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New Pd(II) and Pt(II)-diaminophosphine complexes bearing cyclohexyl or isopropyl moiety: use of Pd(II) complexes as precatalyst in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions

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Abstract: Two new diaminophosphine ligands, *N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline (**1**) and *N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline (**2**) were synthesized by the reaction of 2-(aminomethyl)aniline with two equivalents of Cy_2PCl or $(iPr)_2PCl$, respectively. The reactions of **1** and **2** with $MCl_2(cod)$ (M = Pd, Pt; cod = 1,5-cyclooctadiene) yield complexes [*cis*-$Pd(L_2\mathbf{P}NHC_6H_4CH_2NH\mathbf{P}L_2)Cl_2$] (L = Cy **3**, iPr **4**) and [*cis*-$Pt(L_2\mathbf{P}NHC_6H_4CH_2NH\mathbf{P}L_2)Cl_2$] (L = Cy **5**, iPr **6**), respectively. The catalytic activity of the palladium complexes was investigated in the Suzuki–Miyaura cross-coupling reaction in the presence of Cs_2CO_3 as a base. The palladium complexes were also found to be highly active catalysts in the Mizoroki–Heck reaction.

Key words: Diaminophosphine, palladium, platinum, Suzuki reaction, Heck reaction, stilbene

1. Introduction

Organophosphorus ligands have been extensively used in organometallic and inorganic chemistry,[1] and are mainly important in homogeneous catalysis.[2] In particular, diaminophosphines in which the two phosphorus atoms are connected to a carbon chain and have the same substituents on each phosphorus atom, such as bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) have been widely studied.[3,4] Lately, considerable attention has been devoted to diaminophosphines with a heteroatom or bridge combining two phosphorus atoms.[5–7] Compared to dppe, dppm, and bridged diphosphines, unsymmetrical diphosphines have attracted less attention.[8] Unsymmetrical diaminophosphines exemplify a fascinating series of ligands because the basicity or steric properties of the two phosphorus atoms can be different, which may be used to get different coordination modes, i.e. bidendate versus monodendate.[9]

Considering the advantage of aminophosphines, in recent years our research group has reported the synthesis,[10] characterization and coordination properties, and catalytic activity of this type of ligand.[11–13] Since we obtained high catalytic activity with these ligands, herein we describe the preparation of novel diaminophosphine ligands and their transition metal complexes {Pd(II) and Pt(II)}.[14–16] As far as we know, there are not many reports on the use of these complexes, which include diaminophosphines carrying cyclohexyl or isopropyl moiety on the phosphorus atom, in carbon–carbon coupling reactions. All new compounds were characterized by multinuclear NMR spectroscopy, IR spectroscopy, and microanalysis. Furthermore, continuing

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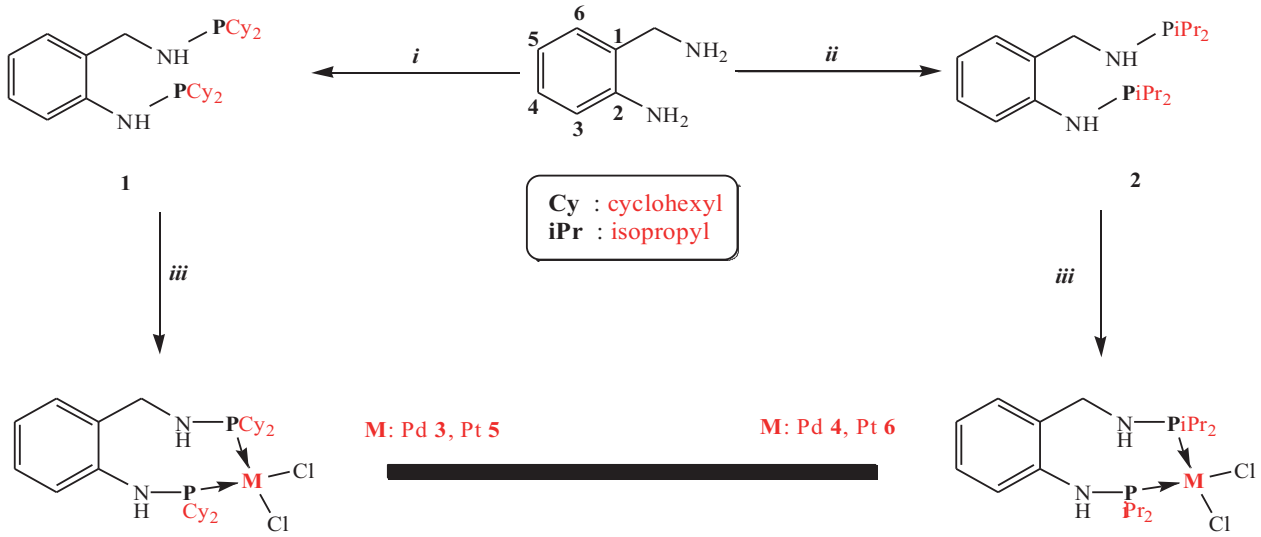
our program involving the design and development of useful catalysts for the carbon–carbon coupling reaction, the catalytic activity of palladium complexes was assessed in Suzuki and Heck type coupling reactions.

2. Results and discussion

2.1. Synthesis and characterization of the diaminophosphine ligands

Diaminophosphine ligands *N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline (**1**) and *N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline (**2**) were prepared from the starting material 2-aminobenzylamine by aminolysis (Scheme).[17]



Scheme. Synthesis of *N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline (**1**) and ***N***,***N***'-bis(diisopropylphosphino)-2-(aminomethyl)aniline (**2**) and their complexes. (i) Cy_2PCl, CH_2Cl_2, rt, 24 h for **1** and **2**; (ii) $(iPr)_2PCl$, CH_2Cl_2; (iii) $[PdCl_2(cod)]$, r.t., 5 h or $[PtCl_2(cod)]$, r.t., 6 h, CH_2Cl_2.

The ^{31}P-$\{^1H\}$ NMR spectra of **1** and **2** displayed single resonances at δ 59.30 and 43.47 ppm and 65.18 and 49.60 ppm, respectively (see electronic supporting information (ESI) Figure 1; on the journal's website). The assignment of the ^1H chemical shifts was derived from 2D HH-COSY spectra and the appropriate assignment of the ^{13}C chemical shifts from DEPT and 2D HMQC spectra. Furthermore, IR spectra and C, H, and N elemental analyses are in accord with the proposed structures (see experimental section for details).

The coordination properties of the ligands *N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline (**1**) and *N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline (**2**) were studied by forming their palladium and platinum complexes. Reaction of **1** or **2** with $[Pd(cod)Cl_2]$ (cod = 1,5-cyclooctadiene) formed Pd(II) complexes **3** and **4** in good yields (88% and 89%, respectively). Both of the isolated dichloropalladium(II) complexes **3** and **4** were found to have *cis*-configuration, characteristic of phosphines having mutually *cis*-arrangement (Figure 1, in ESI).[18,19] In the ^{31}P-$\{^1H\}$ NMR spectra, each of **3** and **4** had two signals at 64.85 and 62.53 ppm and 70.74 and 68.80 ppm, respectively, which are within the expected range of other similar complexes.[20–22] The ^{13}C-$\{^1H\}$ NMR spectrum contained well-resolved signals for the phenyls carbons.[23] Furthermore, IR spectra and C, H, and N elemental analyses, and ^1H NMR and ^{13}C NMR spectral data of the complexes **3** and **4**

are in agreement with the anticipated structures and the compositions of the two complexes were supported by microanalysis.

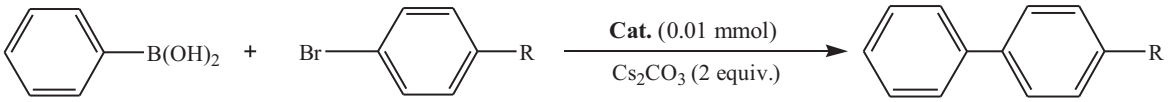
Reaction of [Pt(cod)Cl_2] (cod = 1,5-cyclooctadiene) with one equivalent of **1** or **2** in thf solution yields the respective {*N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline} dichloroplatinum(II) (**5**) and {*N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline} dichloroplatinum(II) (**6**), respectively, by replacement of cod with **1** or **2**. ^{31}P-{^{1}H} -NMR spectra of complexes **5** and **6** contained two singlets for each at δ 66.04 and 55.63 ppm and 72.82 and 61.71 ppm, respectively.[24–26] The large $^{1}J(^{195}$Pt-^{31}P) coupling constants of 4093 and 3905 Hz for **5** and 4092 and 3907 Hz for **6** are indicative of a *cis* arrangement of aminophosphine around the platinum(II) centers.[27–29] Typical spectra of these two platinum complexes are illustrated in the ESI, Figure 2 (Spectra 1.2.). Their ^{1}H NMR and ^{13}C NMR spectra are consistent with the literature values.[30–32] The complexes were able to be isolated as solid materials and characterized by IR as well as microanalysis. Furthermore, we extensively tried to obtain crystals suitable for X-ray analysis, but unfortunately were not successful.

2.2. Suzuki–Miyaura and Mizoroki–Heck coupling reactions

In a pilot study to examine the catalytic activity of palladium complexes, we initially tested the Suzuki cross-coupling reaction between aryl bromides with boronic acid.[33–35] The reaction parameters for the Suzuki cross-coupling reaction were optimized through a series of experiments. The effects of several parameters such as temperature, base, solvent, and ambient atmosphere were systematically studied by using the coupling of *p*-bromoacetophenone and phenylboronic acid as a probe reaction. As can be seen in Table 1, the best catalytic activities were only obtained when the Suzuki reaction was performed at 100 °C in dioxane with Cs_2CO_3. On the other hand, one can easily observe in Table 1 that the efficiency of complexes is not the same for each complex. For instance, the Suzuki reaction with catalyst **3** always afforded higher catalytic activity than that with catalyst **4**. It can also be seen in Table 1 that a typical reaction of *p*-bromoacetophenone and phenylboronic acid indicated that the reaction rate depended on the alkyl substituents on the phosphorus atom, i.e. results of the optimization studies clearly show that complex **3** having cyclohexyl (Cy) moiety on the phosphorus atom is a more active and efficient catalyst leading to nearly quantitative conversions.

With the best conditions in hand, next we conducted further experiments to investigate the scope of the Suzuki cross-coupling of catalysts **3** and **4** with various substrates, including aryl bromides and chlorides having electron-withdrawing or electron-donating substituents (Table 1, entries 3–12). Encouraged by these results, we attempted to study the reactivity between substituted aryl bromides and phenylboronic acid. In this case, the reaction was slower compared to aryl iodides; therefore, we can easily conclude that the electronic nature of the aryl bromides has an obvious influence on the coupling reactions (Table 1, entries 3–10). We also investigated catalytic activity of the complexes in Suzuki coupling reactions of arylchlorides with phenylboronic acid (Table 1, entries 11 and 12). However, the highest conversion was up to 57% in the presence of Cs_2CO_3 within 24 h in dioxane at 100 °C for catalyst **3** and elongation of the reaction time did not afford any further conversion. This can be expected since it is well known that chlorides are often less reactive towards the Suzuki coupling reaction under the same conditions used for the coupling of bromides and iodides.[36] Encouraged by the good catalytic activities obtained in the Suzuki–Miyaura cross-coupling reaction, we next extended our investigations to the Mizoroki–Heck reaction, and the results are given in Tables 2 and 3. It is well known that among the different methods used to form carbon–carbon bonds palladium-catalyzed carbon–carbon bond formation between aryl halides and olefins has become an excellent tool for the synthesis of a variety of styrene derivatives.[37–39]

Table 1. Suzuki coupling reactions of aryl halides with phenylboronic acid catalyzed by palladium(II)-diaminophosphine catalysts **3** and **4**.



Entry	X	R	Cat. Time	Conv. (%)	Yield (%)	TOF (h^{-1})
1	Br	$C(O)CH_3$	**3** 15 min	99	97	396
2	Br	$C(O)CH_3$	**4** 1 s	98	95	98
3	Br	C(O)H	**3** 15 min	97	96	388
4	Br	C(O)H	**4** 1 h	96	92	96
5	Br	H	**3** 30 min	98	97	194
6	Br	H	**4** 2 h	99	96	50
7	Br	OCH_3	**3** 2 h	98	96	50
8	Br	OCH_3	**4** 9 h	99	97	11
9	Br	CH_3	**3** 1 h	98	95	98
10	Br	CH_3	**4** 5 h	99	96	20
11	Cl	$C(O)CH_3$	**3** 24 h	57	52	29
12	Cl	$C(O)\ CH_3$	**4** 48 h	32	27	<5

Reaction conditions: 1.0 mmol *p*-R-C_6H_4X aryl halides, 1.5 mmol phenylboronic acid, 2.0 mmol Cs_2CO_3, 1 mol% complex (**3** or **4**), dioxane (3.0 mL) at 100 °C. The yields are determined by ^1H NMR of the crude reaction. All reactions were monitored by GC; TOF = (mol product/mol Cat.) × h^{-1}.

As expected, the rate of coupling in the Heck reaction depended on different parameters such as temperature, solvent, base, and catalyst loading.[40] The Heck reaction usually requires polar solvents. We tried Cs_2CO_3 and K_2CO_3, which are expected to be the best bases for this reaction. Finally, from the optimum studies, we found that use of 1.0 % mmol, 2 equivalents of Cs_2CO_3 in DMF at 120 °C for **3** and **4** led to the best conversions with the highest TOF values. We firstly investigated the catalytic activities of **3** and **4** for the coupling of *p*-bromoacetophenone with styrene (Table 2). Under the determined reaction conditions, a wide range of aryl bromides bearing electron-donating and electron-withdrawing groups reacted with styrene, affording the coupled products in moderate to good yields. As expected, electron-deficient bromides were more beneficial to obtain high conversions (Table 3, entries 1–8). Using aryl chlorides instead of aryl bromides yielded only small amount of stilbene derivatives under the conditions employed for bromides.

In summary, we prepared two new diaminophosphine ligands, as well as palladium and platinum complexes. All these new compounds were characterized using spectroscopic techniques. The catalytic activities of the Pd(II) complexes were tested in Suzuki coupling and Heck reactions. In general, it appears that {*N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline} dichloropalladium(II) (**3**) is more efficient for Suzuki and Heck reactions of aryl bromides, but its activity is much lower for the coupling of aryl chlorides. The procedure is simple and effective towards various aryl bromides and does not require an induction period.

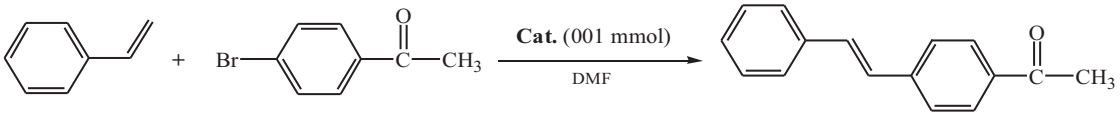
3. Experimental section

3.1. General

All reactions and processes were carried out under inert atmosphere of argon. Cy_2PCl, $(iPr)_2PCl$, 2-aminobenzylamine, and deuterated solvents were purchased from Sigma-Aldrich and used without further purification. The starting materials [MCl_2(cod)] (M = Pd, Pt, cod = 1,5-cyclooctadiene) were synthesized

according to the literature methods.[41,42] Solvents were dried using the appropriate reagents and distilled prior to use. Infrared spectra were measured on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr disks in the range 4000–400 cm^{-1}. ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), and ^{31}P-$\{^{1}H\}$ NMR spectra (162.0 MHz) spectra were recorded on a Bruker AV400 spectrometer, with δ referenced to internal TMS and external 85% H_3PO_4 respectively. Microanalysis was carried out on a Fisons EA 1108 CHNS-O instrument; melting points were determined using a Gallenkamp Model apparatus with open capillaries.

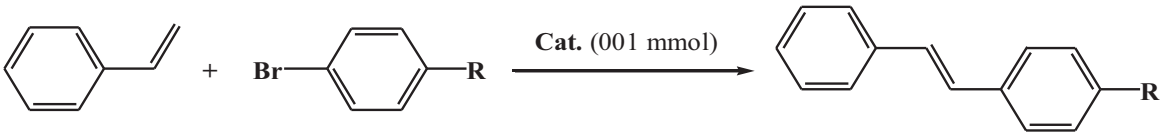
Table 2. Heck coupling reactions of *p*-bromoacetophenone with styrene catalyzed by palladium(II)-diaminophosphine catalysts **3** and **4**.



Entry	Cat.	Time	Base	Temp.	Conv. (%)	Yield (%)	TOF (h^{-1})
1	**3**	1 h	K_2CO_3	90	95	92	48
2	**4**	2 h	K_2CO_3	90	93	90	47
3	**3**	1 h	K_2CO_3	120	99	95	50
4	**4**	2 h	K_2CO_3	120	96	91	48
5	**3**	3/4 h	Cs_2CO_3	90	98	95	74
6	**4**	3/2 h	Cs_2CO_3	90	95	92	63
7	**3**	1/2 h	Cs_2CO_3	120	99	96	50
8	**4**	1 h	Cs_2CO_3	120	98	95	98

Reaction conditions: 1.0 mmol *p*-$CH_3C(O)$-C_6H_4Br aryl bromide, 1.5 mmol styrene, 2.0 mmol base, 1 mol% complex (**3** or **4**), DMF (3.0 mL). All reactions were monitored by GC; TOF = (mol product/mol Cat.) $\times$ h^{-1}.

Table 3. Heck coupling reactions of aryl bromides with styrene catalyzed by palladium(II)-diaminophosphine catalysts **3** and **4**.



Entry	R	Cat.	Time	Conv. (%)	Yield (%)	TOF (h^{-1})
1	C(O)H	**3**	1/2 h	98	96	196
2	C(O)H	**4**	1 h	99	92	99
3	H	**3**	1 h	98	97	98
4	H	**4**	2 h	97	96	49
5	OCH_3	**3**	5 h	98	96	20
6	OCH_3	**4**	5 h	97	96	19
7	CH_3	**3**	4 h	99	99	25
8	CH_3	**4**	4 h	98	97	25

Reaction conditions: 1.0 mmol *p*-R-C_6H_4Br aryl bromide, 1.5 mmol styrene, 2.0 mmol Cs_2CO_3, 1 mol% complex (**3** or **4**), DMF (3.0 mL) at 120 °C. The yields are determined by ^{1}H NMR of the crude reaction. All reactions were monitored by GC; TOF = (mol product/mol Cat.) $\times$ h^{-1}.

3.2. Procedure for the Suzuki–Miyaura cross-coupling reaction

Palladium complexes (**3** and **4**, 0.001 mmol), aryl bromide/chloride/iodide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), and solvent (3 mL) were added to a Schlenk tube under argon atmosphere or in air and the mixture was followed for different conditions and parameters (temperature, time, base, etc.). After completion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated, and purified by flash chromatography on silica gel. The purity of the compounds was checked immediately by GC and ^{1}H NMR and yields are based on aryl halides.

3.3. Procedure for the Heck coupling reaction

Palladium complexes (**3** and **4**, 0.01 mmol), aryl bromide/chloride/iodide (1.0 mmol), styrene (1.5 mmol), base (2 mmol), and solvent (3 mL) were added to a Schlenk tube under argon atmosphere or in air and the mixture was monitored for different conditions and parameters (temperature, time, base, etc.). After completion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silica gel with copious washing, concentrated, and purified by flash chromatography on silica gel. The purity of the compounds was checked immediately by GC and ^{1}H NMR and yields are based on aryl halides.

3.4. Synthesis and characterization of the ligands and their complexes

3.4.1. General procedure for the synthesis of diaminophosphine ligands (1 and 2)

3.4.1.1. Synthesis of *N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline (1)

Chlorodicyclohexylphosphine (0.39 g, 1.60 mmol) was added dropwise over 20 min to a stirred solution of 2-aminobenzylamine (0.10 g, 0.80 mmol) and triethylamine (0.16 g, 1.60 mmol) in CH_2Cl_2 (20 mL) at 0 °C with vigorous stirring. The mixture was stirred at r.t. for 24 h, and the solvent was removed under reduced pressure. After addition of THF, the white precipitate (triethylammonium chloride) was filtered under argon and the solvent removed in vacuo, which was washed with cold diethyl ether (3 × 15 mL) and dried in vacuo to produce a yellow viscous oil compound **1** (Yield: 0.38 g, 93%). ^{1}H NMR (δ in ppm rel. to TMS, J Hz, in $CDCl_3$): 7.42 [d, 1H, $^3J_{H-H}$ = 7.4 Hz, **H**-3]; 7.20 [t, 1H, $^3J_{H-H}$ = 7.4 Hz, **H**-4]; 7.06 [d, 1H, $^3J_{H-H}$ = 6.6 Hz, **H**-6]; 6.75 [t, 1H, $^3J_{H-H}$ =7.2 Hz, **H**-5]; 6.10 [d, 1H, J = 8.6 Hz, ArN**H**–]; 4.10 [dd, 2H, J = 5.6 and 5.8 Hz, C**H**$_2$–]; 2.22 [d, 1H, J = 1.2 Hz, ArCH$_2$N**H**–]; 1.16–1.77 (m, 44 H, protons of cyclohexyls). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$): 128.8, 128.5, 128.0, 127.5, 125.2, 123.9 (carbons of phenyl), 50.2 (**C**H$_2$–), 26.55, 27.03, 27.16, 27.28, 29.12, 29.30 (**C**H$_2$– of cyclohexyls). ^{31}P-{^{1}H} NMR (δ, $CDCl_3$): 59.30 [s, CH$_2$NH**P**Cy$_2$], 43.37 [s, ArNH**P**Cy$_2$]. Selected IR, υ (cm^{-1}): 912 (P-NH), 1441 (P-Ph), 3306 (N-H). $C_{31}H_{52}N_2P_2$ (514.7 g/mol): calcd. C 72.33, H 10.18, N 5.44; found C 72.02, H 10.14, N 5.39%.

3.4.1.2. Synthesis of *N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline (2)

Chlorodiisopropylphosphine (0.25 g, 1.60 mmol) was added dropwise over 20 min to a stirred solution of 2-aminobenzylamine (0.10 g, 0.80 mmol) and triethylamine (0.16 g, 1.60 mmol) in CH_2Cl_2 (20 mL) at 0 °C with vigorous stirring. The mixture was stirred at r.t. for 24 h, and the solvent was removed under reduced pressure. After addition of THF, the white precipitate (triethylammonium chloride) was filtered under argon and the solvent removed in vacuo, which was washed with cold diethyl ether (3 × 15 mL) and dried in vacuo to produce a yellow viscous oil compound **1** (Yield: 0.27 g, 94%). ^{1}H NMR (δ in ppm rel. to TMS, J Hz, in $CDCl_3$): 7.40

[d, 1H, $^{3}J_{H-H}$ = 7.7 Hz, **H**-3]; 7.21 [t, 1H, $^{3}J_{H-H}$ = 7.5 Hz, **H**-4]; 7.10 [d, 1H, $^{3}J_{H-H}$ = 6.8 Hz, **H**-6]; 6.80 [t, 1H, $^{3}J_{H-H}$ =7.4 Hz, **H**-5]; 6.12 [d, 1H, J = 8.6 Hz, ArN**H**–]; 4.12 [dd, 2H, J = 5.4 and 5.6 Hz, C**H**$_2$–]; 2.20 [d, 1H, J = 1.1 Hz, ArCH$_2$N**H**–]; 1.92 (m, 4H, NH-P(C**H**(CH$_3$)$_2$), 1.12 (m, 24H, NH-P(CH(C**H**$_3$)$_2$). ^{13}C-{^{1}H} NMR (δ, CDCl$_3$): 129.2, 128.1, 128.9, 127.1, 125.4, 123.8 (carbons of phenyl), 48.8 (**C**H$_2$–); 30.16 (d, $^{1}J_{P-C}$ = 18.2 Hz, P**C**H(CH$_3$)$_2$), 29.04 (d, $^{1}J_{P-C}$ = 16.8 Hz, P**C**H(CH$_3$)$_2$), 18.12 (d, $^{2}J_{P-C}$ = 2.8 Hz, PCH(**C**H$_3$)$_2$), 18.02 (d, $^{2}J_{P-C}$ = 2.5 Hz, PCH(**C**H$_3$)$_2$), 17.96 (d, $^{2}J_{P-C}$ = 2.7 Hz, PCH(**C**H$_3$)$_2$), 17.80 (d, $^{2}J_{P-C}$ = 2.4 Hz, PCH(**C**H$_3$)$_2$); ^{31}P-{^{1}H} NMR (δ, CDCl$_3$): 65.18 [s, CH$_2$NH**P**(iPr)$_2$], 49.60 [s, ArNH**P**(iPr)$_2$]. Selected IR, υ (cm^{-1}): 916 (P-N), 1444 (P-Ph), 3308 (N-H). $C_{19}H_{36}N_2P_2$ (354.4 g/mol): calcd. C 64.39, H 10.24, N 7.90; found C 69.28, H 10.19, N 7.83%.

3.4.1.3. Synthesis of {*N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline}dichloropalladium(II) (3)

[Pd(cod)Cl$_2$] (0.21 g, 0.74 mmol) and [Cy$_2$PNHC$_6$H$_4$CH$_2$NHPCy$_2$] (0.38 g, 0.74 mmol) were dissolved in dry CH$_2$Cl$_2$ (15 mL) and stirred at r.t. for 5 h. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of diethyl ether (30 mL) gave a clear yellow solid, **3**. The product was collected by filtration and dried in vacuo (yield: 0.45 g, 88%; mp: 156–158 °C). ^{1}H NMR (δ in ppm rel. to TMS, J Hz, in CDCl$_3$): 7.38 [d, 1H, $^{3}J_{H-H}$ = 7.5 Hz, **H**-3]; 7.20 [t, 1H, $^{3}J_{H-H}$ = 7.6 Hz, **H**-4]; 7.06 [d, 1H, $^{3}J_{H-H}$ = 6.9 Hz, **H**-6]; 6.75 [t, 1H, $^{3}J_{H-H}$ =7.4 Hz, **H**-5]; 6.08 [d, 1H, J = 8.8 Hz, ArN**H**–]; 4.10 [dd, 2H, J = 5.7 and 5.8 Hz, C**H**$_2$–]; 2.22 [d, 1H, J = 1.3 Hz, ArCH$_2$N**H**–]; 1.13–1.72 (m, 44 H, protons of cyclohexyls). ^{13}C-{^{1}H} NMR (δ, CDCl$_3$): 128.2, 128.0, 127.6, 127.9, 125.7, 123.5 (carbons of phenyl), 52.7 (**C**H$_2$–), 28.53, 27.23, 27.46, 27.13, 29.46, 29.48 (**C**H$_2$– of cyclohexyls). ^{31}P-{^{1}H} NMR (δ, DMSO): 64.85 [s, CH$_2$NH**P**Cy$_2$], 62.53 [s, ArNH**P**Cy$_2$]. Selected IR, υ (cm^{-1}): 934 (P-N), 1446 (P-Ph), 3222 (N-H). $C_{31}H_{52}N_2P_2$ PdCl$_2$ (692.0 g/mol): calcd. C 53.80, H 7.57, N 4.05; found C 53.68, H 7.52, N 4.01%.

3.4.1.4. Synthesis of {*N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline}dichloropalladium(II) (4)

[Pd(cod)Cl$_2$] (0.22 g, 0.76 mmol) and [(isopropyl)$_2$PNHC$_6$H$_4$CH$_2$NHP(isopropyl)$_2$] (0.27 g, 0.76 mmol) were dissolved in dry CH$_2$Cl$_2$ (10 mL) and stirred at r.t. for 5 h. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of diethyl ether (30 mL) gave a clear yellow solid, **4**. The product was collected by filtration and dried in vacuo (yield: 0.36 g, 89%; mp: 178–180 °C). ^{1}H NMR (δ in ppm rel. to TMS, J Hz, in CDCl$_3$): 7.40 [d, 1H, $^{3}J_{H-H}$ = 7.6 Hz, **H**-3]; 7.20 [t, 1H, $^{3}J_{H-H}$ = 7.6 Hz, **H**-4]; 7.11 [d, 1H, $^{3}J_{H-H}$ = 6.7 Hz, **H**-6]; 6.80 [t, 1H, $^{3}J_{H-H}$ =7.5 Hz, **H**-5]; 6.10 [d, 1H, J = 8.2 Hz, ArN**H**–]; 4.12 [dd, 2H, J = 5.4 and 5.6 Hz, C**H**$_2$-]; 2.19 [d, 1H, J = 1.2 Hz, ArCH$_2$N**H**–]; 1.92 (m, 4H, NH-P(C**H**(CH$_3$)$_2$), 1.14 (m, 24H, NH-P(CH(C**H**$_3$)$_2$). ^{13}C-{^{1}H} NMR (δ, CDCl$_3$): 128.9, 128.7, 127.9, 126.9, 125.2, 123.9 (carbons of phenyl), 53.6 (**C**H$_2$–); 32.16 (d, $^{1}J_{P-C}$ = 19.8 Hz, P**C**H(CH$_3$)$_2$), 29.48 (d, $^{1}J_{P-C}$ = 17.2 Hz, P**C**H(CH$_3$)$_2$), 18.96 (d, $^{2}J_{P-C}$ = 2.6 Hz, PCH(**C**H$_3$)$_2$), 17.93 (d, $^{2}J_{P-C}$ = 2.4 Hz, PCH(**C**H$_3$)$_2$), 17.22 (d, $^{2}J_{P-C}$ = 2.7 Hz, PCH(**C**H$_3$)$_2$), 17.14 (d, $^{2}J_{P-C}$ = 2.4 Hz, PCH(**C**H$_3$)$_2$); ^{31}P-{^{1}H} NMR (δ, DMSO): 70.74 [s, CH$_2$NH**P**(iPr)$_2$], 68.80 [s, ArNH**P**(iPr)$_2$]. Selected IR, υ (cm^{-1}): 928 (P-N), 1441 (P-Ph), 3216 (N-H). Selected IR, υ (cm^{-1}): 931 (P-N), 1448 (P-Ph), 3314 (N-H). $C_{19}H_{36}N_2P_2$ PdCl$_2$ (531.7 g/mol): calcd. C 42.92, H 6.82, N 5.27; found C 42.86, H 6.78, N 5.23%.

3.4.1.5. Synthesis of {*N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline}dichloroplatinum(II) (5)

[Pt(cod)Cl_2] (0.28 g, 0.74 mmol) and [$Cy_2PNHC_6H_4CH_2NHPCy_2$] (0.38 g, 0.74 mmol) were dissolved in dry CH_2Cl_2 (10 mL) and stirred at r.t. for 6 h. The volume was concentrated to ca. 1–2 mL by evaporation under reduced pressure and addition of diethyl ether (30 mL) gave a white solid, **5**. The product was collected by filtration and dried in vacuo (yield: 0.55 g, 95%; mp: >250 °C). ^{1}H NMR (δ in ppm rel. to TMS, J Hz, in $CDCl_3$): 7.37 [d, 1H, $^3J_{H-H}$ = 7.4 Hz, **H**-3]; 7.22 [t, 1H, $^3J_{H-H}$ = 7.8 Hz, **H**-4]; 7.04 [d, 1H, $^3J_{H-H}$ = 6.8 Hz, **H**-6]; 6.75 [t, 1H, $^3J_{H-H}$ =7.2 Hz, **H**-5]; 6.10 [d, 1H, J = 8.6 Hz, ArN**H**–]; 4.10 [dd, 2H, J = 5.6 and 5.9 Hz, C**H**$_2$–]; 2.20 [d, 1H, J = 1.4 Hz, ArCH_2N**H**–]; 1.16–1.76 (m, 44 H, protons of cyclohexyls). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$): 129.0, 128.5, 127.4, 127.5, 125.2, 123.4 (carbons of phenyl), 54.3 (**C**H$_2$–), 28.47, 27.44, 27.44, 27.35, 29.54, 29.32 (**C**H$_2$– of cyclohexyls). ^{31}P-{^{1}H} NMR (δ, DMSO): 66.04 [d, J_{PtP}: 4093 Hz, CH_2NH**P**Cy_2]; 55.63 [d, J_{PtP}: 3905 Hz, ArNH**P**Cy_2]. Selected IR, υ (cm^{-1}): 924 (P-N), 1440 (P-Ph), 3218 (N-H). $C_{31}H_{52}N_2P_2$ $PtCl_2$ (780.7 g/mol): calcd. C 47.69, H 6.71, N 3.59; found C 47.58, H 6.67, N 3.55%.

3.4.1.6. Synthesis of {*N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline}dichloroplatinum (II) (6)

[Pt(cod)Cl_2] (0.28 g, 0.76 mmol) and [(isopropyl)$_2$PNHC$_6$H$_4$CH$_2$NHP(isopropyl)$_2$] (0.27 g, 0.76 mmol) were dissolved in dry CH_2Cl_2 (15 mL) and stirred at r.t. for 6 h. The volume was concentrated to ca. 1–2 mL by evaporation under reduced pressure and addition of diethyl ether (30 mL) gave a white solid, **6**. The product was collected by filtration and dried in vacuo (yield: 0.42 g, 89%; mp: >250 °C). ^{1}H NMR (δ in ppm rel. to TMS, J Hz, in $CDCl_3$): 7.38 [d, 1H, $^3J_{H-H}$ = 7.4 Hz, **H**-3]; 7.18 [t, 1H, $^3J_{H-H}$ = 7.6 Hz, **H**-4]; 7.12 [d, 1H, $^3J_{H-H}$ = 6.6 Hz, **H**-6]; 6.78 [t, 1H, $^3J_{H-H}$ =7.4 Hz, **H**-5]; 6.10 [d, 1H, J = 8.2 Hz, ArN**H**–]; 4.08 [dd, 2H, J = 5.6 and 5.8 Hz, C**H**$_2$–]; 2.16 [d, 1H, J = 1.4 Hz, ArCH_2N**H**–]; 1.82 (m, 4H, NH-P(C**H**$(CH_3)_2$), 1.07 (m, 24H, NH-P(CH(C**H**$_3)_2$). ^{13}C-{^{1}H} NMR (δ, $CDCl_3$): 128.2, 128.4, 127.1, 126.3, 124.2, 123.1 (carbons of phenyl), 52.0 (**C**H$_2$–); 32.06 (d, $^1J_{P-C}$ = 18.4 Hz, P**C**H$(CH_3)_2$), 30.42 (d, $^1J_{P-C}$ = 17.6 Hz, P**C**H$(CH_3)_2$), 18.82 (d, $^2J_{P-C}$ = 2.3 Hz, PCH(**C**H$_3)_2$), 17.39 (d, $^2J_{P-C}$ = 2.1 Hz, PCH(**C**H$_3)_2$), 17.22 (d, $^2J_{P-C}$ = 2.7 Hz, PCH(**C**H$_3)_2$), 17.14 (d, $^2J_{P-C}$ = 2.4 Hz, PCH(**C**H$_3)_2$); ^{31}P-{^{1}H} NMR (δ, DMSO): 72.82 [d, J_{PtP}: 4092 Hz, CH_2NH**P**(iPr)$_2$]; 61.71 [d, J_{PtP}: 3907 Hz, ArNH**P**(iPr)$_2$]. Selected IR, υ (cm^{-1}): 936 (P-N), 1440 (P-Ph), 3322 (N-H). Selected IR, υ (cm^{-1}): 931 (P-N), 1448 (P-Ph), 3314 (N-H). $C_{19}H_{36}N_2P_2PtCl_2$ (620.39 g/mol): calcd. C 36.78, H 5.85, N 4.52; found C 36.67, H 5.78, N 4.47%.

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References

1. McAuliffle, C. A. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, UK, 1987, *2*, pp. 989–1060.
2. Drent, E.; Van-Brockhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235–251.
3. Joshi, M. J.; Thornburn, S. J.; Retting, S. J.; James, B. R.; *Inorg. Chim. Acta.* **1992,** *283*, 198–200.

4. Kang, Y. B.; Pabel, M.; Pathak, D. D.; Willis, A. C.; Wild, S. B. *Main Group Chem.* **1995**, *1*, 89–98.
5. Ugo, R. *Aspects of Homogeneous Catalysis, A Series of Advances*; Reiedel: Dordrecht, Holland, 1974.
6. Benito-Garagorni, D.; Bocokic, V.; Mereiter, K.; Kirchner, K. *Organometallics* **2006**, *25*, 3817–3823.
7. Biricik, N.; Durap, F.; Kayan, C.; Gümgüm, B. *Heteroatom Chem.* **2007**, *18*, 613–616.
8. Ittel, S.; Parshall, G. *Homogeneous Catalysis, the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, NY, USA, 1992.
9. Appleby, T.; Aucott, S. M.; Clarke, M. L.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2002**, *21*, 2639–2645.
10. Aydemir, M.; Baysal, A.; Gürbüz, N.; Özdemir, İ.; Gümgüm, B.; Özkar, S.; Çaylak, N.; Yıldırım, L. T. *Appl. Organomet. Chem.* **2010**, *24*, 17–24.
11. Akba, O.; Durap, F.; Aydemir, M.; Baysal, A.; Gümgüm, B.; Özkar, S. *J. Organomet. Chem.* **2009**, *694*, 731–736.
12. Gümgüm, B.; Biricik, N.; Durap F.; Özdemir, İ.; Gürbüz, N.; Ang, W. H.; Dyson, P. J. *Appl. Organomet. Chem.* **2007**, *21*, 711–715.
13. Aydemir, M.; Baysal, A.; Şahin, E.; Gümgüm, B. *Inorg. Chim. Acta* **2011**, *378*, 10–18.
14. Kayan, C.; Biricik, N.; Aydemir, M. *Trans. Met. Chem.* **2012**, *36*, 513–520.
15. Kılıç, A.; Durap, F.; Aydemir, M.; Baysal, A.; Taş, E. *J. Organomet. Chem.* **2008**, *693*, 2835.
16. Elma, D.; Durap, F.; Aydemir, M.; Baysal, A.; Meriç, N.; Baysal, A.; Meriç, N.; Ak, B.; Turgut, Y.; Gümgüm, B. *J. Organomet. Chem.* **2013**, *729*, 46–52.
17. Baysal, A.; Aydemir, M.; Durap, F.; Gümgüm, B.; Özkar, S.; Yıldırım, L. T. *Polyhedron* **2007**, *26*, 3373–3378.
18. Slawin, A. M. Z.; Wheatley, J.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2005**, 713–720.
19. Ly, T. Q.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 1611–1616.
20. Balakrishna, M. S.; Krishnamurthy, S. S.; Murugavel, R.; Netaji, M.; Mathews, I. I. *J. Soc., Dalton Trans.* **1993**, 477–482.
21. Zijs, E. J.; Van der Vlugt, J. I.; Tooke, D. M.; Spek, A. L.; Vogt, D. *J. Chem. Soc., Dalton Trans.* **2005**, 512–517.
22. Zuburi, M. R. I.; Slawin, A. M. Z.; Wainwright, M.; Woollins, J. D. *Polyhedron* **2002**, *21*, 1729–1736.
23. Zuburi, M. R. I.; Milton, H. L.; Cole-Hamilton, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2004**, *23*, 693–699.
24. Aydemir, M.; Baysal, A.; Gümgüm, B. *J. Organomet. Chem.* **2008**, *693*, 3810–3814.
25. Aydemir, M.; Durap, F.; Baysal, A.; Akba, O.; Gümgüm, B.; Özkar, S.; Yıldırım, L. T. *Polyhedron* **2009**, *28*, 2313–2320.
26. Majoumo-Mbe, F.; Lönnecke, P.; Novikova, E. V.; Below, G. P.; Hey-Hawkins, E. *J. Chem. Soc., Dalton Trans.* **2005**, 3326–3330.
27. Gaw, K. G.; Smith, M. B.; Slawin, A. M. Z. *New J. Chem.* **2000**, *24*, 429–435.
28. Slawin, A. M. Z.; Woollins, J. D.; Zhang, Q. *J. Chem. Soc., Dalton Trans.* **2001**, 621–632.
29. Aydemir, M.; Baysal, A.; Durap, F.; Gümgüm, B.; Özkar, S.; Yıldırım, L. T. *Appl. Organomet. Chem.* **2009**, *23*, 467–475.
30. Aydemir, M.; Baysal, A.; Özkar, S.; Gümgüm, B. *Inorg. Chim. Acta* **2011**, *367*, 166–172.
31. Aydemir, M.; Baysal, A.; Şahin, E.; Gümgüm, B.; Özkar, S. *Inorg. Chim. Acta* **2011**, *378*, 10–18.
32. Lindler, E.; Mohr, M.; Nachtigal, C.; Favzi, R.; Henkel, G. *J. Organomet. Chem.* **2000**, *595*, 166–167.
33. Lloyd-Williams, P.; Giralt, E.; *Chem. Soc. Rev.* **2001**, *30*, 145–147.
34. Bedford, R. B. *Chem. Commun.* **2003**, 1787–1796.
35. Najera, C.; Gil-Molto, J.; Karlström, S.; Falvello, L. R. *Org. Lett.* **2003**, *5*, 1451–1454.

36. Galon, B. J.; Kojima, R. W.; Kaner, R. B.; Diaconescu, P. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 7251–7254.

37. Trost, B. M.; Flemming, I.; Semmelhack M. F. *Comprehensive Organic Synthesis, vol. 4*; Pergamon Press: Oxford, UK, 1991.

38. Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2–7.

39. Brunner, H.; Le Cousturier de Courey, N.; Genet, J. P. *Tetrahedron Lett.* **1999**, *40*, 4815–4818.

40. Herrmann, W. A.; Broßmer, C.; Öfele, K.; Reisinger, C.; Riermeier, T.; Beller, M.; Fischer, H. *Angew. Chem.* **1995**, *107*, 1989–1992.

41. Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 47–55.

42. McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.

Supporting Information

1. The ^{31}P-{^{1}H} NMR spectra of diaminophosphine ligands and their transition metal complexes {Pd(II) and Pt(II)}.

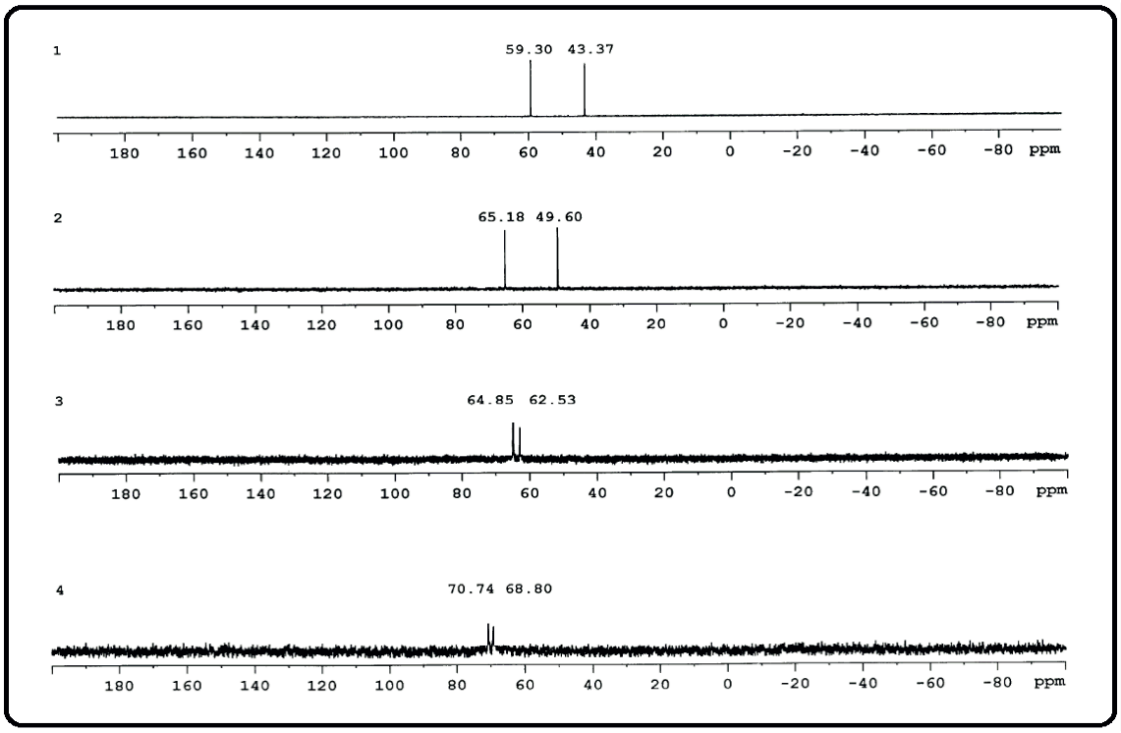

Figure 1. ^{31}P-{^{1}H} NMR spectra of *N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline (**1**), *N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline (**2**), {*N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline}dichloropalladium(II) (**3**), and {*N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl) aniline}dichloropalladium(II) (**4**).

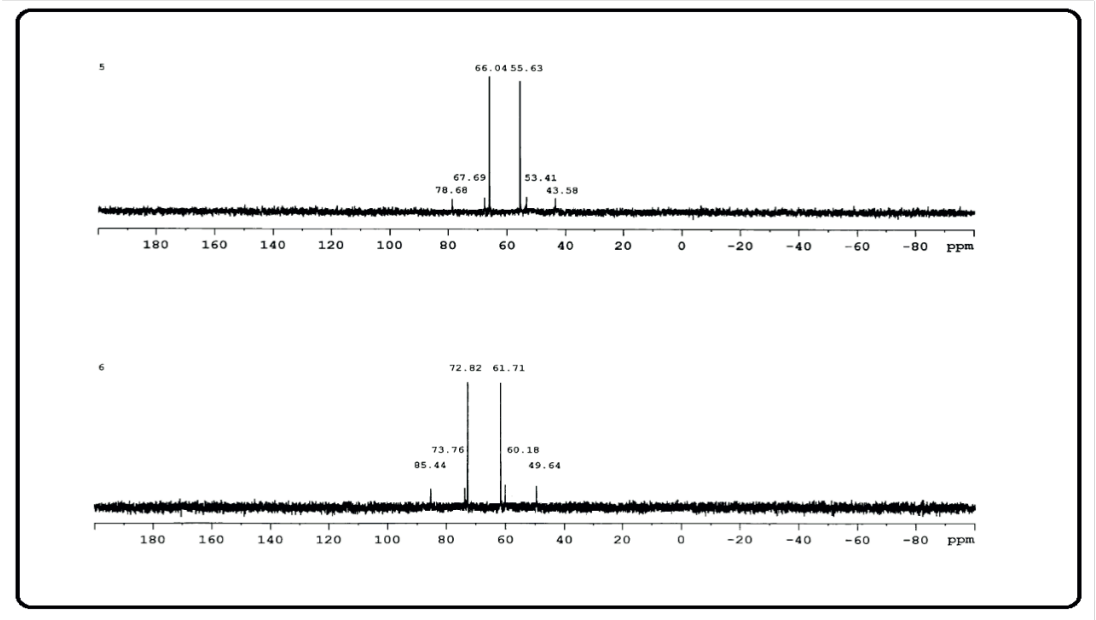

Figure 2. ^{31}P-{^{1}H} NMR spectra of {*N*,*N*'-bis(dicyclohexylphosphino)-2-(aminomethyl)aniline} dichloroplatinum(II) (**5**) and {*N*,*N*'-bis(diisopropylphosphino)-2-(aminomethyl)aniline} dichloroplatinum(II) (**6**).