Efficient Synthesis of Novel N-Substituted Bulky Diphosphinoamines

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Abstract: A convenient procedure for the facile preparation of electron-rich bulky diphosphinoamines from alkylamines and chlorodiphenylphosphine has been developed. The choice of solvent proved to be critical to the successful synthesis of the diphosphinoamine (PNP) products.

Key words: alkylamines, ethylene oligomerisation catalysis, solvent effects, diphoshinoamine ligands, steric hindrance

Since its first commercial application in 1966, ethylene oligomerisation has become a major industrial route towards the preparation of linear α-olefins.[1] The first industrial oligomerisation process based on transition metal catalysis was the Shell Higher Olefin Process (SHOP), wherein a neutral nickel catalyst containing a bidentate P–O chelating ligand effects the oligomerisation of ethylene to linear C_4–C_{20} olefins.[2] Following the success of the SHOP process, transition metal complexes containing novel phosphine ligands have received much attention both in academia and industry.[3] We recently reported an ethylene trimerisation system, as well as the unprecedented ethylene tetramerisation reaction using aluminoxane activated catalysts comprising chromium precursors and diphosphinoamine ($Ph_2PN[R]PPh_2$, Figure 1) ligands.[4] These catalyst systems produce mainly hex-1-ene and oct-1-ene, which are important co-monomers used in the production of linear low-density polyethylene.[5]

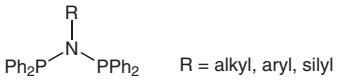
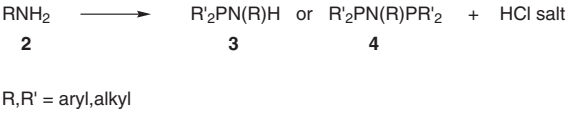


Figure 1 Diphosphinoamine ligands

It has been demonstrated that the nature of the N-substituent has a profound effect on both catalytic activity and selectivity towards C_6 and C_8 alk-1-enes, with the best systems containing bulky groups on the N-atom.[4a,b,6] Although a large number of PNP compounds have been reported in the literature,[7] to the best of our knowledge the synthesis of diphosphinoamine compounds containing very bulky *N*-alkyl groups, such as *tert*-butyl or 1-adamantyl, has not been reported. We describe herein the synthesis of such bulky diphosphinoamines from their respective alkylamines and chlorodiphenylphosphine. The synthetic methodology developed also provides access to a bulky P-substituted PNP, which thus far has been inaccessible via the conventional synthetic methods reported in the literature.[8]The most convenient procedure[7] for the preparation of phosphinoamines [$R'_2PN(H)R$] **3** and diphosphinoamines (PNP) **4** involves the reaction of aryl- or alkylamines with chlorophosphines in the presence of an organic base such as triethylamine (Scheme 1).



Scheme 1

The most commonly used organic solvents for this reaction include THF, diethyl ether, benzene and toluene.[7e–j] The HCl by-product reacts with the base, forming a salt which is often insoluble in these solvents and is thus readily separated from the product by filtration. Unexpectedly, when we adopted this well-established methodology for the use of *tert*-butylamine (**5**, Figure 2), the reaction with two equivalents of chlorodiphenylphoshine (Ph_2PCl) in the above-mentioned solvents yielded exclusively the phosphinoamine $Ph_2PNH(t\text{-Bu})$ (**11**) as was evident from the single peak at δ = 22 ppm in the ^{31}P NMR spectrum. The structure was further confirmed by ^1H NMR spectroscopy.[9]

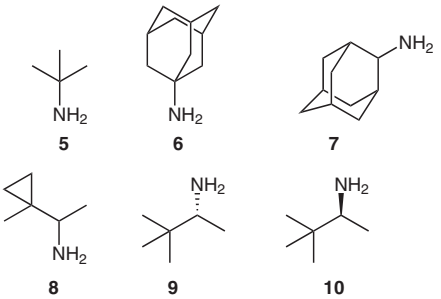


Figure 2 Bulky alkyl- and arylamines used in the synthesis of diphosphinoamine ligands

The use of bulky alkylamines **6**–**10** (Figure 2) also failed to afford the target PNP ligands. In all these instances only the respective phosphinoamines [$Ph_2PNH(R)$] **3** were formed. It became evident that the reaction of sterically

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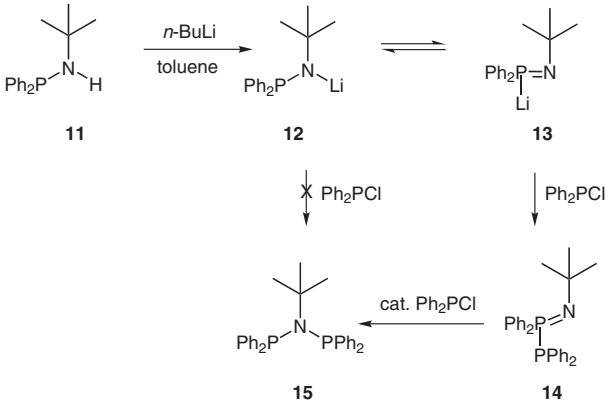
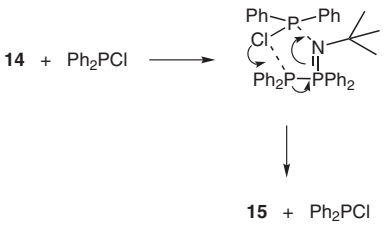
hindered amines and an excess of Ph_2PCl, in solvents such as ethers, paraffins and aromatics, which are typically used for such reactions is not a feasible route to the targeted PNP ligands. The limitations of this methodology, and the absence of suitable procedures for the preparation of $Ph_2PN(t\text{-Bu})PPh_2$ (**15**) and related N-bulky PNP compounds, prompted us to investigate in finding alternative synthetic routes to such systems. We envisaged that the lithium amide nucleophile **12**, generated from the reaction of *n*-butyllithium and $Ph_2PNH(t\text{-Bu})$ (**11**), would afford the PNP ligand **15**, upon reaction with Ph_2PCl (Scheme 2).



Scheme 2

However, this reaction yielded the iminobisphosphine product, $Ph_2PPPh_2{=}N(t\text{-Bu})$ (**14**), as confirmed by two diagnostic doublets resonating at –7 and –22 ppm in the ^{31}P NMR spectrum (Scheme 2). Dyson and co-workers[10] have recently reported similar reactions of aniline-derived amines with Ph_2PCl in the presence of Et_3N or *n*-BuLi that yield predominantly $Ph_2PPh_2P{=}NAr$ (Ar = aniline derivatives) together with PNP product. Interestingly, we observed that the kinetically controlled product, $Ph_2PPPh_2{=}N(t\text{-Bu})$ (**14**), rearranges to the desired isomeric diphosphinoamine (PNP) **15** upon interaction with a catalytic amount of Ph_2PCl. The reaction is fairly slow, as monitored by ^{31}P NMR spectroscopy and the rearrangement of **14** to **15** requires approximately 15 hours at room temperature for complete conversion. The role of Ph_2PCl as an isomerisation catalyst has previously been proposed to reside in its ability to react with the nitrogen atom of the iminobiphosphine **14**, as proposed in Scheme 3.[8]



Scheme 3

Not satisfied with this multi-step approach to the product **15**, a more efficient synthetic procedure was sought. We had noted that 3-methyl-2-butylamine (**16**) (Figure 3) reacted with Ph_2PCl in CH_2Cl_2 as solvent to produce the PNP product *N*,*N*-bis(diphenylphosphanyl)-3-methyl-2-butylamine, in greater than 95% yield within two hours. In contrast, the analogous reactions in toluene and diethyl ether proved to be less effective and resulted only in approximately 50% conversion of **3** to **4** over the same period.

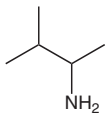


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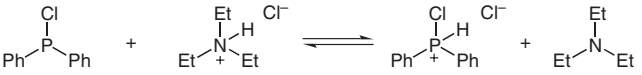
Figure 3 3-Methyl-2-butylamine (**16**)

Dyson and co-workers[10,11] have also reported faster reaction rates with aniline substrates when using CH_2Cl_2 as solvent. We believe that the variance in reaction rates may be explained by considering the likely equilibrium attained between the reaction of triethylammonium chloride and diphenylphosphonium chloride in CH_2Cl_2 as shown in Scheme 4. It is conceivable that the protonated diphenylphosphonium chloride is more electrophilic than its neutral counterpart and hence more reactive. The aforesaid equilibrium presumably lies far to the left in toluene, THF, diethyl ether, dioxane, hexane, and pentane, due to the low solubility of the triethylammonium chloride salt in these solvents, while it has a higher solubility in CH_2Cl_2.



Scheme 4

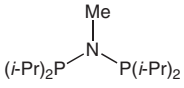
Consequently, we set out to prepare PNP derivative **15** using similar reaction conditions (i.e., with CH_2Cl_2 as solvent). Gratifyingly, the formation of **15** was achieved in approximately 50% yield (by ^{31}P NMR spectroscopy) when two equivalents of Ph_2PCl were reacted overnight with $t\text{-BuNH}_2$ in the presence of two equivalents of Et_3N in CH_2Cl_2 [conducted as a solution (10%; v/v) of this primary amine in the solvent]. Increasing the concentration (from 10% to 20%; v/v), led to a significant improvement in the yield (from 51 to 89%) of **15** as determined by ^{31}P NMR analysis. Furthermore, the amount of Et_3N present in the reaction also influenced the yield and the rate of formation of **15**. Reactions performed with an excess of Et_3N led to significantly lower yields as compared to when only two equivalents of base were used. Reactions at even higher concentrations were not carried out due to the high viscosity of the reaction mixture thereby resulting in inefficient stirring. This newly developed protocol was extended to include the use of other bulky amines **6**–**10**, affording the desired corresponding products, which in-

Table 1 Formation of PNP **4** at 20% (v/v) Solution of a Reactant Primary Amine in CH_2Cl_2

RNH_2	Solvent	$Ph_2PNRPPh_2$ **4** Yield (%) (^{31}P NMR, ≥20 h)	$Ph_2PNRPPh_2$ **4** Isolated yield (%, ≥20 h)
5	CH_2Cl_2	89	61
6	CH_2Cl_2	50	38
7	CH_2Cl_2	38	25
8	CH_2Cl_2	92	66
9	CH_2Cl_2	54	38
10	CH_2Cl_2	55	39

cluded two chiral products, in yields of 38–92% (by ^{31}P NMR monitoring, Table 1).

Although the reactions with amines **9** and **10** gave excellent conversion of the phosphinoamines, it was accompanied by the simultaneous formation of by-products, including tetraphenylbiphosphine (Ph_2PPPh_2) in amounts varying between 18% and 25%. The material loss (variance in yields, isolated vs ^{31}P NMR analysis in Table 1) was mainly due to oxidation of the PNP products during filtration through an alumina column. Ironically it was also noted that the oxidised by-product could be effectively removed from the desired PNP compound by this simple alumina filtration workup procedure. The present work represents the first account of the synthesis of bulky *N*-substituted diphosphinoamines. It is noteworthy that the synthesis of *N*,*N*-bis(diisopropylphosphanyl)methylamine [*i*-$Pr_2PN(Me)P$*i*-Pr_2] (**17**) (Figure 4) and its *N*-propyl derivative has been reported by means of a method similar to that described in Scheme 2.[8]



17

Figure 4 *N*,*N*-Bis(diisopropylphosphanyl)methylamine (**17**)

Using our new protocol we prepared ligand **17**[8] and its *N*-ethyl derivative[12] in a single step using CH_2Cl_2 as solvent in 88% and 54% yield, respectively, as observed by the ^{31}P NMR analysis. Since these reactions had shown such sensitivity to the solvent being used, a range of other solvents was investigated for the synthesis of **15**. The results are summarised in Table 2, which clearly demonstrate the profound influence of the solvents on the outcome of these reactions. The progresses of the reactions were monitored by ^{31}P NMR analysis. Diisopropyl ketone (DIPK), *N*-methylpyrrolidinone (NMP), and acetonitrile were all found to be effective solvents for this reaction. Acetonitrile proved to be even more effective than CH_2Cl_2 affording 91% of the PNP compound **15** (Table 2, entries 5, 9). Unexpectedly, $CHCl_3$ was less effective for the process, affording only 24% of the desired PNP product, whereas CCl_4 and nitropropane failed altogether to produce the desired products, instead producing by-products. As expected, mixtures of toluene–MeCN (1:1) as well as toluene–CH_2Cl_2 (1:1) were found to be effective combinations of solvents giving 62% and 52% yield, respectively of the desired PNP ligands (entries 10, 11). Similar trends were observed with the 1-adamantanamine PNP formation (68% yield in acetonitrile compared to 50% yield in CH_2Cl_2).

Table 2 Reaction of *t*-Butylamine and Ph_2PCl in Various Solvents[a]

Entry	Solvent	$Ph_2PN(t\text{-Bu})H$[b]	Yield of **15** (%; determined by ^{31}P NMR)
1	toluene	quant	0
2	Et_2O	quant	0
3	THF	quant	0
4	Et_3N	quant	0
5	CH_2Cl_2	n.d.	89 (61)[c]
6	$CHCl_3$	n.d.	24
7	CCl_4	0	0
8	DIPK	n.d.	43
9	MeCN	n.d.	91 (85)[c]
10	toluene–MeCN (1:1)	n.d.	66
12	toluene–CH_2Cl_2 (1:1)	n.d.	52
13	NMP	n.d.	60
14	dioxane	quant	0
15	nitropropane	0	0
16	EtOAc	quant	0

[a] Reaction carried out for 20 h.
[b] n.d. = not determined.
[c] Yield in parenthesis refers to isolated yield.

In summary, we have established an efficient direct protocol for the preparation of a range of bulky N-substituted diphosphinoamines. This methodology also proved to be applicable to the preparation of *P*-alkyl analogues. The solvent is critical to the success of the reaction, with CH_2Cl_2 and acetonitrile being the solvents of choice in the presence of triethylamine as base.

All reactions were carried out under dry argon using standard Schlenk-tube techniques. Chemicals were purchased from either Aldrich Chemical Co., Lancaster, or Merck, and were used as received. Anhydrous, oxygen-free solvents were prepared according to standard procedure. The NMR spectra were recorded in $CDCl_3$ on a Bruker 600 MHz or 500 MHz and a Varian 400 MHz spectrometer. Elemental analyses were performed on a Carlo Erba 1108 (CE1108) elemental analyser. MS (EI, 70 eV) spectra were recorded using MicroMass Autospec-TOF (Magnetic sector used for anal-

yses). Melting points were determined on an Electrothermal Digital Melting Point apparatus and are uncorrected. Yields in tables refer to ^{31}P NMR yield (average of at least three runs) unless otherwise stated. Isolated yields refer to yields of pure compounds.

N,N-Bis(diphenylphosphanyl)*tert*-butylamine (15); Typical Procedure

To a stirred solution of *tert*-butylamine (**5**; 2.0 mL, 19.0 mmol) in MeCN (10.0 mL) was added Et_3N (5.8 mL, 41.6 mmol). Ph_2PCl (7.7 mL, 42.9 mmol) was then added in portions. After the addition, the mixture was stirred overnight at r.t. The mixture was concentrated and the residue was slurried with Et_2O or THF (~100 mL). The Et_3N·HCl salt was filtered by passing through a short activated alumina column. Filtration was repeated until a pure compound was obtained. The solvent was evaporated to give the desired ligand as a white solid (7.15 g, 85%); mp 134–135 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, *t*-C_4H_9), 7.22–7.46 (m, 20 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.6, 63.6, 127.7, 128.1, 132.6, 140.6 (broad signals with unresolved coupling).

^{31}P NMR (162 MHz, $CDCl_3$,): δ = 57.8 (very br s).

MS (EI, 70 eV): *m*/*z* (%) = 442 (6, $[M + H]^+$), 441 (21, $[M]^+$), 384 (100, $[M - t\text{-Bu}]^+$), 306 (39, $[M - t\text{-Bu} - Ph]^+$), 262 (44, $[PPh_3]^+$), 256 (50, $[M - PPh_2]^+$), 185 (59, $[PPh_2]^+$).

Anal. Calcd for $C_{28}H_{29}NP_2$: C, 76.18; H, 6.62; N, 3.17. Found: C, 76.07; H, 6.70; N, 3.15.

N,N-Bis(diphenylphosphanyl)-1-adamantanamine

Prepared according to the Typical Procedure from 1-adamantanamine (**6**; 0.50 g, 3.3 mmol) and Ph_2PCl (1.3 mL, 7.4 mmol) in CH_2Cl_2 (2.5 mL); white solid (0.65 g, 38%); mp 174–175 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.42–1.60 (6 H, m), 2.02–2.10 (3 H, m), 2.22–2.29 (6 H, m), 7.20–7.80 (20 H, m, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.5, 36.0, 44.4 (t, $J_{P,C}$ = 7.0 Hz), 64.6 (t, $J_{P,C}$ = 7.2 Hz), 127.7, 128.0, 132.8 (very br s), 140.9 (d, $J_{P,C}$ = 17 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 53.3 (br s).

MS (EI, 70 eV): *m*/*z* (%) = 520 (25, $[M + H]^+$), 519 (48, $[M]^+$), 384 (100, $[M - adamantyl]^+$), 334 (29, $[M - PPh_2]^+$), 185 (34, $[PPh_2]^+$).

Anal. Calcd for $C_{34}H_{35}NP_2$: C, 78.59; H, 6.79; N, 2.70. Found: C, 78.42; H, 6.65; N, 2.63.

N,N-Bis(diphenylphosphanyl)-2-adamantanamine

Prepared according to the Typical Procedure from 2-adamantanamine hydrochloride (**7**·HCl; 2.00 g, 10.6 mmol) and Ph_2PCl (4.3 mL, 23.9 mmol) in CH_2Cl_2 (10.0 mL); white solid (1.40 g, 25%); mp 138–140 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.49–1.61 (m, 8 H), 1.69 (br s, 3 H), 1.89 (br s, 1 H), 3.03 [d, *J* = 12 Hz, 2 H, $NCH(CH)_2$], 3.65 (t, *J* = 13 Hz, 1 H, NCH), 7.24–7.86 (m, 20 H, ArH).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 27.6 (d, $J_{P,C}$ = 56.8 Hz), 29.7, 31.63 (t, $J_{P,C}$ = 8 Hz), 35.8, 38.6 39.6, 65.2 (t, $J_{P,C}$ = 6 Hz), 127.8 (d, $J_{P,C}$ = 5 Hz), 128.4, 132.8 (d, $J_{P,C}$ = 21.4 Hz), 140.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 56.9 (br s), 60.2 (br s).

MS (EI, 70 eV): *m*/*z* (%) = 520 (25, $[M + H]^+$), 519 (42, $[M]^+$), 384 (100, $[M - adamantyl]^+$), 334 (43, $[M - PPh_2]^+$), 262 (40, $[PPh_3]^+$), 185 (52, $[PPh_2]^+$).

Anal. Calcd for $C_{34}H_{35}NP_2$: C, 78.59; H, 6.79; N, 2.70. Found: C, 78.71; H, 6.80; N, 2.64.

N,N-Bis(diphenylphosphanyl)-1-(1-methylcyclopropyl)ethanamine

Prepared according to the Typical Procedure from 1-(1-methylcyclopropyl)ethanamine hydrochloride (**8**·HCl; 0.37 g, 2.7 mmol) and Ph_2PCl (1.1 mL, 6.1 mmol) in CH_2Cl_2 (2.0 mL); white powder (0.85 g, 66%); mp 112–115 °C.

^1H NMR (400 MHz, $CDCl_3$,): δ = 0.02–0.32 (m, 4 H, cyclopropyl 2 × CH_2), 1.06 (s, 3 H, CCH_3), 1.42 (d, *J* = 6.4, $CHCH_3$, 3 H), 3.26–3.34 (m, 1 H, NCH), 7.20–7.40 (m, 20 H, ArH).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 12.2 (d, $J_{P,C}$ = 3 Hz), 14.6, 21.24 (t, $J_{P,C}$ = 9 Hz), 22.1, 23.0 (t, $J_{P,C}$ = 4 Hz), 61.2 (t, $J_{P,C}$ = 7 Hz), 127.8 (d, $J_{P,C}$ = 12.4 Hz), 128.6, 133.3 (very br s), 140.1 (d, $J_{P,C}$ = 14.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 55.0 (very br s).

MS (EI, 70 eV): *m*/*z* (%) = 468 (10, $[M + H]^+$), 467 (30, $[M]^+$), 452 (14, $[M - CH_3]^+$), 384 (100, $[M - C_6H_{11}]^+$), 306 (26, $[M - C_6H_{11} - Ph]^+$), 262 (34, $[PPh_3]^+$), 185 (51, $[PPh_2]^+$).

Anal. Calcd for $C_{30}H_{31}NP_2$: C, 77.07; H, 6.68; N, 3.00. Found: C, 76.94; H, 6.74; N, 2.97.

N,N-(*R*)-Bis(diphenylphosphanyl)-3,3-dimethyl-2-butylamine

Prepared according to the Typical Procedure from (*R*)-3,3-dimethyl-2-butylamine (**9**; 1.00 g, 9.9 mmol) and Ph_2PCl (4.0 mL, 22.3 mmol) in CH_2Cl_2 (5.0 mL); white solid (1.76 g, 38%); mp 105–106 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.80 (s, 9 H, *t*-C_4H_9), 1.54 (d, *J* = 6.7 Hz, 3 H, $NCHCH_3$), 3.60–3.68 (m, 1 H, NCH), 7.00–7.86 (m, 20 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.0 ($J_{P,C}$ = 17 Hz), 28.4 (t, $J_{P,C}$ = 3 Hz), 36.4, 64.1 (dd, $J_{P,C}$ = 21.0, 8.8 Hz), 127.3–129.5 (m, 12 C), 132.3–133.9 (m, 8 C), 134.2–135.7 (m, 4 C, unresolved multiplet signals in the aromatic region).

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 52.2 (d, $J_{P,P}$ = 21.3 Hz), 58.6 (d, $J_{P,P}$ = 21.2 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 470 (8, $[M + H]^+$), 469 (22, $[M]^+$), 412 (36, $[M - C_6H_{13}]^+$), 384 (100, $[M - C_6H_{13}]^+$), 306 (9, $[M - C_6H_{13} - Ph]^+$), 262 (36, $[PPh_3]^+$), 185 (94, $[PPh_2]^+$).

Anal. Calcd for $C_{30}H_{33}NP_2$: C, 76.74; H, 7.08; N, 2.98. Found: C, 76.60; H, 6.98; N, 2.91.

N,N-(*S*)-Bis(diphenylphosphanyl)-3,3-dimethyl-2-butylamine

Prepared according to the Typical Procedure from (*S*)-3,3-dimethyl-2-butylamine (**10**; 1.00 g, 9.9 mmol) and Ph_2PCl (4.0 mL, 22.3 mL) in CH_2Cl_2 (5.0 mL); white solid (1.81 g, 39%); mp 109–111 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.72 (s, 9 H, *t*-C_4H_9), 1.45 (d, *J* = 6.8 Hz, 3 H, $NCHCH_3$), 3.45–3.61 (m, 1 H, NCH), 6.99–7.80 (m, 20 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.0 (d, $J_{P,C}$ = 17 Hz), 28.6 (t, $J_{P,C}$ = 3 Hz), 36.6, 64.4 (dd, $J_{P,C}$ = 21.2, 8.9 Hz), 127.2–130.5 (m, 12 C), 132.0–133.7 (m, 8 C), 135.0–136.0 (m, 4 C, unresolved multiplet in the aromatic region).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 52.3 (d, $J_{P,P}$ = 21.5 Hz), 58.5 (d, $J_{P,P}$ = 21.3 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 470 (20, $[M + H]^+$), 469 (45, $[M]^+$), 412 (52, $[M - C_6H_{13}]^+$), 384 (100, $[M - C_6H_{13}]^+$), 306 (20, $[M - C_6H_{13} - Ph]^+$), 262 (52, $[PPh_3]^+$), 185 (90, $[PPh_2]^+$).

Anal. Calcd for $C_{30}H_{33}NP_2$: C, 76.74; H, 7.08; N, 2.98. Found: C, 76.66; H, 7.07; N, 2.83.

***N*,*N*-Bis(diisopropylphosphanyl)methylamine (17)[8]**

Prepared according to the Typical Procedure from $MeNH_2$ (0.49 g, 15.8 mmol) and $(i\text{-Pr})_2PCl$ (5.7 mL, 35.8 mmol) in CH_2Cl_2 (2.5 mL).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.00–1.12 [m, 24 H, $CH(CH_3)_2$], 1.88–1.94 [m, 4 H, $PCH(CH_3)_2$] 2.58–2.61 (3 H, m, NCH_3).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 92.7 (s).[8]

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(12) *N*,*N*-Bis(diisopropylphosphanyl)ethylamine: ^{31}P NMR (162 MHz, $CDCl_3$): δ = 83.9 (s).