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Synthesis of New Diphosphine Ligands and their Application in Pd-Catalyzed Alkoxycarbonylation Reactions

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Abstract: Carbocyclic and *N*-heterocyclic analogues of the industrially applied ligand bis(di-*tert*-butylphosphinomethyl)benzene (**1**) have been synthesized in moderate to very good yields. The new ligands are based on benzene, tetralin, lutidine, pyrazine, quinoxaline, and maleimide backbones. Electronic and steric variations of the phosphorous donor sites were performed. As a benchmark reaction, the palladium-catalyzed methoxycarbonylation of 1-octene has been tested. Ester yields up to 64% and high linear selectivities up to 92% were achieved.

Keywords: alkoxycarbonylation · homogenous catalysis · ligands · palladium · phosphine

Introduction

Palladium phosphine complexes represent powerful catalytic systems for numerous C–C bond formations in contemporary organic chemistry.[1] Among the different coupling reactions, carbonylation reactions allow for a straightforward synthesis of all kinds of carboxylic acid derivatives. As a result, significant efforts have been dedicated to the development of new phosphine ligands for carbonylation catalysts, which are widely used both in academic laboratories and for industrially relevant processes.[2] As a more recent example, bis(di-*tert*-butylphosphinomethyl)benzene[3] (dtbpmb) (**1**) as well as its (un)symmetrical analogues,[4] have become important for diverse carbonylation reactions (Figure 1). More specifically, their palladium complexes with weakly or non-coordinating anions constitute efficient catalyst systems for highly chemo- and regioselective CO–alkene copolymerization,[5] hydroformylation of both aliphatic and functionalized alkenes,[6] and alkoxycarbonylation[7] of alkynes,[8] nitriles,[9] unsaturated esters,[10] as well as terminal and internal alkenes.[11] Notably, this "state-of-the-art" ligand provides the basis for the so-called Lucite α-process, which is applied on an industrial scale for the synthesis of methyl methacrylate.

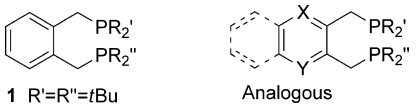

Figure 1. Bis(diphosphinomethyl)benzene ligands and their analogues.

We have been interested for more than a decade in the development of novel phosphorus ligands[12] and their catalytic application in various carbonylations.[13] Some of our palladium catalysts also have found industrial application in the production of active pharmaceutical ingredients.[14]

Based on our long lasting interest in the synthesis and application of such kind of ligands, recently we became attracted to synthesize carbo- and heterocyclic analogues of **1** (Figure 1) and to test their activity in methoxycarbonylation reactions of alkenes. Herein, we report the preparation of novel carbocyclic and *N*-heterocyclic diphosphine ligands and their initial catalytic performance in methoxycarbonylation reactions.

Results and Discussion

Ligand synthesis

So far, there are few examples of dtbpmb-like ligands known, where two phosphorus atoms are connected to each other by a semi-rigid C_4 bridge. In addition, catalytic reactions in the presence of such dtbpmb derivatives are scarcely explored. Some of the first examples of carbocyclic analogues[15] of this kind of diphosphine ligands have been synthesized already more than four decades ago by Hayashi et al. and were tested in hydroformylation[16] and in one case also in methoxycarbonylation[17] reactions. To the best of our knowledge, the corresponding *N*-heterocyclic ligands, for ex-

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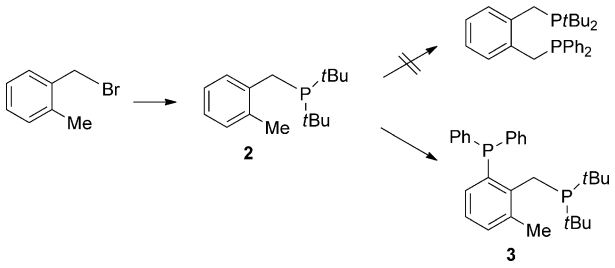
ample, based on lutidine, pyrazine, quinoxaline, and maleimide backbones, are not known except for one example,[18] where 2,3-bis((diisopropylphosphino)methyl)pyrazine was synthesized as an intermediate for further transformations without isolation and any characterization.

In general, the novel ligands were prepared by selective deprotonation at the methyl groups of the corresponding carbocyclic or *N*-heterocyclic substrate by using *n*-butyllithium (*n*BuLi) in the presence of tetramethylenethylendiamine (TMEDA) followed by trapping the resulting lithium intermediate with dialkyl- or diarylchlorophosphines. Advantageously, all substrates and reagents are commercially available or can be conveniently prepared on multi-gram scale using known procedures.

At the beginning of this project, we were interested in the synthesis of (un)symmetrical analogues of bis(di-*tert*-butylphosphinomethyl)benzene (**1**) (Scheme 1). Starting from 1-



Scheme 1. Stepwise phosphorylation of 1-(bromomethyl)-2-methylbenzene.

(bromomethyl)-2-methylbenzene we aimed to take advantage of the different reactivity of the bromomethyl and the methyl groups. Hence, di-*tert*-butyl(2-methylbenzyl)phosphine (**2**) was synthesized in a straightforward manner via the corresponding phosphonium salt, which was subsequently deprotonated with an excess of base (Scheme 1, see the Experimental procedures A and B).

Next, we performed metallation of the monophosphine **2**. Surprisingly, X-ray analysis of single crystals of the lithiated intermediate showed that deprotonation took place on the CH_2–P group and that the lithium atom is located between the methylene group and *ortho*-aromatic hydrogen atoms (Figure 2). The length of C1–C2 and C2–C3 bonds with 1.442 Å and 1.446 Å, respectively, indicates the existence of an allylic structure. Due to steric hindrance, further reaction with chlorodiphenylphosphine led to the formation of product **3**.

Next, we attempted the synthesis of ligands with a tetralin backbone. Thus, 1,4-dibromo-1,2,3,4-tetrahydronaphthalene was synthesized by refluxing 1,2,3,4-tetrahydronaphthalene with *N*-bromosuccinimide in carbon tetrachloride in the presence of benzoyl peroxide (Scheme 2).[19] This bromination reaction was completed before any appreciable dehydrobromination to naphthalene took place. The dibromotetralin derivative was immediately reacted with freshly prepared borane-protected lithium diphenylphosphide to give

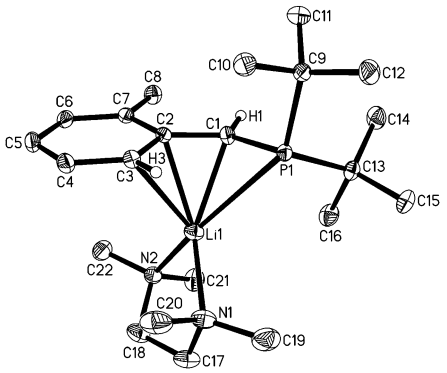
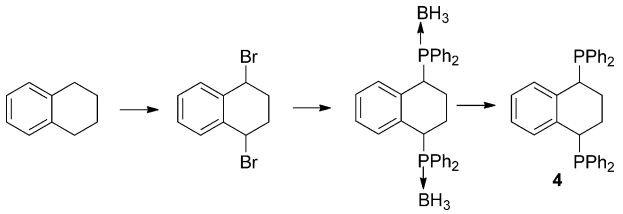


Figure 2. Molecular structure of the lithium complex with phosphine **2** and TMEDA. Displacement ellipsoids are drawn at the 30% probability level.



Scheme 2. Synthesis of tetralin backbone-based diphosphine ligand **4**.

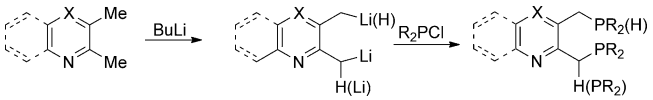
the borane-protected diphosphine, which upon treatment with pyrrolidine yielded the desired ligand **4**.

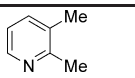
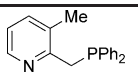
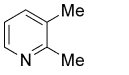
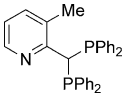
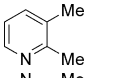
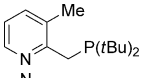
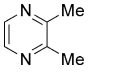
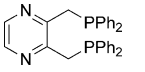
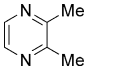
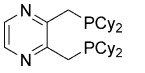
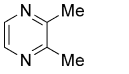
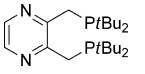
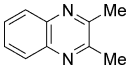
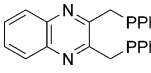
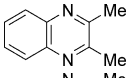
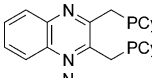
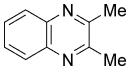
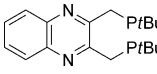
Furthermore, nine different *N*-heterocyclic mono- and diphosphines were synthesized. Preliminary experiments showed that the reaction of 2,3-dibromomethylenequinoxaline with potassium diphenylphosphide or diphenylphosphine led to mixtures of products. To our delight, the metallation of 2,3-dimethyllutidine, 2,3-dimethylpyrazine, and 2,3-dimethylquinoxaline proceeded smoothly at low temperature (−78 °C). When both metallation of 2,3-dimethyllutidine and subsequent phosphorylation reaction with chlorodiphenylphosphine were performed at elevated temperatures, namely above 0 °C, the main product was the monophosphorylated ligand **5** (Table 1, entry 1).

In addition, the unexpected product **6** was formed (Table 1, entry 2), which is a result of double metallation at the methyl group in *ortho*-position to the nitrogen atom. X-ray analysis of single crystals and NMR investigations proved the structure of ligand **6** (Figure 3, structure a). However, decreasing the reaction temperature to −78 °C (see the Experimental Section, procedure D) led to the selective formation of **5** in high yield. Although two equivalents of chlorodiphenylphosphine were used, the monophosphorylated product at the C-2 methyl group was exclusively formed. Similar behavior was observed in the synthesis of the more basic ligand **7** (Table 1, entry 3). Again, the structure of this ligand was confirmed by X-ray analysis (Figure 3, structure b).

Having a reliable protocol in hand (procedure D), we continued our experiments with 2,3-dimethylpyrazine (Table 1, entries 4–6) and 2,3-dimethylquinoxaline (Table 1, entries 7–

Table 1. Synthesis of heterocyclic mono- and diphosphine ligands.[a]



Entry	Substrate	Product		Procedure	Yield[b] [%]
1			**5**	D	57[c,d]
2			**6**	E	35[c,e]
3			**7**	D	88
4			**8**	D	75
5			**9**	D	86
6			**10**	D	53
7			**11**	D	49
8			**12**	D	43
9			**13**	D	51

[a] Reaction conditions were not optimized: Heterocyclic substrate (20 mmol), *n*BuLi (2.2 equiv), TMEDA (2.2 equiv), −78 °C to RT, then disubstituted chlorophosphine (2.2 equiv), −78 °C to RT. [b] Isolated yield. [c] Partly calculated from NMR data. [d] Along with 7 % of product **6**. [e] Along with 20 % of product **5**.

9). The targeted diphosphine ligands were obtained in good to very good yields without any modifications. Notably, all products were isolated by crystallization with a purity $>95\,\%$.

Pyrazine-based aryl- or alkyldiphosphines (Table 1, entries 4–5) were obtained in better yields compared to the corresponding bulky, electron-rich ligand **10** with *tert*-butyl groups at the phosphorus atoms (Table 1, entry 6). In case of the quinoxaline backbone-based ligands the yields were not affected by electronic or steric factors of substituents (Table 1, entries 7–9). Interestingly, we observed that 2,3-bis((di-tert-butylphosphino)methyl)quinoxaline **13** (Table 1, entry 9) forms in methanol fast growing large yellow single crystals. Their X-ray analysis showed the existence of two crystal forms in an asymmetric unit, which differ in the arrangement of the methylene-bridged di-*tert*-butylphosphine groups to the aromatic ring (Figure 3, structure c).

Finally, we attempted the synthesis of related maleimide-derived diphosphines (Scheme 3). Starting from the corresponding maleinanhydrid, more stable *N*-alkylated and *N*-arylated 3,4-dimethylmaleimide substrates were synthesized on a multi-gram scale according to known literature procedures.[20] To our surprise, metallation and phosphorylation of *N*-cyclohexyl 3,4-dimethylmaleimide gave the unknown

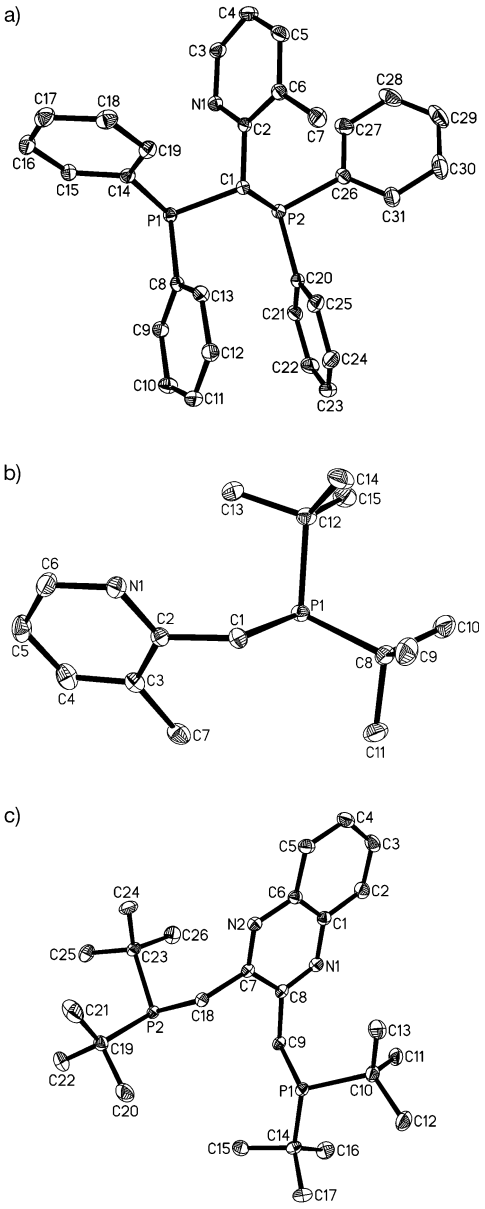
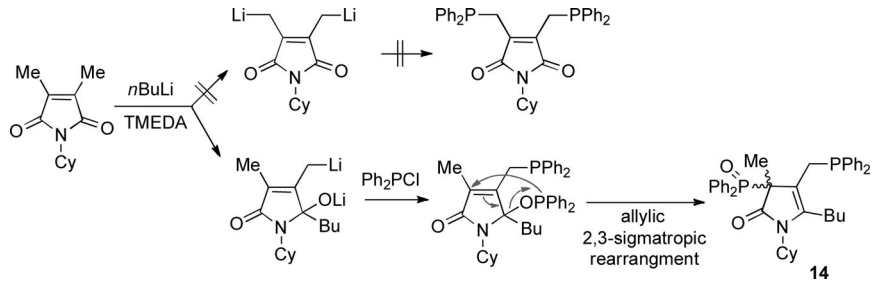


Figure 3. Molecular structures of ligands **6** (a), **7** (b), and **13** (c, only one of two molecules in the asymmetric unit is depicted). Displacement ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity.

product **14**, which combines both phosphine and phosphine oxide moieties in one molecule (Scheme 3). The ^{31}P NMR signals are observed as doublets with a coupling constant ^{4}J(P,P) of 5.8 Hz, for the phosphine moiety at −15.1 ppm and for the phosphine oxide at 30 ppm, respectively. The different oxidation states of the P atoms are also evident from the heteronuclear coupling constants ^{1}J(P,Ph-C_{ipso}) [>90 Hz for P^{V}, about 16 Hz for P^{III}].

Based on the structure of **14**, we assume that the following reaction sequence takes place: First, addition of *n*BuLi to the carbonyl group, then deprotonation of the vicinal methyl group. Subsequent phosphorylation leads to the formation of the phosphinite–phosphine intermediate, which



Scheme 3. Transformations of *N*-cyclohexyl 3,4-dimethylmaleimide according to experimental procedure F.

undergoes allylic 2,3-sigmatropic rearrangement to form compound **14** with both phosphine–phosphine oxide functions. In agreement with this proposal, recently Knochel and co-workers described 2,3-sigmatropic rearrangements of cyclic and open-chain allylic phosphinites to chiral phosphine oxides.[21] To confirm our proposal, we performed the reaction with 1 equivalent of *n*BuLi. In fact, only phosphinoxide was formed and no traces of monophosphine or compound **14** were observed. An attempt to introduce *tert*-butyl groups at phosphorus atoms was unsuccessful probably due to the increased sterical demand.

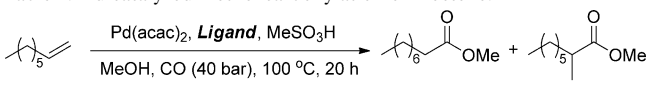
Catalytic Investigations: Methoxycarbonylation

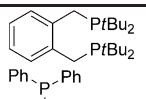
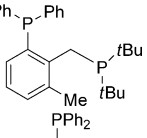
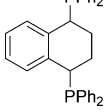
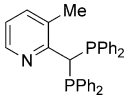
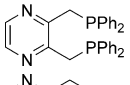
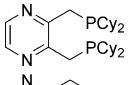
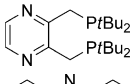
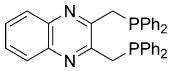
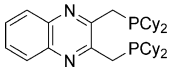
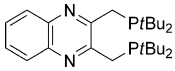
As a benchmark reaction, the methoxycarbonylation of 1-octene was carried out using 0.04 mol% $Pd(acac)_2$ and 0.16 mol% of the new ligands in the presence of 0.6 mol% methane sulfonic acid in methanol under 40 bar of CO pressure. As expected, the ligand structure has a significant influence on the conversion and regioselectivity. Alkyl- and aryl-substituted monophosphine ligands, such as **2**, **5**, **7**, and **14** did not show any catalytic activity. Similarly, diphenylphosphine ligands show almost no activity (Table 2, entries 3 and 4) or gave only very low conversions at moderate linear selectivity (Table 2, entries 5 and 8). However, conversions and selectivity to methyl nonanoate were considerably improved parallel to increased ligand basicity and bulkiness of substituents. Interestingly, ligands **9** and **12** with cyclohexyl substituents were quite active and gave full conversion. Unfortunately, they were not able to convert internal olefins (formed by isomerization from 1-octene) into the desired ester with a significant reaction rate (Table 2, entries 6 and 9). Gratifyingly, the better σ-donor di-*tert*-butylphosphino ligands **10** and **13** led to improved results (Table 2, entries 7 and 10), and total ester yields up to 64% and linear regioselectivites up to 92% were reached. Variations of electronic effects from pyrazine to quinoxaline backbones led to somewhat improved alkoxycarbonylation yields relative to competing olefin isomerization at retained linear selectivity.

Conclusions

We synthesized 9 new carbocyclic and *N*-heterocyclic analogues of bis(di-*tert*-butylphosphinomethyl)benzene (**1**) in moderate to very good yields. All substrates and reagents for the ligand syntheses are commercially available or easily accessible on multi-gram scale. The ligands are constructed on benzene, tetralin, lutidine, pyrazine, quinoxaline, and maleimide backbones. In addition, we performed electronic and steric variations of the phosphorous substituents, which enables a "fine tuning" of the resulting homogeneous palladium catalysts. To demonstrate a catalytic application, alkoxycarbonylation of 1-octane was performed at low catalyst loadings. Obviously, these ligands have additional potential for a variety of other catalytic applications.

Table 2. Pd-catalyzed methoxcarbonylation of 1-octene.[a]



Entry	Ligand		Conv. [%][b]	Olefin isomers yield [%][b]	Total ester yield [%][b]	Linear selec. [%][b]
1		1	>98	–	93	96
2		3	1–2	trace amounts	0	-
3		4	1–2	trace amounts	0	-
4		6	1–2	trace amounts	0	-
5		8	8–10	4–6	4	69
6		9	>98	65–70	26	83
7		10	>98	35–40	56	92
8		11	22–25	8–10	13	70
9		12	>98	55–60	31	83
10		13	>98	25–30	64	92

[a] Reaction conditions: 1-Octene (2 mmol), $Pd(acac)_2$ (0.04 mol%), diphosphine ligand (0.16 mol%), $MeSO_3H$ (0.6 mol%), MeOH (1.25 mL), 100 °C, 20 h. [b] Conversion, yield, and regioselectivity were determined by GC analysis using isooctane as internal standard.

Experimental Section

General Information

All reactions were carried out under argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros, AlfaAsar, or Strem and, unless otherwise noted, were used without further purification. Solvents were additionally purified, degased, or distilled under argon atmosphere. All compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, and by GC-MS and HRMS. ^{1}H NMR spectra were recorded on Bruker AV 300 and AV 400 spectrometers. ^{13}C NMR and ^{31}P NMR spectra were recorded at 75.5 or 101 MHz and 121 or 162 MHz, respectively. Chemical shifts are reported in ppm relative to the center of solvent resonance. Electron ionization (EI) (70 eV) mass spectra were recorded on a MAT 95XP instrument (Thermo Electron Corporation). GC was performed on Agilent 6890 chromatograph with a 30 m HP5 column. HRMS was performed on MAT 95XP (EI) and Agilent 6210 Time-of-Flight LC/MS (ESI) system. GC-MS was performed on an Agilent 5973 chromatography mass selective detector system. All yields reported refer to isolated yields under non-optimized reaction conditions.

Procedure A

A toluene solution (30 mL) of 2-methylbenzylbromide (20 mmol) and di-*tert*-butylphosphine (1 equiv) was refluxed for 4 h. After a few minutes of heating, a white precipitate was formed. After cooling to room temperature, heptane (20 mL) was added, and the hydrobromide salt of the product was filtered off as a white powder (^{31}P NMR signal at 27 ppm). Then, a KOH solution (1.1 equiv, in 10 mL water) was added slowly to the water solution of the hydrobromide salt (20 mL). The formed suspension was extracted with diethyl ether (4×20 mL) and dried over Na_2SO_4. The solvent was evaporated and the product was isolated by vacuum distillation (b.p. 105 °C at 0.67 mbar pressure) to give the desired product as a colorless syrup.

*Di-tert-butyl(2-methylbenzyl)phosphine (**2**)*: Yield: 87 %, 4.36 g; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.47 (m, 1H), 7.19–7.01 (m, 3H), 2.87 (d, J = 3.1 Hz, 2H), 2.46 (s, 3H), 1.17 ppm (d, J = 10.8 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.10 (d, J = 9.9 Hz), 135.96 (d, J = 3.1 Hz), 130.48 (d, J = 12.9 Hz), 130.22, 125.55, 125.38 (d, J = 1.9 Hz), 31.85 (d, J = 22.2 Hz, 2C), 29.77 (d, J = 13.0 Hz, 6C), 25.61 (d, J = 24.3 Hz), 20.57 ppm (d, J = 5.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 28.41 ppm; GC-MS (EI, 70 eV): m/z (%) 250 (40) [M^+]; HRMS (ESI$^+$): calcd for $C_{16}H_{28}P$ [M+H]$^+$: 251.1923; found: 251.1925.

Procedure B

Step 1: An ethereal solution (3 mL) of di-*tert*-butyl(2-methylbenzyl)phosphine (**2**, 1.27 mmol) was slowly added via a syringe to a previously prepared ethereal solution of *n*BuLi (5 mL, 1.2 equiv, 1.6 M in *n*-hexane, which was replaced with diethyl ether) and TMEDA (1.2 equiv) at room temperature. The yellow solution was cooled to −78 °C for 4 h and the formed lithium salt was isolated. Step 2: Heptane (5 mL) was added to the lithiated compound , and then chlorodiphenylphosphine (2.2 equiv) was slowly added via a syringe at room temperature. Conversion was complete after heating of the reaction mixture for 30 min at 50 °C. Then, water was slowly added and the product was extracted with toluene (4× 20 mL). After drying over Na_2SO_4 and solvent evaporation, the crude product was recrystallized from methanol.

*Di-tert-butyl(2-(diphenylphosphino)-6-methylbenzyl)phosphine (**3**)*: Yield: 46 %, 254 mg; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.46 (dt, J = 7.9, 1.8 Hz, 1H), 7.38–7.20 (m, 10H), 7.10 (dd, J = 8.6, 1.6 Hz, 1H), 7.00 (td, J = 7.6, 1.7 Hz, 1H), 2.86 (d, J = 2.8 Hz, 2H), 2.39 (s, 3H), 1.14 ppm (d, J = 10.7 Hz, 18H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 141.22 (d, J = 10.2 Hz), 138.21 (d, J = 11.5 Hz, 2C), 136.98 (dd, J = 8.0, 2.8 Hz), 136.04 (d, J = 22.5 Hz), 133.93 (d, J = 19.5 Hz, 4C), 133.80–133.41 (m), 131.42–131.02 (m, 2C), 128.97–128.63 (m, 6C), 32.22 (d, J = 23.4 Hz, 2C), 29.95 (d, J = 13.3 Hz, 6C), 26.25 (d, J = 26.0 Hz), 20.78 ppm (d, J = 5.8 Hz); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 28.61, −6.16 ppm; GC-MS (EI, 70 eV): m/z (%) 434 (32) [M^+]; HRMS (EI): calcd for $C_{28}H_{37}P_2$: 435.2365; found: 435.2369.

Procedure C

Step 1: To a solution of diphenylphosphine (3.6 mmol) in THF (7 mL) at 0 °C was slowly added via a syringe a solution of BH_3·THF (3.6 mmol, 1 M in THF). The resulting solution of $PPh_2H{\cdot}BH_3$ was cooled to −78 °C, and then a solution of *n*BuLi (3.6 mmol, 1.6 M in *n*-hexane) was added dropwise via a syringe over 10 min. The light-yellow reaction mixture was allowed to warm slowly to room temperature. Step 2: This solution was added dropwise to a cooled (−25 °C) solution of 1,4-dibromo-1,2,3,4-tetrahydronaphthalene[18] (1.8 mmol, freshly prepared) in THF (5 mL). The reaction mixture was again allowed to warm slowly to room temperature. A white precipitate was formed overnight, which was isolated. Step 3: The borane complex was dissolved in THF (25 mL) to which pyrrolidine (18 mL) was added. Deprotection was complete after 15 h at room temperature. Pyrrolidine was removed under vacuum, and the crude product was recrystallized from THF/methanol/heptane and washed with cold methanol to give the desired product as white, shiny crystals.

*1,4-Bis(diphenylphosphino)-1,2,3,4-tetrahydronaphthalene (**4**)*: Yield: 74 %, 665 mg; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.38 (m, 4H), 7.33–7.09 (m, 16H), 6.69 (dd, J = 5.7, 3.4 Hz, 2H), 6.50–6.38 (m, 2H), 3.72 (dq, J = 4.6, 2.6, 2.0 Hz, 2H), 2.09 (dtd, J = 12.6, 7.3, 5.9, 3.0 Hz, 2H), 1.65 ppm (tt, J = 6.6, 2.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.80–137.20 (m, 4C), 137.13–136.55 (m, 2C), 133.89 (ddd, J = 23.5, 14.0, 4.0 Hz, 8C), 129.80–129.38 (m, 4C), 128.74 (d, J = 19.4 Hz, 4C), 128.21 (dt, J = 30.7, 3.4 Hz, 8C), 125.19 (m, 2C), 37.76–37.22 (m, 2C), 24.14 ppm (t, J = 9.9 Hz, 2C); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 0.76 ppm; MS (EI): m/z (%) 500 (9) [M^+]; HRMS (EI): calcd for $C_{34}H_{30}P_2$: 500.1817; found: 500.1814.

General Procedure for the Synthesis of Symmetric Bis-disubstituted Phosphines and Mono-disubstituted Phosphines: Procedure D

Step 1: To 40 mL of an ethereal solution or suspension of the corresponding 2,3-dimethyl pyrazine or quinoxaline (20 mmol) was slowly added an ethereal solution of *n*BuLi (15 mL, 2.2 equiv, 1.6 M in *n*-hexane, which was replaced with diethyl ether) and TMEDA (2.2 equiv) at −78 °C. The intensively colored reaction mixture was allowed slowly to warm to room temperature. After stirring overnight, heptane (20 mL) was added, and the heterogeneous reaction mixture was refluxed at 60–80 °C for 2 h. Step 2: The reaction mixture was again cooled to −78 °C, and an ethereal solution (15 mL) of di-*tert*-butylchlorophosphine, chlorodiphenylphosphine, or chlorodicyclohexylphosphine (2.2 equiv) was slowly added via a syringe. After 1 h at that temperature, the reaction mixture was allowed to warm slowly to room temperature overnight. Then, water was slowly added and the product was extracted with CH_2Cl_2 (4×20 mL). After drying over Na_2SO_4 and solvent evaporation, the crude product was recrystallized from ether or methanol.

*2-((Diphenylphosphino)methyl)-3-methylpyridine (**5**):* Yield: 57 %, 3.32 g; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.37–8.17 (m, 1H), 7.47 (ddtd, J = 7.1, 5.3, 2.9, 1.3 Hz, 5H), 7.41–7.37 (m, 1H), 7.34 (dq, J = 4.5, 1.8, 1.3 Hz, 5H), 7.02 (dd, J = 7.6, 4.9 Hz, 1H), 3.64 (s, 2H), 2.25 ppm (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2):): δ = 157.09 (d, J = 6.8 Hz), 146.79, 139.32 (d, J = 15.5 Hz, 2C), 137.73, 133.21 (d, J = 19.2 Hz, 4C), 132.16 (d, J = 3.0 Hz), 128.87 (2C), 128.61 (d, J = 6.4 Hz, 4C), 121.56 (d, J = 2.7 Hz), 36.54 (d, J = 15.6 Hz), 19.29 ppm (d, J = 4.4 Hz); ^{31}P NMR (121 MHz, CD_2Cl_2):): δ = −15.58 ppm; GC-MS (EI, 70 eV): m/z (%) 291 (78) [M^+]; HRMS (EI): calcd for $C_{19}H_{18}N_1P_1$: 291.1171; found: 291.1170.

Procedure E

The product was synthesized using general procedure D with steps 1 and 2 carried out at room temperature instead of −78 °C.

*2-(Bis(diphenylphosphino)methyl)-3-methylpyridine (**6**):* Yield: 35 %, 3.33 g; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.29 (dd, J = 4.8, 1.8 Hz, 1H), 7.42 (dtd, J = 7.8, 3.7, 1.6 Hz, 5H), 7.21–7.06 (m, 15H), 7.04–7.00 (m, 1H), 6.77 (dd, J = 7.6, 4.7 Hz, 1H), 4.82 (t, J = 3.0 Hz, 1H), 1.91 ppm (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 158.60, 146.95, 137.59, 137.43 (t, J = 4.2 Hz, 2C), 136.89 (t, J = 7.5 Hz, 2C), 134.77 (t, J = 11.6 Hz, 4C), 133.92 (t, J = 10.6 Hz, 4C), 132.19, 129.16 (2C), 128.54 (2C), 128.07 (dt, J = 23.7, 3.8 Hz, 8C), 120.64, 43.32 (t, J = 24.7 Hz), 19.51 ppm; ^{31}P NMR

(121 MHz, CD_2Cl_2): $\delta = 0.95$ ppm; MS (EI): *m/z* (%) 475 (1) [M^+]; HRMS (ESI$^+$): calcd for $C_{31}H_{28}N_1P_2$ [M+H]$^+$: 476.1692; found: 476.1702.

*2-((Di-tert-butylphosphino)methyl)-3-methylpyridine (**7**):* Yield: 88%, 4.43 g; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.29$ (dd, $J = 4.9$, 1.7 Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 6.97 (dd, $J = 7.6$, 4.9 Hz, 1H), 3.12 (d, $J = 2.5$ Hz, 2H), 2.45 (s, 3H), 1.13 ppm (d, $J = 10.9$ Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 159.38$ (d, $J = 8.9$ Hz), 146.04, 137.76, 131.77, 120.92, 32.00 (d, $J = 22.7$ Hz, 2C), 30.35 (d, $J = 27.0$ Hz), 29.71 (d, $J = 13.2$ Hz, 6C), 19.95 ppm (d, $J = 10.1$ Hz); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 26.20$ ppm; GC-MS (EI, 70 eV): *m/z* (%) 194 (100) [M-*t*Bu]; HRMS (ESI$^+$): Calcd for $C_{15}H_{27}N_1P_1$ [M+H]$^+$: 252.1876; found: 252.1872.

*2,3-Bis((diphenylphosphino)methyl)pyrazine (**8**):* Yield: 75%, 7.15 g; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.12$ (s, 2H), 7.28–7.18 (m, 20H), 3.41 ppm (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 152.93$–152.74 (m, 2C), 141.31 (2C), 137.74 (d, $J = 15.0$ Hz, 4C), 132.77 (d, $J = 19.4$ Hz, 8C), 128.78 (4C), 128.38 (d, $J = 6.4$ Hz, 8C), 35.57 ppm (dd, $J = 17.4$, 5.0 Hz, 2C); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -14.00$ ppm; GC-MS (EI, 70 eV): *m/z* (%) 476 (30) [M^+]; HRMS (ESI$^+$): calcd for $C_{30}H_{27}N_2P_2$ [M+H]$^+$: 477.1644; found: 477.1652; HRMS (ESI$^+$): calcd for $C_{30}H_{26}N_2NaP_2$ [M+Na]$^+$: 499.1463; found: 499.1454.

*2,3-Bis((dicyclohexylphosphino)methyl)pyrazine (**9**):* Yield: 86%, 8.61 g;^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.22$ (s, 2H), 3.26 (s, 4H), 1.81–1.56 (m, 24H), 1.31–1.07 ppm (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 154.84 (d, $J = 7.2$ Hz, 2C), 140.68 (2C), 33.68 (d, $J = 15.3$ Hz, 4C), 30.12 (dd, $J = 23.1$, 9.6 Hz, 2C), 29.59 (dd, $J = 22.7$, 11.2 Hz, 8C), 27.29 (dd, $J =$ 9.5, 6.4 Hz, 8C), 26.41 ppm (4C); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta =$ −2.57 ppm; GC-MS (EI, 70 eV): *m/z* (%) 499 (1) [M^+], 417 (100) [M-Cy]; HRMS (ESI$^+$): calcd for $C_{30}H_{51}N_2P_2$ [M+H]$^+$: 501.3522; found: 501.3521.

*2,3-Bis((di-tert-butylphosphino)methyl)pyrazine (**10**):* Yield: 53%, 4.2 g;^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.23$ (s, 2H), 3.32–3.29 (m, 4H), 1.10 ppm (d, $J = 10.9$ Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 155.36$ (d, $J = 8.6$ Hz, 2C), 140.36 (2C), 31.84 (d, $J = 23.6$ Hz, 4C), 29.77 (d, $J =$ 13.4 Hz, 12C), 29.54 ppm (d, $J = 6.8$ Hz, 2C); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 27.00$ ppm; GC-MS (EI, 70 eV): *m/z* (%) 339 (100) [M-*t*Bu]; HRMS (ESI$^+$): calcd for $C_{22}H_{43}N_2P_2$ [M+H]$^+$: 397.2896; found: 397.2902.

*2,3-Bis((diphenylphosphino)methyl)quinoxaline (**11**):* Yield: 49%, 5.17 g; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$–7.85 (m, 2H), 7.60–7.55 (m, 2H), 7.42–7.37 (m, 8H), 7.30–7.25 (m, 12H), 3.75 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 153.23$ (d, $J = 8.4$ Hz, 2C), 140.76 (2C), 137.77 (d, $J = 14.8$ Hz, 4C), 133.04 (4C), 132.79 (4C), 128.98–128.31 (m, 16C), 36.59 ppm (dd, $J = 17.6$, 5.9 Hz, 2C); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta =$ −14.09 ppm; GC-MS (EI, 70 eV): *m/z* (%) 526 (15) [M^+], 341 (100) [M-PPh_2]; HRMS (ESI$^+$): calcd for $C_{34}H_{29}N_2P_2$ [M+H]$^+$: 527.1801; found: 527.1811; HRMS (ESI$^+$): calcd for $C_{34}H_{28}N_2NaP_2$ [M+Na]$^+$: 549.1620; found: 549.1611.

*2,3-Bis((dicyclohexylphosphino)methyl)quinoxaline (**12**):* Yield: 43%, 4.74 g; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (dd, $J = 6.3$, 3.5 Hz, 2H), 7.61 (dt, $J = 6.4$, 3.4 Hz, 2H), 3.51 (s, 4H), 1.86–1.61 (m, 24H), 1.37–1.08 ppm (m, 20H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 155.40$ (d, $J =$ 6.4 Hz, 2C), 140.65 (2C), 128.45 (2C), 128.20 (2C), 33.77 (d, $J = 15.5$ Hz, 4C), 31.13 (dd, $J = 23.6$, 10.7 Hz, 2C), 29.64 (dd, $J = 21.1$, 11.3 Hz, 8C), 27.28 (dd, $J = 9.7$, 6.3 Hz, 8C), 26.39 ppm (4C); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -2.80$ ppm; GC-MS (EI, 70 eV): *m/z* (%) 467 (100) [M−Cy]; HRMS (ESI$^+$): calcd for $C_{34}H_{53}N_2P_2$ [M+H]$^+$: 551.3679; found: 551.3678.

*2,3-Bis((di-tert-butylphosphino)methyl)quinoxaline (**13**):* Yield: 51%, 4.55 g; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (dd, $J = 6.3$, 3.5 Hz, 2H), 7.61 (dt, $J = 6.4$, 3.3 Hz, 2H), 3.65 (t, $J = 1.6$ Hz, 4H), 1.13 ppm (d, $J =$ 11.0 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 156.07$ (d, $J = 7.8$ Hz, 2C), 140.34 (2C), 128.53 (2C), 128.30 (2C), 32.04 (d, $J = 23.6$ Hz, 4C), 31.07 (dd, $J = 28.0$, 9.9 Hz, 2C), 29.91 ppm (d, $J = 13.3$ Hz, 12C); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 25.86$ ppm; GC-MS (EI, 70 eV): *m/z* (%) 389 (100) [M-*t*Bu]; HRMS (ESI$^+$): calcd for $C_{26}H_{45}N_2P_2$ [M+H]$^+$: 447.3053; found: 447.3054.

Procedure F

This product was synthesized from prepared 1-cyclohexyl-3,4-dimethyl-1*H*-pyrrole-2,5-dione (5 mmol) and chlorodiphenylphosphine (2.2 equiv) using the general procedure D without heating at the end of step 1.

*5-Butyl-1-cyclohexyl-4-((diphenylphosphino)methyl)-3-(diphenylphosphoryl)-3-methyl-1H-pyrrol-2(3H)-one (**14**):* Yield: 51%, 1.61 g; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.35$–8.26 (m, 2H), 7.78–7.70 (m, 2H), 7.48–7.20 (m, 16H), 4.00 (dd, $J = 14.2$, 2.2 Hz, 1H), 3.01 (dt, $J = 14.2$, 2.1 Hz, 1H), 2.83 (t, $J = 12.2$ Hz, 1H), 2.20–1.89 (m, 2H), 1.68 (td, $J = 7.2$, 6.7, 3.3 Hz, 2H), 1.59–1.46 (m, 2H), 1.41 (dd, $J = 16.0$, 1.6 Hz, 3H), 1.34–1.18 (m, 2H), 1.13–0.94 (m, 4H), 0.91–0.81 (m, 2H), 0.63 (t, $J = 7.2$ Hz, 3H), 0.55 ppm (ddd, $J = 10.3$, 4.9, 2.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 177.76$ (d, $J = 3.0$ Hz), 142.26 (dd, $J = 10.4$, 7.6 Hz), 139.24 (d, $J = 17.5$ Hz), 138.36 (d, $J = 15.6$ Hz), 133.64 (d, $J = 18.9$ Hz, 2C), 132.96 (d, $J = 9.0$ Hz, 2C), 132.71 (d, $J = 17.7$ Hz, 2C), 131.80 (d, $J = 8.7$ Hz, 2C), 131.73 (d, $J = 3$ Hz, 2C), 131.54 (d, $J = 2.8$ Hz), 130.70 (d, $J = 94.5$ Hz), 130.50 (d, $J = 97.1$ Hz), 128.66, 128.31 (d, $J = 5.4$ Hz, 2C), 128.20, 128.16 (d, $J = 6.6$ Hz), 128.06 (d, $J = 11.9$ Hz, 2C), 127.66 (d, $J = 11.9$ Hz, 2C), 110.92 (t, $J = 6.4$ Hz), 56.16 (d, $J = 57.9$ Hz), 54.08, 29.62 (t, $J = 3.3$ Hz), 28.93, 28.47, 26.33 (d, $J = 16.0$ Hz), 26.22, 25.94, 24.94, 23.55, 22.32, 17.57 (dd, $J = 7.8$, 3.5 Hz), 13.57 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 30.02$ (d, $J = 5.9$ Hz), −15.12 ppm (d, $J = 5.3$ Hz); MS (EI): *m/z* (%) 633 (4) [M^+], 448 (100) [M−PPh_2]; HRMS (ESI$^+$): Calcd for $C_{40}H_{46}NO_2P_2$ [M+H]$^+$: 634.2998; found: 634.2991; HRMS (ESI$^+$): calcd for $C_{40}H_{45}NNaO_2P_2$ [M+Na]$^+$: 656.2818; found: 656.2807. More information on NMR signal assignment can be found in the Supporting Information.

Catalytic Experiments: Methoxycarbonylation of 1-Octene

A vial (4 mL) was charged with monophosphine (0.32 mol%) or diphosphine ligand (0.16 mol%) and a stirring bar was added. Then, 1.25 mL of a clear, light-yellow stock solution (prepared from $Pd(acac)_2$ (2.92 mg, 0.04 mol%), $MeSO_3H$ (9.4 μL, 0.6 mol%), and MeOH (15 mL)) and 1-octene (315 μL, 2 mmol) were injected by using a syringe. The vial was placed in an alloy plate, which was transferred into an autoclave (600 mL) from Parr Instruments under an argon atmosphere. After flushing three times with nitrogen, the autoclave was pressurized by CO at 40 bar. The reaction was performed for 20 h at 100 °C. Then, the autoclave was cooled to room temperature and the pressure was carefully released. Isooctane (200 μL) was added as an internal standard to the solution before the conversion, yield, and regioselectivity were determined by GC analysis.

*X-ray Crystal Structure Analysis of the Lithium Salt of Compound **2** and Products **6**, **7**, and **13***

Data were collected on a STOE-IPDS II (for the lithium salt of compound **2** and product **6**) or on a Bruker Kappa APEX II Duo (for products **7** and **13**) diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[22] XP (Bruker AXS) was used for graphical representations.

Crystal data for the lithium salt of compound **2**: $C_{22}H_{42}LiN_2P$, $M = 372.49$, monoclinic, space group $P2_1/c$, $a = 11.0250(4)$, $b = 16.5445(4)$, $c =$ 13.6678(5) Å, $\beta = 109.189(3)°$, $V = 2354.53(13)$ Å^3, $T = 150(2)$ K, $Z = 4$, 44566 reflections collected, 6358 independent reflections ($R_{int} = 0.0348$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0350$, $wR_2 = 0.0886$, final R values (all data): $R_1 = 0.0495$, $wR_2 = 0.0918$, 254 parameters.

Crystal data for **6**: $C_{31}H_{27}NP_2$, $M = 475.48$, monoclinic, space group $P2_1/c$, $a = 7.8660(2)$, $b = 22.4909(5)$, $c = 14.3707(4)$ Å, $\beta = 98.184(2)°$, $V =$ 2516.48(11) Å^3, $T = 293(2)$ K, $Z = 4$, 44527 reflections collected, 6781 independent reflections ($R_{int} = 0.037$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0322$, $wR_2 = 0.0811$, final R values (all data): $R_1 = 0.0445$, $wR_2 = 0.0834$, 308 parameters.

Crystal data for **7**: $C_{15}H_{26}NP$, $M = 251.34$, orthorhombic, space group $Aba2$, $a = 21.6794(5)$, $b = 15.0690(3)$, $c = 9.5202(2)$ Å, $V = 3110.13(12)$ Å^3, $T = 150(2)$ K, $Z = 8$, 51602 reflections collected, 2045 independent reflections ($R_{int} = 0.0404$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0239$, $wR_2 = 0.0608$, final R values (all data): $R_1 = 0.0269$, $wR_2 = 0.0628$, 161 parameters.

Crystal data for **13**: $C_{26}H_{44}N_2P_2$, $M=446.57$, triclinic, space group $P\bar{1}$, $a=12.3690(2)$, $b=15.1086(3)$, $c=15.8064(3)$ Å, $\alpha=92.094(1)$, $\beta=99.194(1)$, $\gamma=112.064(1)°$, $V=2687.28(9)$ Å^3, $T=150(2)$ K, $Z=4$, 70125 reflections collected, 12333 independent reflections ($R_{int}=0.0338$), final R values ($I>2\sigma(I)$): $R_1=0.0327$, $wR_2=0.0806$, final R values (all data): $R_1=0.0437$, $wR_2=0.0887$, 565 parameters.

CCDC 976293 (**13**), CCDC 976294 (**7**), CCDC 976295 (lithium complex with **2** and TMEDA), and CCDC 976296 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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