



Synthesis and characterizations of *N,N,N',N'*-tetrakis(diphenylphosphino)ethylenediamine derivatives: Use of palladium(II) complex as pre-catalyst in Suzuki coupling and Heck reactions

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ABSTRACT

Oxidation of *N,N,N',N'*-tetrakis(diphenylphosphino)ethylenediamine (**1**) with elemental sulfur and selenium gives the corresponding sulfide and selenide, respectively, [(Ph₂P(E))₂NCH₂CH₂N(P(E)Ph₂)₂] (E: S **1a**, Se **1b**). Complexes of **1** [(M₂Cl₄){(Ph₂P)₂NCH₂CH₂N(PPh₂)₂}] (M: Ni(II) **1c**, Pd(II) **1d**, Pt(II) **1e**) were prepared by the reaction of **1** with NiCl₂ or [MCl₂(COD)] (M = Pd, Pt). The new compounds were characterized by NMR, IR spectroscopy and elemental analysis. The catalytic activity of Pd(II) complex **1d** was tested in the Suzuki coupling reaction and Heck reaction. The palladium complex **1d** catalyses the Heck reaction between styrene and aryl bromides as well as Suzuki coupling reaction between phenylboronic acid and aryl bromides affording stilbenes and biphenyls in high yield, respectively.

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1. Introduction

There is enormous interest in the chemistry of bis(phosphino)amines bearing P–N–P backbone due to their wide range of applications in coordination chemistry [1–5]. Small variations in the electron density on the donor atoms of these ligands can cause significant changes in their coordination behaviors and structural features of resulting complexes [6–10]. Potentially this ligand family is extremely attractive since their various structural modifications are accessible via simple P–N bond formation. The improved catalytic activity of transition metal complexes with hemilabile ligands has been extensively reviewed [11–14]. There has been recently increasing interest in the synthesis of highly active transition metal based catalysts derived from aminophosphines that can be used in different catalytic reactions including allylic alkylation [15–18], amination [19–21], Heck [22–30], Suzuki [31–35], hydroformylation [36–39] and hydrogenation reactions [40–44]. Palladium containing catalysts serve as straightforward and extremely powerful reagents for the carbon–carbon bond formation [45–47]. Among palladium-catalyzed coupling processes, reaction of aryl halides with olefins (the Heck reaction) and with boronic acid (the Suzuki coupling reaction) are emerging as a favorite methods for the C–C bond formation and have found

widespread applications in synthetic organic chemistry and materials science [48,49].

Herein, we report the synthesis of chalcogenides (sulfide and selenide) as well as the (Ni²⁺, Pd²⁺ and Pt²⁺) complexes of *N,N,N',N'*-tetrakis(diphenylphosphino)ethylenediamine **1**. We also report on the catalytic activity of palladium(II) complex of **1** as pre-catalysts in the Suzuki coupling reactions and Heck reactions. The compounds were fully characterized by elemental analysis, IR, ¹H NMR, ³¹P–{¹H} NMR spectroscopy.

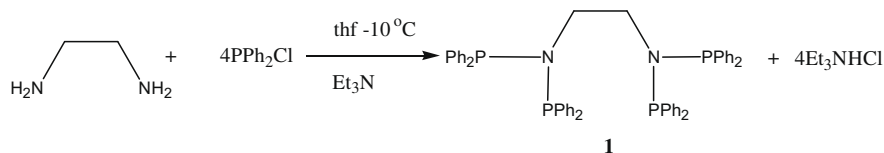
2. Results and discussion

N,N,N',N'-Tetrakis(diphenylphosphino)ethylenediamine, [(Ph₂P)₂NCH₂CH₂N(PPh₂)₂] (**1**) was prepared from the reaction of H₂N–CH₂CH₂–NH₂ and 4 equiv. Ph₂PCl in thf at –10 °C (Scheme 1) and identified by NMR spectral data as reported elsewhere [50].

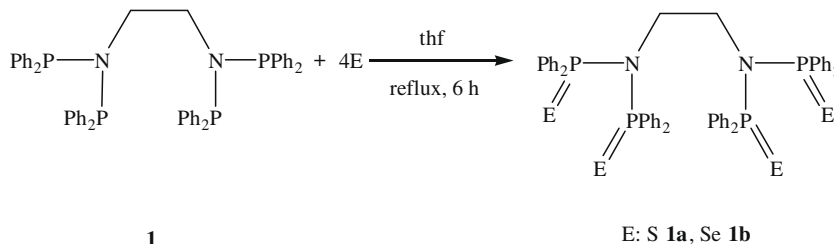
Oxidation of **1** with elemental sulfur and selenium gave the corresponding sulfide **1a** and selenium **1b**, respectively (Scheme 2). Oxidation with sulfur or selenium had to be carried out at elevated temperatures, as expected because elemental sulfur and selenium are weaker oxidizing agents than hydrogen peroxide, especially towards the phosphorus atoms with bulky phenyl groups [51–54]. *N,N,N',N'*-tetrakis(diphenylphosphino)ethylenediamine have already been reported in our previous paper [50].

The oxidation reactions were followed by monitoring the changes in ³¹P–{¹H} NMR signal. The ³¹P NMR spectrum of **1** shows

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Scheme 1. Aminolysis reaction of ethylenediamine with Ph_2PCl in thf.



Scheme 2. Oxidation reaction of **1** with elemental sulfur and selenium.

a singlet resonance at $\delta = 61.3$ ppm. Oxidation of **1** with elemental sulfur and selenium in thf gave the corresponding sulfide and selenide, respectively: $(\text{Ph}_2\text{P}(\text{E}))_2\text{NCH}_2\text{CH}_2\text{N}(\text{P}(\text{E})\text{Ph}_2)_2$ (E: S **1a**, Se **1b**). In $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum, **1a** shows a singlet at $\delta = 69.6$ ppm while **1b** exhibits a singlet at $\delta = 72.3$ ppm, accompanied with selenium satellites ($J(^{31}\text{P}\{-^{77}\text{Se}\})$: 784 Hz).

The reactions of **1** with 2 equiv. of anhydrous NiCl_2 in the mixed solvents of CH_2Cl_2 –methanol (1:1 in volume) at room temperature led to the formation of the corresponding dinuclear nickel(II) diphosphinoamine complex **1c** in high yield (Scheme 3). The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **1c** exhibits only a singlet at 54.1 ppm which is within the range expected for structurally similar complexes [55].

In the reaction of **1** with 2 equiv. $[\text{M}(\text{cod})\text{Cl}_2]$ (M = Pd, Pt; cod = 1,5-cyclooctadiene) in thf solution, cod is replaced by $(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2$ coordinating to each of two metal centers as bidentate ligand and yielding the respective $[\text{Cl}_2\text{M}(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2\text{-MCl}_2]$ complexes **1d**, **1e** (M = Pd, Pt, respectively) (Scheme 4).

The palladium complex **1d** shows a singlet at 35.9 in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum which is shifted upfield ($\Delta\delta$: -25.9 ppm) compared to the free ligand **1** (61.3 ppm) [50]. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of the **1e** exhibits a signal at 16.5 ppm accompanied by the ^{195}Pt satellite ($J(^{195}\text{Pt}\{-^{31}\text{P}\}) = 3392$ Hz) which is also shifted upfield ($\Delta\delta$: -44.4 ppm) compared to the free ligand **1** (61.3 ppm). The large $^1J(^{135}\text{Pt}\{-^{31}\text{P}\})$ coupling constant of 3392 Hz for **1e** is indicative of a *cis* arrangement of phosphines around a platinum(II) centre [56]. The $^{31}\text{P}\{-^1\text{H}\}$ NMR chemical shifts of complexes **1d** and **1e** are within the range expected for structurally similar complexes having P–N–P bond.

All the three complexes **1c**, **1d**, **1e** could be isolated as analytically pure solid material and characterized by elemental analysis, IR, ^1H NMR and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy. Their ^{13}C NMR spectra could not be attained due to the low solubility of the complexes in all common solvents.

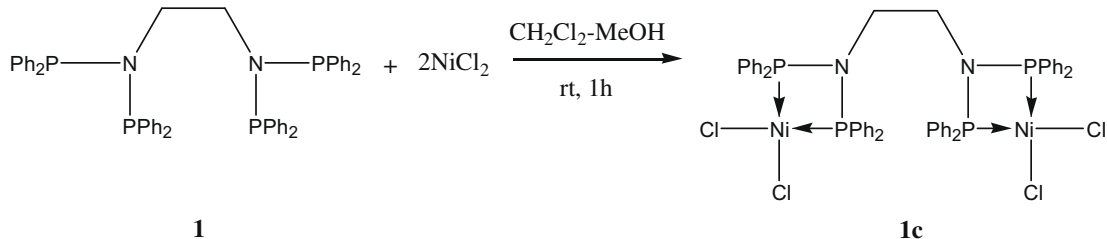
3. The Suzuki coupling reactions

Palladium-catalysed coupling via Suzuki reaction has become, over the last ten years, the method of choice for biaryl and heterobiaryl synthesis [57,58]. These moieties are widely present in numerous classes of organic compounds, such as natural product, pharmaceuticals, agrochemicals and ligands for asymmetric synthesis and in new materials, such as liquid crystals [59]. The reaction generally results in excellent yields when performed at temperatures of 80–100 °C with aryl iodides and bromides. Recently, the Suzuki reaction of aryl chlorides catalysed by palladium-tertiary phosphine [60] systems has been studied extensively due to economically attractive nature of the starting materials.

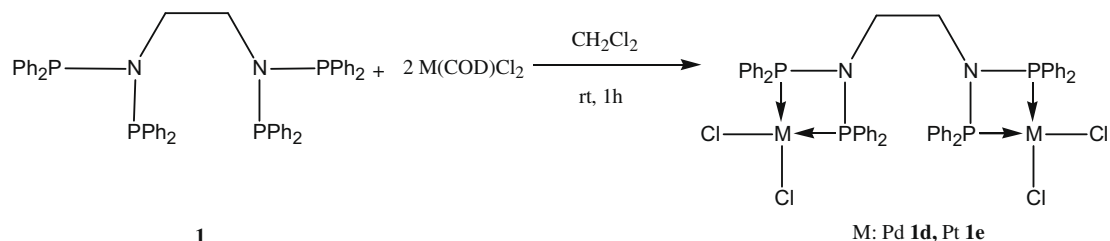
In order to survey the reaction parameters for the catalytic Suzuki reaction, we examined Cs_2CO_3 , K_2CO_3 and K^tOBU as base and DMF and dioxane as solvent. We found that the reaction performed in dioxane, with Cs_2CO_3 as the base at 80 °C appeared to provide the best results. We initially tested the catalytic activity of the complex **1d** for the coupling of *p*-bromoacetophenone with phenylboronic acid and the control experiments showed that the coupling reaction did not occur in the absence of the catalyst. Under these conditions, *p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromoanisole and *p*-bromotoluene react with phenylboronic acid in good yields (Table 1).

4. The Heck coupling reactions

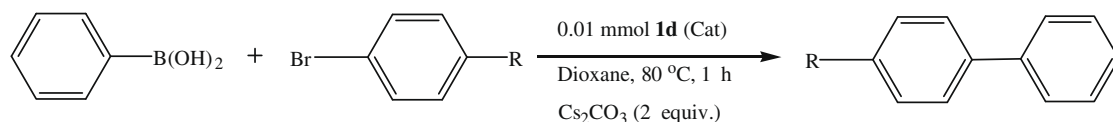
Heck reactions, typically catalysed by palladium complexes in solution, are of growing interest in organic and fine-chemical synthesis [61]. In the last thirty years, the Heck reactions has been extensively explored and used in several diverse areas such as the preparation of hydrocarbons, novel polymers, pharmaceuticals,



Scheme 3. The reactions of **1** with 2 equiv. anhydrous NiCl_2 .

**Scheme 4.** The reactions of **1** with 2 equiv. M(COD)Cl₂.**Table 1**

The Suzuki coupling reactions of aryl bromides with phenylboronic acid.



Entry	R	Conversion (%)	Yield (%)
1	COCH ₃	98.3	97.6
2	CHO	99.4	98.8
3	H	92.3	90.8
4	OCH ₃	54.6	53.8
5	CH ₃	59.6	57.2

Reaction conditions: 1.0 mmol of *p*-R-C₆H₄Br aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol Cs₂CO₃, 0.01 mmol **1d** (Cat.), dioxane 3.0 (mL). Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 80 °C, 1 h.

agrochemicals, dyes and new enantioselective syntheses of natural products, because of the mild conditions required for the reaction [62–66]. The Heck reaction [67,68] has been shown to be very useful for the preparation of disubstituted olefins. The rate of coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Generally, the Heck reactions conducted with tertiary phosphine complexes require high temperatures (higher than 120 °C) and polar solvents. For the choice of base, we surveyed Cs₂CO₃, K₂CO₃ and K^tOBu. Finally, we found that use of 1.0 mol% **1d** and 2 equiv. K₂CO₃ in DMF at 110 °C led to the highest conversion within 1 h. We initially tested the catalytic activity of **1d** for the coupling of 4-bromoacetophenone with styrene.

A control experiment indicated that the coupling reaction did not occur in the absence of **1d**. Under the predetermined reaction conditions, a wide range of aryl bromides bearing electron-releasing and electron-withdrawing groups reacted with styrene, affording the coupled products in excellent yields. As expected,

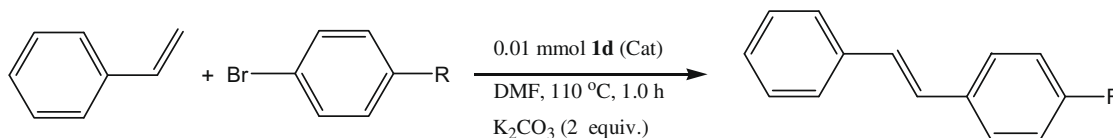
electron-deficient bromides were beneficial for the conversions (Table 2).

Only the palladium complex **1d** was found to be catalytically active in Suzuki coupling and Heck reactions, while nickel and platinum complexes **1c** and **1e** exhibited no catalytic activities in line with the previous observations [69]. This might be attributed to the different metal-ligand bond strengths in palladium complexes from those in nickel and platinum complexes. Depending on the type of coupling reaction, high yields of the desired products were obtained but using **1d** as catalyst. The palladium complex **1d** appears to be a more efficient catalyst for the Heck reactions of aryl bromides than that of aryl chlorides (yields 0.5–20%).

The complex **1d** exhibits relatively higher activity in both Suzuki and Heck reactions of aryl bromides with electron-withdrawing substituents than that with electron-releasing substituent on the aryl bromides in both reactions. It is generally believed that electron-withdrawing groups (R = EWG) on the aryl or alkenyl moiety will enhance the oxidative addition rate by weakening the Ar–X

Table 2

The Heck coupling reactions of aryl bromides with styrene.



Entry	R	Conversion (%)	Yield (%)
1	COCH ₃	96.6	92.1
2	CHO	95.7	93.4
3	H	63.6	59.2
4	OCH ₃	54.7	48.1
5	CH ₃	56.9	53.8

Reaction conditions: 1.0 mmol of *p*-R-C₆H₄Br aryl bromide, 1.5 mmol of styrene, 2.0 mmol K₂CO₃, 0.01 mmol Pd (Cat.), DMF 3.0 (mL). Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 110 °C, 1.0 h.

bond [70–72]. $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy suggests that in the both catalytic reactions aminophosphine ligand decomposes to $\text{PPh}_2(\text{O})\text{H}$ as indicated by signal at $\delta = 20$ ppm [73–75].

5. Conclusion

The dinuclear nickel, palladium and platinum complexes as well as the sulfide and selenide chalcogenides of N,N,N',N' -tetrakis(diphenylphosphino)ethylenediamine were prepared and characterized. Because of the strength of the Pt–C bonds, Pt(II)-bis(phosphino)amine **1e** system exhibited no catalytic activity [76]. Only the palladium complex was found to show catalytic activity in both the Suzuki coupling and Heck reactions of aryl bromides. In both cases, the catalytic activity of complex **1d** was found to be higher in reactions of aryl bromides with electron-withdrawing substituent than that with electron-releasing substituent. The catalytic activity and the yield of coupling reactions could be controlled over a wide range by variation of the coupling parameters.

6. Experimental

All reactions and manipulations were performed under argon atmosphere unless otherwise stated. $\text{Ph}_2\text{P}\text{Cl}$, ethylenediamine were purchased from Fluka and anhydrous nickel, palladium and platinum salts were purchased from Aldrich and used as received. Analytical grade and deuterated solvents were purchased from Merck. Solvents were dried using the appropriate reagents and distilled prior to use. Infrared spectra were recorded from KBr pellet in the range $4000\text{--}400\text{ cm}^{-1}$ on a Mattson 1000 ATI UNICAM FT-IR spectrometer. NMR spectra were taken on Bruker AC 400 spectrometer (400.1 MHz for ^1H , 100.6 MHz for ^{13}C , and 162.0 MHz for ^{31}P). Chemical shifts were referenced to the internal TMS for ^1H and ^{13}C , and to the signal of external 85% H_3PO_4 in capillary for ^{31}P . GC analyses were performed on a HP 6890N Gas Chromatograph equipped with a capillary column (5% diphenyl, 95% dimethylsiloxane) (30 m \times 0.32 mm \times 0.25 μm). Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were determined on a Gallenkamp Model apparatus with open capillaries.

The starting materials [$\text{MCl}_2(\text{COD})$] ($\text{M} = \text{Pd}, \text{Pt}$, COD = 1,5-cyclooctadiene) were prepared according to literature procedures [77,78]. N,N,N',N' -tetrakis(diphenylphosphino)ethylenediamine **1** and N,N,N',N' -tetrakis(diphenylselenophosphino)ethylenediamine were prepared following the procedure given in the previous study [50].

6.1. Synthesis of N,N,N',N' -tetrakis(diphenylphosphino)ethylenediamine

$[(\text{Ph}_2\text{P}(\text{S}))_2\text{NCH}_2\text{CH}_2\text{N}(\text{P}(\text{S})\text{Ph}_2)_2]$ (**1a**)

To a solution of N,N,N',N' -tetrakis(diphenylphosphino)ethylenediamine **1** (50 mg, 0.0628 mmol) in thf (20 mL), S_8 (8.0 mg, 0.251 mmol) was added and this mixture was refluxed for 6 h. The hot solution was filtered through Celite to remove a small amount of insoluble material. Volume of the filtrate solution was reduced to ca. 1–2 mL by evaporating the volatiles in vacuum. Addition of *n*-hexane (20 mL) to this solution gave **1a** as white solid which was collected by suction filtration. $(\text{Ph}_2\text{P}(\text{S}))_2\text{NCH}_2\text{CH}_2\text{N}(\text{P}(\text{S})\text{Ph}_2)_2$ (**1a**) 33 mg (57% yield); m.p. $>250^\circ\text{C}$ (dec.). Anal., Calc. for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{P}_4\text{S}_4$: C, 64.92; H, 4.80; N, 3.03. Found: C, 64.61; H, 4.51; N, 2.93%. ^1H NMR (ppm rel. to TMS in CDCl_3) δ : 3.66 (s, 4H, N- CH_2 -), 7.21 (m, 16H, *o*-hydrogens of phenyls), 7.34 (m, 8H, *p*-hydrogens of phenyls) and 7.66 (m, 16H, *m*-hydrogens of phenyls). ^{13}C NMR (ppm in CDCl_3) δ : 49.48 (N- CH_2 -), 127.74 (d, $J(^{31}\text{P}\text{--}^{13}\text{C})$: 14 Hz, *o*-carbons of phenyls),

131.31 (s, *p*-carbons of phenyls), 132.33 (s, *i*-carbons of phenyls), 133.27 (d, $J(^{31}\text{P}\text{--}^{13}\text{C})$: 12 Hz, *m*-carbons of phenyls), assignment was based on the $^1\text{H}\text{--}^{13}\text{C}$ HETCOR spectrum. $^{31}\text{P}\{-^1\text{H}\}$ NMR (ppm rel. to H_3PO_4 in CDCl_3) δ : 73.1. Selected IR (cm^{-1} from KBr pellet): $\nu_{\text{N-P-N}}$: 881, $\nu_{\text{P-S}}$: 650.

6.2. Synthesis of N,N,N',N' -tetrakis(diphenylselenophosphino)ethylenediamine

$[(\text{Ph}_2\text{P}(\text{Se}))_2\text{NCH}_2\text{CH}_2\text{N}(\text{P}(\text{Se})\text{Ph}_2)_2]$ (**1b**)

To a solution of N,N,N',N' -tetrakis(diphenylphosphino)ethylenediamine (50 mg, 0.0628 mmol) in thf (20 mL), grey Se (19.8 mg, 0.251 mmol) was added and this mixture was refluxed for 6 h. The volume of the reaction solution was reduced to ca. 1–2 mL by evaporating the volatiles in vacuum. Addition of *n*-hexane (20 mL) to this solution gave **1b** as white solid which was collected by suction filtration. $(\text{Ph}_2\text{P}(\text{Se}))_2\text{NCH}_2\text{CH}_2\text{N}(\text{P}(\text{Se})\text{Ph}_2)_2$ 38 mg (55% yield); m.p. 156–158 $^\circ\text{C}$. Anal., Calc. for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{P}_4\text{Se}_4$: C, 53.98; H, 3.99; N, 2.52. Found: C, 53.37; H, 3.78; N, 2.28%. ^1H NMR (ppm rel. to TMS in CDCl_3) δ : 3.73 (s, 4H, N- CH_2 -), 7.20 (m, 16H, *o*-hydrogens of phenyls), 7.32 (m, 8H, *p*-hydrogens of phenyls) and 7.73 (m, 16H, *m*-hydrogens of phenyls). ^{13}C NMR (ppm in CDCl_3) δ : 50.62 (N- CH_2 -), 127.75 (d, $J(^{31}\text{P}\text{--}^{13}\text{C})$: 13 Hz, *o*-carbons of phenyls), 131.45 (s, *p*-carbons of phenyls), 132.49 (s, *i*-carbons of phenyls), 133.88 (d, $J(^{31}\text{P}\text{--}^{13}\text{C})$: 11 Hz, *m*-carbons of phenyls), assignment was based on the $^1\text{H}\text{--}^{13}\text{C}$ HETCOR spectrum. $^{31}\text{P}\{-^1\text{H}\}$ NMR (ppm rel. to H_3PO_4 in CDCl_3) δ : 72.3, ($J(^{31}\text{P}\text{--}^{77}\text{Se})$: 784 Hz). Selected IR (cm^{-1} from KBr pellet): $\nu_{\text{N-P-N}}$: 887, $\nu_{\text{P-Se}}$: 567.

6.3. Synthesis of $\mu\text{-}N,N,N',N'$ -tetrakis(diphenylphosphino)ethylenediamine bis(dichloronickel(II))

(**1c**)

A solution of $(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2$ **1** (100 mg, 0.125 mmol) in CH_2Cl_2 (10 mL) was added to the solution of anhydrous NiCl_2 (33 mg, 0.25 mmol) in CH_3OH (10 mL). Upon stirring for 1 h at room temperature, the mixture was turned to dark red. The volume of the solution was reduced by evaporation of volatiles in vacuum to ca. 1–2 mL and addition of *n*-hexane (20 mL) gave **1c** as a red solid which was collected by suction filtration and dried in vacuum. $\text{Cl}_2\text{Ni}\text{--}(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2\text{--NiCl}_2$ 125 mg, (94% yield); m.p. 223 $^\circ\text{C}$ (dec.). Anal., Calc. for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{P}_4\text{Ni}_2\text{Cl}_4$: C, 56.87; H, 4.20; N, 2.65. Found: C, 56.57; H, 4.08; N, 2.48%. ^1H NMR (ppm rel. to TMS in CDCl_3) δ : 6.88–7.71 (m, 40H, phenyl hydrogens), 3.63 (s, 4H, N- CH_2 -). ^{13}C NMR spectrum could not be taken due to the low solubility of **1c** in all common solvents. $^{31}\text{P}\{-^1\text{H}\}$ NMR (ppm rel. to H_3PO_4 in CDCl_3) δ : 54.1 (s). Selected IR (cm^{-1} from KBr pellet): $\nu_{\text{N-P-N}}$: 888.

6.4. Synthesis of $\mu\text{-}N,N,N',N'$ -tetrakis(diphenylphosphino)ethylenediamine bis(dichloropalladium(II))

(**1d**)

A solution of $\text{Pd}(\text{COD})\text{Cl}_2$ (24 mg, 0.088 mmol) in CH_2Cl_2 (5 mL) was added to the solution of $(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2$ **1** (35 mg, 0.044 mmol) in CH_2Cl_2 (10 mL) and mixture was stirred for 1.5 h at room temperature. Volume of the solution was reduced by evaporation of volatiles in vacuum to ca. 1–2 mL and addition of diethyl ether (20 mL) gave **1d** as yellow solid which was collected by suction filtration and dried in vacuum. $\text{Cl}_2\text{Pd}\text{--}(\text{Ph}_2\text{P})_2\text{NCH}_2\text{CH}_2\text{N}(\text{PPh}_2)_2\text{--PdCl}_2$ 45 mg, (89% yield); m.p. 300 $^\circ\text{C}$ (dec.). Anal., Calc. for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{P}_4\text{Pd}_2\text{Cl}_4$: C, 52.16; H, 3.85; N, 2.43. Found: C, 51.94; H, 3.78; N, 2.38%. ^1H NMR (ppm rel. to TMS in $\text{DMSO-}d_6$) δ : 7.45–7.75 (m, 40H, phenyl hydrogens), 3.70 (s, 4H, N- CH_2 -). ^{13}C NMR spectrum could not be taken due to the low solubility of **1d** in all common solvents. $^{31}\text{P}\{-^1\text{H}\}$ NMR (ppm

rel. to H₃PO₄ in DMSO-*d*₆) δ: 35.9 (s). Selected IR (cm⁻¹ from KBr pellet): ν_{N-P-N}: 889.

6.5. Synthesis of μ-N,N,N',N'-tetrakis(diphenylphosphino)ethylenediamine bis(dichloroplatinum(II)) (1e)

A solution of Pt(COD)Cl₂ (33 mg, 0.088 mmol) in CH₂Cl₂ (5 mL) was added to the solution of (Ph₂P)₂NCH₂CH₂N(PPh₂)₂ **1** (35 mg, 0.044 mmol) in CH₂Cl₂ (10 mL) and mixture was stirred for 1.5 h at room temperature. Volume of the solution was reduced by evaporation of volatiles in vacuum to ca. 1–2 mL and addition of diethyl ether (20 mL) gave **1e** as yellow solid which was collected by suction filtration and dried in vacuum. Cl₂Pt-(Ph₂P)₂NCH₂CH₂N(PPh₂)₂-PtCl₂ 39 mg, (67% yield); m.p. 300 °C (dec.). Anal., Calc. for C₅₀H₄₄N₂P₄Pt₂Cl₄: C, 45.20; H, 3.34; N, 2.11. Found: C, 44.92; H, 2.99; N, 1.89%. ¹H NMR (ppm rel. to TMS in DMSO-*d*₆) δ: 7.39–8.32 (m, 40H, phenyl hydrogens), 3.60 (s, 4H, N-CH₂-). ¹³C NMR spectrum could not be taken due to the low solubility of **1e** in all common solvents. ³¹P-{¹H} NMR (ppm rel. to H₃PO₄ in DMSO-*d*₆) δ: 16.5, J_(Pt-P): 3392 Hz. Selected IR (cm⁻¹ from KBr pellet): ν_{N-P-N}: 887.

7. General procedure for the Suzuki coupling reactions

Suzuki coupling reactions were conducted as follows: μ-N,N,N',N'-Tetrakis(diphenylphosphino)ethylenediaminebis(dichloropalladium(II)) (**1d**) (0.01 mmol), arylbromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs₂CO₃ (2.0 mmol) and 1,4-dioxane (3 mL) were put into a small Schlenk tube and mixture was heated at 80 °C for 1 h. The progress of the reaction was monitored by GC. Upon completion, the mixture was cooled, the product 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 by NMR and GC, and yields are based on arylbromide.

8. General procedure for the Heck coupling reactions

Heck coupling reactions were conducted as follows: μ-N,N,N',N'-tetrakis(diphenylphosphino)ethylenediaminebis(dichloropalladium(II)) (**1d**) (0.01 mmol), arylbromide (1.0 mmol), styrene (1.5 mmol), K₂CO₃ (2.0 mmol) and DMF (3 mL) were put into a Schlenk tube and the mixture was heated to 110 °C for 1.0 h. The progress of the reaction was monitored by GC. Upon completion, the mixture was cooled, and the product 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 by NMR and GC, and yields are based on arylbromide.

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