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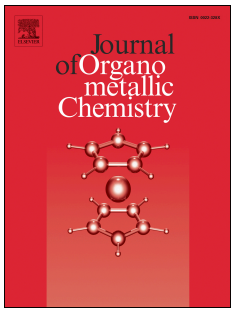

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Synthesis and use of α-aminophosphine oxides and *N*,*N*-bis(phosphinoyl-methyl)amines – A study on the related ring platinum complexes

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ABSTRACT

The Kabachnik–Fields condensation was extended using secondary phosphine oxides, such as dibenzylphosphine oxide and bis(4-methylphenyl)phosphine oxide as the P-reactant in reaction with formaldehyde and different primary amines. Besides the α-aminophosphine oxides, the corresponding bisproducts, *N*,*N*-bis(phosphinoylmethyl)amines were also synthesized under appropriate conditions. The bis(phosphinoyl)amines were then converted to ring platinum complexes after double deoxygenation. The substituent dependence of the energetics of the complexation reaction using bidentate P-ligands, and the stereostructure of a few complexes were evaluated by B3LYP/6-31G(d,p) calculations using the effective core potential (ECP) basis set (SDD). The crystal structure of a few ring Pt species was studied by X-ray analysis. Catalytic activity of the complexes synthesized was investigated in hydroformylation.

Keywords:

Kabachnik–Fields reaction; α-aminophosphine oxides, *N*,*N*-bis(phosphinoylmethyl)amines; Bidentate P-ligand, Ring platinum complex; Hydroformylation.

1. Introduction

α-Aminophosphonates and related derivatives, such as α-aminophosphine oxides are structural analogues of α-amino acids. Due to their versatile bioactivity, they have attracted much attention [1-3].

One of the most convenient and widespread methods for the synthesis of α-aminophosphonates is the Kabachik–Fields (phospha-Mannich) reaction which is based on the condensation of an amine, an aldehyde or ketone and a >P(O)H species, such as dialkyl phosphite or secondary phosphine oxide [4-7]. Usually, the reactions are carried out in the presence of a catalyst and solvent [2,8–13]. However, it was found that, especially under solvent-free conditions, there is no need for a catalyst [14,15]. The efficiency could be further increased by the application of the microwave (MW) technique [16–19].

There are only a few examples in the literature for the synthesis of α-aminophosphine oxides. Petrov and co-workers synthesized (phenylaminomethyl)-dibenzylphosphine oxide in the condensation of aniline, paraformaldehyde and diphenylphosphine oxide [20]. The reaction was carried out at 150 °C for 9 h and the yield was 73%. The (phenylaminomethyl)-dibenzylphosphine oxide was also prepared via (hydroxymethyl)phosphine oxide [21]. Cherkasov and his research group applied the Kabachnik-Fields reaction to obtain (butylaminomethyl)-di(*p*-tolyl)phosphine oxide [22]. The condensation was carried out in benzene.

As a modification, the double Kabachnik–Fields reaction was also elaborated starting from primary amines or amino acid derivatives to make available bis(phosphonomethyl)- or bis(phosphinoylmethyl)amines [23–29]. The latter species were also synthesized via a

methylene insertion reaction into a P–N bond followed by oxidation [30]. Bis(phosphinoylmethyl)amines may be potential bisphosphine ligands after double deoxygenation. There are a few examples for such bidentate P-ligands synthesized by the condensation of amines, paraformaldehyde and diphenylphosphine [31–33]. These bisphosphines were applied successfully in the synthesis of transition metal complexes [34–37]. A number of Pt, Ru and Au complexes show significant anticancer activity [38,39]. The transition metal complexes incorporating P-ligands may also be used as catalyst in hydroformylations [40–44].

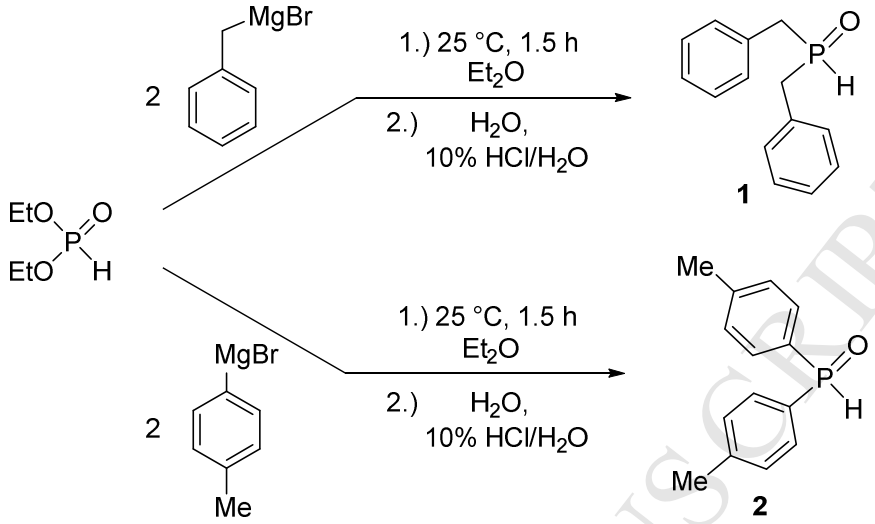
We have developed a catalyst-free MW-assisted method for the synthesis of *N*,*N*-bis(diphenylphosphinoylmethyl)amines that were converted to ring platinum complexes after double deoxygenation [25–27]. In this paper, new *N*-(phosphinoylmethyl)- and *N*,*N*-bis(phosphinoylmethyl)amines, as well as the related bidentate P-ligands and ring platinum complexes are described. The latter complexes were tested as catalysts in the hydroformylation of styrene.

2. Results and discussion

2.1. Synthesis of dibenzyl- and di(p-tolyl)phosphine oxides

First, the secondary phosphine oxides (**1** and **2**) used as P-reagents in the three component condensations were synthesized by the Grignard reaction of diethyl phosphite applying benzyl- or *p*-tolylmagnesium bromide (Scheme 1). Two equivalents of the Grignard reagent were added to the diethyl ether solution of diethyl phosphite at 0 °C, and the mixture was stirred at 25 °C for 1.5 h. Then, the mixture was hydrolyzed with 10% HCl solution, and the aqueous phase was extracted with diethyl ether. After purification of the crude product so obtained by column chromatography, the secondary phosphine oxides (**1** and **2**) were obtained in yields of 84-86%. The dibenzyl- and isomeric di(*p*-tolyl)phosphine oxide (**1** and **2**) are

known compounds [45,46]. The above synthesis elaborated by us represents a simple and attractive approach.

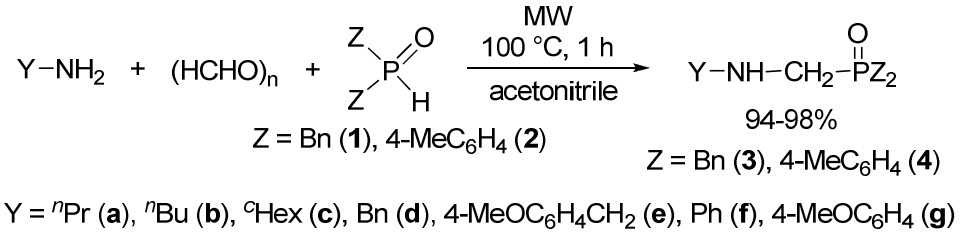


Scheme 1.

2.2. Microwave-assisted synthesis of (aminomethyl)dibenzyl- or di(p-tolyl)phosphine oxides and N,N-bis(dibenzyl- or di(p-tolyl)phosphinoylmethyl)amines

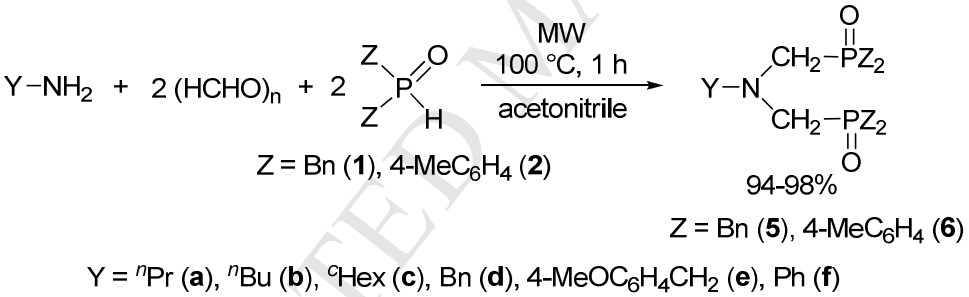
In the first approach, the Kabachnik–Fields reaction of primary amines, such as *n*-propyl-, *n*-butyl-, cyclohexyl-, benzyl-, 4-methoxy-benzylamine, aniline or 4-methoxyaniline was studied with paraformaldehyde and dibenzylphosphine oxide (**1**) at 100 °C for 1 h under MW conditions (Scheme 2). The condensations were carried out without any catalyst in acetonitrile as the solvent to overcome the heterogeneity of the reaction mixture. The solvent and the water formed were removed in vacuum, and the crude products so obtained were passed through a 1 cm silica layer using ethyl acetate as the eluent. After evaporating the solvent in vacuum, the (aminomethyl-)dibenzylphosphine oxides (**3a-g**) were obtained in yields of 94–98% in a pure form.

In the next round, the primary amines (*n*-butyl-, cyclohexyl-, benzyl-amine and aniline) were reacted with paraformaldehyde and di(*p*-tolyl)phosphine oxide (**2**) in a similar way described above. After an irradiation of 1 h at 100 °C, the corresponding products (**4b-d** and **4f**) were isolated in 94–98% yields.



Scheme 2.

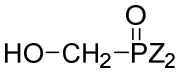
The double Kabachnik–Fields condensation was also investigated. In these cases, the primary amines were reacted with two equivalents of the paraformaldehyde and two equivalents of the dibenzyl- (**1**) or di(*p*-tolyl)phosphine oxide (**2**) under MW conditions (Scheme 3). The reactions were performed in acetonitrile, at 100 °C for 1 h, without any catalyst in a similar way, as the condensations discussed above. Except for the condensation of aniline, the *N*,*N*-bis(phosphinoylmethyl)amines (**5a-e** and **6b-d**) were obtained in yields of 94–98%.



Scheme 3.

The outcome of the double Kabachnik–Fields reaction of aniline, paraformaldehyde and phosphine oxides **1** and **2** was somewhat different, as besides the expected bisproduct (**5f** or **6f**), the mono-adduct (**3f** or **4f**) and a by-product, hydroxymethylphosphine oxide **7** or **8** were also formed. In the reaction of aniline with two equivalents of paraformaldehyde and dibenzylphosphine oxide (**1**), the product composition was 6% of bisadduct (**5f**) {δ_P ($CDCl_3$) 41.3, $[M + H]^+_{found}$ = 578.2381, $C_{36}H_{38}NO_2P_2$ requires 578.2372}, 63% of monoadduct (**3f**), and 31% of hydroxymethyldibenzylphosphine oxide **7** {δ_P ($CDCl_3$) 44.0, $[M + H]^+_{found}$ = 261.1048, $C_{15}H_{18}O_2P$ requires 261.1039}. Using di(*p*-tolyl)phosphine oxide

(**2**) as the P-reagent, 60% of bisproduct (**6f**) {δ_P ($CDCl_3$) 27.8, $[M + H]^+_{found}$ = 578.2373, $C_{36}H_{38}NO_2P_2$ requires 578.2372}, 23% of mono derivative (**4f**) and 17% of by-product (**8**) {δ_P ($CDCl_3$) 31.5, $[M + H]^+_{found}$ = 261.1044, $C_{15}H_{18}O_2P$ requires 261.1039} were formed.

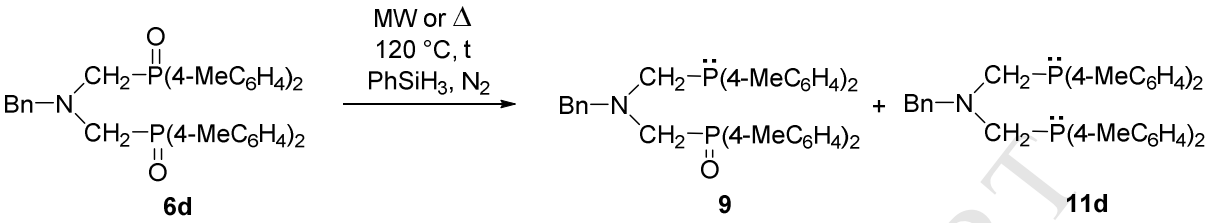


Z = Bn (**7**), 4-MeC_6H_4 (**8**)

2.3. Utilization of bis(phosphinoylmethyl)amines as precursors for bidentate P-ligands

The bis(phosphinoylmethyl)amines (**5** and **6**) were utilized as precursors for bidentate P-ligands in the synthesis of transition metal complexes. First, the double deoxygenation of *N*,*N*-bis(phosphinoylmethyl)benzylamines **5** and **6** was investigated. In our earlier studies [26,27], the deoxygenation of similar *N*,*N*-bis(diphenylphosphinoylmethyl)amines was carried out using phenylsilane in benzene at 80 °C for 3 days. Under these conditions, the deoxygenations were not complete. Recently, a better method was elaborated for the deoxygenation of phosphine oxides in our research group. According to this, phenylsilane was used under MW irradiation in the absence of any solvent [47]. This method has now been applied to the reduction of bis(phosphinoylmethyl)amines **5** and **6**. First, the reduction of bis(di-*p*-tolyl-phosphinoylmethyl)benzylamine **6d** was optimized at 120 °C under different conditions (Scheme 4, Table 1). After a 1 h reaction time, the deoxygenation was not complete, and 27% of phosphine-phosphine oxide **9** and 27% of bisphosphine **11d** were formed (Table 1/Entry 1). Prolonging the irradiation to 2 h, the conversion was almost complete (95%) (Table 1/Entry 2). The best result was obtained after 2.5 h (Table 1/Entry 3). To see the effect of the solvent, the reaction was also carried out in toluene. It was found that the conversion decreased to 87%, and only 74% of bisphosphine **11d** was formed (Table 1/Entry 4). A comparative thermal experiment was also carried out, and it was experienced that after 2.5 h, the reaction mixture contained only 30% of bisphosphine **11d** (Table 1/Entry

5). The 40% lower conversion of the thermal control experiment refers to the role of MW irradiation.



Scheme 4.

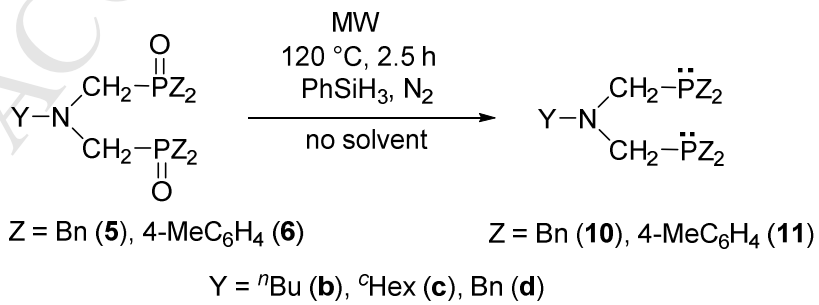
Table 1

Deoxygenation of bis(phosphine oxide) **6d** under different conditions.

Entry	Mode of heating	Solvent	t (h)	Composition (%)		
				6d	**9**	**11d**
1	MW	–	1	46	27	27
2	MW	–	2	5	15	80
3	MW	–	2.5	0	0	**100**
4	MW	toluene	2.5	13	13	74
5	Δ	–	2.5	40	30	30

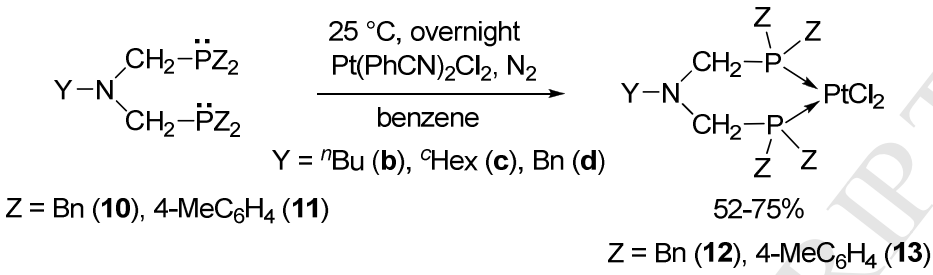
Phosphine-phosphine oxide **9** and bisphosphine **11d** were identified by ^{31}P NMR (**9**: δ_P ($CDCl_3$) –29.4 and 29.5; **11d**: δ_P ($CDCl_3$) –30.4).

Based on the above experiences, the deoxygenation of bis(phosphine oxides) **5b-d** and **6b-d** was carried out at 120 °C for 2.5 h under solvent-free MW-assisted conditions (Scheme 5).



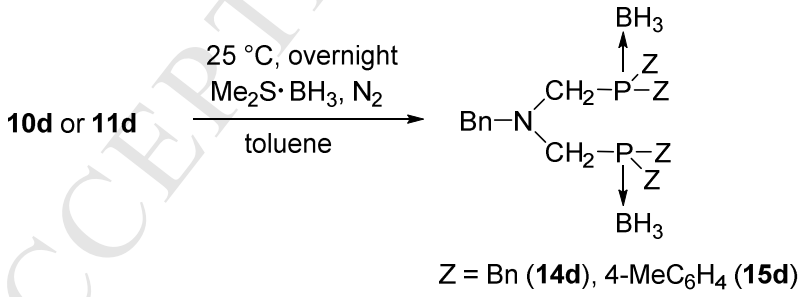
Scheme 5.

The air sensitive bisphosphines (**10b-d** and **11b-d**) so formed were reacted further immediately with dichlorodibenzonitrile platinum to furnish the ring platinum(II) complexes **12b-d** and **13b-d** in yields of 52-75%, and in a purity of *ca.* 99% (Scheme 6).



Scheme 6.

The bis(phosphinomethyl)amines **10d** and **11d** were also converted to the corresponding bis(phosphine boranes) (**14d** or **15d**) by reaction with an excess of dimethyl sulfide borane (Scheme 7). The complexations were performed in toluene at 25 °C. After column chromatography, the borane complexes **14d** or **15d** were obtained in yields of 60/69%. The phosphine boranes can be regarded as the precursors of the corresponding phosphines, as the P(III)-ligand can be liberated from them on treatment with secondary amines in an aromatic solvent [48].



Scheme 7.

All compounds synthesized (**3a-g**, **4b-d**, **4f**, **5a-g**, **6b-d**, **6f**, **7**, **8**, **12b-d**, **13b-d**, **14d** and **15d**) were characterized by ^{31}P, ^{13}C and ^{1}H NMR, as well as mass spectral data.

2.4. Theoretical calculations

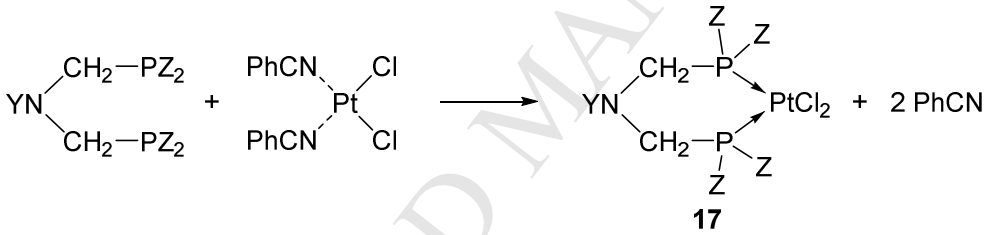
All computations, energy calculations, geometry optimizations and subsequent frequency analyses were carried out using B3LYP/6-31G(d,p) for CHNP and B3LYP/SDD(MWB60) for Pt including effective core potential (ECP) [49–51], applying the Gaussian09 program package (G09) [52]. The method and basis sets were chosen for the characterization of the compounds in agreement with studies published earlier [53].

2.4.1. Stability of the Pt-complexes

The geometry around the Pt^{2+} ion is square planar, where the two phosphorus atoms bind from one side in *cis* configuration, while the two chlorines from the opposite side also in *cis* configuration. The energetics of the complexation process (**16** → **17**) are influenced significantly by Z and moderately by Y. If Z is an alkyl type substituent, like benzyl group (Table 2/Entries 1–7), the electron density on the P atom is much larger, resulting complexation enthalpies of 157–167 kJ mol^{-1}, while aryl substituents (Table 2/Entries 8–11), decrease the electron density, decreasing the benefit of the process by 44–54 kJ mol^{-1}. As expected, the 4-MeC_6H_4 group (Table 2/Entries 12–15) has a somewhat more positive effect on the complexation, as compared to the phenyl case. According to this study, Y has much less effect on the complexation process. Here, one can also find analogous differences between the alkyl and aryl type of substituents, but the effect is less significant. *N*-alkyl substituents resulted in somewhat higher complexation enthalpies, while in the case of aryl groups the enthalpy values were significantly lower. A small decrease in the enthalpies may be observed that may be due to the smaller extent of flexibility of the *N*-aryl substituents. Flexible *N*-propyl and butyl groups may be accommodated without any sterical repulsion with the closer P-benzyl substituents (Table 2/Entries 1 and 2). However, the *N*-phenyl substituent results in a steric repulsion due to its orientation caused by the intensive conjugation with the

nitrogen atom (Table 2/Entry 5). Slightly more negative enthalpy values can be observed for the 4-MeC_6H_4 and 4-$MeOC_6H_4$ derivatives that may be the consequence of the smaller extent of conjugation in these cases (Table 2/Entries 6 and 7). Cyclohexyl and benzyl groups exhibited ΔH values that are close to the value obtained for the butyl or propyl groups (Table 2/Entries 3 and 4), however, due to the lower entropy values ($\Delta\Delta S$ = –17.0 and –16.7 J mol^{-1} K^{-1}, as compared to the Bu case), the final ΔG is less negative, consequently the driving force is somewhat less. These entropy deviations can be attributed to the limited flexibility of these *N*-functional groups in the course of the complexation process.

Table 2
Computed absolute and relative enthalpy (ΔH in kJ mol^{-1}), Gibbs free energy (ΔG in kJ mol^{-1}), and entropy values (ΔS in J mol^{-1} K^{-1}) for the **16** → **17** complexation using B3LYP/6-31G(d,p) for CHNP and B3LYP/SDD(MWB60) for Pt including effective core potential (ECP)



17

Entry	Z	Y	Absolute values (16 → 17)		
			ΔH	**ΔG**	**ΔS**
1	Bn	^{n}Pr	–163.7	–187.5	80.0
2	Bn	^{n}Bu	–166.5	–191.1	82.6
3	Bn	^{c}Hex	–160.9	–180.5	65.6
4	Bn	Bn	–166.7	–186.3	65.9
5	Bn	Ph	–157.1	–183.2	87.6
6	Bn	4-MeC_6H_4	–159.8	–186.3	88.8
7	Bn	4-$MeOC_6H_4$	–161.0	–189.4	95.4
8	Ph	^{c}Hex	–113.0	–134.4	71.9
9	Ph	Ph	–112.4	–133.5	70.8
10	Ph	4-MeC_6H_4	–114.5	–135.6	71.0
11	Ph	4-$MeOC_6H_4$	–114.9	–140.4	85.4
12	4-MeC_6H_4	^{n}Bu	–126.7	–144.6	82.8
13	4-MeC_6H_4	^{c}Hex	–138.3	–155.3	56.9
14	4-MeC_6H_4	Bn	–135.1	–157.3	74.3
15	4-MeC_6H_4	Ph	–131.1	–148.8	59.5

2.4.2. Stereostructure of the ring Pt-complexes

Stereostructures of the *N*-butyl and *N*-cyclohexyl *P*,*P*-tetrabenzyl ring Pt complexes (**12b** and **12c**, respectively), and that of the *N*-cyclohexyl *P*,*P*-tetratolyl derivative (**13c**) were calculated by the B3LYP/6-31G(d,p) method. The optimized structures are shown in Fig. 1, while selected bond lengths, bond angles and torsion angles were collected in Table S1 (Supplementary material). It can be seen clearly that the *N*-substituent may cause a steric interaction with the two closer P-benzyl groups. The *N*-butyl complex (**12b**) strives to form a mirror symmetry structure. This is logical, as the calculations represent isotropic environment conditions, thus the ensuing models can hardly have different “left” or “right” side molecules. However, the *N*-cyclohexyl derivative (**12c**) somewhat breaks this symmetry due to the asymmetrical arrangement. The central six membered hetero ring exhibits a distorted chair conformation in its lowest energy conformer. Noteworthy, that a significant structural difference can be observed between **12c** and **13c**. The six-membered hetero ring with four sterically demanding aryl groups on the two phosphorus atoms (**13c**) adopts a chair-like conformation. At the same time, the P-benzyl species (**12c**) takes up a half-chair conformation. The steric hindrance between the benzyl groups and the N substituent is significant.

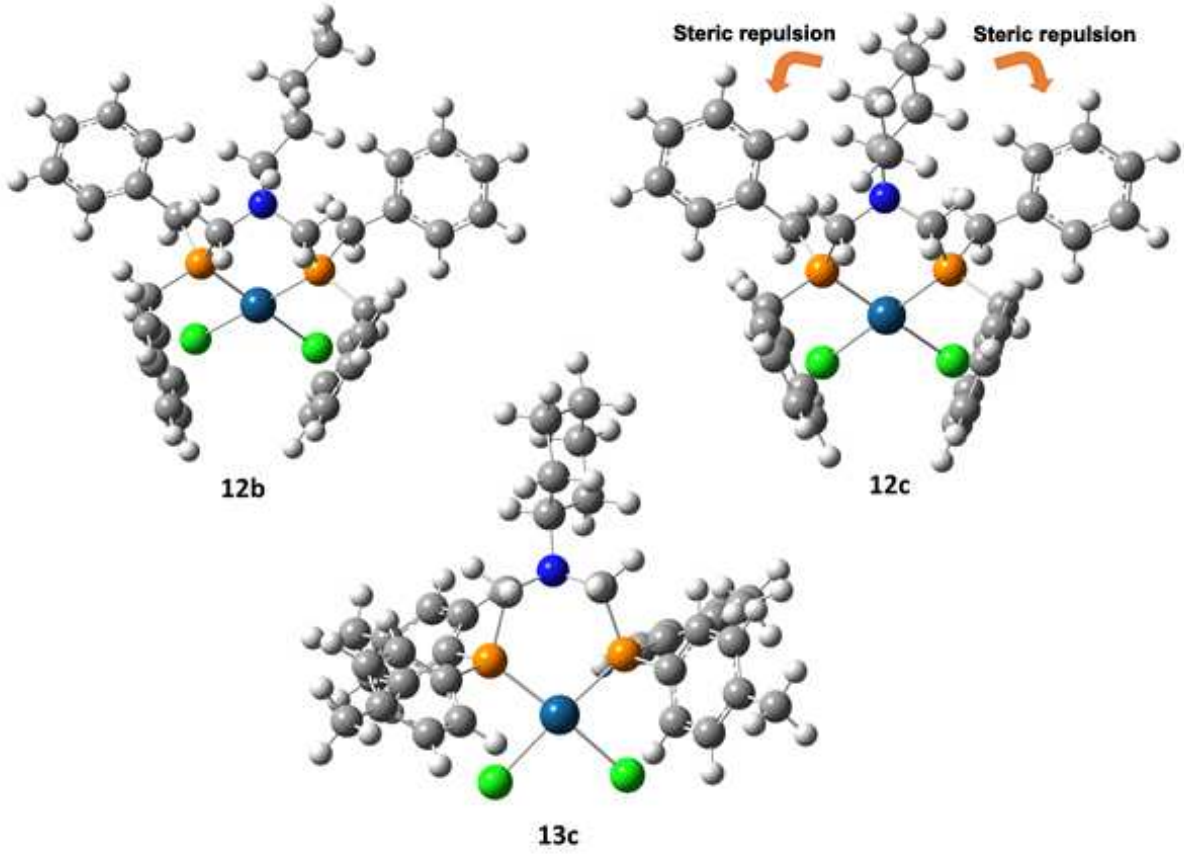


Fig. 1. Computed lowest energy 3D structure of *N*,*N*-[bis(dibenzylphosphinomethyl)-butylamine]dichloroplatinum(II) (**12b**), *N*,*N*-[bis(dibenzylphosphinomethyl)-cyclohexylamine]dichloroplatinum(II) (**12c**) and *N*,*N*-[bis(ditolylphosphinomethyl)-cyclohexylamine]dichloroplatinum(II) (**13c**)

2.5 An X-ray study

The X-ray study on the crystals of the similar six-membered Pt complexes **12b**, **12c** and **13c** revealed that all these substances crystallized with the DMSO solvent as main component, and also additionally with other trace or co-solvents as well. Most important is that the structures give information on the geometry and shape of the central P-heterocyclic ring (Figs. 2-4). Apart from the two C atoms and the two P atoms coordinating to the central Pt atom, the N atom bearing a cyclohexyl or an *n*-butyl group also plays a role. The Pt serves as a square-planar coordination center for the P atoms and the two Cl atoms. The central ring is of a distorted half-chair like shape with the N atom sitting invariably on the flap. This distortion may also depend on the varying solvent content of the crystals. The Pt-centred three-atom P-Pt-P plane portion of the square-planar coordination lends certain rigidity to this

shape. A study of similar cationic and zwitterionic X($CH_2P)_2$Pt< six-membered heterocyclic rings (where X = B, Si or C) revealed a variety of the ring shape, as well as possible pathways for benzene C–H activation and ligand exchange processes [54]. Inspection of closely related crystal structures reveals the similarity of the -N($CH_2P)_2$Pt< six-membered heterocyclic rings to each other [55-57], and also to those seen in Figs. 2–4 (**12b**, **12c** and **13c**). The earlier described ring Pt complexes incorporate cyclohexyl-, phenyl- or trisubstituted phenyl substituents on the P atom and methyl-, phenyl- or isophthalic acid groups on the N atom [55-57]. The corresponding bidentate P-ligands were prepared by a different approach, and were reacted with dichloro(1,5-cyclooctadiene)platinum(II).

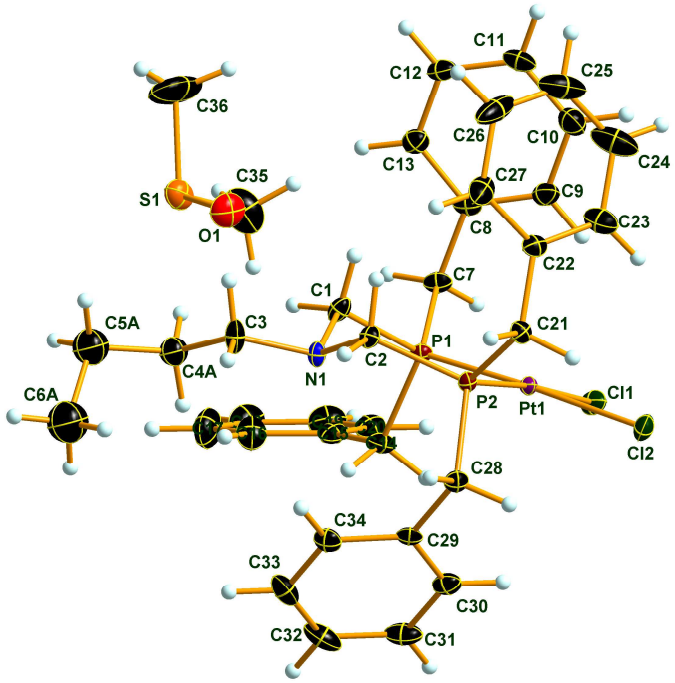


Fig. 2. Atomic displacement plot of *N,N*-[bis(dibenzylphosphinomethyl)-butylamine]-dichloroplatinum(II) (**12b**) DMSO 1:1 solvate with atomic numbering

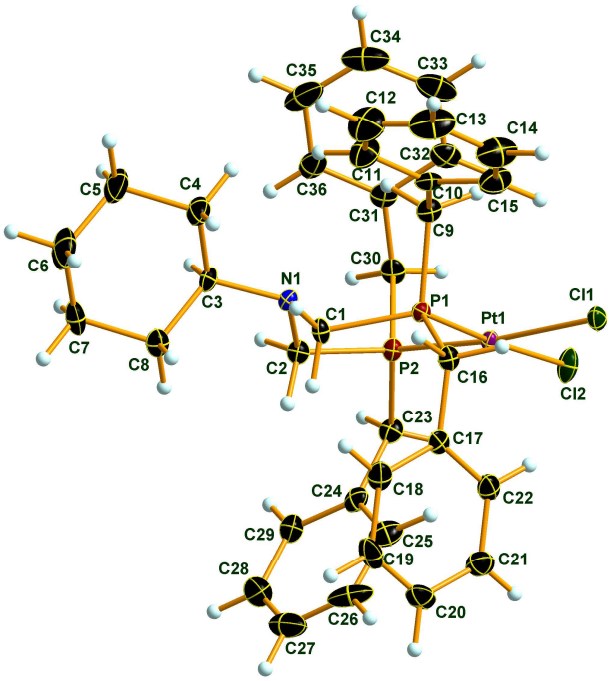


Fig. 3. Atomic displacement plot of *N*,*N*-[bis(dibenzylphosphinomethyl)-cyclohexylamine]-dichloroplatinum(II) (**12c**) with atomic numbering

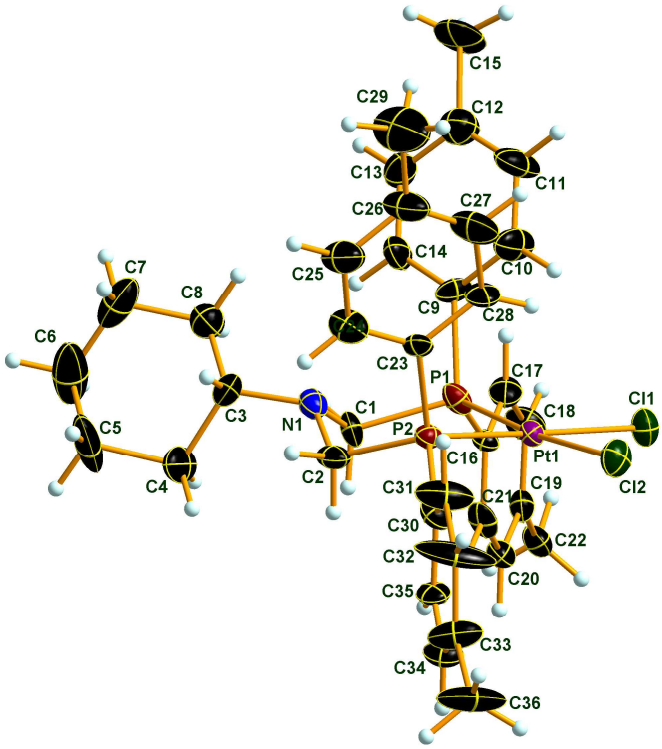


Fig. 4. Atomic displacement plot of *N*,*N*-[bis(ditolylphosphinomethyl)- cyclohexylamine]-dichloroplatinum(II) (**13c**) with atomic numbering

A more detailed analysis of the central ring shape components revealed that the immediate coordination environment of the metal ion is such that the Pt cation is always offset to nearly the same extent from the least-squares (LSQ) plane of its four ligating atoms (*c.f.* Supplementary material, Table S2). It is also visible that the Pt cations are disposed on the opposite side of this plane to the tertiary N atom, except structure **13c**. The N atom in **12b** and in **12c** appears to be almost equally, by 0.36-0.41 Å distant from the LSQ plane of the two Cl and two P atoms, while in **13c**, the N atom is on the same side as the Pt and much less distant. Fig. S1 (Supplementary material) shows the difference between the conformations of these more or less half-chair form heterocyclic rings. As the hetero ring shapes are similar in **12b** and **12c,** only one of them is compared against the heterocyclic ring of **13c**. The side view shows that these heterocyclic rings have visibly different ring shapes.

As is apparent from Fig. S2 (Supplementary material), comparing the least-squares fit of the six atoms of the hetero ring of the theoretical model of **12c** with that of the experimental one, both the central ring and the coordination around Pt, and even the spatial position of the *N*-cyclohexyl substituent agree rather well. Even some benzyl side wings coincide quite close.

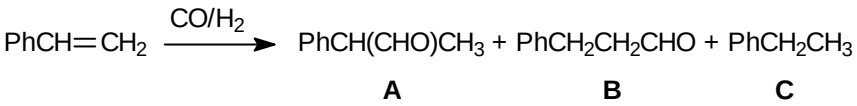
Comparison of the angular values in Table S1 and S3 (Supplementary material) shows that bond angle values agree within the usual significance criteria. This also applies for the torsion angles of **12b** and **12c**, indicating that both rings in both models agree well, and represent closely the flattened half chair-like forms. This is not quite so for **13c**, as the 6-membered heterocycle, in this case, shows significant deviations of the theoretical *vs.* the experimental model. The solid state structures are affected by various effects such as the presence of solvent molecules, the neighbouring host molecules, and the appearance of disordered atomic positions at different *loci* in the studied crystals. The saturated heterocyclic rings may change their shape easily between the chair and half-chair forms, while the pendant aromatic wings are also able to exert a certain extent of motility. It is also obvious that the

appearance of the *n*-butyl group disorder in **12b**, as well as the varying extents of solvent disorders in the crystals of **12c** and also **13c** may bear some relevance to the interplay of the global molecular shapes and their energetics.

A good agreement was observed for the shape of the metalla-heterocycles **12b** and **12c** obtained by theoretical calculations and single crystal X-ray analysis. However, for species **13c,** the conformation obtained by the two methods mentioned were significantly different. This may be the consequence of the different phases of the samples investigated. The data listed in Table S1 (Supplementary material) are related to molecules in the gas phase, while those shown in Table S3 (Supplementary material), came not only simply from solid phase experiments, but even from crystals of associated host and solvent molecules.

*2.6. Hydroformylation of styrene in the presence of the synthesized Pt(II)-complexes (**12b-d, 13b-d**)*

The 'pre-formed' $PtCl_2L_2$-type complexes **12b-d** and **13b-d** containing ligands **10b-d** and **11b-d**, respectively, were tested as catalyst precursors in the hydroformylation of styrene. The catalysts formed *in situ* from **12b-d** or **13b-d** and tin(II)chloride were used at 80 bar [syngas; $p(CO) = p(H_2) = 40$ bar]. In addition to the branched and linear formyl regioisomers (2-arylpropanal (**A**) and 3-arylpropanal (**B**), respectively), ethylbenzene (**C**) as hydrogenation by-product was also formed (Scheme 8). The results are show in Table 3 and Table S4 (Supplementary material).



Scheme 8.

In order to achieve catalytic systems of good performance, tin(II)chloride has to be used in twofold excess. The addition of only one equivalent of tin(II)chloride resulted in a catalyst of negligible activity both at 40 °C and 100 °C reaction temperature. The key lies in *N*-coordination to tin, *i.e.*, the tertiary nitrogen is coordinated to tin(II)chloride, and therefore, no formation of trichlorostannato ligand, resulting in catalytically active Pt(ligand)Cl($SnCl_3$) complex, can be observed in the presence of one equivalent of tin(II)chloride only (Table 3/Entries 3,4; 5,6). The deleterious effect of a tertiary nitrogen, embedded either in the ligand or used as an amine additive in the catalytic system, has been reported [58,59]. The 'second' equivalent of tin(II)chloride is inserted into Pt-Cl bond forming the Pt-$SnCl_3$ moiety which can be considered as a precondition of the catalytic activity. It is worth noting that using a higher Sn to Pt ratio (*e.g.* 5/1), the catalytic activity could not be increased, or in some cases even lower conversions were obtained (Table 3/Entries 6, 7 or 15, 18).

The two types of complexes, *i.e.*, the bis(dibenzylphosphino) derivatives (**12b-d**) with the more basic phosphorus(III) donor atoms and the less basic bis(di(p-tolylphosphino) derivatives (**13b-d**) differ substantially in catalytic activity. The basic bis(trialkylphosphine)-type ligands (**12b**-**12d**) form complexes of lower activity (compare for instance Table 3/Entries 6 and 15, as well as 9 and 20).

The formation of the aldehydes (**A** and **B**) was preferred in all cases. Higher chemoselectivities (up to 88%) were obtained at lower temperature. Typically, chemoselectivities fall in the range of 70-80% at 100 °C. For instance, the use of complex **13c** as a catalyst precursor resulted in 88% and 73-76% chemoselectivities at 40 °C and 100 °C, respectively (Table 3/Entries 14 and 15-17).

The temperature has a pronounced effect also on regioselectivity. The formation of branched aldehyde (**A**) predominated in all cases, however, much higher regioselectivities

towards isomer **A** were obtained at 40 °C (typically about 80%, Table 3/Entries 1, 4, 8, 14) than at 100 °C (typically about 60%, see for instance Table 3/Entries 15–17 or 20, 21).

Table 3

The hydroformylation of styrene in the presence of catalysts formed *in situ* from precursors **12b-d** or **13b-d** and tin(II) chloride.[a]

Entry	Complex	Temp. (°C)	Pt/Sn	R. time (h)	Conv. (%)	R_c [b] (%)	R_{br} [c] (%)
1	**12b**	40	1:2	24	6	73	82
2	**12b**	100	1:2	3	32	72	65
3	**12c**	40	1:1	24	<1	n.d.	n.d.
4	**12c**	40	1:2	24	18	82	76
5	**12c**	100	1:1	3	1	n.d.	n.d.
6	**12c**	100	1:2	3	50	74	61
7	**12c**	100	1:5	3	46	79	62
8	**12d**	40	1:2	24	21	81	79
9	**12d**	100	1:2	3	52	70	65
10	**13b**	40	1:2	24	31	87	75
11	**13b**	100	1:2	3	42	75	64
12	**13b**	100	1:2	6	85	72	63
13	**13b**	100	1:2	8	98	75	63
14	**13c**	40	1:2	24	13	88	78
15	**13c**	100	1:2	3	55	73	62
16	**13c**	100	1:2	6	98	74	63
17	**13c**	100	1:5	3	47	76	65
18	**13d**	40	1:2	24	22	88	76
19	**13d**	40	1:2	72	72	87	76
20	**13d**	100	1:2	2	79	74	61
21	**13d**	100	1:2	3	98	79	56

A: 2-phenylpropanal, **B**: 3-phenylpropanal, **C**: ethylbenzene.

[a] Reaction conditions: Pt/styrene = 1/200, $p(CO) = p(H_2)$ = 40 bar, 1 mmol of styrene, solvent: 5 mL of toluene. (n.d.= not determined)

[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].

In summary, eleven new α-aminophosphine oxides and eight new *N*,*N*-bis(phosphinoylmethyl)amines were synthesized by the Kabachnik-Fields reaction. The latter species were utilized in the preparation of ring platinum complexes after double

deoxygenation. The dependence of the enthalpy gain of the complexation of the bidentate P-ligands on the nature of the *N*-substituents, and the structure of the Pt complexes was calculated using B3LYP/6-31G(d,p) for CHNP and B3LYP/SDD(MWB60) for Pt including effective core potential (ECP). Besides this, the crystal structures of three Pt complexes were solved by X-ray investigation. The complexes were tested as novel catalyst in the hydroformylation of styrene.

Experimental

General (instruments)

The ^{31}P, ^{13}C, ^{1}H NMR spectra were taken in $CDCl_3$ solution 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. Chemical shifts are downfield relative to 85% H_3PO_4 and TMS. The couplings are given in Hz. Mass spectrometric measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode and a Shimadzu LCMS-ITTOF mass spectrometer. The reactions were carried out in a 300 W CEM Discover focused microwave reactor equipped with a pressure controller applying 20–80 W under isothermal conditions.

General procedure for the preparation of dibenzyl- and di(p-tolyl)phosphine oxides

The Grignard reagent formed from 0.97 g (40.0 mmol) of magnesium and 40 mmol of alkyl or aryl halide (benzyl bromide: 4.8 mL, 4-bromotoluene: 6.8 g) in 50 mL of diethyl ether was added dropwise to 1.7 mL (13.0 mmol) of diethyl phosphite in 10 mL of diethyl ether at 0 °C. The resulting mixture was stirred at 25 °C for 1.5 hours. Then, the mixture was hydrolyzed with 10 mL of water and 50 mL of 10% HCl solution, and the aqueous phase was extracted with 2x60 mL of diethyl ether. The combined organic phases were dried (Na_2SO_4). Evaporation of the solvent left a residue that was purified by column chromatography using

silica gel, 1% methanol in dichloromethane as the eluent to give products **1** and **2** as white crystals.

*Dibenzylphosphine oxide (**1**)*

Yield: 84%; white crystals; mp.: 109–110 °C, mp. [45]: 106–107 °C; ^{31}P NMR ($CDCl_3$) δ_P ($CDCl_3$) 36.2, δ_P ($CDCl_3$) [45] 35.5; $[M+H]^+_{found}$ = 231.0937, $C_{14}H_{16}OP$ requires 231.0933.

*Di(p-tolyl)phosphine oxide (**2**)*

Yield: 86%; white crystals; mp.: 98–99 °C, mp. [46]: 95–96 °C; ^{31}P NMR ($CDCl_3$) δ_P ($CDCl_3$) 20.7, δ_P ($CDCl_3$) [46] 21.2; $[M+H]^+_{found}$ = 231.0920, $C_{14}H_{16}OP$ requires 231.0933.

General procedure for the synthesis of (aminomethyl)dibenzyl- or di(p-tolyl)phosphine oxides

A mixture of 0.85 mmol amine (*n*-propylamine: 0.07 mL, *n*-butylamine: 0.08 mL, cyclohexylamine: 0.10 mL, benzylamine: 0.09 mL, 4-methoxybenzylamine: 0.11 mL, aniline: 0.08 mL or 4-methoxyaniline: 0.11 g), 0.026 g (0.85 mmol) of paraformaldehyde, and 0.85 mmol of the secondary phosphine oxide (dibenzylphosphine oxide: 0.20 g or di(*p*-tolyl)phosphine oxide: 0.20 g) and 1.5 mL of acetonitrile was heated at 100 °C in a closed vial in a CEM Discover Microwave reactor equipped with a pressure controller for 1 h. The acetonitrile and the water formed were removed in vacuum. The crude product so obtained was passed through a 1 cm silica gel layer using ethyl acetate. After evaporation of the solvent, the products (**3a-g**, **4b-d** and **4f**) were obtained as crystals. The following products were thus prepared:

*(Propylaminomethyl)dibenzylphosphine oxide (**3a**)*

Yield: 96% (0.25 g) of compound **3a** as white crystals. Mp: 80-82 °C; ^{31}P NMR ($CDCl_3$) δ 44.0; ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 22.9 (CH_3CH_2), 34.3 (d, $^1J_{CP}$ = 60.0, P(O)CH_2), 45.2 (d, $^1J_{CP}$ = 79.2, NHCH_2P), 53.7 (d, $^3J_{CP}$ = 14.4, $CH_3CH_2CH_2$NH), 126.9 (d, J_{CP} = 2.8, C_4), 128.8 (d, J_{CP} = 2.4, C_3), 129.7 (d, $^3J_{CP}$ = 5.1, C_2), 131.9 (d, $^2J_{CP}$ = 7.0, C_1); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J_{HH} = 7.4, 3H, CH_3), 1.41–1.50 (m, 2H, CH_3CH_2), 1.65 (s, 1H, NH), 2.54 (t, J_{HH} = 7.1, 2H, $CH_3CH_2CH_2$NH), 2.73 (d, $^1J_{PH}$ = 7.8, 2H, NHCH_2P), 3.10–3.25 (m, 4H, P(O)CH_2), 7.23–7.35 (m, 10H, ArH); $[M+H]^+_{found}$ = 302.1676, $C_{18}H_{25}$NOP requires 302.1668.

*(Butylaminomethyl)dibenzylphosphine oxide (**3b**)*

Yield: 97% (0.26 g) of compound **3b** as slightly yellow crystals. Mp: 75–76 °C; ^{31}P NMR ($CDCl_3$) δ 44.6; ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 20.0 (CH_3CH_2), 31.6 ($CH_3CH_2CH_2$), 34.1 (d, $^1J_{CP}$ = 60.0, P(O)CH_2), 45.0 (d, $^1J_{CP}$ = 79.1, NHCH_2P), 51.3 (d, $^3J_{CP}$ = 14.3, $CH_3(CH_2)_2CH_2$NH), 126.7 (d, J_{CP} = 2.8, C_4), 128.5 (d, J_{CP} = 2.4, C_3), 129.5 (d, $^3J_{CP}$ = 5.1, C_2), 131.7 (d, $^2J_{CP}$ = 7.1, C_1); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J_{HH} = 7.2, 3H, CH_3), 1.25–1.48 (m, 4H, $CH_3CH_2CH_2$), 1.47 (s, 1H, NH), 2.56 (t, J_{HH} = 6.6, 2H, $CH_3(CH_2)_2CH_2$NH), 2.74 (d, $^1J_{PH}$ = 7.7, 2H, NHCH_2P), 3.07–3.28 (m, 4H, P(O)CH_2), 7.23–7.36 (m, 10H, ArH); $[M+H]^+_{found}$ = 316.1832, $C_{19}H_{27}$NOP requires 316.1825.

*(Cyclohexylaminomethyl)dibenzylphosphine oxide (**3c**)*

Yield: 95% (0.28 g) of compound **3c** as white crystals. Mp: 125–126 °C; ^{31}P NMR ($CDCl_3$) δ 44.4; ^{13}C NMR ($CDCl_3$) δ 24.8 (C_3), 26.0 (C_4), 33.2 (C_2), 34.3 (d, $^1J_{CP}$ = 60.1, P(O)CH_2), 42.5 (d, $^1J_{CP}$ = 79.5, NHCH_2P), 58.5 (d, $^3J_{CP}$ = 13.7, C_1), 126.9 (d, J_{CP} = 2.9, $C_{4'}$), 128.8 (d, J_{CP} = 2.4, $C_{3'}$), 129.7 (d, $^3J_{CP}$ = 5.1, $C_{2'}$), 132.0 (d, $^2J_{CP}$ = 7.0, $C_{1'}$); ^{1}H NMR ($CDCl_3$) δ 0.95–1.10 (m, 2H, $C_2H_{ax.}$), 1.11–1.29 (m, 3H, $C_4H_{ax.}$,$C_3H_{ax.}$), 1.53–1.63 (m, 2H, $C_2H_{eq.}$),

1.64–1.75 (m, 3H, $C_4H_{eq.}$, $C_3H_{eq.}$), 1.81 (s, 1H, NH), 2.22–2.34 (m, 1H, C_1H), 2.75 (d, $^1J_{HP}$ = 8.3, 2H, NHC*H*$_2$P), 3.17 (pt, $^1J_{HP}$ =14.8, 4H, P(O)CH_2), 7.22–7.36 (m, 10H, ArH); $[M+H]^+_{found}$ = 342.1989, $C_{21}H_{29}NOP$ requires 342.1981.

*(Benzylaminomethyl)dibenzylphosphine oxide (**3d**)*

Yield: 98% (0.29 g) of compound **3d** as white crystals. Mp: 119–121 °C; ^{31}P NMR ($CDCl_3$) δ 43.8; ^{13}C NMR ($CDCl_3$) δ 34.3 (d, $^1J_{CP}$ = 60.2, P(O)CH_2), 44.4 (d, $^1J_{CP}$ = 78.9, NHCH_2P), 55.5 (d, $^3J_{CP}$ = 15.2, CH_2NH), 126.9 (d, J_{CP} = 2.8, $C_{4'}$), 127.3 (C_4), 128.4 (d, J_{CP} = 2.5, $C_{3'}$), 128.79 (C_3)*, 128.82 (C_2)*, 129.7 (d, $^3J_{CP}$ = 5.1, $C_{2'}$), 131.8 (d, $^2J_{CP}$ = 7.1, $C_{1'}$), 139.2 (C_1), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 1H, NH), 2.74 (d, $^1J_{HP}$ =7.8, 2H, NHC*H*$_2$P), 3.15 (pt, $^1J_{HP}$ =14.7, 4H, P(O)CH_2), 3.75 (s, 2H, C*H*$_2$NH), 7.19–7.32 (m, 15H, ArH); $[M+H]^+_{found}$ = 350.1677, $C_{22}H_{25}NOP$ requires 350.1668.

*(4-Methoxybenzylaminomethyl)dibenzylphosphine oxide (**3e**)*

Yield: 95% (0.31 g) of compound **3e** as white crystals. Mp: 103–105; ^{31}P NMR ($CDCl_3$) δ 43.9; ^{13}C NMR ($CDCl_3$) δ 34.3 (d, $^1J_{CP}$ = 60.2, P(O)CH_2), 44.2 (d, $^1J_{CP}$ = 79.1, NHCH_2P), 54.9 (d, $^3J_{CP}$ = 15.4, CH_2NH), 55.3 (OCH_3), 113.8 (C_2), 126.9 (d, J_{CP} = 2.8, $C_{4'}$), 128.8 (d, J_{CP} = 2.3, $C_{3'}$), 129.6 (d, $^3J_{CP}$ = 4.6, $C_{2'}$), 129.7 (C_3), 131.3 (C_1), 131.8 (d, $^2J_{CP}$ = 7.0, $C_{1'}$), 158.9 (C_4); ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 1H, NH), 2.72 (d, $^1J_{HP}$ = 7.8, 2H, NHC*H*$_2$P), 3.14 (pt, $^1J_{HP}$ = 14.4, 4H, P(O)CH_2), 3.69 (s, 2H, C*H*$_2$NH), 3.81 (s, 3H, OCH_3), 6.86 (d, J_{HH} =8.4, 2H, C_3H), 7.17–7.32 (m, 12H, ArH); $[M+H]^+_{found}$ = 380,1782, $C_{23}H_{27}NO_2P$ requires 380,1774.

*(Phenylaminomethyl)dibenzylphosphine oxide (**3f**)*

Yield: 94% (0.27 g) of compound **3f** as white crystals. Mp: 159–161 °C; Mp[30]: 158-159; ^{31}P NMR ($CDCl_3$) δ 42.9; ^{13}C NMR ($CDCl_3$) δ 34.7 (d, $^1J_{CP}$ = 60.4, P(O)CH_2), 39.9 (d,

$^{1}J_{CP}$ = 75.1, $NHCH_2P$), 113.5 (C_2), 118.8 (C_4), 127.2 (d, J_{CP} = 2.9, $C_{4'}$), 129.0 (d, J_{CP} = 2.4, $C_{3'}$), 129.3 (C_3), 129.7 (d, $^{3}J_{CP}$ = 5.2, $C_{2'}$), 131.3 (d, $^{2}J_{CP}$ = 7.1, $C_{1'}$), 147.6 (d, $^{3}J_{CP}$ = 10.6, C_1); ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 1H, NH), 3.33–3.14 (m, 6H, CH_2), 6.57 (d, J_{HH} = 7.8, 2H, C_2H), 6.78 (t, J_{HH} = 7.0, 1H, C_4H), 7.18 (t, J_{HH} = 8.0, 2H, C_3H), 7.23–7.38 (m, 10H, ArH); $[M+H]^{+}_{found}$ = 336.1516, $C_{21}H_{23}NOP$ requires 336.1512.

*(4-Methoxyanilinomethyl)dibenzylphosphine oxide (**3g**)*

Yield: 95% (0.29 g) of compound **3g** as slightly yellow crystals. Mp: 141–143 °C; ^{31}P NMR ($CDCl_3$) δ 43.0; ^{13}C NMR ($CDCl_3$) δ 34.6 (d, $^{1}J_{CP}$ = 60.4, $P(O)CH_2$), 40.9 (d, $^{1}J_{CP}$ = 75.7, $NHCH_2P$), 55.7 (OCH_3), 114.8 (C_2)*, 114.9 (C_3)*, 127.2 (d, J_{CP} = 2.9, $C_{4'}$), 129.0 (d, J_{CP} = 2.4, $C_{3'}$), 129.7 (d, $^{3}J_{CP}$ = 5.2, $C_{2'}$), 131.4 (d, $^{2}J_{CP}$ =7.1, $C_{1'}$), 141.7 (d, $^{3}J_{CP}$ = 11.4, C_1), 153.0 (C_4), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 1H, NH), 3.13–3.33 (m, 6H, CH_2), 3.75 (s, 3H, OCH_3), 6.54 (d, 2H, J_{HH} = 8.7, C_2H)*, 6.78 (d, 2H, J_{HH} = 8.8, C_3H)*, 7.22–7.38 (m, 10H, ArH), *may be reversed; $[M+H]^{+}_{found}$ = 366,1615, $C_{22}H_{25}NO_2P$ requires 366,1617.

*(Butylaminomethyl)di(p-tolyl)phosphine oxide (**4b**)*

Yield: 96% (0.26g) of compound **4b** as slightly yellow oil. ^{31}P NMR ($CDCl_3$) δ 29.7; δ[32] (C_6D_6) 42.0; ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3CH_2), 20.2 (CH_3CH_2), 21.5 (C_4CH_3) 31.7 ($CH_3CH_2CH_2$), 49.5 (d, $^{1}J_{CP}$ = 80.5, $P(O)CH_2$), 51.4 (d, $^{3}J_{CP}$ = 13.4, $CH_3(CH_2)_2CH_2NH$), 128.9 (d, $^{1}J_{CP}$ = 99.9, C_1), 129.3 (d, $^{2}J_{CP}$ = 12.0, C_2), 131.1 (d, $^{3}J_{CP}$ = 9.5, C_3), 142.2 (d, J_{CP} = 2.7, C_4); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J_{HH} = 7.2, 3H, CH_3CH_2), 1.22–1.35 (m, 2H, $CH_3CH_2CH_2$), 1.37–1.49 (m, 2H, $CH_3CH_2CH_2$), 1.45 (s, 1H, NH), 2.40 (s, 6H, C_4CH_3), 2.67 (t, J_{HH} = 7.0, 2H, $CH_3(CH_2)_2CH_2NH$), 3.43 (d, $^{1}J_{HP}$ = 8.0, 2H, $NHCH_2P$), 7.27 (d, $^{3}J_{HP}$ = 5.6, 4H, C_3H), 7.68 (dd, $^{2}J_{HP}$ = 11.1, J_{HP} = 8.1, 4H, C_2H); $[M+H]^{+}_{found}$ = 316.1828, $C_{19}H_{27}NOP$ requires 316.1825.

*(Cyclohexylaminomethyl)di(p-tolyl)phosphine oxide (**4c**)*

Yield: 98% (0.28 g) of compound **4c** as slightly yellow oil. ^{31}P NMR ($CDCl_3$) δ 29.6; ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 22.5 (C_3), 26.7 (C_4), 31.6 (C_2), 49.5 (d, $^1J_{CP}$ = 80.5, P(O)CH_2), 51.7 (d, $^3J_{CP}$ = 13.3, C_1), 128.9 (d, $^1J_{CP}$ = 99.9, $C_{1'}$), 129.2 (d, $^2J_{CP}$ = 12.0, $C_{2'}$), 131.1 (d, $^3J_{CP}$ = 9.6, $C_{3'}$), 142.2 (d, J_{CP} = 2.7, $C_{4'}$); ^{1}H NMR ($CDCl_3$) δ 0.83–0.89 (m, 3H, $C_4H_{ax.}$,$C_3H_{ax.}$), 1.19–1.30 (m, 5H, $C_2H_{ax.}$, $C_4H_{eq.}$, C_3H_{eq}), 1.37–1.49 (m, 2H, $C_2H_{eq.}$), 1.75 (s, 1H, NH), 2.39 (s, 6H, CH_3), 2.66 (t, $^3J_{HP}$ = 7.1, 1H, C_1H), 3.43 (d, $^1J_{HP}$ = 7.8, 2H, NHCH_2P), 7.22–7.31 (m, 14H, $C_{3'}$), 7.67 (d, $^2J_{HP}$ = 11.1, J_{HP} = 8.1, 4H, C_2H); $[M+H]^+_{found}$ = 342.1987, $C_{21}H_{29}$NOP requires 342.1981.

*(Benzylaminomethyl)di(p-tolyl)phosphine oxide (**4d**)*

Yield: 95% (0.28 g) of compound **4d** as slightly yellow crystals. Mp: 115–117 °C; ^{31}P NMR ($CDCl_3$) δ 29.9; ^{13}C NMR ($CDCl_3$) δ 21.5 (C_4CH_3), 48.3 (d, $^1J_{CP}$ = 81.2, P(O)CH_2), 55.1 (d, $^1J_{CP}$ = 14.3, CH_2NHCH_2P), 127.1 (C_4), 128.2 (C_2), 128.3 (C_3), 128.8 (d, $^1J_{CP}$ = 100.4, $C_{1'}$), 129.3 (d, $^2J_{CP}$ = 12.0, $C_{2'}$), 131.1 (d, $^3J_{CP}$ = 9.6, $C_{3'}$), 139.2 (C_1), 142.3 (d, J_{CP} = 2.8, $C_{4'}$); ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 1H, NH), 2.40 (s, 6H, CH_3), 3.39 (d, $^1J_{HP}$ =8.0, 2H, NHCH_2P), 3.87 (s, 2H, CH_2NH), 7.22–7.34 (m, 9H, ArH, C_3H), 7.65 (dd, $^2J_{HP}$ = 11.1, J_{HP} = 8.1, 4H, C_2H); $[M+H]^+_{found}$ = 350.1669, $C_{22}H_{25}$NOP requires 350.1668.

*(Phenylaminomethyl)di(p-tolyl)phosphine oxide (**4f**)*

Yield: 94% (0.27 g) of compound **3f** as yellow crystals. Mp: 139–141 °C; ^{31}P NMR ($CDCl_3$) δ 30.1; ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 43.9 (d, $^1J_{CP}$ = 78.8, P(O)CH_2), 113.4 (C_2), 118.5 (C_4), 127.9 (d, $^1J_{CP}$ = 102.8, $C_{1'}$), 129.2 (C_3) 129.5 (d, $^2J_{CP}$ = 12.3, $C_{2'}$), 131.1 (d, $^3J_{CP}$ = 9.9, $C_{3'}$), 142.9 (d, J_{CP} = 2.8, $C_{4'}$), 147.7 (d, $^3J_{CP}$ = 11.2, C_1); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 6H,

CH_3), 3.88 (d, J_{PH} = 9.0, 2H, P(O)CH_2), 3.99 (s, 1H, NH), 6.65 (d, J_{HH} = 8.3, 2H, C_2H), 6.74 (t, J_{HH} = 7.1, 1H, C_4H), 7.16 (t, J_{HH} = 7.7, 2H, C_3H), 7.24–7.31 (m, 4H, $C_{3'}$H), 7.66 (dd, $^2J_{HP}$ = 11.4, J_{HP} = 8.0, 4H, $C_{2'}$H); $[M+H]^+_{found}$ = 336.1507, $C_{21}H_{23}NOP$ requires 336.1512.

General procedure for the synthesis of N,N-bis(dibenzyl- or di-p-tolylphosphinoylmethyl)amines

A mixture of 0.85 mmol amine (*n*-propylamine: 0.07 mL, *n*-butylamine: 0.08 mL, cyclohexylamine: 0.10 mL, benzylamine: 0.09 mL, 4-methoxybenzylamine: 0.11 mL, aniline: 0.08 mL or 4-methoxyaniline: 0.11 g), 0.05 g (1.7 mmol) of paraformaldehyde, and 1.7 mmol of the secondary phosphine oxide (dibenzylphosphine oxide: 0.40 g or di(*p*-tolyl)phosphine oxide: 0.40 g) and 2.5 mL of acetonitrile was heated at 100 °C in a closed vial in a CEM Discover Microwave reactor equipped with a pressure controller for 1 h. The acetonitrile and the water formed were removed in vacuum. The crude products were passed through a 1 cm silica gel layer using ethyl acetate. After evaporation of the solvent, the products (**5a-e** and **6b-d**) were obtained as crystals. The following products were thus prepared:

*N,N-Bis(dibenzylphosphinoylmethyl)propylamine (**5a**)*

Yield: 95% (0.44 g) of compound **5a** as white crystals. Mp: 183–185 °C; ^{31}P NMR ($CDCl_3$) δ 40.4; ^{13}C NMR ($CDCl_3$) δ 11.6 (CH_3), 19.8 (CH_3CH_2), 35.5 (d, $^1J_{CP}$ = 60.0, P(O)CH_2), 53.5 (dd, $^1J_{CP}$ = 87.9, $^3J_{CP}$ = 7.9, NCH_2P), 60.6 (d, $^3J_{CP}$ = 6.1, $CH_3CH_2CH_2N$), 126.8 (d, J_{CP} = 2.6, C_4), 128.7 (d, J_{CP} = 2.0, C_3), 129.8 (d, $^3J_{CP}$ = 5.3, C_2), 131.8 (d, $^2J_{CP}$ = 7.3, C_1); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J_{HH} = 7.2, 3H, CH_3), 1.28–1.44 (m, 2H, CH_3CH_2), 2.73 (t, J_{HH} =7.2, 2H, $CH_3CH_2CH_2$), 2.94 (d, $^1J_{HP}$ = 7.4, 4H, NCH_2P), 3.02–3.30 (m, 8H, P(O)CH_2), 7.18–7.39 (m, 20H, ArH); $[M+H]^+_{found}$ = 544.2523, $C_{33}H_{40}NO_2P_2$ requires 544.2529.

*N,N-Bis(dibenzylphosphinoylmethyl)butylamine (**5b**)*

Yield: 96% (0.45 g) of compound **5b** as white crystals. Mp: 174–176 °C; ^{31}P NMR ($CDCl_3$) δ 40.5; ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3CH_2), 20.2 (CH_3CH_2), 28.9 ($CH_3CH_2CH_2$), 35.5 (d, $^1J_{CP}$ = 60.1, $P(O)CH_2$), 53.4 (dd, $^1J_{CP}$ = 87.9, $^3J_{CP}$ = 7.1, NCH_2P), 58.5 (d, $^3J_{CP}$ = 6.1, $CH_3(CH_2)_2CH_2N$), 126.8 (d, J_{CP} = 2.5, C_4), 128.7 (d, J_{CP} = 1.8, C_3), 129.8 (d, $^3J_{CP}$ = 5.2, C_2), 131.8 (d, $^2J_{CP}$ = 7.3, C_1); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J_{HH} = 6.0, 3H, CH_3), 1.21–1.32 (m, 4H, CH_3CH_2), 2.73 (t, J_{HH} =7.1, 2H, $CH_3CH_2CH_2N$), 2.91 (d, $^1J_{HP}$ = 4.4, 4H, NCH_2P), 3.02–3.27 (m, 8H, $P(O)CH_2$), 7.19–7.33 (m, 20H, ArH); $[M+H]^+_{found}$ = 558.2701, $C_{37}H_{39}NO_2P_2$ requires 558.2691.

*N,N-Bis(dibenzylphosphinoylmethyl)cyclohexylamine (**5c**)*

Yield: 95% (0.47 g) of compound **5c** as white crystals. Mp: 205–207 °C; ^{31}P NMR ($CDCl_3$) δ 40.3; ^{13}C NMR ($CDCl_3$) δ 25.6 (C_3), 26.1 (C_4), 28.2 (C_2), 35.4 (d, $^1J_{CP}$ = 60.3, $P(O)CH_2$), 50.1 (dd, $^1J_{CP}$ = 91.0, $^3J_{CP}$ = 7.6, NCH_2P), 61.9 (t, $^3J_{CP}$ = 10.7, C_1), 126.7 (d, J_{CP} = 2.5, $C_{4'}$), 128.6 (d, J_{CP} = 2.1, $C_{3'}$), 129.8 (d, $^3J_{CP}$ = 5.2, $C_{2'}$), 132.0 (d, $^2J_{CP}$ = 7.3, $C_{1'}$); ^{1}H NMR ($CDCl_3$) δ 0.84–1.33 (m, 5H, $C_2H_{ax.}$, $C_4H_{ax.}$,$C_3H_{ax.}$), 1.55–1.77 (m, 5H, $C_2H_{eq.}$, $C_4H_{eq.}$, $C_3H_{eq.}$), 2.92 (d, $^1J_{HP}$ = 4.7, 4H, NCH_2P), 2.99–3.32 (m, 9H, C_1H, $P(O)CH_2$), 7.19–7.33 (m, 20H, ArH); $[M+H]^+_{found}$ = 584.2835, $C_{36}H_{44}NO_2P_2$ requires 584.2842.

*N,N-Bis(dibenzylphosphinoylmethyl)benzylamine (**5d**)*

Yield: 97% (0.49 g) of compound **5d** as slightly yellow crystals. Mp: 175–177 °C; ^{31}P NMR ($CDCl_3$) δ 40.4; ^{13}C NMR ($CDCl_3$) δ 35.3 (d, $^1J_{CP}$ = 60.4, $P(O)CH_2$), 52.5 (dd, $^1J_{CP}$ = 87.5, $^3J_{CP}$ = 6.9, NCH_2P), 63.6 (t, $^3J_{CP}$ = 6.3, CH_2N), 126.7 (d, J_{CP} = 2.6, $C_{4'}$), 127.6 (C_4), 128.4 (C_3), 128.6 (d, J_{CP} = 2.1, $C_{3'}$), 129.7 (d, $^3J_{CP}$ = 5.1, $C_{2'}$), 130.1 (C_2), 131.7 (d, $^2J_{CP}$ = 7.3, $C_{1'}$), 137.5 (C_1); ^{1}H NMR ($CDCl_3$) δ 2.92 (d, 4H, $^1J_{HP}$ = 4.5, NCH_2P), 3.05 (pt, 8H, $^1J_{HP}$ =

14,8, P(O)CH_2), 3.88 (s, 2H, CH_2N), 7.08–7.15 (m, 5H, ArH), 7.18–7.34 (m, 20H, Ar'H); $[M+H]^+_{found}$ = 592.2535, $C_{37}H_{40}NO_2P_2$ requires 592.2529.

*N,N-Bis(dibenzylphosphinoylmethyl)-4-methoxybenzylamine (**5e**)*

Yield: 94% (0.50 g) of compound **5e** as white crystals. Mp: 128–130 °C; ^{31}P NMR ($CDCl_3$) δ 40.5; ^{13}C NMR ($CDCl_3$) δ 35.4 (d, $^1J_{CP}$ = 60.3, P(O)CH_2), 52.3 (dd, $^1J_{CP}$ = 88.0, $^3J_{CP}$ = 7.5, NCH_2P), 55.2 (OCH_3), 62.3 (t, $^3J_{CP}$ = 6.7, CH_2N), 113.8 (C_3), 126.7 (d, J_{CP} = 2.4, $C_{4'}$), 128.6 (d, J_{CP} = 1.9, $C_{3'}$), 129.6 (C_1), 129.8 (d, $^3J_{CP}$ = 5.2, $C_{2'}$), 131.3 (C_2), 131.8 (d, $^3J_{CP}$ = 7.3, $C_{1'}$), 159.1 (C_4); ^{1}H NMR ($CDCl_3$) δ 2.91 (d, 4H, $^1J_{HP}$ =3.8, NCH_2P), 3.06 (pt, 8H, $^1J_{HP}$ =14.0, P(O)CH_2), 3.80 (s, 2H, CH_2N), 3.81 (s, 3H, OCH_3), 6.82 (d, J_{HH} =8.1, 2H, C_3H), 7.09–7.29 (m, 22H, ArH); $[M+H]^+_{found}$ = 622.2648, $C_{38}H_{42}NO_3P_2$ requires 622.2640.

*N,N-Bis(di-p-tolylphosphinoylmethyl)butylamine (**6b**)*

Yield: 98% (0.46 g) of compound **6b** as slightly yellow oil. ^{31}P NMR ($CDCl_3$) δ 29.5; ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3CH_2), 19.9 (CH_3CH_2), 21.4 (C_4CH_3), 28.5 ($CH_3CH_2CH_2$), 55.9 (dd, $^1J_{CP}$ = 85.1, $^3J_{CP}$ = 7.7, NCH_2P), 58.3 (t, $^3J_{CP}$ = 6.9, $CH_3(CH_2)_2CH_2N$), 128.9 (d, $^2J_{CP}$ = 11.8, C_2), 129.2 (d, $^1J_{CP}$ = 99.9, C_1), 131.1 (d, $^3J_{CP}$ = 9.5, C_3), 141.7 (d, J_{CP} = 2.8, C_4); ^{1}H NMR ($CDCl_3$) δ 0.73 (t, J_{HH} = 7.2, 3H, CH_3CH_2), 0.95–1.09 (m, 2H, CH_3CH_2), 1.16–1.29 (m, 2H, $CH_3CH_2CH_2$), 2.32 (s, 12H, C_4CH_3), 2.93 (t, $^3J_{HH}$ =7.1, 2H, $CH_3CH_2CH_2CH_2N$), 3.62 (d, $^1J_{HP}$ = 5.5, 4H, NCH_2P), 7.12 (d, $^3J_{HP}$ = 7.8, 8H, C_3H), 7.59 (dd, $^2J_{HP}$ = 11.0, J_{HP} = 8.1, 8H, C_2H); $[M+H]^+_{found}$ = 558.2680, $C_{34}H_{42}NO_2P_2$ requires 558.2685.

*N,N-Bis(di-p-tolylphosphinoylmethyl)cyclohexylamine (**6c**)*

Yield: 95% (0.47 g) of compound **6c** as slightly yellow oil. ^{31}P NMR ($CDCl_3$) δ 30.2; ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 24.6 (C_3), 25.6 (C_4), 27.7 (C_2), 51.8 (dd, $^1J_{CP}$ = 87.2, $^3J_{CP}$ = 8.0,

NCH_2P), 61.7 (t, $^3J_{CP}$ = 5.9, C_1), 128.9 (d, J_{CP} = 12.0, $C_{2'}$), 129.1 (d, $^2J_{CP}$ = 99.9, $C_{1'}$), 131.2 (d, $^3J_{CP}$ = 9.4, $C_{2'}$), 141.6 (d, J_{CP} = 2.8, $C_{4'}$); ^{1}H NMR ($CDCl_3$) δ 0.88–1.07 (m, 3H, $C_4H_{ax.}$,$C_3H_{ax.}$), 1.20–1.35 (m, 3H, $C_2H_{ax.}$), 1.58–1.77 (m, 5H, $C_2H_{eq.}$, $C_4H_{eq.}$, $C_3H_{eq.}$), 2.34 (s, 12H CH_3), 3.42 (t, $^3J_{HP}$ = 11.5, 1H, C_1H), 3.69 (d, $^1J_{HP}$ = 6.5, 4H, NCH_2P), 7.14 (d, $^3J_{HP}$ = 6.2, 8H, $C_{3'}H$), 7.62 (dd, $^2J_{HP}$ = 10.8, J_{HP} = 8.1, 8H, $C_{2'}H$); $[M+H]^+_{found}$ = 584.2836, $C_{36}H_{44}NO_2P_2$ requires 584.2842.

*N,N-Bis(di-p-tolylphosphinoylmethyl)benzylamine (**6d**)*

Yield: 94% (0.47 g) of compound **6d** as slightly yellow oil. ^{31}P NMR ($CDCl_3$) δ 30.2; ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 55.1 (dd, $^1J_{CP}$ = 85.0, $^3J_{CP}$ = 7.7, NCH_2P), 63.1 (t, $^3J_{CP}$ = 7.5, CH_2N), 127.1 (C_4), 127.9 (C_2), 128.9 (d, $^1J_{CP}$ = 100.7, $C_{1'}$), 129.0 (d, $^2J_{CP}$ = 12.1, $C_{2'}$), 129.8 (C_3), 131.1 (d, $^3J_{CP}$ = 9.5, $C_{3'}$), 137.7 (C_1), 141.7 (d, J_{CP} = 2.8, $C_{4'}$); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 12H, CH_3), 3.67 (d, 4H, $^1J_{HP}$ = 6.2, NCH_2P), 4.08 (s, 2H, CH_2N), 6.88 (d, 2H, J_{HH} = 7.0, C_2H), 7.07–7.28 (m, 11H, $C_{3'}H$, C_3H, C_4H), 7.50 (dd, $^2J_{HP}$ = 11.0, J_{HP} = 8.1, 8H, $C_{2'}H$); $[M+H]^+_{found}$ = 592.2522, $C_{37}H_{40}NO_2P_2$ requires 592.2529.

General procedure for the synthesis of ring platinum complexes

To 0.20 mmol of the bis(>P(O)CH_2)amine **5** or **6** (**5b** or **6b**: 0.11 g, **5c** or **6c**: 0.11 g or **5d** or **6d**: 0.12 g) was added 0.15 mL (1.20 mmol) of phenylsilane under nitrogen. The mixture was stirred at 120 °C in a vial in a CEM Discover Microwave reactor equipped with a pressure controller for 2.5 h. Then the mixture was diluted by the addition of 1 mL of degassed benzene. To the solution of phosphine **10b-d** or **11b-d** so obtained was added 0.10 g (0.21 mmol) of dichlorodibenzonitrile platinum and the mixture stirred at 25 °C for overnight. The solid crystallized from the mixture was separated by filtration to afford complex **12b-d** or **13b-d** after washing with pentane–acetone (8:2) and drying.

*[Bis(dibenzylphosphinomethyl)butylamine-dichloroplatinum(II) (**12b**)*

Yield: 75% (0.12 g) of compound **12b** as white powder. ^{31}P NMR (d-DMSO) δ –4.6 ($^{1}J_{P\text{-}Pt}$ = 3400); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3CH_2), 20.3 (CH_3CH_2), 30.0 (d, $^{1}J_{CP}$ = 37.3, PCH_2), 30.5 ($CH_3CH_2CH_2$), 52.0 (dd, $^{1}J_{CP}$ = 68.8, $^{3}J_{CP}$ = 5.6, NCH_2P), 61.6 ($CH_3(CH_2)_2CH_2N$), 126.5 (C_4), 128.2 (C_3), 129.9 (C_2), 132.9 (d, $^{2}J_{CP}$ = 7.3, C_1); ^{1}H NMR ($CDCl_3$) δ 0.82-0.92 (m, 3H, CH_3), 1.11–1.26 (m, 4H, CH_3CH_2, $CH_3CH_2CH_2$), 2.16 (s, 2H, $CH_3CH_2CH_2CH_2N$), 2.44 (s, 4H, NCH_2P), 3.01–3.14 and 3.51–3.64 (m, 8H, PCH_2), 7.15–7.35 (m, 20H, ArH); $[M–Cl]^{+}_{found}$ = 754.2061, $C_{34}H_{41}NP_2ClPt$ requires 754.2051.

*[Bis(dibenzylphosphinomethyl)cyclohexylamine]dichloroplatinum(II) (**12c**)*

Yield: 58% (0.09 g) of compound **12c** as white powder. ^{31}P NMR ($CDCl_3$) δ –6.1 ($^{1}J_{P\text{-}Pt}$ = 3404); ^{13}C NMR ($CDCl_3$) δ 25.2 (C_3), 25.3 (C_4), 26.9 (C_2), 31.0 (d, $^{1}J_{CP}$ = 35.7, PCH_2), 56.2 (dd, $^{1}J_{CP}$ = 73.8, $^{3}J_{CP}$ = 4.9, NCH_2P), 67.2 (bs, C_1), 126.5 ($C_{4'}$), 128.2 ($C_{3'}$), 129.9 ($C_{2'}$), 133.1 ($C_{1'}$); ^{1}H NMR ($CDCl_3$) δ 0.90–1.13 (m, 5H, $C_2H_{ax.}$, $C_4H_{ax.}$,$C_3H_{ax.}$), 1.23–1.32 (m, 2H, $C_2H_{eq.}$), 1.49–1.56 and 1.65–1.73 (m, 3H $C_4H_{eq.}$, $C_3H_{eq.}$), 1.71 (s, 1H, C_1H), 2.58 (s, 4H, NCH_2P), 3.03–3.14 and 3.53–3.64 (m, 8H, PCH_2), 7.15–7.38 (m, 20H, ArH); $[M–Cl]^{+}_{found}$ = 780.2217, $C_{36}H_{43}NP_2ClPt$ requires 780.2207.

*[Bis(dibenzylphosphinomethyl)benzylamine]dichloroplatinum(II) (**12d**)*

Yield: 69% (0.11 g) of compound **12d** as white powder. ^{31}P NMR (d-DMSO) δ –5.2 ($^{1}J_{P\text{-}Pt}$ = 3404); ^{13}C NMR ($CDCl_3$) δ 30.7 (d, $^{1}J_{CP}$ = 35.9, PCH_2), 46.8 (dd, $^{1}J_{CP}$ = 55.2, $^{3}J_{CP}$ = 3.2, NCH_2P), 65.4 (t, $^{3}J_{CP}$ = 10.9, CH_2N), 126.6 ($C_{4'}$), 127.9 (C_4), 128.4 ($C_{3'}$), 129.4 (C_3), 129.7 ($C_{2'}$), 130.3 (C_2), 133.3 ($C_{1'}$), 135.5 (C_1); ^{1}H NMR ($CDCl_3$) δ 2.96–3.06 (m, 2H, CH_2N),

3.29–3.51 (m, 12H, NCH_2P, PCH_2), 7.05–7.24 (m, 16H) and 7.33–7.48 (m, 9H) (ArH, Ar'H); $[M–Cl]^+_{found}$ = 788.1910, $C_{37}H_{39}NP_2ClPt$ requires 788.1894.

*[Bis(di-p-tolylphosphinomethyl)butylamine]dichloroplatinum(II) (**13b**)*

Yield: 74% (0.12 g) of compound **13b** as slightly yellow powder. ^{31}P NMR ($CDCl_3$) δ –9.6 ($^1J_{P\text{-}Pt}$ = 3408); ^{13}C NMR ($CDCl_3$) δ 13.8 (CH_3CH_2), 20.1 (CH_3CH_2), 21.4 (C_4CH_3), 29.2 ($CH_3CH_2CH_2$), 56.6 (dd, $^1J_{CP}$ = 61.6, $^3J_{CP}$ = 5.0, NCH_2P), 62.8 (t, $^3J_{CP}$ = 11.4, $CH_3(CH_2)_2CH_2N$), 125.1 (dd, $^1J_{CP}$ = 72.6, $^3J_{CP}$ = 5.3, C_1), 129.05 (d, $^2J_{CP}$ = 5.8), 129.10 (d, $^2J_{CP}$ = 5.7) (C_2), 133.68 (d, $^3J_{CP}$ = 4.9), 133.72 (d, $^3J_{CP}$ = 4.9 (C_3), 141.6 (C_4); ^1H NMR ($CDCl_3$) δ 0.78 (t, J_{HH} = 7.3, 3H, CH_3CH_2), 1.01–1.10 (m, 2H, CH_3CH_2), 1.25–1.32 (m, 2H, $CH_3CH_2CH_2$), 2.38 (s, 12H, C_4CH_3), 2.51 (t, $^3J_{HH}$ =7.0, 2H, $CH_3CH_2CH_2CH_2N$), 3.31 (d, $^1J_{HP}$ = 2.6, 4H, NCH_2P), 7.20 (d, $^3J_{HP}$ = 7.2, 8H, C_3H), 7.70 (dd, $^2J_{HP}$ = 10.9, J_{HP} = 8.1, 8H, C_2H); $[M–Cl]^+_{found}$ = 754.2038, $C_{34}H_{41}NP_2ClPt$ requires 754.2030.

*[Bis(di-p-tolylphosphinomethyl)cyclohexylamine]dichloroplatinum(II) (**13c**)*

Yield: 59% (0.09 g) of compound **13c** as white powder. ^{31}P NMR ($CDCl_3$) δ –11.7 ($^1J_{P\text{-}Pt}$ = 3448); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 25.7 (C_3), 27.9 (C_2), 29.2 (C_4), 54.4 (dd, $^1J_{CP}$ = 62.5, $^3J_{CP}$ = 5.6, NCH_2P), 69.0 (t, $^3J_{CP}$ = 9.5, C_1), 125.1 (dd, $^1J_{CP}$ = 71.7, $^3J_{CP}$ = 4.6, $C_{1'}$), 129.01 (d, $^2J_{CP}$ = 5.8), 129.05 (d, $^2J_{CP}$ = 5.7) ($C_{2'}$), 133.78 (d, $^3J_{CP}$ = 4.8), 133.82 (d, $^3J_{CP}$ = 4.9 ($C_{3'}$), 141.6 (d, J_{CP} = 2.8, $C_{4'}$); ^1H NMR ($CDCl_3$) δ 0.92–1.17 (m, 5H, $C_2H_{ax.}$, $C_4H_{ax.}$,$C_3H_{ax.}$), 1.49–1.76 (m, 5H, $C_2H_{eq.}$, $C_4H_{eq.}$, $C_3H_{eq.}$), 2.17 (s, 1H, C_1H), 2.39 (s, 12H CH_3), 3.38 (d, $^1J_{HP}$ = 2.5, 4H, NCH_2P), 7.20 (d, $^3J_{HP}$ = 7.1, 8H, $C_{3'}H$), 7.72 (dd, $^2J_{HP}$ = 11.0, J_{HP} = 8.1, 8H, C_2H); $[M–Cl]^+_{found}$ = 780.2193, $C_{36}H_{43}NP_2ClPt$ requires 780.2186.

*[Bis(di-p-tolylphosphinomethyl)benzylamine]dichloroplatinum(II) (**13d**)*

Yield: 52% (0.09 g) of compound **13d** as slightly yellow powder. ^{31}P NMR ($CDCl_3$) δ –9.4 ($^1J_{P\text{-}Pt}$ = 3406); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 55.7 (dd, $^1J_{CP}$ = 53.4, $^3J_{CP}$ = 2.0, NCH_2P), 67.3 (t, $^3J_{CP}$ = 11.9, CH_2N), 124.6 (dd, $^1J_{CP}$ = 73.5, $^3J_{CP}$ = 6.2, $C_{1'}$), 128.0 (C_4), 128.6 (C_2), 129.04 (d, $^2J_{CP}$ = 5.8), 129.08 (d, $^2J_{CP}$ = 5.7) ($C_{2'}$), 129.6 (C_3), 133.68 (d, $^3J_{CP}$ = 5.0), 133.72 (d, $^3J_{CP}$ = 5.0 ($C_{3'}$), 135.2 (C_1), 141.6 ($C_{4'}$); ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 12H, CH_3), 3.19–3.29 (m, 4H, NCH_2P), 3.46 (s, 2H, CH_2N), 6.83 (d, 2H, J_{HH} = 7.0, C_2H), 7.04 (d, 8H, $^3J_{HP}$ = 7.1, $C_{3'}H$), 7.07–7.11 (m, 3H, C_3H, C_4H), 7.44–7.52 (m, 8H, $C_{2'}H$); $[M–Cl]^+_{found}$ = 788.1880, $C_{37}H_{39}NP_2ClPt$ requires 788.1873.

General procedure for the synthesis of bis(dibenzyl- or di-p-tolylphosphinomethyl)-benzylamine-borane complexes

To 0.12 g (0.20 mmol) of the bis(>P(O)CH_2)benzylamine (**5d** or **6d**) was added 0.15 mL (1.20 mmol) of phenylsilane under nitrogen. The mixture was stirred at 120 °C in a vial in a CEM Discover Microwave reactor equipped with a pressure controller for 2.5 h.

Then, the mixture was diluted by the addition of 1 mL of degassed toluene. To the solution of phosphine **10d** or **11d** so obtained was added 0.40 mL of 2M THF solution of $BH_3{\cdot}SMe_2$ (0.80 mmol), and the mixture was stirred at 25 °C for overnight. After this, 3 mL of water was added dropwise and contents of the flask were stirred for 10 minutes. The precipitated boric acid was removed by filtration and the organic phase was dried (Na_2SO_4). The residue obtained after evaporation of the volatile components was purified by column chromatography (silica gel, 3% methanol in dichloromethane) to give borane complex (**14d** or **15d**).

*Bis(dibenzylphosphinomethyl)benzylamine-borane complex (**14d**)*

Yield: 74% (0.09 g) of compound **14d** as slightly yellow oil. ^{11}B NMR ($CDCl_3$) δ -34.6; ^{31}P NMR ($CDCl_3$) δ 12.1; ^{13}C NMR ($CDCl_3$) δ 31.1 (d, $^1J_{CP}$ = 29.3, PCH_2), 50.9 (dd, $^1J_{CP}$ = 41.3, $^3J_{CP}$ = 5.3, NCH_2P), 61.6 (t, $^3J_{CP}$ = 4.5, CH_2N), 127.0 (d, J_{CP} = 2.6, $C_{4'}$), 127.7 (C_4), 128.51 (d, J_{CP} = 2.2, $C_{3'}$), 128.52 (C_3)*, 129.8 (C_2)*, 129.9 (d, $^3J_{CP}$ = 4.1, $C_{2'}$), 131.9 (d, $^2J_{CP}$ = 5.4, $C_{1'}$), 137.3 (C_1), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 0.35–1.30 (m, 6H, BH_3), 2.88–3.04 (m, 12H, NCH_2P and PCH_2), 3.77 (s, 2H, CH_2N), 7.07–7.12 (m, 5H, ArH), 7.20–7.35 (m, 20H, Ar'H); $[M+H]^+_{found}$ = 588.3333, $C_{37}H_{46}B_2NP_2$ requires 588.3328.

*Bis(di-p-tolylphosphinomethyl)benzylamine-borane complex (**15d**)*

Yield: 69% (0.08 g) of compound **15d** as slightly yellow oil. ^{11}B NMR ($CDCl_3$) δ -34.8; ^{31}P NMR ($CDCl_3$) δ 9.3; ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 53.2 (dd, $^1J_{CP}$ = 40.0, $^3J_{CP}$ = 3.6, NCH_2P), 60.9 (t, $^3J_{CP}$ = 4.0, CH_2N), 125.3 (d, $^1J_{CP}$ = 54.9, $C_{1'}$), 127.1 (C_4), 127.9 (C_2)*, 129.2 (C_3)*, 129.4 (d, $^2J_{CP}$ = 10.0, $C_{2'}$), 132.5 (d, $^3J_{CP}$ = 8.9, $C_{3'}$), 137.5 (C_1), 141.4 (d, J_{CP} = 2.2, $C_{4'}$), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 0.80–1.45 (m, 6H, BH_3), 2.36 (s, 12H, CH_3), 3.83 (s, 4H, NCH_2P), 3.90 (s, 2H, CH_2N), 6.88 (d, 2H, J_{HH} = 7.1, C_2H), 7.09–7.20 (m, 11H, $C_{3'}H$, C_3H, C_4H), 7.42–7.48 (m, 8H, $C_{2'}H$); $[M+H]^+_{found}$ = 588.3333, $C_{37}H_{46}B_2NP_2$ requires 588.3328.

Calculation on the Pt-complexes

All computations were carried out with the Gaussian09 program package (G09) [52], using convergence criteria of 3.0×10^{-4}, 4.5×10^{-4}, 1.2×10^{-3} and 1.8×10^{-3}, for the gradients of the root mean square (RMS) Force, Maximum Force, RMS displacement and maximum displacement vectors, respectively. Computations were carried out using B3LYP/6-31G(d,p) for CHNP and B3LYP/SDD(MWB60) for Pt including effective core potential

(ECP) [49-51]. The vibrational frequencies were computed at the same levels of theory, in order to properly confirm all structures as residing at minima on their potential energy hypersurfaces (PESs). Thermodynamic functions *U, H,* G and S were computed at 298.15 K.

SCXRD measurements

General procedures: Crystals were mounted on a glass fibres. Cell parameters were determined by least-squares from the respective setting angles as quoted. Intensity data were collected on a high flux Bruker D8 Venture diffractometer at 100K(2) K (monochromatized Mo-Kα radiation, λ = 0.71069 Å) at 100K(2) and a mix of ω and φ scans for **12b**, **12c** and **13c**. Multi-scan absorption corrections were applied to the data. Initial structure models were obtained by direct methods [60,61] and subsequent difference syntheses. Anisotropic full-matrix least-squares refinement on F^2 were applied [60,61] for all non-hydrogen atoms except some isotropic treated disordered atomic sites and the models were refined to convergence. Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but they were not refined. H atoms were kept riding on their anchor atoms, with isotropic displacement parameters of these hydrogen atoms were approximated from the U(eq) value of the atom to which they were bonded to.

12b: Space group was determined as monoclinic $P2_1/c$ (No. 14), with a = 9.6517(3), b = 24.1859(7), c = 15.9487(5) [Å] and β = 100.738(1)^o . Final R indices [I > 2σ(I)] are R_1 = 0.0211, wR^2 = 0.0424. Hydrogen atomic positions were calculated from assumed geometries. The maximum and minimum residual electron densities in the final difference maps are 1.05 and –0.60 e.Å^{-3} and are acceptable due to disorder in the *n* -butyl chain.

12c: Space group was determined as monoclinic $P2_1/c$ (No. 14), with a = 9.7858(3), b = 15.9750(5), c = 25.1121(9) [Å] and β = 98.130(1)^o . Final R indices [I > 2σ(I)] are R_1 = 0.0420, wR^2 = 0.0934. Hydrogen atomic positions were calculated from assumed geometries.

The maximum and minimum residual electron densities in the final difference maps are 5.7 and –4.6 e.Å^{-3} and are acceptable due to extensive solvent disorder.

13c: It was clear from the first data collection that these crystals suffer from serious twinning. Thus data were recollected and the twin law derived. Space group was determined as monoclinic $P2_1/c$ (No. 14), with a = 19.090(3), b = 10.9159(17), c = 20.821(3) [Å] and β = 103.651(5)^{o}. Final R indices [I > 2σ(I)] are R_1 = 0.0508, wR^2 = 0.1163. Hydrogen atomic positions were calculated from assumed geometries. The maximum and minimum residual electron densities in the final difference maps are 2.3 and –1.1 e.Å^{-3} and are acceptable due to extensive solvent disorder.

All further calculations and drawings were done by using PLATON [62] and SCHAKAL [63]. Crystal structure data are deposited with the Cambridge Crystallographic Data Centre under CCDC 1414765, 1414766 and 1416216 and can be obtained free of charge upon application to CCDC.

Hydroformylation experiments

In a typical experiment, a solution of $PtCl_2$(ligand) (**12b-d** or **13b-d**), 0.005 mmol) and tin(II) chloride (1.9 mg; 0.01 mmol) in toluene (5 mL) containing styrene (0.115 mL, 1.0 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.

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Graphical abstract

Synthesis and use of α-aminophosphine oxides and *N,N*-bis(phosphinoyl-methyl)amines – A study on the related ring platinum complexes

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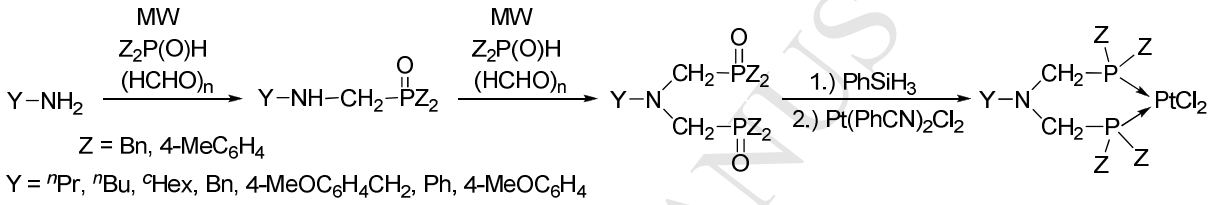

Research Highlights

- New α-aminophosphine oxides and *N*,*N*-bis(phosphinoylmethyl)amines were prepared by efficient microwave-assisted Kabachnik-Fields reactions.

- The bis(phosphinoyl)amines, precursors for bidentate P-ligands were then converted to the corresponding borane and ring platinum complexes after double deoxygenation.

- Stereostructure of a few Pt complexes was evaluated by quantum chemical calculations. Complexation enthalpies were determined.

- The crystal structure of a few ring Pt species was studied by X-ray analysis. The factors controlling the conformation were evaluated.

- The Pt complexes were tested as novel catalyst in the hydroformylation of styrene.