Synthesis and characterization of tris{2-(*N*,*N*-bis(diphenylphosphino) aminoethyl} amine derivatives: Application of a palladium(II) complex as a pre-catalyst in the Heck and Suzuki cross-coupling reactions

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ABSTRACT

The polydendate bis(phosphino)amine, tris{2-(*N*,*N*-bis(diphenylphosphino)aminoethyl}amine **1** has been prepared in a single step from the reaction of tris(2-aminoethyl)amine with six equivalents of PPh$_2$Cl in the presence of NEt$_3$ in THF. Oxidation of **1** with aqueous H$_2$O$_2$, elemental sulfur or grey selenium gave the corresponding oxide, sulfide or selenide derivatives. [{(P(E)Ph$_2$)$_2$NCH$_2$CH$_2$)$_3$N] (E: **2a** O, **2b** S, **2c** Se), respectively. Reaction of [{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] with 3 equiv. of PdCl$_2$(cod) or PtCl$_2$(cod) gave the corresponding chelate complexes, [Pd$_3$Cl$_6$**1**] or [Pt$_3$Cl$_6$**1**]. The new compounds were fully characterized by NMR, IR spectroscopy and elemental analysis. The catalytic activity of the Pd(II) complex was tested in the Suzuki coupling and Heck reactions. The Pd(II) complex catalyzed the Suzuki coupling and Heck reaction affording biphenyls and stilbenes, respectively, in high yields.

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1. Introduction

There is immense interest in the development of new phosphorus(III) ligands for various applications principally those of homogeneous metal-catalyzed reactions [1]. It is without a doubt that tertiary mono- and diphosphines are the most extensively used ligands throughout inorganic and organometallic chemistry [2–6]. The coordination chemistry of bis(phosphino)amines, RN(PR$_2$)$_2$, has attracted considerable interest in recent years, due to their chemical and structural proximity to the widely used Ph$_2$PCH$_2$PPh$_2$, [bis(diphenylphosphino)methane] [7,8]. Compared to diphosphines with the P–C–P linkage, bis(phosphine)amines P–N–P skeletons have proved to be much more versatile ligands, and varying the substituents on both the P- and N-centers gives rise to changes in the P–N–P angle and conformation around the P-centers [9,10]. Small variations in these ligands can cause significant changes in their coordination behaviour and the structural features of the resulting complexes [11]. This feature enables the synthesis of a wide range of four membered ring systems containing transition metals such as Cu, Mo, Ni, Pd, Pt and Ru which have potential uses in catalysis [12–14]. There has been recently an increasing interest in the synthesis of new and highly active transition metal based catalysts derived from aminophosphines which can be used in different catalytic reactions including allylic alkylation [15–18], amination [19–21], Heck [22–28], Suzuki [29–33], and hydrogenation reactions [34–38].

During the final quarter of the 20th century, among palladium-catalyzed coupling processes, reaction of aryl halides with olefins (the Heck reaction) and with boronic acid (the Suzuki reaction) have been emerging as favourite methods for formation of C–C bonds and have found widespread applications in synthetic organic chemistry and materials science [39]. The popularity stems in part from their tolerance of many functional groups, which allows them to be employed in the synthesis of highly complex molecules [40].

Herein, we describe the synthesis of a new bis(phosphino)-amine ligand and the corresponding oxides and transition metal complexes {Pd(II) and Pt(II)}. The compounds were fully characterized by elemental analysis, IR, ^{13}C NMR, ^{1}H NMR, ^{31}P-{^{1}H} NMR spectroscopy. We also report on the catalytic activity of Pd(II) complex of **1** as a pre-catalyst in the Heck and Suzuki cross-coupling reactions.

2. Results and discussion

Several methods have been developed for the synthesis of phosphinoamines and bis(phosphino)amines, and aminolysis seems to be most commonly used [41]. The new hexadentate phosphinoamine was prepared from the commercially available starting material tris(2-aminoethyl)amine by the aminolysis

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method [42–45]. It has been found that the solvent has a signifi-
cant influence on the reaction rate and on the reaction product.
[{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] was prepared by the aminolysis method
using diethyl ether or toluene as a solvent. However, this synthesis
route requires 24–36 h stirring at room temperature. With THF as a
solvent for the synthesis of **1**, the reaction was completed in 3 h at
room temperature. THF is also a more-appropriate solvent for this
aminolysis reaction because of the fact that all the components
formed in the reaction are soluble in the reaction media, also
allowing the reaction to be monitored by ^{31}P-{H} NMR spectros-
copy. In a typical reaction, 6 equiv. of PPh$_2$Cl were added slowly
to a THF solution of [{H$_2$NCH$_2$CH$_2$}$_3$N] containing Et$_3$N to afford
the hexadendate bis(phosphino)amine [{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] **1**
in high yield (93.5%) (Scheme 1). The ^{31}P-{H} NMR spectrum of
the reaction solution shows a singlet resonance at 62.0 ppm for
1, indicating that all of the six P-atoms are equivalent. The ^{31}P-
{H} NMR spectrum also displays two doublets at 16.5 ppm and
−21.3 ppm with a $^1J_{(PP)}$ value of 282 Hz indicating the formation
of iminobiphosphine [N(CH$_2$)$_2$N=PPh$_2$–PPh$_2$] structure. In addi-
tion, formation of PPh$_2$PPh$_2$ and P(O)Ph$_2$PPh$_2$ were observed, as
indicated by signals at δ −14.3 ppm as singlet and δ 34.4 ppm
and δ −23.7 ppm as doublets with $^1J_{(PP)}$ 220 Hz, respectively. These
by products were easily eliminated by washing the solid residue
with copious amounts of dry diethyl ether. Solution of **1** in CDCl$_3$,
prepared under anaerobic conditions, is unstable and decompose
gradually to give oxide [{(P(O)Ph$_2$)$_2$NCH$_2$CH$_2$}$_3$N] and bis(diphen-
ylphosphino)monoxide [P(O)Ph$_2$PPh$_2$] derivatives. **1** is also not sta-
ble in the solid state and decomposes rapidly on exposure to air or
moisture.

In the ^{1}H NMR spectrum of **1**, both of the methylene groups ap-
pear as triplets at 1.80 ppm (N*CH*$_2$CH$_2$NPPh$_2$, $^3J_{(H–H)}$ 7.6 Hz) and
3.59 ppm (NCH$_2$*CH*$_2$NPPh$_2$, $^3J_{(H–H)}$ 8.0 Hz). In addition, in the ^{13}C
NMR spectrum the ligand displays four aromatic resonances at

139.7 ppm (d, $^1J_{(31P-13C)}$ 13.0 Hz, *i*-carbons of phenyls), 132.8 ppm
(d, $^2J_{(31P13C)}$ 21.0 Hz, *o*-carbons of phenyls), 128.5 ppm (d,
$^3J_{(31P13C)}$ 6.0 Hz, *m*-carbons of phenyls) and 128.8 ppm (s, *p*-car-
bons of phenyls), together with two resonances at 55.3 ppm
(N*CH*$_2$CH$_2$NPPh$_2$) and 50.9 ppm (NCH$_2$*CH*$_2$NPPh$_2$) for methylene
carbons. The structure of **1** was further confirmed by using IR spec-
troscopy and microanalysis, and found to be in good agreement
with the theoretical values.

Oxidation of **1** with aqueous hydrogen peroxide, elemental sul-
fur or grey selenium gave the corresponding oxide **2a**, sulfide **2b** or
selenide **2c** derivatives, respectively (Scheme 1). With the excep-
tion of **2a** (δ 31.7 ppm) there is a negligible change in ^{31}P chemical
shift upon oxidation (δ 69.6 ppm for **2b**, δ 67.5 ppm, $^1J_{(PSe)}$ = 775 Hz
for **2c**). As expected, the oxidation reaction using aqueous hydro-
gen peroxide was very rapid for **2a** and takes place at ambient con-
ditions spontaneously. In addition a small amount of hydrolysis
product Ph$_2$P(O)H formed as evidenced by the signal at about
20.0 ppm in the ^{31}P-{^{1}H} NMR spectra. The structures of the oxi-
dized derivatives **2a–c** were further confirmed by ^{1}H, ^{13}C NMR,
IR spectroscopy and also microanalysis, and found to be in good
agreement with the theoretical values.

The coordination chemistry of **1** with selected transition-metals
(Pd and Pt) was explored. Reaction of **1** with MCl$_2$(cod) (where
M = Pd, Pt; cod = 1,5-cyclooctadiene) in THF afforded the corre-
sponding metal(II) complexes **3a** and **3b** in high yields (90%) and
(86%), respectively (Scheme 1). In both complexes **3a** and **3b**, coor-
dination to the metal center takes place preferentially at the phos-
phorus atoms. The ^{31}P-{^{1}H} NMR spectra **3a** and **3b** displayed
singlets at 30.7 ppm and 16.9 ppm in DMSO, respectively. The
chemical shifts of **3a** and **3b** are similar and within the expected
range of other reported structurally similar complexes [46–49].
For Pt complexes **3b**, the ^{31}P-^{195}Pt coupling constant (3400 Hz)
agrees with *cis* ligand arrangement [50]. In the ^{1}H NMR spectra
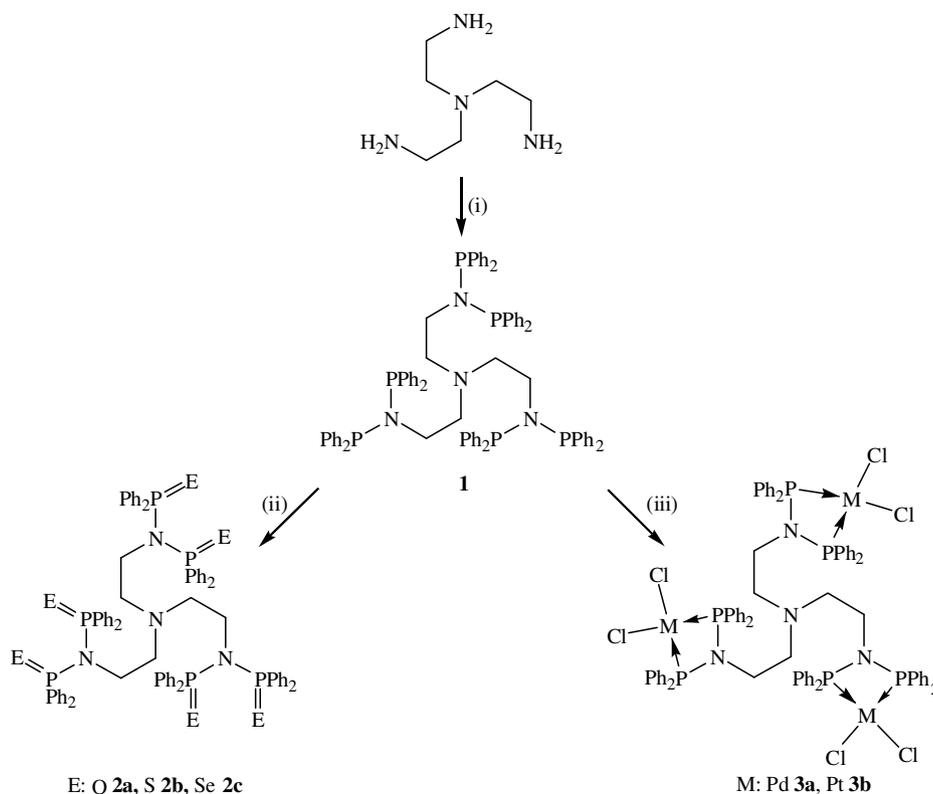
Scheme 1. Synthesis of tris{2-(*N,N*-bis(diphenylphosphino)aminoethyl)amine} and its derivatives.(i) Ph$_2$PCl, THF; (ii) H$_2$O$_2$, elemental S or grey Se, THF; (iii) [MCl$_2$[cod]]
(M = Pd or Pt), THF.

of **3a** and **3b**, the chemical shifts of the both of the CH_2 groups were slightly shifted to lower field with respect to the free ligand. Characteristic $J_{(31P-13C)}$ coupling constants of the carbons of the phenyl rings were observed in the ^{13}C NMR spectra, which are consistent with the literature values [51,52]. The complexes **3a and b** could be isolated as analytically pure solid materials and fully characterized by IR spectroscopy and microanalysis as well, and found to be in good agreement with the theoretical values.

3. The Suzuki coupling

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 70 °C for 1 h appeared to be best. We initially tested the catalytic activity of the complex **3a** 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 high yields (Table 1).

4. The Heck coupling

Generally, Heck reaction conducted with tertiary phosphine complexes requires high temperatures (higher than 120 °C) and polar solvents. For the choice of base, we surveyed Cs_2CO_3, K_2CO_3 and K^tOBu. Finally, we found that use of 0.01 mmol (1%) **3a** and 2 equiv. of K_2CO_3 in DMF at 100 °C led to the best conversion within 1 h. We initially tested the catalytic activity **3a** for the coupling of 4-bromoacetophenone with styrene and a control experiment indicated that the coupling reaction did not occur in the absence of **3a**. 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 excellent yields. As expected, electron-deficient bromides were beneficial for the conversions (Table 2).

5. Conclusion

In summary, a versatile and inexpensive bis(phosphino)amine ligand **1** and its derivatives including oxide, sulfide and selenide, as well as transition metal complexes containing Pd(II), Pt(II) centers were synthesized. All of these new compounds were characterized using NMR, IR spectroscopy and microanalysis. Complex **1** is a precursor for the different functionalization of aryl halides, in particular aryl bromides for Suzuki and Heck reaction. The catalytic behaviour of the **3a** was investigated in Suzuki coupling and Heck reactions. Because of the strength of the Pt–C bonds, Pt(II)-bis(phosphine)amine system **3b** exhibited no catalytic activity [53], but with Pd(II) complex, depending on the type of coupling reaction, excellent yields of the desired products were obtained. In general, **1**-based catalyst appears to be more efficient for the Heck reactions of aryl bromides, but its activity is much lower for the coupling of aryl chlorides (05–20%). The complex **3a** displayed relatively higher activity with electron-withdrawing substituents than electron-donating substituents on the aryl bromides in both reactions.

6. Experimental

All reactions and manipulations were performed under argon unless otherwise stated. Ph_2PCl and tris(2-aminoethyl)amine were purchased from Fluka and used directly. Analytical grade and deuterated solvents were purchased from Merck. The starting materials $[MCl_2(cod)]$ (M = Pd, Pt; cod = 1,5-cyclooctadiene) were prepared according to literature procedures [54–55]. Solvents were

Table 1
The Suzuki coupling reactions of aryl bromides with phenylboronic acid
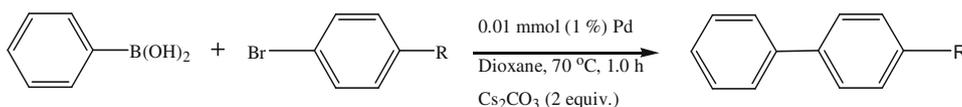
Entry	R	Conversion (%)	Yield (%)
1	COCH₃	96.4	94.8
2	CHO	98.0	98.3
3	H	63.3	61.6
4	OCH₃	60.6	59.7
5	CH₃	74.6	71.3

Reaction conditions: 1.0 mmol of *p*-R-C₆H₄Br aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol Cs₂CO₃, 0.01 mmol (1%) Pd (Cat.), dioxane 3.0 (mL). Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 70 °C. 1.0 h.

Table 2
The Heck coupling reactions of aryl bromides with styrene
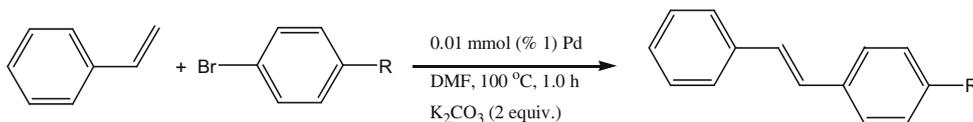
Entry	R	Conversion(%)	Yield(%)
1	COCH₃	94.6	90.6
2	CHO	98.7	96.3
3	H	71.3	87.7
4	OCH₃	56.3	55.3
5	CH₃	70.8	60.4

Reaction conditions: 1.0 mmol of *p*-R-C₆H₄Br aryl bromide, 1.5 mmol of styrene, 2.0 mmol K₂CO₃, 0.01 mmol (1%) 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; 100 °C, 1.0 h.

dried using the appropriate reagents and distilled prior to use. Infrared spectra were recorded as KBr pellet in the range 4000–400 cm^{-1} on a Mattson 1000 ATI UNICAM FT-IR spectrometer. ^{1}H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P-{^{1}H} NMR spectra (162.0 MHz) were recorded spectra on a Bruker Avance 400 spectrometer, with δ referenced to external TMS and 85% H$_3$PO$_4$, respectively. GC analyses were performed on a HP 6890N Gas Chromatograph equipped with capillary column (%5 biphenyl, %95 dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument; melting points by Gallenkamp Model apparatus with open capillaries.

6.1. Synthesis of tris{2-(N,N-bis(diphenylphosphino)amino-ethyl)amine} 1

Chlorodiphenylphosphine (2.74 g, 11.76 mmol) was added dropwise over a period 10 min to a solution of tris(2-amino-ethyl)amine (0.29 g, 1.96 mmol) and triethylamine (1.21 g, 11.76 mmol) in THF (50 mL) at room temperature with vigorous stirring. The mixture was stirred at room temperature for 3 h, and then the white precipitate (triethylamine hydrogen chloride) was filtered off under argon and the solvent removed in *vacuum*. The remaining solid was washed with cold diethyl ether (3 × 15 mL) and dried in *vacuum* to produce a clear, white solid compound **1** (yield: 2.32 g, 93.5%); mp. 71–73 °C). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.32 (m, 24H, *o*-protons of phenyls), 7.29 (d, 12H, *J* = 2.0 Hz, *p*-protons of phenyls), 7.26 (br, 24H, *m*-protons of phenyls), 3.01 (t, 6H, *J* = 8.0 Hz, NCH$_2$CH$_2$NPPh$_2$), 1.80 (t, 6H, $^3J_{H-H}$ = 7.6 Hz, NCH$_2$CH$_2$NPPh$_2$). ^{13}C-{^{1}H} NMR (CDCl$_3$) δ (ppm): 139.7 (d, $^1J_{31P-13C}$ = 13.0 Hz, *i*-carbons of phenyls), 132.8 (d, $^2J_{31P-13C}$ = 21.0 Hz, *o*-carbons of phenyls), 128.8 (s, *p*-carbons of phenyls), 128.5 (d, $^3J_{31P-13C}$ = 6.0 Hz, *m*-carbons of phenyls), 55.3 (NCH$_2$CH$_2$NPPh$_2$), 50.93 (NCH$_2$CH$_2$NPPh$_2$), assignment was based on the ^{1}H-^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR (CDCl$_3$) δ (ppm): 62.0 (s). Selected IR, υ (cm^{-1}): 869 (P–N–P), 1439 (P–Ph). C$_{78}$H$_{72}$N$_4$P$_6$: Calc. C, 74.87; H, 5.80; N, 4.48. Found: C, 74.51; H, 5.52; N, 4.17%.

6.2. Synthesis of tris{2-(N,N-bis(diphenyloxophosphino)aminoethyl)-amine} 2a

Aqueous hydrogen peroxide (30%, w/w, 0.09 mL, 0.96 mmol) was added drop wise to a suspension of [{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] (0.20 g, 0.16 mmol) in THF and the mixture was stirred for 2 h at room temperature. The volume was concentrated in *vacuum* to ca. 1–2 mL and addition *n*-hexane (25 mL) gave **2a** as a white solid which was collected by suction filtration (yield: 0.18 g, 83.6%); mp. 119–121 °C). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.73 (dd, 24H, *J* = 6.4 and 11.2 Hz), 7.41 (t, 12 Hz, *J* = 7.0 Hz, *p*-protons of phenyls), 7.31 (d, 24H, *J* = 6.8 Hz, *m*-protons of phenyls), 2.93 (t, 6H, $^3J_{H-H}$ = 8.0 Hz, NCH$_2$CH$_2$NPPh$_2$). 1.94 (t, 6H, $^3J_{H-H}$ = 7.6 Hz, NCH$_2$CH$_2$NPPh$_2$). ^{13}C-{^{1}H} NMR (CDCl$_3$) δ (ppm): 139.3 (d, $^1J_{31P-13C}$ = 12.6 Hz, *i*-carbons of phenyls), 132.5 (d, $^2J_{31P-13C}$ = 17.7 Hz, *o*-carbons of phenyls), 131.3 (s, *p*-carbons of phenyls), 128.7 (d, $^3J_{31P-13C}$ = 10.8 Hz, *m*-carbons of phenyls), 53.4 (NCH$_2$CH$_2$NPPh$_2$), 44.5 (NCH$_2$CH$_2$NPPh$_2$), assignment was based on the ^{1}H-^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR (CDCl$_3$) δ (ppm): 31.7 (s). Selected IR, υ (cm^{-1}): 912 (P–N–P), 1447 (P–Ph), 1200 (P=O). C$_{78}$H$_{72}$N$_4$P$_6$O$_6$: Calc. C, 69.54; H, 5.39; N, 4.16. Found: C, 69.17; H, 5.10; N, 3.93%.

6.3. Synthesis of tris{2-(N,N-bis(diphenylthiophosphino)aminoethyl)-amine} 2b

[{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] (0.20 g, 0.16 mmol) and elemental sulfur (0.04 g, 0.96 mmol) were heated to reflux in THF (25 mL) for 2 h.

After allowing mixture to cool room temperature, the white solid **2b** was collected by suction filtration and dried in *vacuum* (yield: 0.19 g, 82.3%); mp.: 135–137 °C). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.79 (dd, 24H, *J* = 7.2 and 14.2 Hz, *o*-protons of phenyls), 7.37 (t, 12H, *J* = 6.8 Hz, *p*-protons of phenyls), 7.28 (br, 24H, *m*-protons of phenyls), 3.13 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, NCH$_2$CH$_2$NPPh$_2$), 1.86 (t, 6H, $^3J_{H-H}$ = 7.2 Hz, NCH$_2$CH$_2$NPPh$_2$). ^{13}C-{^{1}H} NMR (CDCl$_3$) δ (ppm): 138.9 (d, $^1J_{31P-13C}$ = 16.2 Hz, *i*-carbons of phenyls), 132.2 (d, $^2J_{31P-13C}$ = 11.0 Hz, *o*-carbons of phenyls), 131.5 (s, *p*-carbons of phenyls), 127.8 (d, $^3J_{31P-13C}$ = 14.3 Hz, *m*-carbons of phenyls), 52.9 (NCH$_2$CH$_2$NPPh$_2$), 47.2 (NCH$_2$CH$_2$NPPh$_2$), assignment was based on the ^{1}H-^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR (CDCl$_3$) δ (ppm): 69.6 (s). Selected IR, υ (cm^{-1}): 871 (P–N–P), 1438 (P–Ph), 647 (P=S). C$_{78}$H$_{72}$N$_4$P$_6$O$_6$: Calc. C, 64.89; H, 5.03; N, 3.88. Found: C, 64.55; H, 4.73; N, 3.60%.

6.4. Synthesis of tris{2-(N,N-bis(diphenylselenophosphino)amino-ethyl)amine} 2c

[{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] (0.20 g, 0.16 mmol) and grey selenium (0.08 g, 0.96 mmol) were heated to reflux in THF (25 mL) for 2 h. After allowing mixture to cool room temperature the dirty white solid **2c** was collected by suction filtration and dried in *vacuum* (yield: 0.24 g, 87.0%); mp.: 189–191 °C). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.79 (dd, 24H, *J* = 7.1 and 13.2 Hz, *o*-protons of phenyls), 7.36 (d, 12H, *J* = 7.2 Hz, *p*-protons of phenyls), 7.27 (br, 24H, *m*-protons of phenyls), 3.42 (t, 6H, $^3J_{H-H}$ = 7.4 Hz, NCH$_2$CH$_2$NPPh$_2$), 2.03 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, NCH$_2$CH$_2$NPPh$_2$). ^{13}C-{^{1}H} NMR (CDCl$_3$) δ (ppm): 140.1 (d, $^1J_{31P-13C}$ = 15.4 Hz, *i*-carbons of phenyls), 133.5 (t, $^2J_{31P-13C}$ = 5.7 Hz, *o*-carbons of phenyls), 131.6 (s, *p*-carbons of phenyls), 127.8 (t, $^3J_{31P-13C}$ = 6.5 Hz, *m*-carbons of phenyls), 53.0 (NCH$_2$CH$_2$NPPh$_2$), 50.0 (NCH$_2$CH$_2$NPPh$_2$), assignment was based on the ^{1}H-^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR (CDCl$_3$) δ (ppm): 67.5 (s, $^1J_{PSe}$: 775 Hz). Selected IR, υ (cm^{-1}): 869 (P–N–P), 1439 (P–Ph), 561 (P=Se). C$_{78}$H$_{72}$N$_4$P$_6$Se$_6$: Calc. C, 54.31; H, 4.21; N, 3.25. Found: C, 53.89; H, 3.95; N, 3.01%.

6.5. Synthesis of tris{2-(N,N-bis(diphenylphosphino)aminoethyl)-amine}tripalladium(II) chloride, 3a

[Pd(cod)Cl$_2$] (0.17 g, 0.60 mmol) and [{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] (0.25 g, 0.20 mmol) were dissolved in THF (25 mL) and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of diethyl ether (20 mL) gave as **3a** yellow solid. The product was collected by suction filtration and dried in *vacuum* (yield: 0.32 g, 89.8%); mp.: 181–182 °C). ^{1}H NMR (DMSO) δ (ppm): 7.72 (dd, 24H, *J* = 7.6 and 16.0 Hz), 7.59 (br, 12H, *p*-protons of phenyls), 7.45 (br, 24H, *m*-protons of phenyls), 3.11 (t, 6H, $^3J_{H-H}$ = 7.2 Hz, NCH$_2$CH$_2$NPPh$_2$), 2.09 (t, 6H, $^3J_{H-H}$ = 7.4 Hz, NCH$_2$CH$_2$NPPh$_2$). ^{13}C-{^{1}H} NMR (DMSO) δ (ppm): 139.7 (d, $^1J_{31P-13C}$ = 14.6 Hz, *i*-carbons of phenyls), 133.5 (s, *o*-carbons of phenyls), 128.9 (s, *m*-carbons of phenyls), 54.9 (NCH$_2$CH$_2$NPPh$_2$), 46.3 (NCH$_2$CH$_2$NPPh$_2$), assignment was based on the ^{1}H-^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR (DMSO) δ (ppm): 30.7 (s). Selected IR, υ (cm^{-1}): 862 (P–N–P), 1439 (P–Ph). C$_{78}$H$_{72}$N$_4$P$_6$Pd$_3$Cl$_6$: Calc.: C, 52.54; H, 4.07; N, 3.14. Found: C, 52.11; H, 3.69; N, 2.92%.

6.6. Synthesis of tris{2-(N,N-bis(diphenylphosphino)aminoethyl)-amine}triplatinum(II)chloride, 3b

[Pt(cod)Cl$_2$] (0.22 g, 0.60 mmol) and [{(PPh$_2$)$_2$NCH$_2$CH$_2$}$_3$N] (0.20 g, 0.20 mmol) were dissolved in dry THF (25 mL) and stirred for 1 h. The volume was concentrated to ca. 1–2 mL by evaporation under reduced pressure and addition of diethyl ether (20 mL) afforded **3b** as a white solid. The product was collected by suction filtra-

tion and dried in *vacuum* (yield: 0.35 g, 85.5%; mp.: >300 °C). ^{1}H NMR (DMSO) δ (ppm): 7.41–7.68 (m, 60H, *o,m,p*-protons of phenyls), 3.08 (t, 6H, NCH$_2$CH_2NPPh$_2$), 2.15 (br, 6H, NCH_2CH$_2$NPPh$_2$). ^{13}C-$\{^1$H$\}$ NMR (DMSO) δ (ppm): 139.8 (s, *i*-carbons of phenyls), 132.9 (s, *o*-carbons of phenyls), 130.6 (s, *p*-carbons of phenyls), 129.8 (s, *m*-carbons of phenyls), 54.2 (NCH$_2$CH$_2$NPPh$_2$), 43.5 (NCH$_2$CH$_2$NPPh$_2$), assignment was based on the ^{1}H-^{13}C HETCOR spectrum. ^{31}P-$\{^1$H$\}$ NMR (DMSO) δ (ppm): 16.9 (s, $^1J_{\text{PPt}}$: 3400 Hz). Selected IR, υ (cm^{-1}): 875 (P–N–P), 1440 (P–Ph). C$_{78}$H$_{72}$N$_4$P$_6$Pt$_3$Cl$_6$: Calc. C, 45.72; H, 3.54; N, 2.73. Found: C, 45.43; H, 3.27; N, 2.52%.

7. General procedure for the Suzuki coupling reaction

Bis(phosphino)amine-palladium complex {**3a**, 0.01 mmol}, aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs$_2$CO$_3$ (2 mmol), dioxane (3 mL) were added to a small Schlenk tube in argon atmosphere and the mixture was heated at 70 °C for 1.0 h. After completion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silicagel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and NMR and yields are based on aryl bromide.

8. General procedure for the Heck coupling reaction

Bis(phosphino)amine-palladium complex {**3a**, 0.01 mmol}, aryl bromide (1.0 mmol), styrene (1.5 mmol), K$_2$CO$_3$ (2 mmol), DMF (3 mL) were added to a small Schlenk tube in argon atmosphere and the mixture was heated to 100 °C for 1.0 h. After completion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silicagel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and NMR and yields are based on aryl bromide.

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