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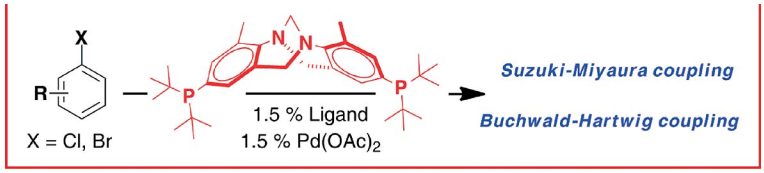
SHORT COMMUNICATION

Tröger's Base P Ligands



Easily accessible bisphosphane ligands based on the 2,8-substituted Tröger's base scaffold are synthesized and effectively applied in palladium-catalyzed C–C and C–N bond-forming reactions of aryl chlorides and bromides.

Keywords: Ligand design / Phosphane ligands / Cross-coupling / Palladium / Homogeneous catalysis

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Tröger's Base Derived Phosphanes for Suzuki–Miyaura and Buchwald–Hartwig Cross-Coupling Reactions

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Keywords: Ligand design / Phosphane ligands / Cross-coupling / Palladium / Homogeneous catalysis

A library of bis(phosphane) ligands based on the 2,8-substituted Tröger's base scaffold was synthesized through an efficient two-step protocol by starting from a commercially available aniline. The new ligands proved their efficiency in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions and Buchwald–Hartwig aminations of aryl chlorides and bromides.

Introduction

Palladium-catalyzed cross-coupling reactions between organometallic reagents and organic electrophiles have developed over the years into a sophisticated synthetic tool.[1] This methodology helped chemists to access complex architectures ranging from natural products and medicinal compounds to those in materials chemistry.[2] Organic phosphane ligands typically play a prominent role in these transformations.[3] The ever-increasing demand to access new and more challenging targets has advanced the field of ligand design. Thus, the phosphane family of ligands consisting of simple representatives, such as 1,1′-bis(diphenylphosphany)ferrocene (dppf) and PPh_3, which were frequently used at the infancy of palladium-catalyzed cross-coupling reactions, recently expanded with the addition of tailor-made members. The development of meticulously designed electron-rich bulky phosphanes[4] allowed for the sluggish reactivity of aryl chlorides and sterically hindered coupling partners[5] to be addressed and also expanded the substrate scope to form bonds other than carbon–carbon, most notably carbon–nitrogen bonds.[6]

Despite significant achievements, the quest for alternative motifs in ligand design should not be abated if a reasonable balance between the complexity of the ligand and its performance is achieved. Tröger's base (2,8-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine) is a dissymmetric molecule belonging to the C_2 point group.[7] Probably the most interesting feature of Tröger's base is that pyramidal inversion at the nitrogen atom is structurally prohibited, and this gives rise to two enantiomers that are configurationally stable and that can be separated at room temperature. We recently exploited the 4,10-disubstituted Tröger's base scaffold as a structural backbone for a new class of ligands.[8] X-ray crystallography and NMR spectroscopy revealed that such structures behave as doubly bidentate ligands coordinating two metal atoms within a single ligand molecule. The corresponding phosphane ligands were catalytically active in Suzuki–Miyaura cross-coupling reactions of aryl bromides. However, any attempt to employ aryl chlorides proved fruitless. Herein, we provide a solution to this issue and present a concise strategy for the synthesis of 2,8-bis(phosphane) Tröger's base derived ligands that can effectively involve aryl chlorides in palladium-catalyzed C–C and C–N bond-forming reactions.

Results and Discussion

Tröger's base derived bis(phosphanes) **2a**–**c** were efficiently synthesized by starting from *rac*-2,8-dibromo-4,10-dimethyl Tröger's base analogue **1** (Scheme 1).[9] The lithium/bromine exchange on **1** followed by quenching with chlorodiphenylphosphane or chlorodicyclohexylphosphane afforded bis(phosphanes) **2a** and **2c**. Whereas **2a** was isolated in 75% yield without any issues, the purification of **2c** proved troublesome. Therefore, it was directly protected as its BH_3 adduct **2c′** in 74% overall yield to prevent oxidation during workup and purification. Adduct **2c′** was then readily deprotected, typically immediately prior to its use in catalysis, with morpholine to give **2c** in 70% yield. In the case of *tert*-butyl derivative **2b**, transmetalation to organocuprate[10] and an elevated reaction temperature were necessary to introduce the di-*tert*-butylphosphane moiety effectively. Omission of CuCl resulted in no product formation. In analogy to the previous ligand, **2b** was directly treated with BH_3·THF and purified as borane adduct **2b′** (88%). Deprotection with morpholine yielded **2b** in 80% yield. Ac-

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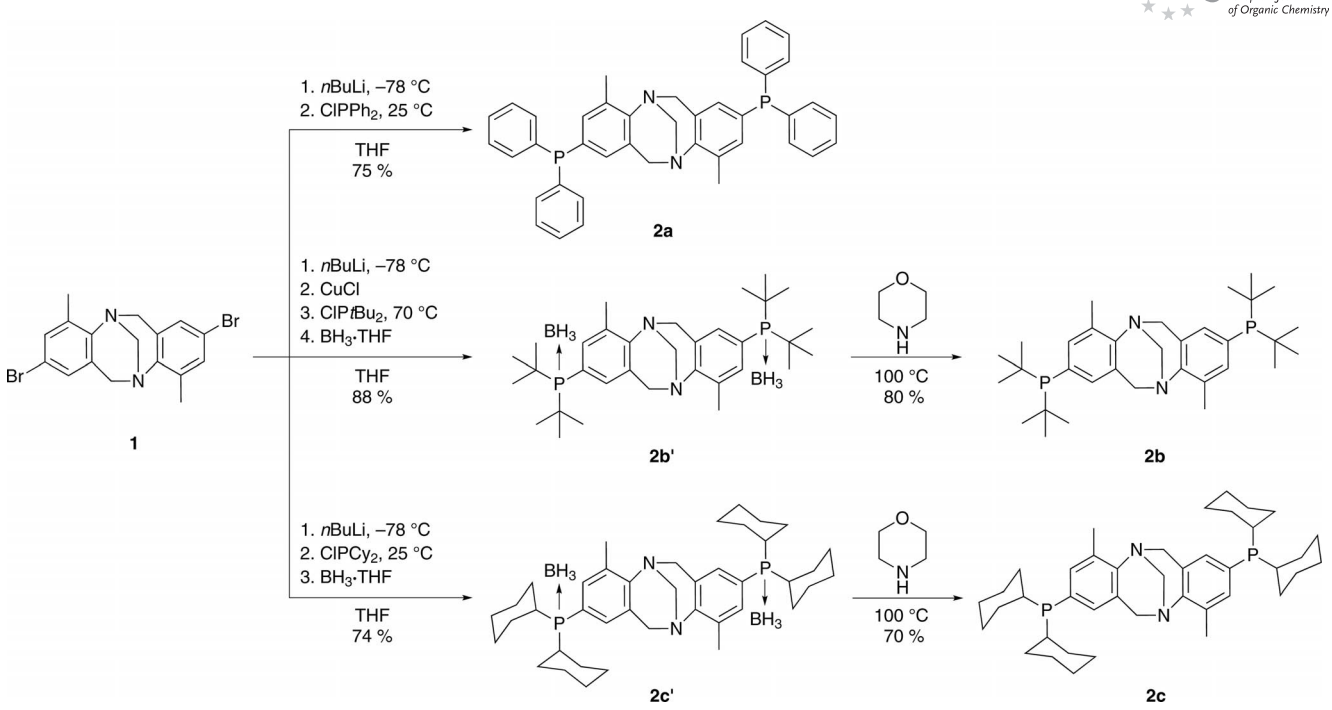


Scheme 1. Synthesis of ancillary phosphane ligands based on a Tröger's base scaffold.

cording to our observations, bis(phosphanes) **2b** and **2c** are bench-stable in the solid state, but their sensitivity towards oxygen increases in solution. Their ease of preparation from cheap starting materials and the high modularity of the presented strategy bodes well for further development and tuning of this family.

With a small library of bis(phosphanes) in hand, their efficiency was first tested in Suzuki–Miyaura cross-coupling reactions. A brief screening of reaction conditions revealed that the use of $Pd(OAc)_2$ as the palladium precursor, potassium phosphate (tribasic) as the base, and toluene as the solvent were critical for an efficient outcome of the coupling reaction.[11]

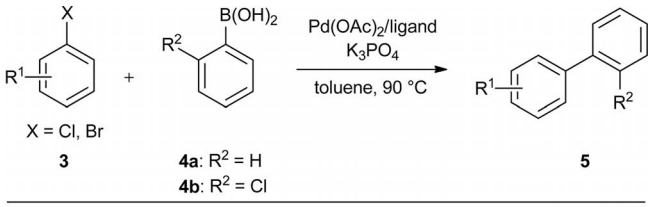
As summarized in Table 1 the palladium complexes with ligands **2a**–**c** efficiently catalyzed the cross-coupling of aryl bromides and chlorides with arylboronic acids in short periods of time. The palladium/ligand ratio turned out to be crucial (Table 1, Entry 5). Although 1-chloro-2-methylbenzene (**3e**) could be coupled with phenylboronic acid (**4a**) to provide the product in 80% yield if equimolar amounts of $Pd(OAc)_2$ and **2b** were used, an excess amount of palladium slowed down the reaction, and an excess amount of the ligand almost completely deactivated the catalyst. Substituents in the *ortho* position were tolerated both on the haloarene and on the boronic acid (Table 1, Entries 2–5). Moreover, the presence of electron-withdrawing groups at aryl chlorides is not necessary (Table 1, Entries 5 and 9). On the basis of the results obtained, *t*Bu ligand **2b** was identified to be the most active followed by cyclohexyl (Cy) analogue **2c**, and both ligands were capable of effecting the cross-coupling of aryl chlorides. Bis(diphenylphosphane) **2a** turned out to be the least active in terms of its substrate scope, and its use was limited to aryl bromides.

Subsequently, we turned our attention to catalytic C–N bond-forming reactions. On the basis of our results from the Suzuki–Miyaura coupling reaction, we tested most-potent ligand **2b** in Buchwald–Hartwig cross-coupling reactions of aryl bromides and chlorides with morpholine. We were delighted to observe that the combination of **2b** with $Pd(OAc)_2$ in refluxing toluene with sodium *tert*-butoxide as the base cleanly yielded the anticipated products in high yields (Table 2). Also in this case, *ortho* substituents did not hamper the outcome of the reaction. Only in the presence of strongly electron-donating groups on the aryl chloride were lower yields obtained (Table 2, Entries 6 and 7).

Conclusions

We have developed an efficient two-step synthetic route to novel C_2-symmetric bis(phosphane) ligands based on a Tröger's base scaffold. The synthesis is highly modular, as the phosphane moiety is introduced in the last step. We have shown that these ligands form a versatile catalytic system with $Pd(OAc)_2$ for Suzuki–Miyaura cross-coupling and Buchwald–Hartwig amination reactions of aryl bromides and chlorides. Intense efforts are currently dedicated to the clarification of the coordination properties of the reported ligands. Additionally, we are focusing on their preparation in enantiomerically pure form for applications in asymmetric catalysis. The results will be reported in due course.

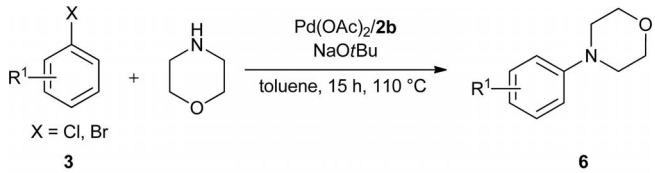
Table 1. Suzuki–Miyaura cross-coupling.[a]



Entry	Aryl-X	R^2	Product	Ligand	Time [h]	Yield[b] [%]
1	Br **3a**	H	**5aa**	**2a**	1.5	98
				2b	0.16	99
2	**3b** Br	H	**5ba**	**2a**	2	98
3	Br **3c**	H	**5ca**	**2a**	2	98
4	Br **3d** NH_2	Cl	H_2N **5db** Cl	**2b**	0.66	90
5	Cl **3e**	H	**5ea**	**2b**	5	80
					5	60[c]
					5	8[d]
6	Cl **3f** CN	H	NC **5fa**	**2b**	1.5	94
				2c	1.5	96
7	Cl **3g** $COCH_3$	H	**5ga** $COCH_3$	**2b**	1.5	96
8	Cl **3h** NO_2	H	O_2N **5ha**	**2c**	1.5	94
9	Cl **3i** MeO OMe	H	OMe **5ia** MeO	**2b**	24	50 (94)[e]

[a] Reactions conditions: aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), K_3PO_4 (2.0 mmol), $Pd(OAc)_2$ (1.5 mol-%), ligand (1.5 mol-%), toluene (2.5 mL), argon. [b] Yield of isolated product after column chromatography. [c] Ligand/Pd = 1:2. [d] Ligand/Pd = 2:1. [e] In xylene at 130 °C.

Table 2. Amination of aryl bromides and chlorides.[a]



Entry	Aryl-X	Product	Yield[b] [%]
1	Br **3k** OMe	MeO **6a**	96
2	**3b** Br	**6b**	93
3	Br **3l** NO_2	O_2N **6c**	95
4	Cl **3e**	**6d**	80
5	Cl **3h**	**6e**	93
6	Cl **3m** OMe	MeO	45
7	Cl **3i** MeO OMe	OMe **6f** MeO	51

[a] Reactions conditions: aryl halide (1.0 mmol), morpholine (1.2 mmol), NaO*t*Bu (1.2 mmol), $Pd(OAc)_2$ (1.5 mol-%), ligand (1.5 mol-%), toluene (2.5 mL), 110 °C, 15 h, argon.

Experimental Section

***rac*-2,8-Bis(diphenylphosphanyl)-4,10-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (2a):** THF (16 mL) was added to a Schlenk flask charged with **1** (0.82 g, 2 mmol) under argon. The mixture was cooled to –78 °C, and *n*BuLi (1.6 M in hexane, 2.8 mL, 4.4 mmol, 2.2 equiv.) was added dropwise to form a pale-yellow

clear solution. After 10 min, chlorodiphenylphosphane (0.78 mL, 4.4 mmol, 2.2 equiv.) was added in one portion. Stirring was continued at ambient temperature overnight. A saturated aqueous solution of NH_4Cl (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3× 20 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography [SiO_2 (40 g), ethyl acetate/hexane (1:10 to 20:80) containing 0.1% Et_3N] to give **2a** (747 mg, 75%) as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.30 (s, 6 H, CH_3), 3.92 (d, ^2J = 17.0 Hz, 2 H, CH_2N), 4.26 (s, 2 H, NCH_2N), 4.50 (d, ^2J = 16.9 Hz, 2 H, CH_2N), 6.75 (d, $^3J_{H,P}$ = 7.9 Hz, 2 H, Ar-*H*), 7.02 (d, $^3J_{H,P}$ = 7.9 Hz, 2 H, Ar-*H*), 7.29 (m, 20 H, Ar-*H*) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 17.5 (Ar-*C*H$_3$), 55.4 (*C*H$_2$N), 67.9 (N*C*H$_2$N), 128.8, 128.9, 129.0, 129.1, 130.6 (d, $J_{C,P}$ = 21.4 Hz), 132.1 (d, $J_{C,P}$ = 10.3 Hz), 133.9, 134.1 (d, $J_{C,P}$ = 19.6 Hz), 134.8 (d, $J_{C,P}$ = 20.2 Hz), 138.28 (d, $J_{C,P}$ = 11.4 Hz), 138.31 (d, $J_{C,P}$ = 11.3 Hz), 147.71 ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = –5.8 ppm. HRMS (ESI): calcd. for $C_{41}H_{37}N_2P_2$ [M + H]$^+$ 619.2426; found 619.2430.

***rac*-4,10-Bis(di-*tert*-butylphosphanyl)-2,8-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (2b):** THF (8 mL) was added to a Schlenk flask charged with **1** (0.41 g, 1 mmol) under argon. The mixture was cooled to –78 °C, and *n*BuLi (1.6 M in hexane, 1.5 mL, 2.4 mmol, 2.4 equiv.) was added dropwise to form a pale-yellow clear solution. After 5 min, the flask was opened, CuCl (0.198 g, 2.0 mmol) was quickly added, and the resulting suspension was stirred for 5 min after which di-*tert*-butylphosphane (0.44 g, 2.4 mmol, 2.2 equiv.) was added in one portion. The resulting mixture was warmed to ambient temperature within 60 min. Stirring was continued at 70 °C for 36 h. The mixture was then cooled to 0 °C, and BH_3·THF (1 M in THF, 10 mL, 10 mmol) was added. The reaction mixture was allowed to reach room temperature, and it was then stirred for an additional 6 h. The reaction mixture was poured into a saturated aqueous solution of NH_4Cl (25 mL) under argon, and the resulting mixture was stirred for 5 min and then extracted with CH_2Cl_2 (3× 75 mL). The combined organic layers were filtered through a Whatman filter paper, dried with $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography [SiO_2 (30 g), hexane/ethyl acetate (4:1) containing 0.1% Et_3N] to give borane-protected phosphane **2b′** (500 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.22–0.99 [br., 6 H, (BH_3)$_2$], 1.25 [d, ^3J = 12.8 Hz, 18 H, (CH_3)$_3$], 1.26 [d, ^3J = 12.8 Hz, 18 H, (CH_3)$_3$], 2.44 (s, 6 H, CH_3), 4.08 (d, ^2J = 17.0 Hz, 2 H, CH_2N), 4.27 (s, 2 H, NCH_2N), 4.62 (d, ^2J = 17.0 Hz, 2 H, CH_2N), 7.45 (d, $^3J_{H,P}$ = 8.0 Hz, 2 H, Ar-*H*), 7.59 (d, $^3J_{H,P}$ = 9.7 Hz, 2 H, Ar-*H*) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 17.7 (Ar-*C*H$_3$), 29.1 [d, $J_{C,P}$ = 1.8 Hz, C(*C*H$_3$)$_3$], 29.2 [d, $J_{C,P}$ = 1.8 Hz, C(*C*H$_3$)$_3$], 33.4 [d, $J_{C,P}$ = 27.1 Hz, *C*(CH$_3$)$_3$], 33.5 [d, $J_{C,P}$ = 27.1 Hz, *C*(CH$_3$)$_3$], 55.3 (*C*H$_2$N), 67.5 (N*C*H$_2$N), 122.2 (d, $J_{C,P}$ = 46.2 Hz), 128.3 (d, $J_{C,P}$ = 10.3 Hz), 132.5 (br. s), 133.3 (d, $J_{C,P}$ = 8.4 Hz), 135.3 (br. s), 149.4 (d, $J_{C,P}$ = 2.5 Hz) ppm. ^{31}P NMR (162.1 MHz, CD_2Cl_2): δ = 43.2 (d, $J_{B,P}$ = 66.3 Hz) ppm. HRMS (ESI): calcd. for $C_{38}H_{59}B_2N_2P_2$ [M + H]$^+$ 567.4345; found 567.4343.

Prior to the catalytic test, borane-protected phosphane **2b′** (260 mg, 0.46 mmol) was placed into a Schlenk flask under argon. Degassed morpholine (5 mL) was added, and the flask was sealed. The reaction mixture was stirred at 100 °C for 3 h. It was then cooled to room temperature, and the excess amount of morpholine was removed under reduced pressure. The residue was treated with degassed ethanol and cooled to –78 °C. The clear yellow supernatant was carefully removed by cannula filtration under argon to give **2b** (197 mg, 80%) as a white solid, which was briefly checked by ^{1}H NMR and ^{31}P NMR spectroscopy and immediately used in catalysis. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.12 [d, ^3J = 11.4 Hz, 18 H, (CH_3)$_3$], 1.13 [d, ^3J = 11.7 Hz, 18 H, (CH_3)$_3$], 2.39 (s, 6 H, CH_3), 4.02 (d, ^2J = 16.9 Hz, 2 H, CH_2N), 4.26 (s, 2 H, NCH_2N), 4.58 (d, ^3J = 16.8 Hz, 2 H, CH_2N), 7.07 (d, $^3J_{H,P}$ = 7.6 Hz, 2 H, Ar-*H*), 7.35 (d, $^3J_{H,P}$ = 5.2 Hz, 2 H, Ar-*H*) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 38.5 ppm.

***rac*-2,8-Bis(dicyclohexylphosphanyl)-4,10-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (2c):** THF (8 mL) was added to a 50 mL Schlenk flask charged with **1** (0.4 g, 1.0 mmol) under argon. The mixture was cooled to –78 °C, and *n*BuLi (1.6 M in hexane, 1.5 mL, 2.4 mmol, 2.4 equiv.) was added dropwise to form a pale-yellow clear solution. After 10 min, a solution of chlorodicyclohexylphosphane (560 mg, 2.4 mmol) in THF (5 mL) was used to quench the lithiated species. The reaction mixture was allowed to reach room temperature overnight. It was then cooled to 0 °C, and BH_3·THF (1 M in THF, 10 mL, 10 mmol) was added. The reaction mixture was allowed to reach room temperature, and it was then stirred for an additional 6 h. The reaction mixture was then poured into a saturated aqueous solution of NH_4Cl (20 mL) under argon, and the resulting mixture was stirred for 5 min and then extracted with CH_2Cl_2 (3× 50 mL). The combined organic layers were dried with $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography [SiO_2 (30 g), hexane/ethyl acetate (4:1 to 3:1) containing 0.1% Et_3N] to give borane-protected phosphane **2c′** (495 mg, 74%) as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = –0.26–0.94 [br., 6 H, (BH_3)$_2$], 0.99–1.39 [m, 20 H, (C$_6H_{11}$)$_2$], 1.41–2.08 [m, 24 H, (C$_6H_{11}$)$_2$], 2.43 (s, 6 H, CH_3), 4.09 (d, ^2J = 17.0 Hz, 2 H, CH_2N), 4.28 (s, 2 H, NCH_2N), 4.63 (d, ^2J = 17.0 Hz, 2 H, CH_2N), 7.16 (d, $^3J_{H,P}$ = 9.2 Hz, 2 H, Ar-*H*), 7.28 (d, $^3J_{H,P}$ = 8.2 Hz, 2 H, Ar-*H*) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 17.7 (Ar-*C*H$_3$), 26.5, 26.7, 26.8, 26.9, 27.0, 27.1, 27.19, 27.22, 27.24, 27.33 27.36, 27.4, 31.6 (d, $J_{C,P}$ = 34.2 Hz), 31.9 (d, $J_{C,P}$ = 33.9 Hz), 55.1 (*C*H$_2$N), 67.5 (N*C*H$_2$N), 120.6 (d, $J_{C,P}$ = 49.4 Hz), 128.7 (d, $J_{C,P}$ = 10.4 Hz), 131.0 (d, $J_{C,P}$ = 10.3 Hz), 133.4 (d, $J_{C,P}$ = 5.7 Hz), 133.9 (d, $J_{C,P}$ = 8.6 Hz), 149.6 ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 24.8 (br. s) ppm. HRMS (ESI): calcd. for $C_{41}H_{67}B_2N_2P_2$ [M + H]$^+$ 671.4974; found 671.4966.

Prior to the catalytic test, borane-protected phosphane **2c′** (200 mg, 0.3 mmol) was placed into a Schlenk flask under argon. Degassed morpholine (3 mL) was added, and the flask was sealed. The reaction mixture was stirred at 100 °C for 3 h. It was then cooled to room temperature, and the excess amount of morpholine was removed under reduced pressure. The residue was treated with degassed ethanol and cooled to –78 °C. The clear yellow supernatant was carefully removed by cannula filtration under argon. Degassed CH_2Cl_2 and silica (1 g) were added to the white precipitate, and the volatiles were removed. The residue was placed at the top of a short silica column (5 g) and eluted with hexane/ethyl acetate (1:2) + 0.1% Et_3N to give **2c** (138 mg, 70%) as a white solid, which was briefly checked by ^{1}H NMR and ^{31}P NMR spectroscopy and immediately used in catalysis. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.86–1.32 [m, 22 H, (C$_6H_{11}$)$_2$], 1.52–1.84 [m, 22 H, (C$_6H_{11}$)$_2$], 2.39 (s, 6 H, CH_3), 4.02 (d, ^3J = 16.9 Hz, 2 H, CH_2N), 4.26 (s, 2 H, NCH_2N), 4.57 (d, ^3J = 16.8 Hz, 2 H, CH_2N), 6.87 (d, $^3J_{P,H}$ = 7.4 Hz, 2 H, Ar-*H*), 7.12 (d, $^3J_{P,H}$ = 6.3 Hz, 2 H, Ar-*H*) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 2.5 ppm.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data and copies of the NMR spectra.

Acknowledgments

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