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N-Benzyl and *N*-aryl bis(phospha-Mannich adducts): Synthesis and catalytic activity of the related bidentate chelate platinum complexes in hydroformylation

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ABSTRACT

The microwave-assisted double Kabachnik–Fields (phospha-Mannich) reaction of benzylamine and arylamines, two equivalents of paraformaldehyde and the >P(O)H reagent, such as dialkyl phosphites, ethyl phenyl-*H*-phosphinate and diphenylphosphine oxide gave the bis(>P(O)CH_2)amine derivatives in good yields. The bis(diphenylphosphinoxido) derivatives were converted to the corresponding ring platinum complexes after deoxygenation whose catalytic activity was tested in the hydroformylation of styrene. Crystal structure analysis of one of the complexes reveals interesting correlations between complex structure and solvent inclusion.

1. Introduction

α-Aminophosphonates and related derivatives are evergreen targets in biochemistry due to their versatile bioactivity [1–3]. The most common approach to α-aminophosphonates is the condensation of an amine, an aldehyde or ketone and a dialkyl phosphite that is called the Kabachnik–Fields (phospha-Mannich) reaction [4–6].

A number of catalytic versions of the Kabachnik–Fields reaction were developed. However, it was found that, especially under solvent-free conditions, there is no need for catalysts [7,8]. The efficiency could be further increased by the microwave (MW) technique [9–11].

A novel preparation of α-aminophosphonates involves the substitution of α-hydroxyphosphonates by amines. This reaction takes place with an unexpected ease as a consequence of a neighbouring group effect [12].

The mechanism of the Kabachnik–Fields reaction has been the subject of a lot of studies [6]. One of the authors of this article with co-workers could prove the intermediacy of the imine intermediate in a few cases studied utilizing the method of *in situ* Fourier Transform Infrared spectroscopy [13,14].

Bis(phosphonomethyl)amines may be interesting building blocks in synthetic organic chemistry. The double Kabachnik–Fields condensation made available lipophilic derivatives [15]. The use of phosphorous acid as the P-reactant led to bis(phosphonic acids) [16,17]. Bis(phosphinoxido)derivatives were synthesized via a surprising methylene insertion reaction into a P–N bond followed by oxidation [18].

We have elaborated a MW-assisted solvent-free method for the synthesis of *N*-alkyl bis(>P(O)CH_2)amino derivatives [19,20]. The stereostructure of a related *N*-cyclohexyl ring platinum complex was studied in detail [20]. In this paper, new *N*-benzyl and *N*-aryl bis(>P(O)CH_2)amino species and the bidentate chelate platinum complexes of the corresponding bis(phosphino) derivatives are discussed. The latter ring platinum complexes were tested as catalysts in the hydroformylation of styrene.

2. Results and discussion

2.1. Synthesis of new bis(phospha-Mannich adducts)

To extend the scope of the efficient synthesis of bis(>P(O)CH_2)amino derivatives, first benzylamine and 4-methoxyaniline were reacted with two equivalents of paraformaldehyde and the >P(O)H species, such as dialkyl phosphites and ethyl phenyl-*H*-phosphinate on MW irradiation at 100 °C for 1 h without using any solvent to afford the corresponding products **1a**–**e** and **2a**–**d**, respectively, in

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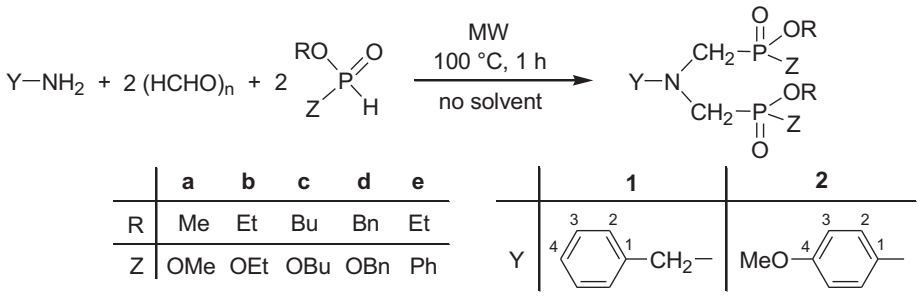
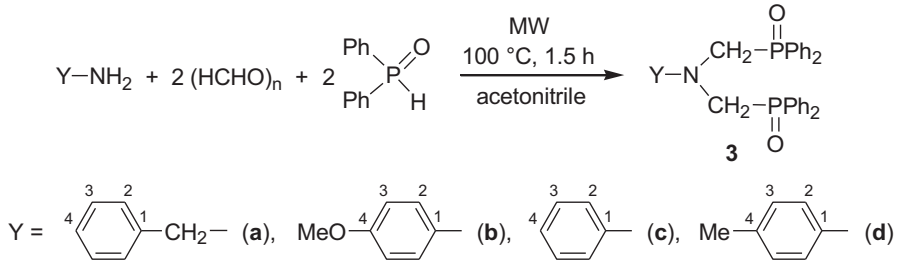


Scheme 1.

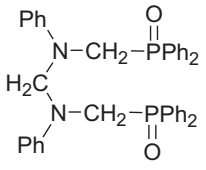


Scheme 2.

81–98% yields after flash column chromatography (Scheme 1). Due to the stereogenic center in ethyl phenyl-*H*-phosphinate, the related bis(phospha-Mannich adduct) **1e** was obtained as a 51:49 mixture of two stereoisomers.

In the next round, benzylamine and arylamines were reacted with two equivalents of paraformaldehyde and diphenylphosphine oxide as above with the only difference that acetonitrile was used as the solvent due to the heterogeneity of the reaction mixture. After an irradiation of 1.5 h, chromatography afforded the products **3a**–**d** in 55–95% yields (Scheme 2).

In the reaction of aniline, paraformaldehyde and diphenylphosphine oxide, a by-product with an elemental composition of $C_{39}H_{36}N_2O_2P_2$ ($[M + H]^+$ = 627.2325 (found) and 627.2330 (calculated)) and with a δ_P of 27.7 ($CDCl_3$) was also identified in a quantity of *ca.* 15%. Its structure was substantiated as bis(aminophosphine oxide) **4**.



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The bis(phosphine oxides) **3a**–**d** were subjected to double deoxygenation and the diphosphines **5a**–**d** so obtained were reacted with dichlorodibenzonitrile platinum to furnish *cis* chelate platinum complexes **6a**–**d** in yields of 45–60% (Scheme 3).

All compounds prepared (**1a**–**e**, **2a**–**d**, **3a**–**d** and **6a**–**d**) were characterized by ^{31}P, ^{13}C and ^{1}H NMR, as well as mass spectral data.

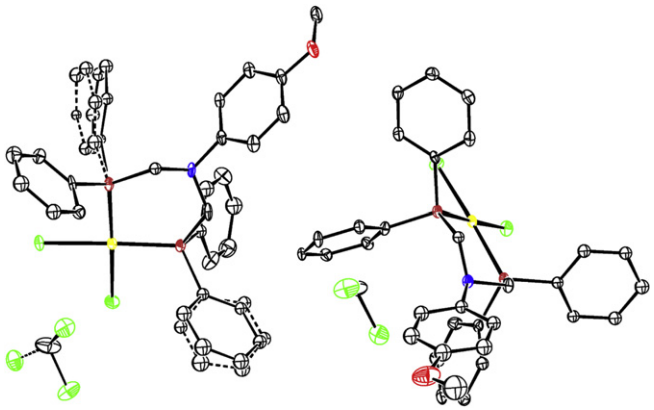
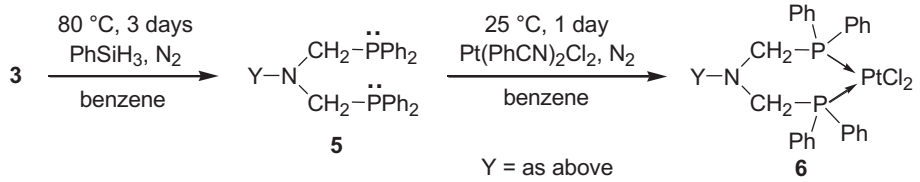


Fig. 1. An atomic displacement (ORTEP-style) plot of the asymmetric unit in the **6b** crystal.



Scheme 3.

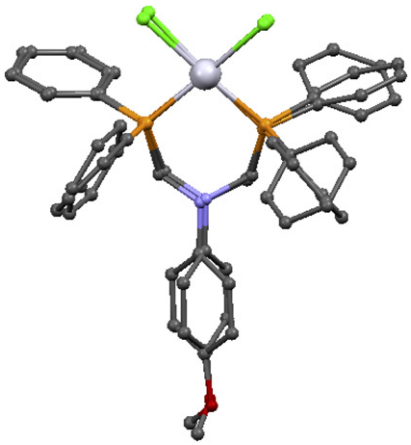


Fig. 2. Overlay of the two independent **6b** molecules through their least-square fit of the respective six-membered heterocycles (for the sake of clarity only major disorder sites are used and H-atoms omitted from the drawing).

Crystal structure of ring platinum complex **5b** was determined by single crystal X-ray analysis. The resulting structure (Fig. 1) corroborates molecular structure of ring Pt-complex **6b**.

2.2. Intermolecular relations of molecular structure *6b* and the solvent inclusion

At the onset of the crystal structure analysis it was unknown that the crystals contain solvent from the crystal growth. The crystals of complex **6b** were grown from dichloromethane (DCM) and crystallized with two **6b** molecules as well as two solvent molecules in the asymmetric unit of the orthorhombic *Pbca* space group. One of the **6b** molecules as well as one of the solvent molecules shows clear signs of conformational disorder, apparent in the rotation of some of the phenyl rings in complex **6b**. The disorder was modelled by 2/3:1/3 major:minor atomic positions for these appropriate molecular entities. An overlay of the two independent **6b** molecules of the asymmetric unit reveals close similarity in the shape and dimensions of the central 6-membered heterorings (see Fig. 2), but also accentuates differently twisted phenyl rings, hence giving a good reason for the appearance of more than one molecule in the asymmetric unit. The role of the included DCM solvent appears to be unequal, too. The *ordered solvent* molecule provides three interesting short contacts to the neighbouring *ordered host* **6b** molecules in the crystal. One of these is a phenyl C–H···Cl contact at 2.91 Å, (C–H···Cl 135°) (where C···Cl 3.644(9) Å) another Cl···C(phenyl) short distance at 3.438(9) Å (C–Cl···C 137.2(5)°) is just shorter than the van der Waals' radii sum. These two probably productive interactions are of both well-known types of C–H···X type hydrogen bridges and dispersive interactions, respectively. A bit more unusual is the 2.87 Å DCM C–H···Pt (C–H···Pt1 150°) distance as the third interaction possibility. However, such contacts fall entirely in the range of the so-called *anagostic* contact types [21]. As shown by inseminating analyses by Braga and Desiraju [22] as well as a more recent one [23] these short contact types may rather be termed as somewhat rare C–H···M type H-bridges. Apparently as even a study from 2006 [23] listed only two of the Pt-type metal acceptors we deemed appropriate to extend this study for more recent examples of square planar d_8 – metal examples with more Pt-centres found since then. Thus a Cambridge Structural Database [24] study was additionally performed. These then also include our recent structure studies of complex **6b** of this paper. Fig. 3 shows the

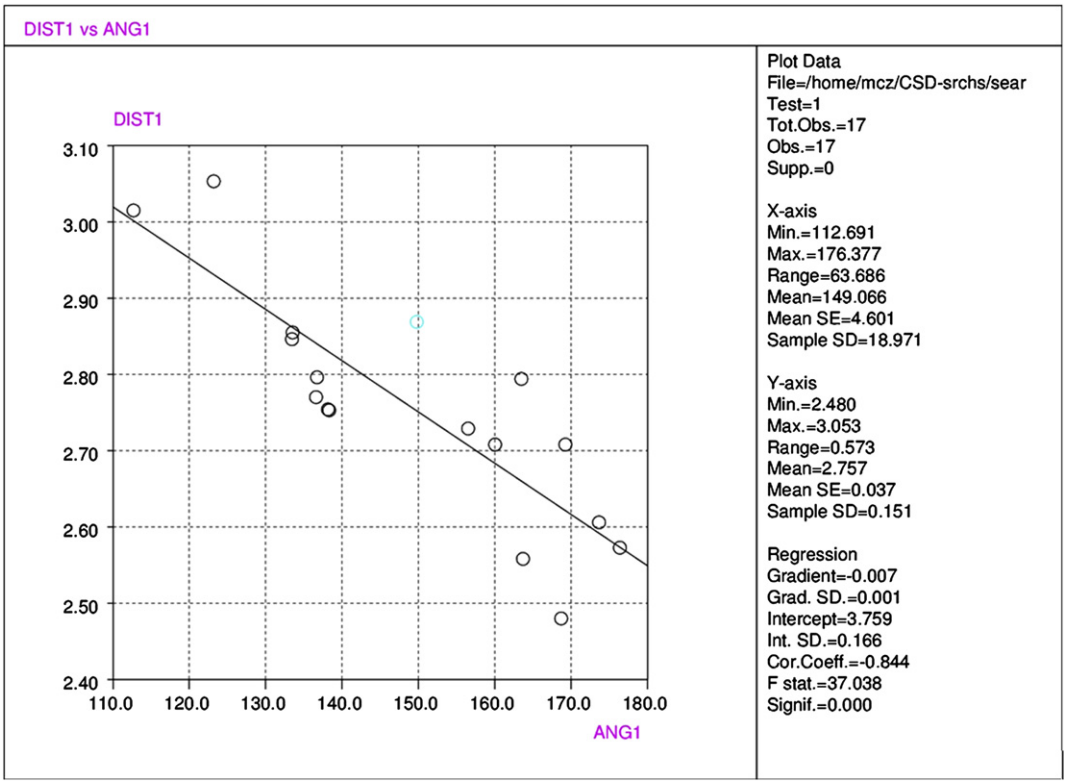


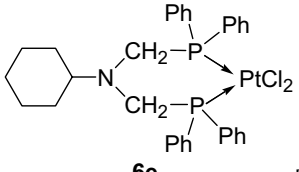
Fig. 3. Correlation of the H···M (M = Ni, Pd, Pt) distances and C–H···M (M = Ni, Pd, Pt) angles in **6b** (blue circle) and in recent literature data from using the CSD database [32]. The database hits are mostly from Pt, Pd and Ni are represented with 3 and 2 entries. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

correlation of the H···M (M = Ni, Pd and Pt) contact distances plotted against the respective C–H···M angles, suggesting acceptable correlations of these parameters and corresponding to H-bridge-like interactions. **6b** Performs close to the correlations line and as expected on its H···Pt distance.

It is presumably these three close contacts that mutually help stabilizing both one of the **6b** molecules as well as the of the DCM solvent in the crystal structure. The second disordered DCM molecule has contacts to only the other **6b** molecule, so these two entities appear to be fairly isolated in that there are no cross-contacts at all. There is, however, no contact to the Pt and the three C–H···Cl contacts are split such that the minor disorder position is also involved (i.e. there are only two interactions per DCM molecules of the second types). It is also to be noted that the phenyl rings maintaining the two $C_{(phenyl)}$–H···Cl contacts give rise to the two ordered phenyl rings while the other two rings, apparently lacking such contacts, are disordered thus may provide yet another hint on the inter-dependence of disorder and productive interactions. These data call for attention to the role of the corresponding solvent in complexes of this type and may also provide some insight into the fairly intricate relations that may exist in such systems not only in the solid phase.

2.3. Catalytic activity of the $PtCl_2(\eta^1,\eta^1$-(P,P)–PNP) complexes (**6a**, **6b**, **6d** and **6e**) in the hydroformylation of styrene

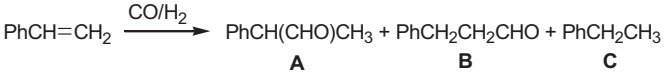
The earlier experiences of *Kollár* and *Keglevich* showed that the wide variety of platinum–phosphine complexes may reveal interesting catalytic activity in the hydroformylation of styrene derivatives [25,26]. For this, the ring Pt complexes *cis*-[(benzyl-bis(diphenylphosphinomethyl)amine)-dichloro-platinum(II)] **6a** and *cis*-[(aryl-bis(diphenylphosphinomethyl)amine)-dichloro-platinum(II)] **6b**,**d** along with the earlier reported *N*-cyclohexyl derivative (**6e**) [20] were tested as catalyst precursors in the hydroformylation of styrene.



6e [20]

The platinum-containing *in situ* catalysts formed either from **6a**, **6b**, **6d** or **6e** and tin(II) chloride under standard 'oxo-conditions' ($p(CO)=p(H_2)$ = 40 bar, reaction temperature varied from 40 °C to 100 °C) were used. As generally observed, in addition to the branched and linear formyl regioisomers (2-phenylpropanal (**A**) and 3-phenylpropanal (**B**), respectively), the hydrogenation by-product ethylbenzene (**C**) was also formed (Scheme 4).

The catalytic activity of the above system is comparable to that of the best platinum–diphosphine–tin(II) chloride catalysts. The use of 1% platinum precursor related to the substrate proved to be an active catalyst in the temperature range of 40–100 °C (Table 1). The *in situ* catalysts, formed from complexes **6a**, **6b**, **6d** and **6e**, have shown remarkable activity already at 40 °C (entries 1, 6/7, 10/11 and 14, respectively). Although the presence of various amines (in excess to platinum) reduced substantially the catalytic activity [27], in case of these PNP ligands with a non-coordinating *N*-atom, highly active catalysts were obtained with an $SnCl_2$/Pt ratio being as low as 1/1. The catalytic activities of the *in situ* catalysts, containing the tin(II) chloride additive in various amounts, are similar. A slight decrease of activity with increasing amount of tin(II) chloride was observed in the case of **6a**, **6b** and **6e**. (Table 1/entries 2, 3 and 6, 7 and 17–19, respectively). An opposite trend for the change in the activity was observed with **6d**.



Scheme 4. General scheme for the hydroformylation of styrene.

Table 1
Hydroformylation of styrene in the presence of *in situ* catalysts formed from $PtCl_2$(PNP) complexes (**6a**, **6b**, **6d**, **6e**) and tin(II) chloride.[a]

Entry	Complex	Temp. (°C)	Pt/$SnCl_2$	R. time (h)	Conv. (%)	R_c[b] (%)	R_{br}[c] (%)
1	**6a**	40	1/2	20	63	79	80
2	**6a**	60	1/1	5	87	76	77
3	**6a**	60	1/2	5	85	76	76
4	**6a**	100	1/1	1	65	56	68
5	**6a**	100	1/2	1	73	65	67
6	**6b**	40	1/1	20	92	80	79
7	**6b**	40	1/2	20	73	81	79
8	**6b**	100	1/1	1	89	67	68
9	**6b**	100	1/2	1	93	70	67
10	**6d**	40	1/1	20	33	79	77
11	**6d**	40	1/2	20	71	80	78
12	**6d**	100	1/1	1	36	65	69
13	**6d**	100	1/2	1	96	73	70
14	**6e**	40	1/1	20	63	78	79
15	**6e**	60	1/1	20	>99.8	78	74
16	**6e**	60	1/1	5	85	77	76
17	**6e**	100	1/1	3	>99.8	64	63
18	**6e**	100	1/2	1.5	94	67	66
19	**6e**	100	1/5	1.5	87	66	67

A: 2-phenylpropanal, **B**: 3-phenylpropanal, **C**: ethylbenzene.
[a] Reaction conditions: Pt/styrene = 1/100, $p(CO)=p(H_2)$ = 40 bar, 0.005 mmol catalyst, 0.5 mmol of substrate, solvent: 5 mL of toluene.
[b] Chemoselectivity towards aldehydes (**A**, **B**). [(moles of **A** + moles of **B**)/(moles of **A** + moles of **B** + moles of **C**) × 100].
[c] Regioselectivity towards branched aldehyde (**A**). [moles of **A**/(moles of **A** + moles of **B**) × 100].

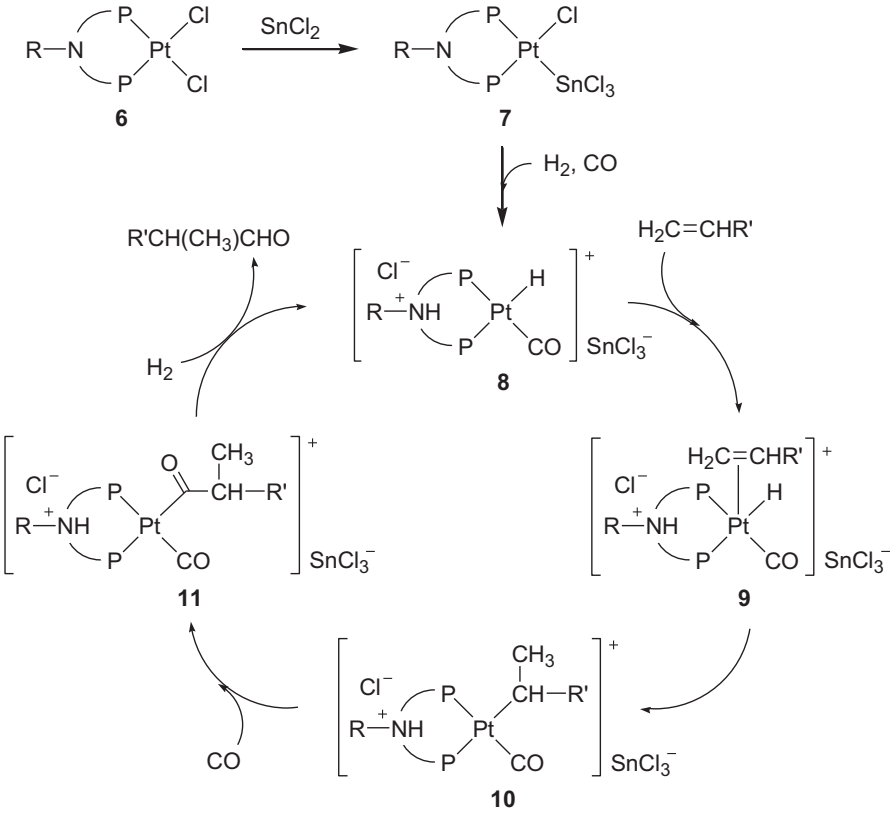
The formation of the aldehyde regioisomers (**A** and **B**) was preferred in all cases that is numberized by chemoselectivities of 70–79%, 67–81%, 65–80% and 64–78% using complexes **6a**, **6b**, **6d** and **6e** as catalyst precursors, respectively. The known tendency of increasing chemoselectivity towards aldehydes with decreasing reaction temperature was observed. For example, in the presence of **6a** as the catalytic precursor, slightly decreasing chemoselectivities of 79, 76 and 56% were obtained at 40, 60, and 100 °C, respectively (Table 1/entries 1, 2 and 4). A similar influence of the temperature on the chemoselectivity was observed also with **6b**, **6d** and **6e** as the catalyst precursors (Table 1/entries 6, 8 and 10,12 and 14, 16, 17). It is worth noting, that the $SnCl_2$/Pt ratio has practically no influence on the chemoselectivity using **6a** (Table 1/entries 2 and 3), **6b** (Table 1/entries 6 and 7), **6d** (Table 1/entries 10 and 11) or **6e** (Table 1/entries 17–19).

As regards the regioselectivity, the branched aldehyde (**A**) predominated over the linear one (**B**) in all cases. Regarding platinum-catalyzed hydroformylations, surprisingly high regioselectivities towards branched aldehyde (**A**) were obtained. In our previous studies we have demonstrated that the application of some monodentate *P*-heterocycles, such as phosphole, phospholene or phospholane ligands resulted in similar "branched selectivities" in the platinum-catalyzed hydroformylation of styrene [28]. It should be added that even higher preference for the branched aldehyde (2-phenylpropanal) is characteristic for the rhodium-catalyzed hydroformylation of styrene [29]. With all catalytic precursors, the dependence of the regioselectivities on the reaction

temperature has shown the same tendency. That is, decrease of the branched selectivity with increasing temperature was observed. For example, regioselectivities of 79, 74 and 63% were obtained using precursor **6e** at 40, 60 and 100 °C, respectively, while the other conditions were kept constant (Table 1/entries 14, 15 and 17). A similar decrease of the branched selectivity with increasing temperature was observed also with catalytic precursor **6a**, **6b** and **6d** (Table 1/entries 2, 4 and 6, 8 and 10, 12, respectively). The influence of $SnCl_2$/Pt ratio on the activity of platinum complexes was also studied. It has to be mentioned that in most examples published up to now [30], the $SnCl_2$/Pt ratio was kept either on 2 or 5. Its role is to form the trichlorostannato ligand, a facile leaving group from the Pt(PP)R($SnCl_3$) complex. It has been proved that the dissociation of the $SnCl_3^-$ ligand provides a vacant coordination site in an ionic complex, while the trichlorostannate ion serves as a counterion [31]. The vacant coordination site enables the coordination of carbon monoxide and therefore leads to catalytically active species.

In our case, the investigation of the effect of tin(II) chloride cocatalyst on the catalytic activity is of special importance since the non-coordinated nitrogen atom of the PNP ligands may act as a Lewis base coordinating to $SnCl_2$, or as an HCl/$HSnCl_3$ acceptor. The reactions should lead to decreased catalytic activities at low $SnCl_2$/Pt ratios because the tin(II) chloride is attached to the central tertiary N atom of the ligand, and as a consequence of that, there would be no chance to form trichlorostannato ligand of key importance in providing active cationic species (*vide supra*). However, we have found that all precursors (**6a**, **6b**, **6d** and **6e**) are active even at low $SnCl_2$/Pt ratios (~1). This behaviour is rationalized on the basis of the simplified mechanistic scheme below (Scheme 5). The close proximity of the basic, non-coordinating tertiary N acts as an HCl acceptor formed upon the hydrogenolysis of the Pt–Cl bond. After protonation, the ligand behaves as a *cis*-coordinating bidentate diphosphine ligand with an ammonium moiety throughout the reaction. In this way, instead of coordinating the tin(II) halide cocatalyst and leading to catalysts of low activities, the nitrogen atom will be protonated by the HCl liberated to form the platinum-hydrido species (**8**), the 'starting' complex of the catalytic cycle. According to a generally accepted mechanism of platinum-catalyzed hydroformylation, the coordination of the substrate provides the five-coordinated alkene complex (**9**). The insertion of alkene into the Pt–H bond results in the formation of the alkyl complex (**10**). The insertion of carbon monoxide and the immediate coordination of the 'second' carbon monoxide results in the platinum-acyl-carbonyl complex (**11**) which undergoes hydrogenolysis in the product forming step.

To check whether tin(II) chloride insertion into Pt–Cl bond takes place even at low $SnCl_2$/Pt ratio, *in situ* NMR experiments were carried out using tin(II) chloride in equimolar amount to platinum. The formation of the PtCl($SnCl_3$)(PNP) complexes (**7**) of key catalytic importance was unequivocally proved by ^{31}P NMR spectroscopy. The chemical shift of phosphorus atoms *trans* to tin has a characteristic downfield shift related to that of the phosphorus atoms *trans* to chloride [32]. That is, approximately 5 ppm downfield shift was observed on the phosphorus atoms *trans* to the trichlorostannato ligand in **7a**, **7b**, **7d** and **7e**. In the same time, a typical $^1J_{Pt,P}$ coupling of about 2700 Hz can be observed on the phosphorus *trans* to tin reflecting to the presence of a trichlorostannato ligand with stronger *trans* influence. (^{31}P NMR ($CDCl_3$) **7a**: δ: −8.07 ($^1J_{P(A),Pt}$ = 3285), −2.04 ($^1J_{P(B),Pt}$ = 2694), $^2J_{P,P}$ = 16.0; **7b**: δ: −6.34 ($^1J_{P(A),Pt}$ = 3262), −0.54 ($^1J_{P(B),Pt}$ = 2728), $^2J_{P,P}$ = 16; **7d**: δ: −6.09 ($^1J_{P(A),Pt}$ = 3255), −0.19 ($^1J_{P(B),Pt}$ = 2685),



Scheme 5. Simplified mechanism of the platinum-catalyzed hydroformylation of an alkene in the presence of catalytic precursor **6** containing PNP ligands (for clarity reasons, the formation of the branched regioisomer is depicted only).

$^{2}J_{P,P}$ = 16; **7e**: δ: −8.80 ($^{1}J_{P(A),Pt}$ = 3287), −3.23 ($^{1}J_{P(B),Pt}$ = 2725), $^{2}J_{P(A),P(B)}$ = 16.5).

3. Conclusion

In conclusion, a series of new *N*-benzyl and *N*-aryl bis(phospha-Mannich adducts) were prepared and characterized. After double deoxygenation, the bis(diphenylphosphinoxido) derivatives were converted to the corresponding 6-ring platinum complexes.

The crystal structure determination of the *N*-(4-methoxyphenyl) complex from a slightly decayed solvent inclusion crystal suggests a direct correlation between the number and type of productive interactions of the solvent guest from/to the complex host molecules and the appearance of motility as expressed by structural disorder.

The *in situ* formed platinum–PNP–tin(II)chloride systems proved to be active catalysts in the hydroformylation of styrene providing the branched aldehyde in high regioselectivities.

4. Experimental

4.1. General (instruments)

The ^{31}P, ^{13}C, ^{1}H NMR spectra were taken on a Bruker AV-300 or DRX-500 spectrometer operating at 121.5, 75.5 and 300 or 202.4, 125.7 and 500 MHz, respectively. The couplings are given in Hz. Mass spectrometric measurements were performed using a Q-TOF Premier mass spectrometer (Waters Corporation, 34 Maple St, Milford, MA, USA) in positive electrospray mode.

4.2. General procedure for the preparation of bis(>P(O)CH$_2$)amines

A mixture of 1.70 mmol amine (0.19 mL of benzylamine or 0.21 g of 4-methoxyaniline), 3.40 mmol (0.10 g) of paraformaldehyde and 3.40 mmol of the >P(O)H species (0.31 mL of dimethyl phosphite, 0.44 mL of diethyl phosphite, 0.67 mL of dibutyl-phosphite and 0.75 mL of dibenzyl phosphite) was heated at 100 °C in a vial in a CEM Discover Microwave reactor equipped with a pressure controller for 1 h. The water formed was removed in vacuum. Column chromatography (silica gel 3% methanol in chloroform) of the residue afforded the products (**1a**–**e** and **2a**–**d**) as oils. The following products were thus prepared:

4.2.1. N,N-Bis(dimethoxyphosphonylmethyl)benzylamine (*1a*)

Yield: 82% (0.49 g); ^{31}P NMR ($CDCl_3$) δ: 27.3; ^{13}C NMR ($CDCl_3$) δ: 48.9 (dd, $^{1}J_{CP}$ = 158.0, $^{3}J_{CP}$ = 7.7, CH_2P), 52.8 (m, OCH_3), 61.3 (t, $^{3}J_{CP}$ = 7.7, CH_2N), 127.8 (C_4), 128.6 (C_3)*, 129.5 (C_2)*, 138.0 (C_1), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 3.17 (d, $^{2}J_{PH}$ = 9.4, 4H, CH_2P), 3.74 (d, $^{3}J_{PH}$ = 10.7, 12H, OCH_3), 3.95 (s, 2H, CH_2N), 7.26–7.39 (m, 5H, ArH); $[M + H]^{+}_{found}$ = 352.1083, $C_{13}H_{24}NO_6P_2$ requires 352.1079.

4.2.2. N,N-Bis(diethoxyphosphonylmethyl)benzylamine (*1b*)

Yield: 98% (0.68 g); ^{31}P NMR ($CDCl_3$) δ: 26.1; ^{13}C NMR ($CDCl_3$) δ: 16.6 (m, CH_2CH_3), 49.7 (dd, $^{1}J_{CP}$ = 156.0, $^{3}J_{CP}$ = 6.7, CH_2P), 61.2 (t, $^{3}J_{CP}$ = 7.9, CH_2N), 62.1 (m, CH_2CH_3), 127.6 (C_4), 128.4 (C_3)*, 129.4 (C_2)*, 138.2 (C_1), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.31 (t, $^{3}J_{HH}$ = 6.9, 12H, CH_2CH_3), 3.16 (d, $^{2}J_{PH}$ = 9.4, 4H, CH_2P), 3.97 (s, 2H, CH_2N), 4.07–4.16 (m, 8H, CH_2CH_3), 7.25–7.39 (m, 5H, ArH); $[M + H]^{+}_{found}$ = 408.1706, $C_{17}H_{32}NO_6P_2$ requires 408.1705.

4.2.3. N,N-Bis(dibutoxyphosphonylmethyl)benzylamine (*1c*)

Yield: 98% (0.87 g); ^{31}P NMR ($CDCl_3$) δ: 25.1; ^{13}C NMR ($CDCl_3$) δ: 13.8 (CH_2CH_3), 18.9 (CH_2CH_3), 32.8 (m, OCH_2CH_2), 49.6 (dd, $^{1}J_{CP}$ = 156.1, $^{3}J_{CP}$ = 7.3, CH_2P), 61.1 (t, $^{3}J_{CP}$ = 7.9, CH_2N), 65.8 (m, OCH_2), 127.6 (C_4), 128.4 (C_3)*, 129.4 (C_2)*, 138.2 (C_1), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.94 (t, $^{3}J_{HH}$ = 7.4, 12H, CH_2CH_3), 1.34–1.46 (m, 8H, CH_2CH_3), 1.60–1.69 (m, 8H, OCH_2CH_2), 3.17 (d, $^{2}J_{PH}$ = 9.1, 4H, CH_2P), 3.97–4.10 (m, 10H, OCH_2, CH_2N (overlapped)), 7.26–7.40 (m, 5H, ArH); $[M + H]^{+}_{found}$ = 520.2963, $C_{25}H_{48}NO_6P_2$ requires 520.2957.

4.2.4. N,N-Bis(dibenzyloxyphosphonylmethyl)benzylamine (*1d*)

Yield: 91% (1.0 g); ^{31}P NMR ($CDCl_3$) δ: 26.4; ^{13}C NMR ($CDCl_3$) δ: 50.1 (dd, $^{1}J_{CP}$ = 156.3, $^{3}J_{CP}$ = 7.5, CH_2P), 61.1 (t, $^{3}J_{CP}$ = 7.8, CH_2N), 67.6 (m, OCH_2), 128.0 (C_3)[a], 128.2 ($C_{3'}$)[b], 128.50 (C_4), 128.55 ($C_{4'}$), 128.6 (C_2)[a], 128.7 ($C_{2'}$)[b], 136.46 (d, $^{3}J_{CP}$ = 3.1), 136.50 (d, $^{3}J_{CP}$ = 3.2) ($C_{1'}$), 137.9 (C_1), [a,b]may be reversed; ^{1}H NMR ($CDCl_3$) δ: 3.20 (d, $^{2}J_{HP}$ = 8.8, 4H, CH_2P), 3.95 (s, 2H, CH_2N), 4.91–5.03 (m, 8H, OCH_2), 7.19–7.37 (m, ArH); $[M + H]^{+}_{found}$ = 656.2311, a $C_{37}H_{40}NO_6P_2$ requires 656.2331.

4.2.5. N,N-Bis(dimethoxyphosphonylmethyl)-4-methoxyaniline (*2a*)

Yield: 85% (0.53 g); ^{31}P NMR ($CDCl_3$) δ: 26.3; ^{13}C NMR ($CDCl_3$) δ: 47.4 (d, $^{1}J_{CP}$ = 157.4, CH_2P), 52.8 (t, $^{1}J_{CP}$ = 3.4 $POCH_3$), 55.8 (CH_3O), 114.7 (C_3)*, 116.4 (C_2)*, 142.2 (C_1), 153.2 (C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 3.66 (d, $^{3}J_{PH}$ = 10.5, 12H, $POCH_3$), 3.72 (s, 3H, CH_3O), 3.87 (d, $^{2}J_{PH}$ = 6.0, 4H, CH_2P), 6.78–6.81 and 6.87–6.90 (m, 4H, ArH); $[M + H]^{+}_{found}$ = 368.1028, $C_{13}H_{24}NO_7P_2$ requires 368.1028.

4.2.6. N,N-Bis(diethoxyphosphonylmethyl)-4-methoxyaniline (*2b*)

Yield: 89% (0.64 g); ^{31}P NMR ($CDCl_3$) δ: 23.9; ^{13}C NMR ($CDCl_3$) δ: 16.6 (t, $^{3}J_{CP}$ = 2.7, CH_2CH_3), 47.8 (d, $^{1}J_{CP}$ = 157.5, CH_2P), 55.8 (CH_3O), 62.2 (t, $^{2}J_{CP}$ = 3.4, OCH_2), 114.5 (C_3)*, 116.0 (C_2)*, 142.4 (C_1), 152.9 (C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 1.22 (t, $^{3}J_{HH}$ = 7.1, 12H, CH_2CH_3), 3.71 (s, 3H, CH_3O), 3.87 (d, $^{2}J_{PH}$ = 5.6, 4H, CH_2P), 3.97–4.08 (m, 8H, CH_2CH_3), 6.75–6.78 and 6.87–6.90 (m, 4H, ArH); $[M + H]^{+}_{found}$ = 424.1649, $C_{17}H_{32}NO_7P_2$ requires 424.1654.

4.2.7. N,N-Bis(dibutoxyphosphonylmethyl)- 4-methoxyaniline (*2c*)

Yield: 85% (0.77 g); ^{31}P NMR ($CDCl_3$) δ: 24.7; ^{13}C NMR ($CDCl_3$) δ: 13.8 (CH_2CH_3), 18.9 (CH_2CH_3), 32.8 (t, $^{3}J_{CP}$ = 2.8 OCH_2CH_2), 47.7 (d, $^{1}J_{CP}$ = 157.1, CH_2P), 55.9 (CH_3O), 66.0 (t, $^{2}J_{CP}$ = 3.5, OCH_2), 114.6 (C_3)*, 116.1 (C_2)*, 142.5 (C_1), 152.9 (C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, $^{3}J_{HH}$ = 7.4, 12H, CH_2CH_3), 1.28–1.41 (m, 8H, CH_2CH_3), 1.53–1.63 (m, 8H, OCH_2CH_2), 3.91 (d, $^{2}J_{PH}$ = 5.2, 4H, CH_2P), 3.94–4.05 (m, 8H, OCH_2), 6.79–6.82 and 6.91–6.94 (m, 4H, ArH); $[M + H]^{+}_{found}$ = 536.2908, $C_{25}H_{48}NO_7P_2$ requires 536.2906.

4.2.8. N,N-Bis(dibenzyloxyphosphonylmethyl)-4-methoxyaniline (*2d*)

Yield: 81% (0.79 g); ^{31}P NMR ($CDCl_3$) δ: 25.0; ^{13}C NMR ($CDCl_3$) δ: 49.4 (OCH_3), 55.9 (CH_2P), 67.8 (m, OCH_2), 114.7 (C_3)[a], 116.4 (C_2)[a], 128.3 ($C_{3'}$)[b], 128.6 ($C_{4'}$), 128.8 ($C_{2'}$)[b], 136.3 (d, $^{3}J_{CP}$ = 2.7) and 136.4 (d, $^{3}J_{CP}$ = 2.9) ($C_{1'}$), 142.1 (C_1), 153.2 (C_4), [a,b]may be reversed; ^{1}H NMR ($CDCl_3$) δ: 3.73 (s, 3H, CH_3O), 3.84 (d, $^{2}J_{HP}$ = 9.0, 4H, CH_2P), 4.89–4.96 (m, 8H, OCH_2), 6.71–6.74 and 6.84–6.87 (m, 4H, ArH), 7.21–7.37 (m, 20H, Ar'H); $[M + H]^{+}_{found}$ = 672.2285, a $C_{37}H_{40}NO_7P_2$ requires 672.2280.

4.2.9. N,N-Bis(ethoxy-phenylphosphinylmethyl)benzylamine (*1e*)

Compound **1e** was prepared similarly using the same amount of benzylamine and paraformaldehyde along with 3.40 mmol (0.51 mL) of ethyl phenylphosphonate. Yield: 97% (0.78 g) (oil as a 51:49 mixture of two isomers); ^{31}P NMR ($CDCl_3$) δ: 41.2 and 41.3; ^{13}C NMR ($CDCl_3$) δ: 16.7 and 16.8 (CH_2CH_3), 53.9 (dd, $^{1}J_{CP}$ = 126.3, $^{3}J_{CP}$ = 8.9) and 54.0 (dd, $^{1}J_{CP}$ = 123.9, $^{3}J_{CP}$ = 8.0) (CH_2P), 60.7 and 60.9 (m, CH_2CH_3), 61.8 and 61.9 (m, CH_2N), 128.2 (C_4), 128.3 (d, J_{CP} = 11.7) and 128.6 (d, J_{CP} = 12.6) ($C_{2'}$)[a], 128.5 (C_3)[b], 129.3 (C_2)[b], 130.0 (d, $^{1}J_{CP}$ = 123.8) and 130.6 (d, $^{1}J_{CP}$ = 122.6) ($C_{1'}$), 132.1 (d,

$^4J_{CP}$ = 2.7) and 132.2 (d, $^4J_{CP}$ = 2.7) ($C_{4'}$), 132.3 (d, J_{CP} = 10.1) and 132.5 (d, J_{CP} = 10.0) ($C_{3'}$)[a], 137.9 (C_1); ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, $^3J_{HH}$ = 7.0, 6H, CH_2CH_3), 3.00–3.08 (m, 2H) and 3.39–3.51 (m, 2H) CH_2P, 3.77–3.87 (m, 2H) and 3.98–4.09 (m, 2H) CH_2CH_3, 3.96 (s, 2H, CH_2N), 6.91–7.71 (m, 15H, ArH), [a,b]may be reversed; $[M + H]^+_{found}$ = 472.1807, $C_{25}H_{32}NO_4P_2$ requires 472.1807.

4.3. General procedure for the synthesis of N,N-bis(diphenylphosphinoylmethyl)amines **3a–d**

A mixture of 0.85 mmol of the amine (0.09 mL of benzylamine, 0.105 g of 4-methoxyaniline, 0.08 mL of aniline and 0.09 mL of 4-methylaniline), 1.70 mmol (0.05 g) of paraformaldehyde, 1.70 mmol (0.34 g) of diphenylphosphine oxide and 3 mL of acetonitrile was heated at 100 °C in a closed vial in the MW reactor for 1.5 h. The work-up was similar as above to provide products **3a–d**.

4.3.1. N,N-Bis(diphenylphosphinoylmethyl)benzylamine (**3a**)

Yield: 95% (0.86 g) of compound **3a** as white crystals. Mp: 80–82 °C; ^{31}P NMR ($CDCl_3$) δ: 29.8; ^{13}C NMR ($CDCl_3$) δ: 55.1 (dd, $^1J_{CP}$ = 84.4, $^3J_{CP}$ = 7.7, CH_2P), 63.1 (t, $^3J_{CP}$ = 7.7, CH_2N), 127.3 (C_4), 128.1 (C_3)[a], 128.4 (d, J_{CP} = 12.3, $C_{3'}$)[b], 129.8 (C_2)[a], 131.2 (d, J_{CP} = 9.2, $C_{2'}$)[b], 131.6 (d, $^4J_{CP}$ = 2.2, $C_{4'}$), 132.0 (d, $^1J_{CP}$ = 98.0, $C_{1'}$); 137.6 (C_1); ^{1}H NMR ($CDCl_3$) δ: 3.74 (d, $^2J_{PH}$ = 6.4, 4H, CH_2P), 4.09 (s, 2H, CH_2N), 6.80–7.66 (m, 25H, ArH), [a,b]may be reversed; $[M + H]^+_{found}$ = 536.1905, $C_{33}H_{32}NO_2P_2$ requires 536.1908.

4.3.2. N,N-Bis(diphenylphosphinoylmethyl) 4-methoxyaniline (**3b**)

Yield: 94% (0.87 g) of compound **3b** as white crystals. Mp: 158–160 °C; ^{31}P NMR ($CDCl_3$) δ: 28.1; ^{13}C NMR ($CDCl_3$) δ: 54.6 (d, $^1J_{CP}$ = 77.3, CH_2P), 55.7 (CH_3O), 114.3 (C_3)[a], 122.0 (C_2)[a], 128.7 (d, J_{CP} = 11.5, $C_{3'}$)[b], 131.3 (d, J_{CP} = 9.4, $C_{2'}$)[b], 132.0 ($C_{4'}$), 132.2 (d, $^1J_{CP}$ = 95.9, $C_{1'}$), 146.7 (dd, $^2J_{CP}$ = 6.0, $^4J_{CP}$ = 2.9, C_1), 155.0 (C_4); ^{1}H NMR ($CDCl_3$) δ: 3.66 (s, 3H, OCH_3), 4.41 (s, 4H, CH_2P), 6.50–6.53 (m, 2H, C_3H)[a] and 6.72–6.75 (m, 2H, C_2H)[a], 7.34–7.69 (m, 20H, Ar'H), [a,b]may be reversed; $[M + H]^+_{found}$ = 552.1863, $C_{33}H_{32}NO_3P_2$ requires 552.1857.

4.3.3. N,N-Bis(diphenylphosphinoylmethyl)aniline (**3c**)

Yield: 55% (0.48 g) of compound **3c** as white crystals. Mp: 190–192 °C; ^{31}P NMR ($CDCl_3$) δ: 27.6; ^{13}C NMR ($CDCl_3$) δ: 52.2 (d, $^1J_{CP}$ = 76.2, CH_2P), 116.7 (C_2), 119.7 (C_4), 128.5 (C_3), 128.6 (d, J_{CP} = 11.5, $C_{3'}$)[a], 131.1 (d, J_{CP} = 9.3, $C_{2'}$)[a], 131.99 ($C_{4'}$), 132.02 (d, $^1J_{CP}$ = 94.2, $C_{1'}$), 148.8 (C_1); ^{1}H NMR ($CDCl_3$) δ: 4.50 (s, 4H, CH_2P), 6.68–6.71 (m, 2H, C_3H)[a] and 6.91–6.94 (m, 2H, C_2H)[a], 7.36–7.73 (m, 20H, Ar'H), [a]may be reversed; $[M + H]^+_{found}$ = 522.1741, $C_{32}H_{30}NO_2P_2$ requires 522.1752.

4.3.4. N,N-Bis(diphenylphosphinoylmethyl)-4-methylaniline (**3d**)

Yield: 89% (0.81 g) of compound **3d** as white crystals. Mp: 165–167 °C; ^{31}P NMR ($CDCl_3$) δ: 28.0; ^{13}C NMR ($CDCl_3$) δ: 20.6 (CH_3), 53.2 (d, $^1J_{CP}$ = 76.8, CH_2P), 118.3 (C_2), 128.8 (d, J_{CP} = 11.4, $C_{3'}$)[a], 129.5 (C_3), 130.0 (C_4), 131.4 (d, J_{CP} = 9.3, $C_{2'}$)[a], 132.0 ($C_{4'}$), 132.3 (d, $^1J_{CP}$ = 94.5, $C_{1'}$), 147.2 (C_1); ^{1}H NMR ($CDCl_3$) δ: 2.14 (s, 3H, CH_3), 4.44 (s, 4H, CH_2P), 6.63–6.66 (m, 2H, C_3H)[a] and 6.75–6.78 (m, 2H, C_2H)[a], 7.35–7.72 (m, 20H, Ar'H), [a]may be reversed; $[M + H]^+_{found}$ = 536.1908, $C_{33}H_{32}NO_2P_2$ requires 536.1908.

4.4. General procedure for the synthesis of cis[(benzyl- or aryl-bis(diphenylphosphinomethyl)amine)-dichloro-platinum(II)]

To 0.36 mmol of **3a–d** (**3a**: 0.19 g, **3b**: 0.20 g, **3c**: 0.19 g, **3d**: 0.19 g) in 1 mL of degassed benzene was added 1.35 mL (1.07 mmol) of phenylsilane under nitrogen. The mixture was stirred at 80 °C for 3 days. Then the mixture was diluted by the addition of 2 mL of degassed benzene. To the solution of phosphine **5** so obtained was added 0.18 g (0.37 mmol) of dichlorodibenzonitrile platinum and the mixture stirred at 25 °C for 1 day. The solid crystallized from the mixture was separated by filtration to afford complex **6a–d**.

4.4.1. Bis(diphenylphosphinomethyl)benzylamine]-dichloro-platinum(II) (**6a**)

Yield: 60%; ^{31}P NMR ($CDCl_3$) δ: −7.9 ($^1J_{P,Pt}$ = 3395); ^{13}C NMR ($CDCl_3$) δ: 55.7 (dd, $^1J_{CP}$ = 62.0, $^3J_{CP}$ = 5.7, CH_2P), 69.9 (t, $^3J_{CP}$ = 12.1, CH_2N), 127.9 (dd, $^1J_{CP}$ = 72.0, $^3J_{CP}$ = 5.7, $C_{1'}$), 128.4 (C_4), 128.59 (d, $^4J_{CP}$ = 5.7), 128.63 (d, $^4J_{CP}$ = 5.7) ($C_{3'}$)[a], 128.9 (C_3)[b], 129.9 (C_2)[b], 131.6 ($C_{4'}$), 133.98 (d, $^5J_{CP}$ = 4.9), 134.01 (d, $^5J_{CP}$ = 4.9) ($C_{2'}$)[a], 135.2 (C_1); ^{1}H NMR ($CDCl_3$) δ: 3.42 (d, $^2J_{HP}$ = 2.5, $^3J_{HPt}$ = 36.4, 4H, CH_2P), 3.59 (s, 2H, CH_2N), 6.92 (d, $^4J_{HH}$ = 7.5, 2H, C_2H)[a], 7.20 (t, $^3J_{HH}$ = 7.3, 2H, C_3H)[a], 7.28 (t, $^4J_{HH}$ = 7.5, C_4H), 7.34 (t, $^3J_{HH}$ = 7.5, 8H, $C_{3'}H$)[b], 7,44 (t, $^3J_{HH}$ = 7.2, 4H, $C_{4'}H$), 7.70 (dd, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 10.7, 8H, $C_{2'}H$)[b], [a,b]may be reversed; $[M - Cl]^+_{found}$ = 732.1269, $C_{33}H_{31}NP_2PtCl$ requires 732.1247.

4.4.2. Bis(diphenylphosphinomethyl) 4-methoxyaniline]-dichloro-platinum(II) (**6b**)

Yield: 50%; ^{31}P NMR ($CDCl_3$) δ: −6.3 ($^1J_{P,Pt}$ = 3410); ^{13}C NMR ($CDCl_3$) δ: 56.0 (dd, $^1J_{CP}$ = 58.0, $^3J_{CP}$ = 5.5, CH_2P), 55.8 (OCH_3), 115.2 (C_3)[a], 122.6 (C_2)[a], 127.8 (dd, $^1J_{CP}$ = 70.4, $^3J_{CP}$ = 5.6, $C_{1'}$), 128.76 (d, $^4J_{CP}$ = 5.7), 128.84 (d, $^4J_{CP}$ = 5.7) ($C_{3'}$)[b], 131.8 ($C_{4'}$), 134.07 (d, $^5J_{CP}$ = 4.9), 134.13 (d, $^5J_{CP}$ = 4.9) ($C_{2'}$)[b], 146.7 (C_1), 156.9 (C_4); ^{1}H NMR ($CDCl_3$) δ: 3.74 (s, 3H, CH_3O), 3.91 (d, $^2J_{HP}$ = 0.9, $^3J_{HPt}$ = 19.7, 4H, CH_2P), 6.67 (d, $^4J_{HH}$ = 8.9, 2H, C_3H)[a], 6.76 (d, $^3J_{HH}$ = 8.8, 2H, C_3H)[a], 7.40 (t, $^3J_{HH}$ = 6.8, 8H, $C_{3'}H$)[b], 7,45 (t, $^3J_{HH}$ = 6.9, 4H, $C_{4'}H$), 7.83 (dd, $^3J_{HH}$ = 7.6, $^3J_{PH}$ = 17.9 8H, $C_{2'}H$)[b], [a,b]may be reversed; $[M - Cl]^+_{found}$ = 748.1196, $C_{33}H_{31}NOP_2PtCl$ requires 748.1196.

4.4.3. Bis(diphenylphosphinomethyl)aniline]-dichloro-platinum(II) (**6c**)

Yield: 45%; ^{31}P NMR ($CDCl_3$) δ: −5.4 ($^1J_{P,Pt}$ = 3422); ^{13}C NMR ($CDCl_3$) δ: 52.7 (dd, $^1J_{CP}$ = 57.4, $^3J_{CP}$ = 4.9, CH_2P), 118.9 (C_2), 123.4 (C_4), 127.7 (dd, $^1J_{CP}$ = 122.9, $^3J_{CP}$ = 5.7, $C_{1'}$), 128.9 (d, $^4J_{CP}$ = 5.6), 129.0 (d, $^4J_{CP}$ = 5.6) ($C_{3'}$)[a], 130.0 (C_3) 132.0 ($C_{4'}$), 134.0 (d, $^5J_{CP}$ = 4.9), 134.1 (d, $^5J_{CP}$ = 4.8) ($C_{2'}$)[a], 156.7 (C_1); ^{1}H NMR ($CDCl_3$) δ: 4.08 (d, $^2J_{HP}$ = 1.2, $^3J_{HPt}$ = 21.3, 4H, CH_2P), 6.69 (d, $^4J_{HH}$ = 8.1, 2H, C_3H)[a], 6.89–6.93 (m, 1H, C_4H), 7.03 (d, $^3J_{HH}$ = 7.4, 2H, C_3H)[a], 7.44 (t, $^3J_{HH}$ = 6.7, 8H, $C_{3'}H$)[b], 7.49 (t, $^3J_{HH}$ = 6.8, 4H, $C_{4'}H$), 7.85 (dd, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 17.7 8H, $C_{2'}H$)[b], [a,b]may be reversed; $[M - Cl]^+_{found}$ = 718.1101, $C_{32}H_{29}NP_2PtCl$ requires 718.1091.

4.4.4. Bis(diphenylphosphinomethyl)-4-methylaniline]-dichloro-platinum(II) (**6d**)

Yield: 60%; ^{31}P NMR ($CDCl_3$) δ: −5.8 ($^1J_{P,Pt}$ = 3416); ^{13}C NMR ($CDCl_3$) δ: 20.8 (CH_3), 54.1 (dd, $^1J_{CP}$ = 64.3, $^3J_{CP}$ = 5.2, CH_2P), 119.7 (C_2), 127.6 (dd, $^1J_{CP}$ = 76.4, $^3J_{CP}$ = 6.0, $C_{1'}$), 128.8 (d, $^4J_{CP}$ = 5.6), 128.9 (d, $^4J_{CP}$ = 5.7) ($C_{3'}$)[a], 130.6 (C_3) 131.9 ($C_{4'}$), 134.0 (d, $^5J_{CP}$ = 4.9), 134.1 (d, $^5J_{CP}$ = 5.0) ($C_{2'}$)[a], 143.9 (C_4), 150.2 (C_1); ^{1}H NMR ($CDCl_3$) δ: 2.27 (s, 3H, CH_3), 4.00 (d, $^2J_{HP}$ = 1.5, $^3J_{HPt}$ = 20.0, 4H, CH_2P), 6.62 (d, $^4J_{HH}$ = 8.3, 2H, C_3H)[a], 7.04 (d, $^3J_{HH}$ = 8.2, 2H, C_3H)[a], 7.40 (t, $^3J_{HH}$ = 7.9, 8H, $C_{3'}H$)[b], 7.45 (t, $^3J_{HH}$ = 6.7, 4H, $C_{4'}H$), 7.85 (dd, $^3J_{HH}$ = 8.3, $^3J_{PH}$ = 18.1 8H, $C_{2'}H$)[b], [a,b]may be reversed; $[M - Cl]^+_{found}$ = 732.1269, $C_{33}H_{31}NP_2PtCl$ requires 732.1247.

4.5. Hydroformylation experiments

In a typical experiment, a solution of 0.005 mmol of $PtCl_2$(PNP ligand) **6** (**6a**: 3.9 mg, **6b**: 3.9 mg, **6d**: 3.9 mg, **6e**: 3.8 mg) and tin(II) chloride (0.95 mg; 0.005 mmol) in toluene (5 mL) containing styrene (0.058 mL, 0.5 mmol) was transferred under argon into a 100 mL stainless steel autoclave. The reaction vessel was

pressurized to 80 bar total pressure ($CO/H_2 = 1:1$) and placed in an oil bath of constant temperature. The mixture was stirred with a magnetic stirrer for the given reaction time. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC and GC–MS.

4.6. X-ray experimental

A selected colourless prism shaped single crystal ($0.2 \times 0.3 \times 0.1$ mm) of **6b** was mounted on a Rigaku R-AXIS RAPID diffractometer (graphite monochromator Cu–$K\alpha$ radiation, $\lambda = 1.54178$ Å). Data collection was performed at low temperatures ($T = 108(2)$ K). Crystal data for **6b**: $C_{34}H_{33}Cl_4NOP_2Pt$, orthorhombic, space group *Pbca*, $a = 13.8550(3)$ Å, $b = 21.8600(4)$ Å, $c = 44.6567(8)$ Å, $V = 13525.2(4)$ Å^3, $T = 108(2)$ K, $Z = 16$, $F(000) = 6848$, $D_x = 1.710$ Mg/m^3, $\mu = 11.791$ mm^{-1}. Initial structure model was obtained by SHELXS-97,2 completed by successive difference Fourier syntheses and refined to convergence by SHELXL-97,2 $R^1 = 0.0616$ and $wR^2 = 0.1604$ for 1332 [$I > 2\sigma(I)$] and $R^1 = 0.0697$ and $wR^2 = 0.1685$ for all (11,723) intensity data. Crystallographic data for **6b** have been deposited at the Cambridge Crystallographic Data centre under deposition no. CCDC 876164. Copies of these data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 00 44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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