\nu_{AM} = 40J_{AM}$ and $\Delta\nu_{XY} = 4J_{XY}$, corresponding to an AMXY spin system ($^{2}J_{AM}$ = 12.4 Hz and $^{2}J_{XY}$ = 10.5 Hz). The ^{31}P NMR spectrum of **3** in $CDCl_3$ or acetone-d_6 showed a single central signal at 15.48 or 16.25 ppm, respectively, flanked by platinum satellites in a ratio of 1:4:1. The absence of the signal corresponding to the free ligand **1** at –13.80 ppm [16] supports the coordination of the P-atom to the metal center and the formation of a five-membered chelate ring. The value of $^{1}J_{PtP}$ coupling constant (3903 Hz in $CDCl_3$ or 3878 Hz in acetone-d_6) provides a clear evidence for the formation of a *cis*-$PtCl_2$**(1)** complex. The above-mentioned coordination mode and geometry is also supported by the crystal structure of complex **3** as described below. Positive ESI-MS of **3** showed bands corresponding exactly to $[M–Cl]^+$ and $[M+Na]^+$ (see HRMS in the experimental section and also in SI).

Complex **4** was prepared at room temperature in 18 h using dichloromethane as a solvent (Method A) or in toluene at 100 ºC for 3 h (Method B). The ^{31}P NMR spectrum of **4** showed central signals flanked by platinum satellites in a ratio of 1:4:1. The absence of the signal corresponding to the free ligand **2** at –21.22 ppm [17] and the lack of P–P coupling support the coordination of the two equivalent P-atoms to platinum. However, the ^{31}P NMR spectra of the products obtained by each of the above-mentioned methods showed a difference, although the spectra for the products by both syntheses were taken in $CDCl_3$ over several hours (Figure 1). In $CDCl_3$, the ^{31}P NMR spectrum of the product obtained by method A displayed a central signal at 10.37 ppm with a $^{1}J_{PtP}$ coupling constant equal to 3591 Hz and also a central signal at 27.49 ppm with 2712 Hz as a $^{1}J_{PtP}$ coupling constant. In accordance to Hii's (Mimi) observation for Pd complexes with ethylene-linked NP2 ligands [31], we also propose an isomerization between the neutral *cis*(*P*,*P*) and the cationic *trans*(*P*,*N*,*P*) configuration as the ligand alternates between bi- and terdentate modes without cleavage of the Pt–P bonds (Scheme 1). The value of the $^{1}J_{PtP}$ coupling constant for the upfield resonance corresponds to a *cis*(*P*,*P*) geometry (complex **4a**), in which ligand **2** is bound to platinum only *via* the two P-atoms. The downfield resonance corresponds to the *trans*(*P*,*N*,*P*) isomer **4b**, in which N-donor is also coordinated to the metal, forming two five-membered chelate rings in cationic species of the formula $[(PNP)Pt(Cl)]^+$ with chloride as a counterion. Relative integration of the signals showed that the product mixture comprises 86% of **4a** and 14% of **4b**. The small Λ value (1.91 Ω^{-1} cm^2 mol^{-1} in CH_2Cl_2) observed from the conductivity measurement of the product resulting from method A definitely indicates only a partial isomerization of the neutral platinum complex to the corresponding ionic form. Analogous cationic complexes as unique species have previously been reported for palladium [31] and

nickel complexes [23] of ligand **2** at reflux or at room temperature, respectively. Synthesis was also performed at room temperature in a shorter reaction time (3 h), affording complex **4** in a very similar yield with the same molar ratio of isomers (**4a**/**4b** = 86:14). On the other hand, the ^{31}P NMR spectrum in $CDCl_3$ of the product obtained by method B (toluene, 100 ºC, 3 h), provided the same resonances and coupling constants with the percentage of the major component **4a** being 99%. The same isomer ratio (99:1) for the latter method was also found in an overnight ^{31}P NMR experiment using acetone-d_6 or DMSO-d_6 as a solvent (see spectra in SI), and this observation is in contrast to a platinum complex with another ethylene-linked NP2 ligand previously reported by Kollár, in which the coordination mode changes from a *P*,*P*-bidentate to a *P*,*N*,*P*-terdentate fashion in DMSO-d_6 [32]. The multiplet pattern for the PCH_2 carbons in the ^{13}C NMR spectrum of **4a** is characteristic for chemically equivalent but magnetically nonequivalent nuclei [19b]. Negative ESI-MS of **4a** showed a band corresponding exactly to $[M+Cl]^-$ (see HRMS in the experimental section and also in SI). It is obvious from the above-mentioned experiments that the reaction conditions affect the isomer ratio, and that a reaction at 100 ºC leads almost exclusively to the formation of the thermodynamically favoured *cis*-$PtCl_2$**(2)** complex in a *P*,*P*-bidentate mode, which is also supported by the crystal structure of the complex resulting from method B (see below). It should also be pointed out that the temperature effect on the isomer ratio of **4** is opposite to that observed for a palladium complex with ligand **2**, in which heating of the reaction mixture leads to $[(PNP)Pd(Cl)]^+Cl^-$ as the most thermodynamically stable product [31].

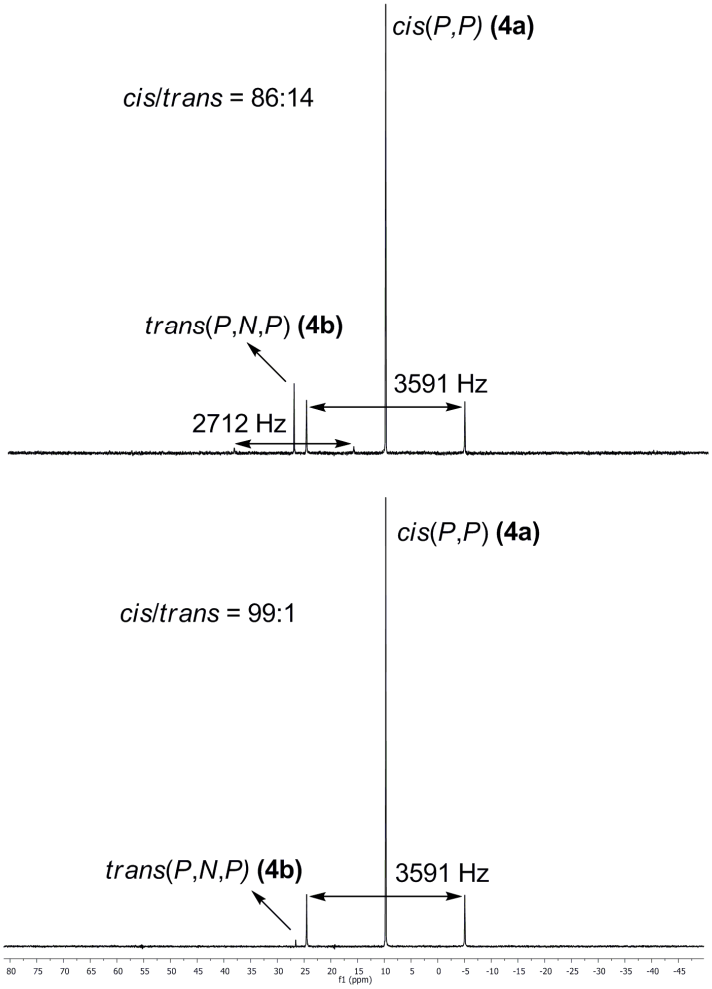


Figure 1. ^{31}P NMR (121.50 MHz, $CDCl_3$) spectrum for complex **4**, synthesized by method A (top) or B (bottom).
[Fig. to be reproduced in a single column]

2.2. Crystal structures

Crystals of complexes **3** and **4a** (synthesized by method B) suitable for X-ray determination were obtained by slow diffusion of diethyl ether through a solution of the complexes in dichloromethane. The molecular structures of **3** and **4a** are shown in Figure 2, and selected bond distances and angles are listed in Table 1.

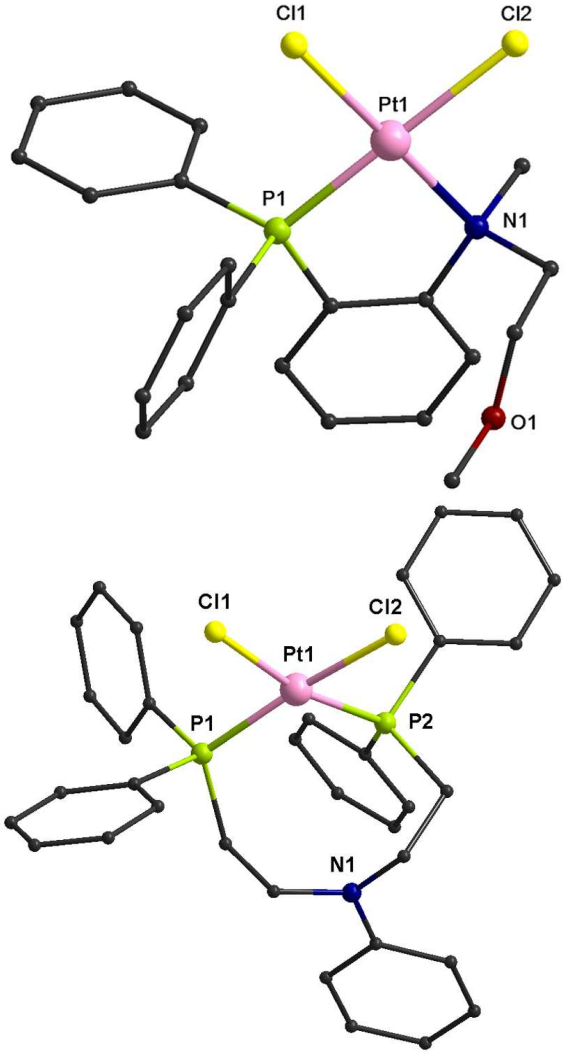


Figure 2. Partially labeled plot of the molecular structure of **3** (top) and **4a** (bottom). [Fig. to be reproduced in a single column]

Complex **3** consists of a Pt^{II} ion in square planar coordination comprised of two chloro ions in a *cis*-arrangement and the P,N-donor atoms of ligand **1**. The bite angle P–Pt–N is 86.98°. The coordination chromophore $PNCl_2$ and the metal ion are coplanar within experimental error. The five-membered ring in the coordination sphere, defined by atoms Pt(1)–P(1)–C(22)–C(17)–N(1), is almost planar with largest deviation 0.13 Å for C(22). The Pt(1)–Cl(1) (*trans* to N(1)) bond is ~2.29 Å, substantially shorter by 0.08 Å than the Pt(1)–Cl(2) (*trans* to P(1)) bond of ~2.37 Å, in conformity with the *trans* effect series, i.e. ligands coordinated through P atoms show higher *trans* influence than those coordinated through N ones [35]. The longer Pt–Cl bond (~2.37 Å) is in agreement with those observed in *cis*-dichloro platimum(II) complexes with PNP ligands which fall in the range 2.35-2.38 Å [19b,c]. Inspection of the Cambridge Structural Database (CSD) revealed only 24 *cis*-

dichloro Pt^{II} complexes with *P*,*N*-ligands such as **1**, with unsymmetrical Pt–Cl bond distances in the range 2.27–2.30 and 2.35–2.38 Å, respectively [36].

Complex **4a** consists of a Pt^{II} ion in a square planar P_2Cl_2 environment. The bite angle P–Pt–P is 99.42°. The PtP_2Cl_2 atoms are almost coplanar with largest deviation 0.20 Å for Cl(2). The two *cis*-chloro ions are bound with almost equal bonds at ~2.36 Å, as expected from the fact that they are *trans* to the same type of atoms (P(1) and P(2)), in agreement with other Pt(*P*,*P*) complexes [19b,c]. Ligand **2** is coordinated through the two phosphorous atoms forming an eight-membered ring with the participation of the metal ion. The eight-membered ring, defined by atoms Pt(1), P(1), P(2), N(1) and the two ethylene groups, is found in the most stable boat-chair conformation. To the best of our knowledge, **4a** and complex *cis*-$[PtCl_2(Ph_2P\text{-}(CH_2)_5\text{-}PPh_2)]$ [37] are the only examples of PtP_2Cl_2 square planar complexes with eight-membered rings in the coordination sphere as determined by crystallographic studies. The Pt–P bond distances are ~2.24 Å, in agreement with analogous complexes [19b,c]. The large distance of the nitrogen atom from the metal ion at ~3.92 Å indicates absence of interaction. The molecular structure of **4a** also contains one molecule of dichloromethane.

Table 1
Selected bond distances [Å] and angles [°] in **3** and **4a**

3		**4a**	
Distances			
Pt(1)–N(1)	2.111(2)	Pt(1)–P(1)	2.2352(5)
Pt(1)–P(1)	2.1844(6)	Pt(1)–P(2)	2.2524(5)
Pt(1)–Cl(1)	2.2890(6)	Pt(1)–Cl(1)	2.3543(5)
Pt(1)–Cl(2)	2.3697(6)	Pt(1)–Cl(2)	2.3578(5)
Angles			
N(1)–Pt(1)–P(1)	86.98(5)	P(1)–Pt(1)–P(2)	99.42(2)
N(1)–Pt(1)–Cl(1)	177.57(6)	P(1)–Pt(1)–Cl(1)	89.73(2)
P(1)–Pt(1)–Cl(1)	91.84(2)	P(2)–Pt(1)–Cl(1)	168.77(2)
N(1)–Pt(1)–Cl(2)	92.13(5)	P(1)–Pt(1)–Cl(2)	171.60(2)
P(1)–Pt(1)–Cl(2)	179.07(2)	P(2)–Pt(1)–Cl(2)	83.35(2)
Cl(1)–Pt(1)–Cl(2)	89.03(2)	Cl(1)–Pt(1)–Cl(2)	88.51(2)

[Table to be reproduced in a single column]

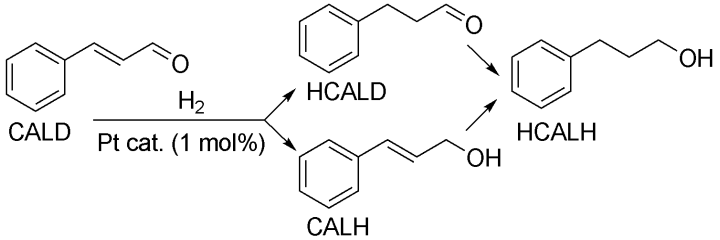
2.3. Hydrogenation of cinnamaldehyde

Platinum complexes **3** and **4** without any promoting additive such as $SnCl_2$, were evaluated as catalysts in the hydrogenation of *trans*-cinnamaldehyde (CALD) which was chosen as a model compound for α,β-unsaturated aldehydes (Scheme 2, Table 2). Hydrogenations were carried out in acetone or dichloromethane as solvent with a substrate/catalyst molar ratio of 100:1. In order to compare the obtained selectivity values at a similar conversion level, selected experiments were performed by using a higher Pt loading at the same concentration (1 mM) and with prolonged reaction times. GC–MS analyses of the

resulting hydrogenation products indicated that the formation of decarbonylation by-products or other side-products was negligible or nonexistent. Unfortunately, a significant amount of hydrocinnamyl alcohol (HCALH) was formed in all experiments due to the hydrogenation of both C=C and C=O bonds.

Catalysis at 40 ºC and 20 bar of hydrogen pressure by complex **3** in acetone for 2 h, afforded 52% conversion with 59% selectivity toward cinnamyl alcohol (CALH) (entry 1), while a reaction time of 24 h was sufficient for a quantitative conversion of CALD, but with a considerable increase in the percentage of HCALH, resulting in a lower selectivity for CALH, and the disappearance of hydrocinnamaldehyde (HCALD) (entry 2). On the other hand, catalysis in dichloromethane under the same reaction conditions, led to 58% conversion of CALD and 72% selectivity for HCALD as the major product (entry 3), and thus, it is clear that acetone enhances the reaction rate compared to dichloromethane as solvent. A higher Pt loading (CALD/Pt = 70:1) for a prolonged reaction time (48 h) in dichloromethane afforded a high CALD conversion (88%), but the major product was HCALH with a selectivity of 74% (entry 4). The effect of temperature and hydrogen pressure in dichloromethane using a CALD/Pt ratio of 100:1 and a reaction time of 24 h was investigated. Reaction at 60 ºC under 20 bar of hydrogen pressure did not improve the CALD conversion (58%) but increased the selectivity for both CALH (from 6 to 46%) and HCALH (from 22 to 34%) against HCALD (compare entries 3 and 5). On the other hand, hydrogenation under a pressure of 50 bar at 40 ºC was sufficient for a quantitative conversion of CALD, forming a product mixture comprised of only CALH and HCALH in a ratio of 34:66 (entry 6).

When complex **4** prepared by method B (**4a**/**4b** = 99:1) was used as a catalyst, replacement of acetone by dichloromethane as a solvent under identical reaction conditions (40 ºC, 20 bar H_2, CALD/Pt = 100:1, 24 h), also decreased CALD conversion from 86 to 60% but the CALH selectivity increased from 53 to 66% (compare entries 8 and 10). A higher Pt loading (CALD/Pt = 70:1) for a prolonged reaction time (70 h) in acetone afforded 95% conversion of CALD with 52% selectivity toward CALH (entry 9). Hydrogenation in dichloromethane for 48 h using a CALD/Pt ratio of 70:1 afforded 80% conversion of CALD with 58% selectivity toward CALH (entry 11). A higher hydrogen pressure (50 bar) at the same temperature (40 ºC) in dichloromethane using a CALD/Pt ratio of 100:1 for a reaction time of 24 h increases the CALD conversion from 60 to 82% (compare entries 10 and 12) and for a similar level of conversion, also increases the CALH selectivity from 58 to 67% (compare entries 11 and 12), while a higher temperature (60 ºC) at the same pressure (50 bar) did not improve the CALD conversion, as in the case of complex **3**, but only increased the amount of HCALH, leading to a lower CALH selectivity (compare entries 12 and 13). Hydrogenation for 24 h by complex **4** prepared by method A (**4a**/**4b** = 86:14) in dichloromethane at 40 ºC and 20 bar of hydrogen pressure using a CALD/Pt ratio of 100:1, dramatically decreased both CALD conversion and CALH selectivity compared to complex **4** synthesized by method B (**4a**/**4b** = 99:1) (compare entries 10 and 14). Catalysis by complex **4** (**4a**/**4b** = 86:14; 40 ºC, 20 bar H_2, CH_2Cl_2) for 68 h using a higher platinum loading (CALD/Pt = 40:1) gave a quantitative conversion of CALD, leading to further full hydrogenation of HCALD to HCALH, while the CALH selectivity remained exactly the same (compare entries 14 and 15).



Scheme 2. Hydrogenation of cinnamaldehyde.
[Scheme to be reproduced in a single column]

Table 2
Hydrogenation of cinnamaldehyde catalyzed by platinum complexes **3** and **4**[a]

Entry	Pt Complex	Solvent	*P* (bar)[b]	Time (h)	Conv. (%)	Selectivity (%)		
						HCALD	CALH	HCALH
1	**3**	acetone	20	2	52	24	59	17
2	**3**	acetone	20	24	100	–	43	57
3	**3**	CH_2Cl_2	20	24	58	72	6	22
4[c]	**3**	CH_2Cl_2	20	48	88	9	17	74
5[d]	**3**	CH_2Cl_2	20	24	58	20	46	34
6	**3**	CH_2Cl_2	50	24	100	–	34	66
7	**4** (**4a**/**4b**=99:1)	acetone	20	2	30	44	36	20
8	**4** (**4a**/**4b**=99:1)	acetone	20	24	86	12	53	35
9[c]	**4** (**4a**/**4b**=99:1)	acetone	20	70	95	6	52	42
10	**4** (**4a**/**4b**=99:1)	CH_2Cl_2	20	24	60	10	66	24
11[c]	**4** (**4a**/**4b**=99:1)	CH_2Cl_2	20	48	80	11	58	31
12	**4** (**4a**/**4b**=99:1)	CH_2Cl_2	50	24	82	5	67	28
13[d]	**4** (**4a**/**4b**=99:1)	CH_2Cl_2	50	24	82	11	41	48
14	**4** (**4a**/**4b**=86:14)	CH_2Cl_2	20	24	37	53	21	26
15[e]	**4** (**4a**/**4b**=86:14)	CH_2Cl_2	20	68	100	–	21	79

[a] Reaction conditions: 1 mM solution of Pt complex (6 mL, 6 μmol); cinnamaldehyde: 75 μL (0.6 mmol); CALD:Pt = 100:1; 40 ºC.
[b] Initial pressure of H_2 at r.t.
[c] CALD:Pt = 70:1.
[d] 60 ºC.
[e] CALD:Pt = 40:1.

[Table to be reproduced in a two-column]

As mentioned above, the conversion of CALD is higher in acetone than dichloromethane as a solvent for both complexes **3** and **4a** under identical conditions, and this observation is not surprising as it is known that the catalytic activity of Pt(II)-chloro complexes toward hydrogenation is much greater in acetone than in halocarbon so1vents [38]. At a high conversion level of over 80%, the selectivity toward CALH was higher using complex **4a** compared to **3** in both solvents (compare entries 2 *vs* 9 and 4 *vs* 11). The higher selectivity for CALH by complex **4a** compared to complex **3** was also observed at a CALD conversion level of ca. 60% (compare entries 3 and 10). In accordance to the above-mentioned experimental results, the type of complex, solvent, temperature and pressure all affect the selectivity for the formation of CALH. The classical mechanism for the hydrogenation of unsaturated aldehydes by metal complexes involves interaction of the substrate with the metal center and also oxidative addition of hydrogen [8b]. Therefore, an explanation for the different selectivities observed should be based on the mechanism, in accordance to which the higher selectivity observed in some experiments for the formation of CALH compared to HCALD is probably attributed to the interaction of CALD with platinum preferentially through the C=O rather than the C=C bond. In complexes **4a** and **3**, platinum is coordinated with the ligand *via* P,P- and P,N-donors, respectively. The higher CALH selectivity observed by complex **4a** should

probably be attributed to the lower electronegativity of P in complex **4a** compared to N in complex **3** resulting in a higher electron density on the metal, and as a consequence, a lower probability for the C=C bond hydrogenation with respect to C=O hydrogenation, in accordance to a previous review describing electronic effects on the heterogeneous selective hydrogenation of α,β-unsaturated aldehydes [5]. Perhaps, the larger bite angle in complex **4a** compared to complex **3** by 12.44° also plays a role in the higher selectivity for the formation of CALH by complex **4a**. Of course, the reasonable mechanistic considerations mentioned above are not completely confirmed by the experimental data presented here, and further experimental and theoretical studies are required for this hydrogenation by using platinum complexes with a number of *P*,*P*- and *P*,*N*-ligands, in order to accurately propose more promising ligands for a higher selectivity toward the C=O hydrogenation of α,β-unsaturated aldehydes. It should also be mentioned that, as shown in Table 2, the higher percentage of the cationic *trans*-Pt(*P*,*N*,*P*) complex **4b** in mixture **4** (**4a**/**4b** = 86:14) is responsible for the lower activity and selectivity compared to **4** (**4a**/**4b** = 99:1), and perhaps complex **4b** also decelerates the oxidative addition of hydrogen during the catalytic cycle.

3. Conclusions

We have found that a methoxy-amino phosphine ligand binds to platinum in a *P*,*N*-bidentate coordination mode without any Pt–O interaction, forming a *cis* five-membered chelate complex $PtCl_2$(L) with a P–Pt–N bite angle of 86.98°, and the Pt–Cl (*trans* to N) bond shorter than the Pt–Cl (*trans* to P) bond. The coordination mode and geometry of the complex is independent of the reaction conditions (room temperature or 100 ºC). On the other hand, the coordination chemistry of an ethylene-linked nitrogen-containing bis(phosphine) ligand with platinum, is temperature dependent. A mixture of a *cis*-Pt(*P*,*P*) complex and the isomeric *P*,*N*,*P*-terdentate cationic complex where the two P atoms are *trans* to each other and with two five-membered chelate rings was formed at room temperature in a molar ratio of 86:14. Synthesis at 100 ºC afforded almost exclusively the *cis P*,*P*-bidentate eight-membered chelate complex with a P–Pt–P bite angle of 99.42°, in contrast to its analogous palladium complex previously reported, in which heating of the reaction mixture leads to the terdentate cationic complex. The observed *P*,*P*-bidentate coordination mode is not common, as the very high majority of ethylene-linked NP2 ligands are bound to transition metals in a *P*,*N*,*P*-terdentate fashion. We also found that after syntheses and isolation of pure products were achieved, the coordination chemistry in complexes was retained at room temperature despite the choice of solvent (chloroform, acetone, dimethyl sulfoxide). Evaluation of complexes without any promoting additive in the hydrogenation of cinnamaldehyde under mild reaction conditions showed that using acetone as a solvent, the catalytic activity is higher than using dichloromethane, and that the selectivity towards the formation of cinnamyl alcohol is higher in acetone for the *cis*-Pt(*P*,*N*) complex, while this selectivity is increased up to 67% in dichloromethane by the use of the *cis*-Pt(*P*,*P*) complex. A significant contamination of the neutral *cis*-Pt(*P*,*P*) complex by the cationic *trans*-Pt(*P*,*N*,*P*) isomer decreases both activity and selectivity. This study provides interesting information for the coordination chemistry of old ligands in new platinum complexes, and although their catalytic activity and selectivity are not as high as several other catalysts for the hydrogenation of α,β-unsaturated aldehydes, the observed selectivity for cinnamyl alcohol of up to 67% should be considered as the highest yet reported for unsupported platinum complexes as homogeneous catalysts for this reaction.

4. Experimental section

4.1. General

Ligands **1** [16] and **2** [17] were synthesized as previously described by us. Bis(benzonitrile)dichloroplatinum was prepared by a known procedure [39]. All other chemicals were commercially available. All syntheses were carried out under argon with dry and degassed reagents and solvents. Diethyl ether, toluene and hexane were distilled over Na, dichloromethane over CaH_2, and acetone over drierite. Hydrogenation studies were performed in a stainless steel autoclave (300 mL) with magnetic stirring. NMR spectra were recorded on a Varian 300 (300.13 MHz, 75.47 MHz and 121.50 MHz for ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$, respectively) or a Varian 600 (599.827 MHz for ^{1}H). The assignment of protons and carbons in the ^{1}H and ^{13}C NMR spectra was performed by HSQC NMR spectra. Chemical shift values in ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances, and the ^{31}P spectra were referenced to external 85% H_3PO_4 in H_2O. Electron impact gas chromatography – mass spectrometry was carried out using a Varian Saturn 2000 with a 30 m × 0.25 mm DB5-MS column; experimental details: initial column temperature 60 °C, initial column hold time 3 min, rate of increasing temperature 10 ºC / min, final column temperature 260 ºC, column hold time 37 min. HRMS was determined by a Thermo Scientific LTQ Orbitrap Velos (ESI); experimental details for the positive ESI–MS of **3** in CH_2Cl_2/MeOH (5:95) and the negative ESI–MS of **4a** in CH_2Cl_2/MeOH (10:90): source voltage 4 KV, source temperature 100 ºC, sheath gas flow rate 15, aux gas flow rate 15, capillary temperature 270 ºC. Melting points were measured on a Büchi melting point apparatus. Conductivity measurement for complex **4** synthesized by method A was carried out at 25 ºC under argon from a solution of the complex in CH_2Cl_2 (3.19 mM) on an Orion (Model 105) instrument; $\Lambda = K \times \kappa \times c^{-1}$, K (cell constant) = 1 cm^{-1}, κ (measured specific conductance) = 6.1 μS, and c = 3.19 × 10^{-6} mol × cm^{-3}.

4.2. cis{o-Diphenylphosphino-[N-(2-methoxyethyl)-N-methyl]aniline}dichloroplatinum(II) ***(3)***

A solution of ligand **1** (35.01 mg, 100 μmol) in dichloromethane (3 mL) was added dropwise under argon to a solution of $(PhCN)_2PtCl_2$ (47.32 mg, 100 μmol) in dichloromethane (3 mL) at room temperature and stirred overnight (18 h). The resulting pale yellow solution was concentrated under reduced pressure to an approximate volume of 0.5 mL. Dry diethyl ether (5 mL) was added to cause precipitation of a solid which was collected after decantation, washed with ether (2 × 10 mL) and then dried under vacuum, yielding **3** (52.6 mg, 86%) as a white solid, m.p. (dec.) > 200 ºC. As determined by the spectral data, the same product with a similar yield was also obtained by a dropwise addition of a solution of ligand **1** (34.93 mg, 100 μmol) in toluene (3 mL) to a solution of $(PhCN)_2PtCl_2$ (47.22 mg, 100 μmol) in toluene (3 mL) at 100 ºC and stirring at this temperature for 3 h.
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82–7.77 (m, 4H, arom), 7.69–7.67 (m, 1H, arom), 7.63–7.61 (m, 1H, arom), 7.56–7.49 (m, 3H, arom), 7.47–7.40 (m, 5H, arom), 4.78 (1H, NCH_AH_M), 3.94 (1H, OCH_XH_Z), 3.77 (1H, OCH_XH_Z) and 3.64 (1H, NCH_AH_M) (NCH_2CH_2O, AMXZ spin system, $^{2}J_{AM}$ = 12.7 Hz, $^{2}J_{XZ}$ = 10.7 Hz, $^{3}J_{AX}$ = 5.0 Hz, $^{3}J_{AZ}$ = 5.0 Hz, $^{3}J_{MX}$ = 6.6 Hz, $^{3}J_{MZ}$ = 5.3 Hz), 3.73 (s, 3H, NCH_3), 2.89 (s, 3H, OCH_3); ^{1}H NMR (600 MHz, acetone-d_6): δ 8.13–8.11 (m, 1H, arom), 7.92–7.89 (m, 2H, arom), 7.85–7.81 (m, 2H, arom), 7.77–7.70 (m, 2H, arom), 7.65–7.51 (m, 7H, arom), 4.68 (1H, NCH_AH_M), 3.85 (1H, NCH_AH_M), 3.80 (1H, OCH_XH_Y) and 3.72 (1H, OCH_XH_Y) (NCH_2CH_2O, AMXY spin system, $^{2}J_{AM}$ = 12.4 Hz, $^{2}J_{XY}$ = 10.5 Hz, $^{3}J_{AX}$ = 4.8 Hz, $^{3}J_{AY}$ = 5.9 Hz, $^{3}J_{MX}$ = 6.3 Hz, $^{3}J_{MY}$ = 6.3 Hz), 3.75 (s, 3H, NCH_3), 2.91 (s, 3H, OCH_3).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 159.79 (d, $^2J_{CP}$ = 14.2 Hz, C_{ipso}(NAr), arom), 132.83–132.73 (m, arom), 132.61 (d, J_{CP} = 3.4 Hz, arom), 132.12–132.11 (m, arom), 131.07 (d, J_{CP} = 2.8 Hz, arom), 130.98 (d, J_{CP} = 2.9 Hz, arom), 129.96 (s, arom), 129.19 (s, arom), 128.92 (d, J_{CP} = 7.2 Hz, arom), 128.74 (s, arom), 128.15 (d, J_{CP} = 4.6 Hz, arom), 127.99 (d, J_{CP} = 4.5 Hz, arom), 127.51 (s, arom), 126.90 (s, arom), 126.60 (s, arom), 126.00 (s, arom), 121.45 (d, J_{CP} = 10.6 Hz, arom), 70.64 (s, OCH_2), 64.56 (s, NCH_2), 59.03 (s, NCH_3), 58.91 (s, OCH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 162.64–162.47 (m, C_{ipso}(NAr), arom), 135.16 (d, J_{CP} = 2.2 Hz, arom), 134.86 (s, arom), 134.74 (d, J_{CP} = 3.2 Hz, arom), 134.61 (s, arom), 134.14–134.13 (m, arom), 132.84–132.77 (m, arom), 131.03 (d, J_{CP} = 7.2 Hz, arom), 129.91 (d, J_{CP} = 1.9 Hz, arom), 129.75 (d, J_{CP} = 1.8 Hz, arom), 123.98 (d, J_{CP} = 10.7 Hz, arom), 71.24 (s, OCH_2), 64.63 (s, NCH_2), 58.83 (s, NCH_3 and OCH_3).
$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 15.48 ($^1J_{PtP}$ = 3903 Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 16.25 ($^1J_{PtP}$ = 3878 Hz).
HRMS (positive ESI-MS): calcd for $C_{22}H_{24}ClNOPPt$ $[M–Cl]^+$ 579.0932, found 579.0927; calcd for $C_{22}H_{24}Cl_2NNaOPPt$ $[M+Na]^+$ 637.0513, found 637.0520.

4.3. cis{N,N-Bis[2-(diphenylphosphino)ethyl]phenylamine}dichloroplatinum(II) ***(4a)*** *and its ionic trans-Pt(P,N,P) isomer* ***(4b)***

Method A: A solution of ligand **2** (51.79 mg, 100 μmol) in dichloromethane (3 mL) was added dropwise under argon to a solution of $(PhCN)_2PtCl_2$ (47.19 mg, 100 μmol) in dichloromethane (3 mL) at room temperature and stirred overnight (18 h). The resulting light pale yellow solution was concentrated under reduced pressure to an approximate volume of 0.5 mL. Dry diethyl ether (5 mL) was added to cause precipitation of a solid which was collected after decantation, washed with ether (2 × 5 mL) and then dried under vacuum, yielding **4** (60.9 mg, 78%) as a white solid. Λ (Ω^{-1} cm^2 mol^{-1}): 1.91. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 27.49 ($^1J_{PtP}$ = 2712 Hz), *trans*-Pt(*P*,*N*,P) **(4b)**; 10.37 ($^1J_{PtP}$ = 3591 Hz), *cis*-Pt(*P*,*P*) **(4a)**; **4a**/**4b** = 86:14. ^1H and ^{13}C NMR spectra showed only very slight differences in the aromatic region compared to those observed for the product synthesized by method B as given below (see spectra in SI). A shorter reaction time (3 h) afforded complex **4** in a very similar yield (80%) with the same isomer ratio (86:14) (see spectra in SI).

Method B: A solution of ligand **2** (51.79 mg, 100 μmol) in toluene (5 mL) was added dropwise under argon to a solution of $(PhCN)_2PtCl_2$ (47.23 mg, 100 μmol) in toluene (5 mL) at 100 ºC and stirred at this temperature for 3 h, forming a white solid. After cooling to room temperature, toluene was removed by vacuum. Dichloromethane (10 mL) was added and the mixture was filtered under argon to remove traces of insoluble species. The filtrate was concentrated under reduced pressure to an approximate volume of 0.5 mL, and addition of dry diethyl ether (5 mL) caused the precipitation of a solid. The solid was collected after decantation, washed with ether (2 × 5 mL), hexane (5 mL) and dried under vacuum, yielding **4** (60.0 mg, 77%) as a white solid, m.p. (dec.) > 200 ºC.
^1H NMR (600 MHz, $CDCl_3$): δ 7.48–7.45 (m, 8H, arom), 7.33–7.29 (m, 6H, arom), 7.15 (t, $^3J_{HH}$ = 7.3 Hz, 8H, arom), 6.86 (t, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{para}(NPh), arom), 6.57 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH_{ortho}(NPh), arom), 4.18 (dm, J = 23.1 Hz, 4H, CH_2NCH_2), 2.60–2.57 (br m, 4H, 2 × CH_2P); ^1H NMR (300.1 MHz, acetone-d_6): δ 7.61–7.55 (m, 8H, arom), 7.38–7.26 (m, 6H, arom), 7.20 (t, $^3J_{HH}$ = 6.9 Hz, 8H, arom), 6.82 (t, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{para}(NPh), arom), 6.76 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_{ortho}(NPh), arom), 4.17 (dm, J = 23.3 Hz, 4H, CH_2NCH_2), 2.81–2.75 (br m, 2 × CH_2P, obscured with HDO); ^1H NMR (300.1 MHz, DMSO-d_6): δ 7.54–7.48 (m, 8H, arom), 7.40–7.35 (m, 6H, arom), 7.27–7.19 (m, 8H, arom), 6.80 (t, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{para}(NPh), arom), 6.64 (d, $^3J_{HH}$ = 8.4 Hz, 2H, CH_{ortho}(NPh), arom), 3.94 (dm, J = 19.8 Hz, 4H, CH_2NCH_2), 2.78–2.72 (br m, 4H, 2 × CH_2P).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 146.89 (s, C_{ipso}(NPh), arom), 132.47–132.35 (br m and virtual triplet, J_{CP} = 4.8 Hz, arom), 130.62 (s, arom), 129.83 (s, arom), 128.17 (virtual triplet, J_{CP} = 5.5 Hz, arom), 117.94 (s, C_{para}(NPh), arom), 112.28 (s, C_{ortho}(NPh), arom), 51.43 (s, CH_2N), 25.14–24.52 (m, CH_2P); $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6): δ 148.81 (s, C_{ipso}(NPh), arom), 133.71–133.59 (br m and virtual triplet, J_{CP} = 4.8 Hz, arom), 131.41 (s, arom), 130.49 (s, arom), 129.01 (virtual triplet, J_{CP} = 5.5 Hz, arom), 118.70 (s, C_{para}(NPh), arom), 114.09 (s, C_{ortho}(NPh), arom), 52.31 (s, CH_2N), 26.22–25.68 (m, CH_2P).
$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 27.20, *trans*-Pt(*P*,*N*,*P*) **(4b)**; 10.38 ($^1J_{PtP}$ = 3591 Hz), *cis*-Pt(*P*,*P*) **(4a)**; $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6): δ 28.12, *trans*-Pt(*P*,*N*,*P*) **(4b)**; 11.16 ($^1J_{PtP}$ = 3580 Hz), *cis*-Pt(*P*,*P*) **(4a)**; $^{31}P\{^1H\}$ NMR (121.5 MHz, DMSO-d_6): δ 28.16, *trans*-Pt(*P*,*N*,*P*) **(4b)**; 10.11 ($^1J_{PtP}$ = 3599 Hz), *cis*-Pt(*P*,*P*) **(4a)**; **4a**/**4b** = 99:1 in all solvents.
HRMS (negative ESI-MS): calcd for $C_{34}H_{33}Cl_3NP_2Pt$ $[M+Cl]^-$ 817.0796, found 817.0802.

4.4. General experimental procedure for the hydrogenation of cinnamaldehyde

A freshly prepared solution of the metal complex (**3** or **4**) in acetone or dichloromethane (1 mM, 6 mL, 6 μmol) and cinnamaldehyde (75 μL, 0.6 mmol) were transferred under argon to an oven-dried autoclave, which was then closed, pressurized and depressurized twice with 5 bar of hydrogen, and then pressurized with hydrogen (20 or 50 bar) and brought to the appropriate temperature (40 or 60 ºC). After stirring for the appropriate time, the autoclave was cooled to room temperature and the pressure was carefully released. The solution was removed, passed through celite and analyzed by GC–MS and ^1H NMR. Conversions and selectivities were determined by ^1H NMR spectroscopy based on the relative integration of substrate and product peaks (see spectra and characteristic ^1H NMR chemical shifts in SI).

*4.5. X-ray crystallographic study of **3** and **4a***

Crystals of **3** (0.11 × 0.23 × 0.31 mm) and **4a** (0.12 × 0.37 × 0.37 mm) were taken from the mother liquor and immediately cooled to –113 and –103 ºC, respectively. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated Mo Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and Empirical absorption correction) were performed using the CrystalClear program package [40]. Important crystallographic data are listed in Table 3. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [41]. Further experimental crystallographic details for **3**: $2\theta_{max}$ = 54°; reflections collected/unique/used, 42229/4861 [R_{int} = 0.0293]/4861; 338 parameters refined; $(\Delta/\sigma)_{max}$ = 0.003; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 1.422/–0.431 e/Å^3; *R*1/w*R*2 (for all data), 0.0184/0.0379. Further experimental crystallographic details for **4a**: $2\theta_{max}$ = 54°; reflections collected/unique/used, 82170/7505 [R_{int} = 0.0185]/7505; 527 parameters refined; $(\Delta/\sigma)_{max}$ = 0.004; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.759/–1.180 e/Å^3; *R*1/w*R*2 (for all data), 0.0171/0.0405. All hydrogen atoms were located by difference maps and were refined isotropically or were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically. Plots of the structure were drawn using the Diamond 3 program package [42].

Table 3
Crystallographic data for **3** and **4a**

	3	**4a** · CH_2Cl_2
Formula	$C_{22}H_{24}Cl_2NOPPt$	$C_{35}H_{35}Cl_4NP_2Pt$

Fw	615.38	868.47
Space group	$P2_1/n$	$P2_1/n$
α (Å)	14.6852(3)	13.4966(3)
b (Å)	10.6060(2)	14.4529(3)
c (Å)	14.7022(3)	17.9852(3)
α (°)	90.0	90.0
β (°)	102.642(1)	101.024(1)
γ (°)	90.0	90.0
V (Å^3)	2234.37(8)	3443.54(12)
Z	4	4
T (ºC)	–113	–103
Radiation	Mo Kα	Mo Kα
ρ_{calcd} (g cm^{-3})	1.829	1.675
μ (mm^{-1})	6.603	4.504
Reflections with $I>2\sigma(I)$	4618	7319
R_1[a]	0.0167	0.0166
$wR2$[a]	0.0374	0.0403

[a] $w = 1/[\sigma^2(F_o^2)+(\alpha P)^2+bP]$ and $P = [\max(F_o^2,0)+2F_c^2]/3$; $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[Table to be reproduced in a single column]

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Appendix A. Supplementary data

CCDC-1486014 (for **3**) and CCDC-1486015 (for **4a**) 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. The Supporting Information related to this article is available free of charge and contain copies of NMR and HRMS spectra of complexes and ^{1}H NMR spectra of hydrogenation products.

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- Complexation of an ethylene-linked NP2 ligand with Pt is temperature dependent.
- At r.t., a mixture of a *cis*-Pt(*P*,*P*) and a *trans*-Pt(*P*,*N*,*P*) complex was formed.
- Synthesis at 100 ºC afforded almost exclusively the *cis*-Pt(*P*,*P*) complex.
- Hydrogenation of cinnamaldehyde with selectivity for cinnamyl alcohol of up to 67%.