P-Chirogenic silylphosphine-boranes: synthesis and phospha-Michael reactions

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Dedicated to Prof. Jürgen Martens for his 65th birthday

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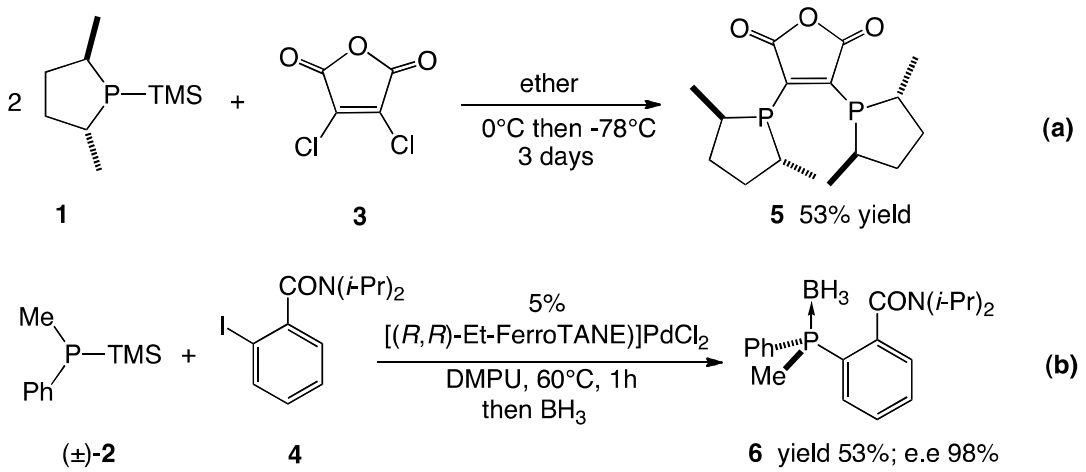
Abstract
Chiral and achiral silylphosphine-boranes were prepared in high yields by reaction of phosphide boranes with halogenosilanes. Their reaction at room temperature with Michael acceptors afforded 1,4-addition products as silylenol ether or ketone derivatives in good to excellent yields. In the case of the 2,3-dihalogeno-maleimides, the double addition of silylphosphine-borane led to the corresponding *trans*-diphosphine-boranes in 86% yield. Noteworthy, the reaction of P-chirogenic silylphosphine-boranes with enones afforded the phospha-Michael adducts without racemization at the P-center. While the silylphosphine-boranes have been scarcely described so far, these compounds demonstrate their great interest for the synthesis of chiral and achiral functionalized organophosphorus compounds.

Keywords: Phosphine-borane, silylphosphine, phospha-Michael reaction, P-chirogenic phosphine, silylenol ether.

Introduction

Organophosphorus chemistry[1] is a very active research field that concerns numerous applications in agrochemistry,[2] health,[3,4] biology,[5] materials[6] and additives,[7] hydrometallurgy,[8] … Chiral organophosphorus compounds are also of particular interest because their properties often depend on their configuration.[2-5] Indeed, they played a significant role as ligands in metal based asymmetric catalysis[9] as well as Brönsted acid or Lewis bases in organocatalysis.[10] Usually, the stereoselective synthesis of chiral organophosphorus compounds with P-C bond formation was

performed using chlorophosphines or phosphides as electrophilic or nucleophilic reagents, respectively.[9,11] In the last decade, the asymmetric hydrophosphination[12,13] and phospha-Michael addition[14] have also emerged as powerful methodologies for the synthesis of functional derivatives such as chiral organophosphorus compounds, that hold promise for applications in asymmetric catalysis. In this last case, typical reactions of Michael acceptor with free secondary phosphines or their oxide, sulfur or other borane derivatives, were achieved either in basic conditions or by heating.[14,15] On the other hand, the asymmetric phospha-Michael addition could also be performed using chiral transition metal catalysts[16-18] or organocatalysts.[19-21] Among the nucleophilic phosphorus reagents, the silylphosphines have recently retained the attention because these compounds are considered more electron-rich than the parent secondary phosphines due to the electrodonating effect of the silicon moiety.[22,23] Usually, the silylphosphines react with electrophiles through nucleophile-induced activation,[24,25] activated electrophile-driven reactions,[26-29] or using transition metal catalysis.[30-33] Thus, the silylphosphines **1** and **2** have been used for the stereoselective synthesis of MalPHOS **5** and P-chirogenic phosphines **6**, by double phospha-Michael addition with the 2,3-dichloromaleic anhydride **3**,[34] or Pd-catalyzed enantioselective arylation of the iodo compound **4**,[35] respectively (Scheme 1a,b).



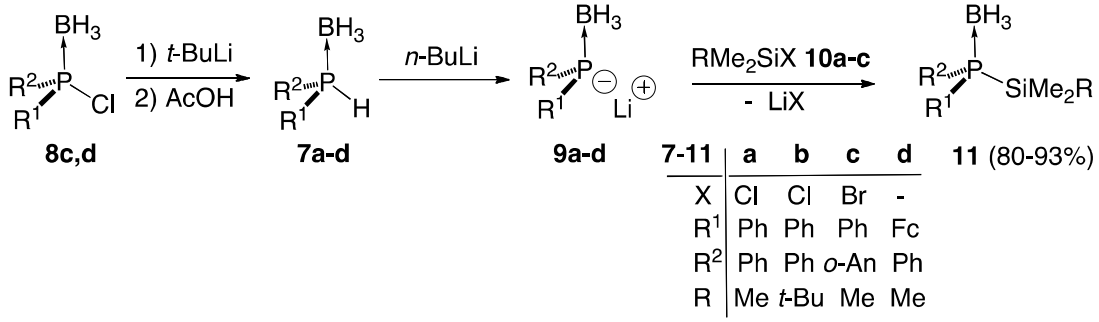
Scheme 1

While in the last decades the use of borane as P(III)-protecting group has resulted in significant breakthroughs for the stereoselective synthesis of tricoordinated organophosphorus compounds, surprisingly the silylphosphine-borane complexes have been scarcely studied.[36]
As part of our on-going program on the stereoselective synthesis of P-chirogenic organophosphorus compounds, we recently reported a new method for the preparation of P-chirogenic phosphide-boranes that involves metal-halide exchange of the corresponding chlorophosphines.[37,38] This method, which proceeds with retention of configuration at the P-center, was used for the synthesis of P-chirogenic phosphines by reaction with alkyl halide or

aryne reagents.[37,38] These results led us to envisage the synthesis and study of silylphosphine-boranes. Herein we report the first examples of P-chirogenic silylphosphane-boranes and their application to the stereoselective synthesis of functionalized phosphine-boranes by phospha-Michael addition under mild uncatalyzed conditions.

Results and Discussion

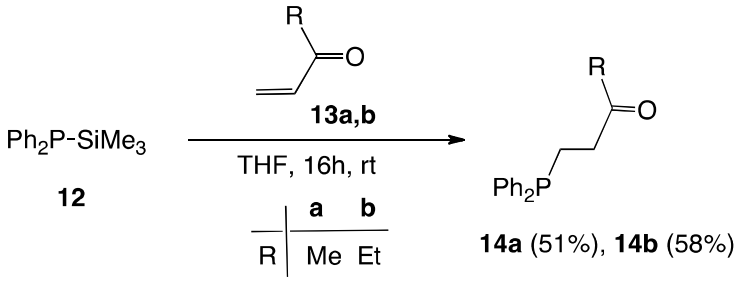
The silylphosphine-boranes **11a,b** were prepared in 80-93% yields by reaction of phosphide-boranes **9**, previously obtained by deprotonation of the secondary diphenylphosphine- borane **7a,** with the corresponding halogenosilane **10a** or **10b** (Scheme 2). After removal of the solvent, the residue was dissolved in toluene, then filtered to afford the silylphosphine-boranes **11a,b** which were used without further purification. In these conditions, when the P-chirogenic (*S*)-*o*-anisyl- or (*R*)-ferrocenylphosphine-boranes **7c**,**d**, previously prepared from the chlorophosphine-boranes **8c**,**d**,[37,38] were used, the corresponding silylphosphine-boranes **11c,d** were obtained with ee up to 87%, by reaction with TMSBr **10c** (Scheme 2). As the deprotonation of secondary P-chirogenic phosphine-boranes **7c**,**d** and their reactions proceed with retention of configuration at the phosphorus center,[37,38] it is reasonable to think that silylation with TMSBr **10c** follows the same stereochemistry. All silylphosphine-boranes **11** could be purified by chromatography, but in low isolated yields. Therefore, they were better used immediately after preparation without further purification.



7-11	a	b	c	d
X	Cl	Cl	Br	-
R^1	Ph	Ph	Ph	Fc
R^2	Ph	Ph	*o*-An	Ph
R	Me	*t*-Bu	Me	Me

Scheme 2

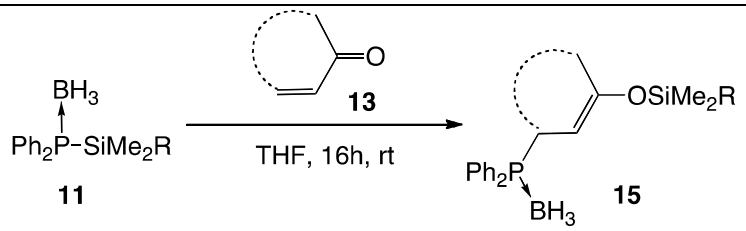
Firstly, the reactivity of the silylphosphine-borane **11a** was investigated in the Michael addition to enones **13** by comparison with the free trimethylsilylphosphine **12** (Scheme 3). When the trimethylsilylphosphine **12** was stirred with the enone **13a** (or **13b**) in THF during 16 hours at room temperature, the β-phosphinoketone **14a** (or **14b**) was obtained after purification by chromatography on silica gel in 51% (or 58%) yield (Scheme 3).[39]



Scheme 3

Surprisingly, when the silylphosphine-borane **11a** was used in the same conditions the reaction with enones **13a**,**b** led to the corresponding trimethylsilylenol ethers **15a** (or **15b**) as an isomeric mixture in 2:1 ratio and with yields up to 48% (Table 1, entries 1,2). In the case where the silylphosphine-borane **11a** was reacted with cyclohexenone **13c** in THF or toluene, the silylenol ether **15c** was successfully isolated in 84 or 63% yields (entries 3,4). Similarly, the reaction of the *t*-butyldimethylsilyl phosphine-borane **11b** with the cyclohexenone **13c** led to the corresponding silylenol ether **15d** in 77 % yield (entry 5).

Table 1. Reaction of silylphosphine-boranes **11** with Michael acceptors **13**



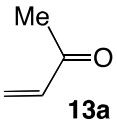
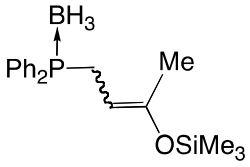
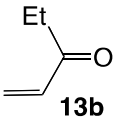
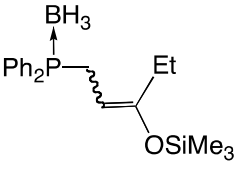
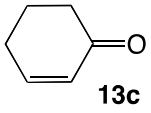
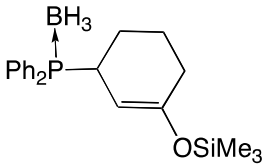
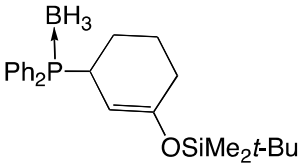
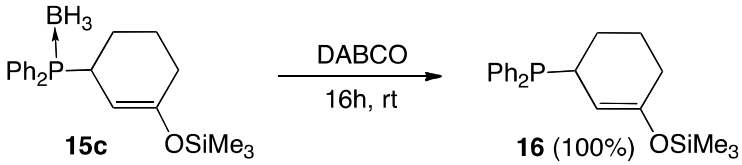
entry	silylphosphine borane	Michael acceptor	conditions[a]	Phosphine-borane	yield (%)[b]
1	**11a** (R= Me)	 **13a**	THF	**15a** 	40[c]
2	"	 **13b**	THF	**15b** 	48[c]

Table 1 (continued)

entry	silylphosphine borane	Michael acceptor	conditions[a]	Phosphine-borane	yield (%)[b]
3	"	 **13c**	THF	**15c** 	84
4	"	**13c**	Toluene	**15c**	"	63
5	**11b** (R= *t*-Bu)	**13c**	THF	**15d** 	77

[a] Reaction at rt for 16 hours. [b] Isolated yield. [c] Obtained as an isomeric mixture in 2:1 ratio.

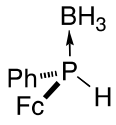
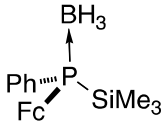
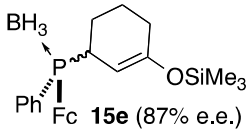
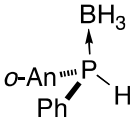
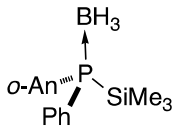
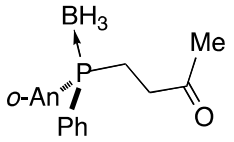
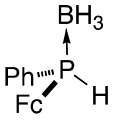
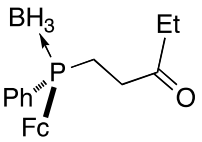
Interestingly, treatment of phosphine-borane **15c** with DABCO led quantitatively to the corresponding free phosphine silylenol ether **16** by decomplexation of the borane moiety (Scheme 4).



Scheme 4

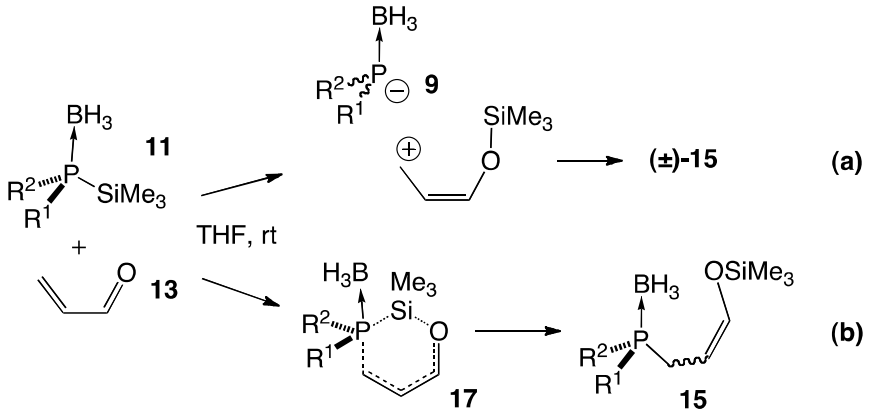
On the other hand, when the reaction of cyclohexenone **13c** was performed with (*S*)-ferrocenylphenyl(trimethylsilyl)phosphine-borane **11d** (85% ee), the silylenol ether **15e** was obtained as an epimeric mixture in 1:1 ratio in 75% yield (Table 2, entry 1). In the case where the (*R*)-*o*-anisylphenyl(trimethylsilyl)phosphine-borane **11c** was reacted with the enone **13a**, the β-(boranato)phosphinoketone **14c** was obtained in 72% yield and with 82% ee (entry 2). Similarly, the reaction of (*S*)-ferrocenylphenyl(trimethylsilyl)phosphine-borane **11d**, prepared from secondary phosphine-borane **7d** (33% ee), with the enone **13b**, led to the β-(boranato)phosphinoketone **14d** in 95% yield and with 33% ee (entry 3). In these cases, the formation of the ketone derivatives **14c**,**d** was explained by an easier hydrolysis of the silylenol intermediates in the conditions of the reaction (entries 2,3).

Table 2. Michael-addition of P-chirogenic silylphosphines **11c**,**d** with enone **13a-c**

entry	*sec*-phosphine boranes (ee %)[a]	silylphosphine boranes	enones	conditions	products (ee %)[a]	yield (%)[b]
1	 **7d** (87% e.e.)	 **11d**	**13c**	Toluene	 **15e** (87% e.e.) d.r. 1:1	75
2	 **7c** (85% e.e.)	 **11c**	**13a**	THF	 **14c** (82% e.e.)	72
3	 **7d** (33% e.e.)	**11d**	**13b**	Toluene	 **14d** (33% e.e.)	95

[a] Determined by HPLC on chiral column. [b] Isolated yield.

Interestingly, the phospha-Michael additions of Table 2 proceeded without racemization as the enantiomeric excesses of **15e**, **14c**, and **14d**, were close to those of the corresponding secondary phosphines **7c** and **7d** used for the preparation of the intermediate silyl phosphines **11c** and **11d**, respectively (entry 1). While the absolute configuration of the products **14c**,**d** or **15e** was not established, we believe that the reaction proceeds with a concerted mechanism involving retention of configuration at the P-center as showed in Scheme 5b.



Scheme 5

Indeed, in the case where the mechanism would lead to the formation of P-chirogenic phosphide-borane **9** by nucleophilic attack of the enone **13** first on the silyl group, a racemized product **15** would be obtained due to the poor configurational stability of **9** at room temperature (Scheme 5a).[37,38] On the contrary, when a concerted transition state **17** is formed by interaction of the enone **13** with the silyphosphine-borane **11** both on the Si- and P-atoms, precisely in anti position of the P-B bond, the product **15** is obtained with retention of configuration at the phosphorus center (Scheme 5b).

Finally, the 1,4-addition of silylphosphine-boranes **11** was investigated with various kinds of electrophilic acceptors such as methyl propiolate **13d**, 2,3-dihalogeno-maleimide **13e**,**f** and quinoxaline derivatives **13g**. In the case of the methyl propiolate **13d**, the reaction with the silylphosphine-borane **11a** led to the (boranato)phosphine-enoate **18**, which is stereoselectively obtained as (*E*)-isomer in 56% isolated yield (Table 3, entry 1).

Table 3. Addition of silylphosphine-borane **11a** to electrophilic acceptors **13d-g**

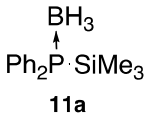
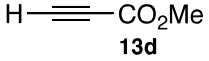
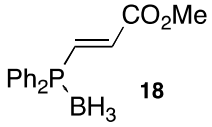
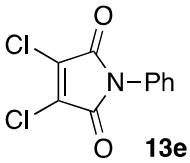
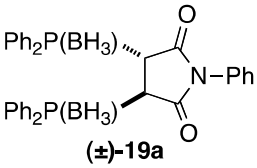
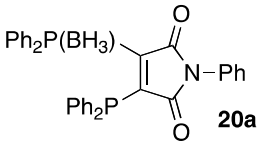
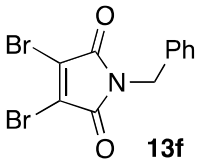
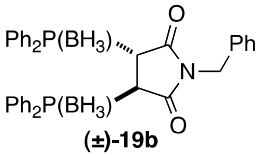
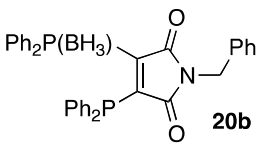
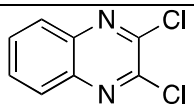
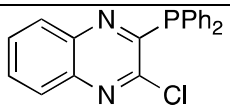
entry	silylphosphine (borane)	Michael acceptor	Conditions[a]	product	Yield[b] (%)
1	 **11a**	 **13d**	THF	 **18**	56
2	"	 **13e**	THF	 **(±)-19a**	47
3	"	**13e**	Et_2O	 **20a**	35
4	"	**13e**	Toluene	**19a**	86
				20a	11
5	"	 **13f**	THF	 **(±)-19b**	50
6	"	**13f**	Et_2O	 **20b**	37
7	"	**13f**	Toluene	**20b**	96

Table 3 (continued)

entry	silylphosphine (borane)	Michael acceptor	Conditions[a]	product	Yield[b] (%)
8	"	 **13g**	THF	 **21**	41
9	"	**13g**	Toluene	**21**	46

[a] Reaction at rt for 16 hours. [b] Isolated yield.

When the reaction of silylphosphine-borane **11a** was performed with 2,3-dichloromaleimide **13e** in THF, the 2,3-di(boranato)phosphinosuccinimide (±)-**19a** was obtained in 47% yield (entry 2). Crystals of diphosphine-diborane **19a** have been obtained and an OLEX view of the X-ray structure is depicted in Figure 1. The compound crystallizes in the C2/c space group with both enantiomers in the unit cell (*i.e.* racemate). The structure of **19a** is chiral and exhibits a C_2 crystallographic axis spanning the ring and both (boranato)diphenylphosphino groups, which are in *trans* relative configuration (Figure 1).

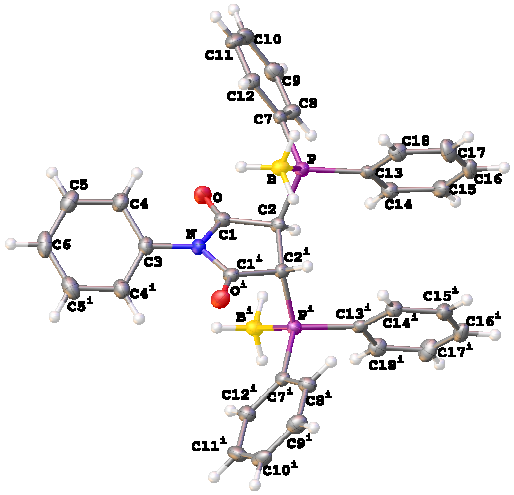
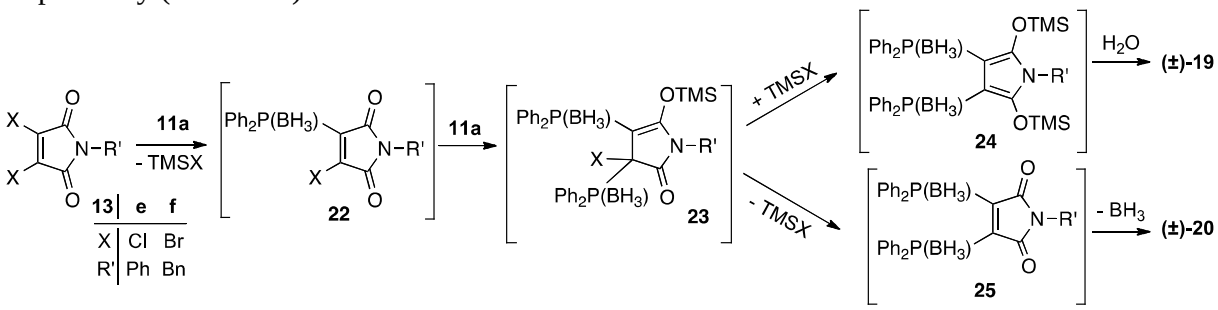


Figure 1. OLEX[40] view of the compound **19a**. Symmetry transformations used to generate equivalent atoms (i): 1-x, y, 3/2-z. Selected bond lengths [Å], angles [°] and dihedral angles [°]: P-B 1.910(2); C2-P 1.8577(18), C2-C2' 1.545(3); C7-P-C2 105.82(8), C13-P-C2 104.54(8), C13-P-C7 106.48(8); C2-P-B 110.54(9); C1-C2-P-B 71.23(14), N-C1-C2-P -100.70(12), C1-C2-P-C13 -163.77(12). C2-C1-N-C1^{i} -7.28(8).

On the other hand, when the silylphosphine-borane **11a** was added to the dichloromaleimide **13e** in Et_2O, the (monoboranato)diphosphinomaleimide derivative **20a** was isolated as major product (35% yield, entry 3). By contrast, when the reaction was performed in toluene the 2,3-

di(boranato)phosphinosuccinimide **19a** and the maleimide derivative **20a** were obtained in 88 and 11% yields, respectively (entry 4). Similarly, the addition of silylphosphine-borane **11a** to the dibromomaleimide **13f** in THF led to the 2,3-di(boranato)phosphinosuccinimide **19b** in 50% yield (entry 5). When the reaction was run in Et_2O, the (monoboranato)diphosphinomaleimide **20b** was obtained as major product (37% yield, entry 6). Finally, when the reaction of **11a** with the 2,3-dibromomaleimide **13f** was performed in toluene, the maleimide derivative **20b** was obtained in 96 % yield (entry 7).

The formation of the succinimide or maleimide derivatives **19** (or **20**) could be explained by two possible pathways *via* the intermediate **23** depending on the substrate **13**, the solvent and the halide. The compound **23** was formed by addition of two equivalents of silylphosphine-borane **11a** to the dihalogenomaleimide **13e** (or **13f**), *via* the diphenylphosphine-borane **22** (Scheme 6). The intermediate **23** can evolve either towards the formation of the bis-silylether derivative **24** by reaction with a trimethylsilyl reagent (*e.g.* TMSX), or the conventional double Michael-addition product **25** (Scheme 6). Finally, the hydrolysis of **24** and the loss of a borane moiety due to steric congestion in compound **25** led to the succinimide and maleimide products **19** and **20**, respectively (Scheme 6).



Scheme 6

On the other hand, when the dichloroquinoxaline **13g** was used as electrophilic acceptor, the reaction with the silylphosphine-borane **11a** in THF (or toluene) led to the monophosphine product **21** in 41 or 46% yield, respectively (entries 8,9). The formation of compound **21** was explained by only one addition of silylphosphine-borane **11a** to the 2,3-dichloroquinoxaline substrate **18** and the decomplexation of borane due to steric hindrance of the 2-chloroquinoxaline substituent. The structure of compound **21** was established by X-ray analysis (Figure 2). This structure shows the chloroquinoxaline substituent in staggered conformation with respect to both phenyl groups borne by the phosphorus atom, the chlorine atom facing the lone pair of the phosphorus atom (Figure 2)

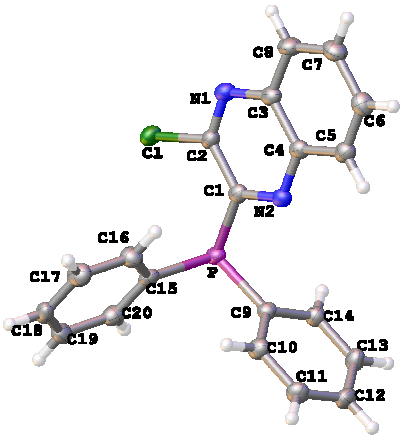


Figure 2. OLEX[40] view of the compound **21**. Selected bond lengths [Å], angles [°] and dihedral angles [°]: C1-P 1.844(3); C9-P 1.822(2), C15-P 1.828(3); C1-C2 1.433(3); C2-Cl 1.741(3); N2-C1-P 120.70(18), C9-P-C1 102.30(11), C9-P-C15 103.87(11); Cl-C2-C1-P 7.0(3), C2-C1-P-C9 175.4(2), C2-C1-P–C15 -77.3(2).

Conclusions

The silylphosphine-boranes were prepared in high yields by reaction of phosphide boranes, previously obtained either by deprotonation of the secondary phosphine-boranes or by metal halide exchange of the chlorophosphine-boranes with halogenosilanes. The reaction of silylphosphine-boranes with various Michael-acceptors led to the addition products in yields up to 96% under uncatalyzed mild conditions. In the case of the reaction with enones the product are mainly isolated as silylenol ether derivatives. Moreover, the silylphosphine-boranes also react with 2,3-dihalogenomaleimides to afford the corresponding *trans* diphosphine-diborane complexes in yields up to 86%. The *trans* configuration of both phosphine-borane moieties has been established by X-ray crystal structure analysis. Interestingly, when P-chirogenic silylphosphine-borane were used, the reaction with enones led to the phospha-Michael products without racemization at the P-center. While the silylphosphine-boranes have been scarcely described so far, these compounds reveal a great potential for the synthesis of chiral and achiral functionalized organophosphorus compounds.

Supporting information available

NMR spectra and crystallographic data in CIF format for compounds **19a** and **21**. This material is available free of charge via the internet at http://www.arkat-usa.org.

Experimental Section

All reactions were carried out under inert atmosphere. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone and stored under argon. Diphenyl(trimethylsilyl)phosphine **12** was purchased from commercial sources and used without purification. The P-chirogenic secondary phosphine-boranes (*S*)-**7c** and (*R*)-**7d** were prepared using the (-)- and (+)-ephedrine methodology, respectively.[37,38] Reactions were monitored by thin-layer chromatography (TLC) using 0.25 mm E. Merck precoated silica gel plates. Flash chromatography was performed with the indicated solvents using silica gel 60 (60AAC, 35-70 µm). NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{29}Si) were recorded on Bruker Avance 600, 500 or 300 MHz spectrometers at ambient temperature and chemical shifts are reported in ppm using TMS as internal reference for ^{1}H, ^{13}C and ^{29}Si NMR or 85% phosphoric acid as external reference for ^{31}P NMR. The signals are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s = broad signal, coupling constant(s) in Hertz and with their integration. The infrared spectra were recorded on a FT-IR Bruker Vector 22 and the bands are reported in cm^{-1}. Melting points were mesured on a Kofler melting points apparatus and are uncorrected. Optical rotation values were determined at 20°C on polarimeter Perkin Elmer 341 at 589 nm (sodium lamp). HPLC analyses were performed on a chromatograph equipped with a UV detector at λ = 210 nm and λ = 254 nm. High Resolution Mass Spectra (HRMS) were performed on Thermo Orbitrap XL under ESI conditions with a micro Q-TOF detector. Elemental analyses were measured on Thermo EA 1112 with a precision superior to 0.3% on a CHNS-O instrument apparatus.

Crystal Structure Determination

Diffraction data were collected on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems low-temperature apparatus operating at T = 115 K. Data were measured using φ and ω scans using MoK$_\alpha$ radiation (λ = 0.71073 Å, X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation the program Collect.[41] Cell parameters were retrieved using the SCALEPACK software and refined using DENZO.[42] Data reduction was performed using the DENZO[42] software which corrects for Lorentz polarisation. The structure was solved by Direct Methods using the SIR92[43] program structure solution program and refined by Least Squares using version of the ShelXL[44,45] (Sheldrick, 2008). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. CCDC Deposition Number: Compound **19a** (CCDC 1048105); Compound **21** (CCDC 1048106).

Trimethylsilyl(diphenyl)phosphine-borane (11a).[36] To a solution of diphenyl phosphine-borane **7a** (R^1 = Ph) (3.31 g, 16.6 mmol) in 30 mL of THF under inert atmosphere, was added dropwise at -78 °C *n*-BuLi (11.4 mL, 18.2 mmol, 1.1equiv). After stirring 30 minutes at -78 °C, a solution of chloro(trimethyl)silane **10a** (2.10 mL, 16.6 mmol) in 10 mL of THF was added. The

reaction mixture was kept at -78 °C during 30 minutes and was stirring at room temperature overnight. After removing the solvent under vacuum, the residue was dissolved in toluene and was filtered off. After new removal of the solvent under vacuum, **11a** was obtained as a colorless uncrystallized compound (4.21 g, 93% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 0.16 (d, $^{3}J_{PH}$ = 6.0 Hz, 9H, $SiMe_3$); 0.90-2.50 (br, 3H, BH_3); 7.01-7.08 (m, 6H, Ph); 7.66-7.70 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ -2.5 (d, $^{2}J_{PC}$ = 9.3 Hz, $SiMe_3$); 129.0 (d, J_{PC} = 9.3 Hz, C-aryl); 130.4 (d, J_{PC} = 2.3 Hz, C-aryl); 133.2 (d, J_{PC} = 9.3 Hz, C-aryl); 133.7 (d, J_{PC} = 8.2 Hz, C-aryl). ^{31}P NMR (121.4 MHz, C_6D_6): δ -23.9 (d, $^{1}J_{PB}$ = 38 Hz). ^{29}Si NMR (99.4 MHz, C_6D_6): δ +4.6 (d, $^{1}J_{SiP}$ = 44.7 Hz). IRFT (neat): 3057, 2959, 2926, 2856, 2383, 1437, 1256, 1112, 1066, 992, 846, 733, 691.

Diphenyl[*t*-butyl(dimethyl)silyl]phosphine-borane (11b). To a solution of diphenyl phosphine-borane **7a** (R^1 = Ph) (0.52 g, 2.6 mmol) in 6 mL of THF under inert atmosphere, was added dropwise at -78 °C *n*-BuLi (1.8 mL, 2.86 mmol, 1.1equiv). After stirring 30 minutes at -78 °C, a solution of *t*-butylchloro(dimethyl)silane **10b** (0.39 g, 2.6 mmol) in 4 mL of THF was added. The reaction mixture was kept at -78 °C during 30 minutes and was allowed to stir at room temperature overnight. After removal of the solvent under vacuum, the resulting crude was dissolved in toluene and was filtered off. After concentration under vacuum, **11b** was obtained as a colorless uncrystallized compound (0.65 g, 80% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 0.19 (d, $^{3}J_{PH}$ = 9.0 Hz, 6H, $SiMe_2$); 0.90-5.50 (br, 3H, BH_3); 0.90 (s, 9H, *t*-Bu); 7.01-7.06 (m, 6H, Ph); 7.82-7.84 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ -5.1 (d, $^{2}J_{PC}$ = 8.3 Hz, $SiMe_2$); 19.9 (d, J_{PC} = 9.3 Hz, *t*-Bu); 27.4 (s, CH_3); 128.8 (d, J_{PC} = 9.3 Hz, C-aryl); 130.5 (d, J_{PC} = 2.3 Hz, C-aryl); 134.1 (d, J_{PC} = 8.2 Hz, C-aryl); 135.3 (d, J_{PC} = 18.6 Hz, C-aryl). ^{31}P NMR (121.4 MHz, C_6D_6): δ -26.6 (d, $^{1}J_{PB}$ = 38 Hz). ^{29}Si NMR (99.4 MHz, C_6D_6): δ +4.7 (d, J_{SiP} = 44.3 Hz).

(*R*)-*o*-Anisyl(trimethylsilyl)phenylphosphine-borane (11c). To a solution of (*S*)-*o*-anisylphenylphosphine-borane **7c** (0.086 g, 0.37 mmol, 85% ee) in 6 mL of THF under inert atmosphere, was added dropwise at -78 °C *n*-BuLi (0.3 mL, 0.41 mmol, 1.1equiv). After stirring 30 minutes at -78 °C, a solution of bromo(trimethyl)silane **10c** (0.1 mL, 0.37 mmol) in 4 mL of THF was added. The reaction mixture was kept at -78 °C during 30 minutes and was stirred at room temperature overnight. After removal under vacuum the solvent, the residue was dissolved in toluene and was filtered off. After concentration under vacuum, **11c** was obtained as a colorless uncrystallized product (0.10 g, 93% yield). $[\alpha]_D^{25}$ = -57.1 (c 0.5, THF); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.29 (d, ^{3}J = 6.0 Hz, 9H, $SiMe_3$); 0.50-1.50 (br, 3H, BH_3); 3.82 (s, OMe); 6.94-7.06 (m, 2H, Ph); 7.32-7.55 (m, 6H, Ph); 7.62-7.73 (m, 1H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ -1.6 (d, $^{2}J_{PC}$ = 9.4 Hz, $SiMe_3$); 54.5 (s, OMe); 110.3 (d, J_{PC} = 3.8 Hz, C-aryl); 116.8 (d, $J_{P\text{-}C}$ = 44.4 Hz, C-aryl); 121.6 (d, J_{PC} = 10.1 Hz, C-aryl); 128.4 (d, J_{PC} = 10.1 Hz, C-aryl); 129.6 (d, J_{PC} = 3.8 Hz, C-aryl); 129.9 (d, J_{PC} = 44.4 Hz, C-aryl); 132.5 (d, J_{PC} = 3.8 Hz, C-aryl); 132.7 (d, J_{PC} = 10.1 Hz, C-aryl); 136.2 (d, J_{PC} = 10.1 Hz, C-aryl); 160.3 (s, C-aryl). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -28.9 (d, $^{1}J_{PB}$ = 48.6 Hz). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ +6.4 (d, $^{1}J_{PSi}$ = 48.7 Hz).

(*S*)-Ferrocenyl(trimethylsilyl)phenylphosphine-borane (11d). To a solution of (*R*)-ferrocenylphenylphosphine-borane **7d** (60 mg, 0.19 mmol, 87% ee) in 2 mL of THF under inert

atmosphere, was added dropwise at -78 °C *n*-BuLi (0.09 mL, 0.21 mmol, 1.1 equiv). After stirring 30 minutes at -78 °C, a solution of bromo(trimethyl)silane **10c** (0.03 mL, 0.23 mmol, 1.2 equiv) in 0.5 mL of THF was added and the reaction was stirred at room temperature overnight. After removal the solvent under vacuum, the residue was dissolved in toluene and was used without further purification. ^{31}P NMR (121.4 MHz, toluene D_8): δ -34.3 (d, $^1J_{PB}$ = 48.6 Hz).

4-Diphenylphosphinobutan-2-one (14a).[46] To a solution of diphenyl(trimethylsilyl) phosphine **12** (0.64 g, 2.47 mmol) in 10 mL of THF under inert atmosphere was added a solution of methylvinylketone **13a** (0.20 mL, 2.47 mmol) in 5 mL of THF at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum. After purification by chromatography on silica gel, **14a** was obtained as a colorless uncrystallized compound (0.32 g, 51% yield). R_f = 0.82 (dichloromethane/pentane 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 3H, Me); 2.33 (m, 2H, CH_2); 2.52 (m, 2H, CH_2); 7.32-7.40 (m, 6H, Ph); 7.41-7.50 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): 21.1 (d, J_{PC} = 11.2 Hz, CH_2); 29.9 (s, Me); 39.8 (d, J_{PC} = 17.7 Hz, C-P); 128.6 (d, J_{PC} = 6.7 Hz, C-aryl); 128.9 (s, C-aryl); 132.7 (d, J_{PC} = 18.5 Hz, C-aryl); 138.2 (d, J_{PC} = 12.5 Hz, C-aryl); 207.7 (d, J_{PC} = 12.5 Hz, C=O). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -15.7 (s). HRMS (ESI-Q-TOF) calcd for $C_{16}H_{17}OPNa$ $[M+Na]^+$: 279.0909, found 279.0911.

5-Diphenylphosphinopentan-3-one (14b).[47] To a solution of diphenyl(trimethylsilyl)phosphine **12** (0.64 g, 2.47 mmol) in 10 mL of THF was added at room temperature under inert atmosphere a solution of ethylvinylketone **13b** (0.17 mL, 2.47 mmol) in 5 mL of THF. After 16 hours stirring, the reaction mixture was concentrated under vacuum. After purification by chromatography on silica gel, **14b** was obtained as colorless uncrystallized product (0.39 g, 58% yield). R_f = 0.76 (dichloromethane/Pentane 80:20). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.02 (t, ^3J = 7.4 Hz, 3H, CH_3); 2.30 (m, CH_2); 2.38 (q, ^3J = 7.4 Hz, 2H, CH_2); 2.49 (td, J = 7.7 Hz, J = 8.4 Hz, 2H, CH_2); 7.33-7.39 (m, 6H, Ph); 7.40-7.50 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 7.8 (s, CH_3); 21.4 (d, $^1J_{PC}$ = 11.2 Hz, CH_2P); 35.9 (s, CH_2); 38.4 (d, $^2J_{PC}$ = 17.7 Hz, CH_2); 128.5 (d, J_{PC} = 6.7 Hz, C-aryl); 128.8 (s, C-aryl); 132.7 (d, J_{PC} = 18.5 Hz, C-aryl); 138.2 (d, J_{PC} = 12.5 Hz, C-aryl); 210.4 (d, J_{P-C} = 12.5 Hz, C=O). ^{31}P NMR (121.4MHz, $CDCl_3$): δ -15.4 (s). HRMS (ESI-Q-TOF) calcd for $C_{17}H_{19}OPNa$ $[M+Na]^+$: 293.0923, found: 293.0916.

(*R*)-4-[(Boranato)-*o*-anisylphenylphosphino]butan-2-one (14c). To a solution of (*R*)-*o*-anisyl(trimethylsilyl)phenylphosphine-borane **11c** (0.05 g, 0.17 mmol) in 5 mL of THF under inert atmosphere was added at -78 °C a solution of methylvinylketone **13a** (14 µL, 0.17 mmol) in 5 mL of THF. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **14c** as a colorless uncrystallized compound (0.04 g, 72% yield). R_f = 0.86 (dichloromethane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.50-1.70 (br, 3H, BH_3); 2.11 (s, CH_3); 2.53 (m, 2H, CH_2); 2.80 (m, 2H, CH_2P); 3.69 (s, 3H, OCH_3); 6.90 (dd, J = 3.0 Hz, J = 6.0 Hz, 1H, Ph); 7.10 (t, J = 6.0 Hz, 1H, Ph); 7.39-7.45 (m, 3H, Ph); 7.53 (t, J = 6.0 Hz, 1H, Ph); 7.68 (dd, J = 3.0 Hz, J = 6.0 Hz, 2H, Ph); 7.91 (dd, J = 6.0 Hz, 1H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 17.7 (d, J_{PC} = 41.5 Hz, CH_2P); 29.8 (s, CH_3); 37.3 (d, J_{PC} = 2.4 Hz, CH_2); 55.4 (s, OCH_3); 111.1 (d, J_{PC} = 4.9 Hz, C-aryl); 115.6 (d, J_{PC} = 51.0 Hz, C-aryl); 121.2 (d, J_{PC} = 12.2 Hz, C-aryl); 128.4 (d, J_{PC} = 12.2 Hz, C-aryl); 129.8 (d, J_{PC} =

57.1 Hz, C-aryl); 130.6 (d, J_{PC} = 2.4 Hz, CH_2); 131.6 (d, J_{PC} = 12.2 Hz, C-aryl); 134.0 (d, J_{PC} = 2.4 Hz, CH_2); 136.4 (d, J_{PC} = 12.1 Hz, C-aryl); 206.7 (d, J_{PC} = 13.4 Hz, C=O). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +15.7 (d, J_{PB} = 76 Hz). HRMS (ESI-Q-TOF) calcd for $C_{17}H_{22}O_2PBNa$ $[M+Na]^+$: 323.1342, found: 323.1335. The enantiomeric excess 82% was determined by HPLC on Chiralcel OK column using a mixture hexane/*i*-propanol 80:20 as eluent, flow 1 mL/min, λ = 230 nm, T = 40 °C. The retention times for the enantiomers were t_1 = 15.3 and t_2 = 30.5 minutes, respectively.[48]

(*S*)-5-[(Boranato)ferrocenylphenylphosphino]pentan-3-one (14d). To a solution of (*R*)-ferrocenyl(trimethylsilyl)phenylphosphine-borane **11d** (0.07 g, 0.19 mmol, 33% ee) in 2 mL of THF under inert atmosphere, was added at -78 °C a solution of ethylvinylketone **13b** (38.6 μL, 0.39 mmol) in 0.5 mL of THF. The reaction mixture was then allowed to warm up at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **14d** as an orange uncrystallized compound (0.07 g, 95% yield). R_f = 0.74 (dichloromethane/ethyl acetate 97:3); $[\alpha]_D^{25}$ = -10.1 (c 1.4, $CHCl_3$), 33% ee uncorrected. ^{1}H NMR (300 MHz, C_6D_6): δ 0.70 (t, *J* = 7.20 Hz, 3H, CH_3); 1.40-1.90 (m, 3H, BH_3); 1.54 (AB, *J* = 17.9 Hz, *J* = 7.2 Hz, 1H, CH_2); 1.62 (AB, *J* = 17.9 Hz, *J* = 7.2 Hz, 1H, CH_2); 2.05-2.20 (m, 1H, CH_2); 2.25-2.36 (m, 2H, CH_2); 2.45-2.60 (m, 1H, CH_2); 3.92-3.95 (m, 1H, Fc); 3.95 (s, 5H, Fc); 3.97-4.00 (m, 1H, Fc); 4.14-4.17 (m, 1H, Fc); 4.36-4.38 (m, 1H, Fc); 6.93-6.99 (m, 3H, Ph); 7.69-7.76 (m, 2H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ 7.6 (s, CH_3); 21.5 (d, J_{PC} = 40.6 Hz, CH_2P); 35.2 (s, CH_2); 35.6 (d, J_{PC} = 2.1 Hz, CH_2); 70.0 (s, CH_{Fc}); 70.5 (d, J_{PC} = 64.9 Hz, Fc); 71.2 (d, J_{PC} = 7.5 Hz, Fc); 71.8 (d, J_{PC} = 8.8 Hz, Fc); 71.8 (d, J_{PC} = 7.9 Hz, Fc); 71.9 (d, J_{PC} = 9.8 Hz, Fc); 128.6 (d, J_{PC} = 9.7 Hz, Ph); 130.7 (d, J_{PC} = 54.0 Hz, Ph); 131.0 (d, J_{PC} = 2.4 Hz, Ph); 132.4 (d, J_{PC} = 9.1 Hz, Ph); 207.3 (d, J_{PC} = 12.0 Hz, C=O). ^{31}P NMR (121.4 MHz, C_6D_6): δ +26.0 (m). HRMS (ESI-Q-TOF) calcd for $C_{21}H_{26}BFeOPNa$ $[M+Na]^+$: 415.10601, found: 415.10756. FTIR (neat): 3056, 2976, 2937, 2373, 1714, 1436, 1413, 1172, 1107, 1063, 1026, 742. The enantiomeric excess 33% was determined by HPLC on Chiralcel OD-H column using a mixture hexane/*i*-propanol 97:3 as eluent, flow 0.7 mL/min., λ = 210 nm, T = 40 °C. The retention times for the enantiomers were t_1 = 17.07 and t_2 = 20.25 minutes, respectively.[48]

3-(Trimethylsilyloxy)but-2-enyl-diphenylphosphine-borane (15a). To a solution of diphenyl(trimethylsilyl)phosphine-borane **11a** (0.65 g, 3.33 mmol) in 10 mL of THF under inert atmosphere was added a solution of methylvinylketone **13a** (0.30 mL, 3.33 mmol) in 5 mL of THF at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **15a** as a mixture of isomers in 2:1 ratio and colorless uncrystallized compound (0.45 g, 40% yield). R_f = 0.79 (dichloromethane/pentane 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): 0.50-1.50 (br, 3H, BH_3); Major isomer, δ 0.20 (s, 6H, $SiMe_3$); 1.76 (dd, *J* = 1.0 Hz, *J* = 3.9 Hz, 1.3H, CH_3); 3.06 (dd, *J* = 7.3 Hz, *J* = 12.0 Hz, 1.3H, CH_2); 4.50 (q, *J* = 7.2 Hz, 0.7H, CH=CO); [Minor isomer, 0.10 (s, 3H, $SiMe_3$); 1.60 (dd, *J* = 0.6 Hz, *J* = 3.2 Hz, 0.7H, CH_3); 2.99 (dd, *J* = 8.1 Hz, *J* = 11.9 Hz, 0.7H, CH_2); 4.60 (q, *J* = 6.3 Hz, 0.3 H, CH=CO)]; 7.43-7.49 (m, 6H, Ph); 7.67-7.74 (m, 4H, Ph). ^{13}C

NMR (75.4 MHz, C_6D_6): major isomer, δ 1.10 (s, $SiMe_3$); 22.4 (d, J_{PC} = 2.3 Hz, CH_3); 23.4 (d, J_{PC} = 38.5Hz, CH_2); 97.2 (d, J_{PC} = 4.6 Hz, CH=C-O); 128.6 (d, J_{PC} = 10.4 Hz, C-aryl); 129.7 (d, J_{PC} = 54.3 Hz, C-aryl); 130.9 (d, J_{PC} = 5.2 Hz, C-aryl); 132.3 (d, J_{PC} = 2.3 Hz, C-aryl); 150.3 (d, J_{PC} = 11.0 Hz, C-OSiMe_3). Minor isomer, δ 1.06 (s, $SiMe_3$); 18.1 (d, J_{PC} = 2.3 Hz, CH_3); 25.9 (d, J = 38.5 Hz, CH_2); 97.3 (d, J_{PC} = 4.6 Hz, CH=C-O); 129.1 (d, J_{PC} = 10.4 Hz, C-aryl); 129.8 (d, J_{PC} = 54.3 Hz, C-aryl); 131.2 (d, J_{PC} = 5.2 Hz, C-aryl); 132.5 (d, J_{PC} = 2.3 Hz, C-aryl); 152.1 (d, J_{PC} = 11.0 Hz, C-OSiMe_3). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +16.8 (d, J = 58.3 Hz). ^{29}Si NMR (99.4 MHz, C_6D_6): δ +17.3. MS (ESI) m/z (relative intensity %): 293 [M-$SiMe_3$; 100], 279[M-BH_3-$SiMe_3$; 60].

3-(Trimethylsilyloxy)pent-2-enyl-diphenylphosphine-borane (15b). To a solution of diphenyl(trimethylsilyl)phosphine-borane **11a** (0.51 g, 1.85 mmol) in 5 mL of THF was added a solution of ethylvinylketone **13b** (0.13 mL, 1.85 mmol) in 5 mL of THF at room temperature under inert atmosphere. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **15b** as a mixture of isomers in 2:1 ratio and colorless uncrystallized compound (0.31 g, 48% yield). R_f = 0.73 (dichloromethane/pentane 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): 0.50-1.50 (br, 3H, BH_3); Major isomer, 0.20 (s, 6H, $SiMe_3$); 0.93 (t, J = 6 Hz, 2H, CH_3); 1.98 (m, 1.3H, CH_2); 3.02 (dm, J = 6 Hz, 1.3H, CH_2P); 4.56 (m, 0.7H, CH=C); [Minor isomer, δ 0.15 (s, 3H, $SiMe_3$); 0.87 (t, J = 6 Hz, 1H, CH_3); 1.99 (m, 0.7H, CH_2); 2.98 (dm, J = 6 Hz, 0.7H, CH_2-P); 4.58 (m, 0.3H, CH=C)]; 7.41-7.48 (m, 6H, Ph); 7.67-7.74 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): Major isomer, δ 0.4 ($SiMe_3$); 10.7 (s, CH_3); 22.5 (d, J_{PC} = 37.7 Hz, CH_2-P); 28.4 (d, J_{PC} = 2.3 Hz, CH_2); 95.2 (d, J = 4.5 Hz, CH=C); 127.8 (d, J_{PC} = 19.6 Hz, C-aryl); 128.8 (d, J_{PC} = 53.6 Hz, C-aryl); 130.1 (d, J_{PC} = 3.0 Hz, C-aryl); 131.5 (d, J_{PC} = 9.0 Hz, C-aryl); 154.7 (d, J_{PC} = 11.3 Hz, C-OSiMe_3); Minor isomer, δ 0.2 ($SiMe_3$); 10.3 (s, CH_3); 22.6 (d, J_{PC} = 37.7 Hz, CH_2); 24.7 (d, J_{PC} = 2.3 Hz, CH_2-P); 94.8 (d, J = 4.5 Hz, CH=C); 128.0 (d, J_{PC} = 19.6 Hz, C-aryl); 130.3 (d, J_{PC} = 3.0 Hz, C-aryl); 131.2 (d, J_{PC} = 9.1 Hz, C-aryl); 155.9 (d, J_{PC} = 12.1 Hz, C-OSiMe_3). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +16.7 (sl). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ +17.3. MS (ESI) m/z (relative intensity %): 307 [M-$SiMe_3$; 100], 293 [M-BH_3-$SiMe_3$; 60].

(±)-[3-(Trimethylsilyloxy)cyclohex-2-enyl]diphenylphosphine-borane (15c). To a solution of diphenyl(trimethylsilyl)phosphine-borane **11a** (0.32 g, 1.19 mmol) in 5 mL of THF under inert atmosphere was added at room temperature a solution of cyclohex-2-enone **13c** (0.13 mL, 1.31 mmol) in 5 mL of THF. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **15c** as a colorless uncrystallized compound (0.43 g, 84% yield). R_f = 0.83 (dichloromethane/ethyl acetate 95:5). ^{1}H NMR (300 MHz, C_6D_6): δ 0.17 (s, 9H, $SiMe_3$); 0.90-2.20 (br, 3H, BH_3); 1.30 (m, 2H, CH_2); 1.55 (m, 2H, CH_2); 1.85 (m, 2H, CH_2); 3.26 (m, 1H, CH-P); 4.64 (dm, J = 8 Hz, 1H, CH=CO); 6.98-7.09 (m, 6H, Ph); 7.67-7.87 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ 0.2 (s, $SiMe_3$); 22.3 (d, J_{PC} = 9.8 Hz, CH_2); 23.1 (s, CH_2); 29.7 (d, J_{PC} = 2.6 Hz, CH_2); 32.7 (d, J_{PC} = 36.2 Hz, CH-P); 99.6 (d, J_{PC} = 2.3 Hz, CH=CO); 128.5 (d, J_{PC} = 3.0 Hz, C-aryl); 128.7 (d, J_{PC} = 3.0 Hz, C-aryl); 130.7 (d, J_{PC} = 2.3 Hz, C-aryl); 131.0 (d, J_{PC} = 2.3 Hz, C-aryl); 132.6 (d, J_{PC} = 8.3 Hz, C-aryl);

133.3 (d, J_{PC} = 8.3 Hz, C-aryl); 154.5 (d, J_{PC} = 9.8 Hz, C-OSiMe$_3$). ^{31}P NMR (121.4 MHz, C_6D_6): δ +22.6 (sl). ^{29}Si NMR (99.4 MHz, C_6D_6): δ +16.8. HRMS (ESI-Q-TOF) calcd for $C_{21}H_{30}BOPSiNa$ $[M+Na]^+$: 391.1792, found: 391.1768.

(±)-3-[*t*-Butyl(dimethyl)silyloxy]cyclohex-2-enyl(diphenyl)phosphine-borane (15d). To a solution of diphenyl[*t*-butyl(dimethyl)silyl]phosphine-borane **11b** (0.88 g, 2.8 mmol) in 6 mL of THF was added to a solution of cyclohex-2-enone **13c** (0.28 mL, 2.9 mmol) at room temperature and under inert atmosphere. After 16h of stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel (toluene/pentane 70:30) to afford **15d** as a colorless uncrystallized compound (0.88 g, 77% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 0.03 (s, 6H, SiMe$_2$); 0.15 (s, 9H, Si*t*-Bu); 0.90-2.30 (br, 3H, BH$_3$); 1.20 (m, 2H, CH$_2$); 1.55 (m, 2H, CH$_2$); 1.80 (m, 2H, CH$_2$); 3.13 (m, 1H, CH-P); 4.67 (dd, 1H, *J* = 8.4 Hz, *J* = 1.3Hz, CH=CO); 6.80-7.10 (m, 6H, Ph); 7.50-7.80 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ 0.2 (s, SiMe$_2$); 1.0 (s, Si*t*-Bu); 22.5 (d, J_{PC} = 9.8 Hz, CH$_2$); 23.4 (s, CH$_2$); 29.9 (d, J_{PC} = 2.3 Hz, CH$_2$); 32.9 (d, J_{PC} = 36.8 Hz, CH-P); 99.8 (d, J_{PC} = 2.3 Hz, CH=CO); 129.2 (d, J_{PC} = 10.4 Hz, C-aryl); 131.6 (d, J_{PC} = 2.2 Hz, C-aryl); 132.9 (d, J_{PC} = 9.9 Hz, C-aryl); 136.6 (s, C-aryl); 137.2 (s, C-aryl); 137.3 (d, J_{PC} = 3.8 Hz, C-aryl); 154.7 (d, J_{PC} = 10.4 Hz, C-OSiMe$_3$). ^{31}P NMR (121.4 MHz, C_6D_6): δ +21.3 (sl).

(*S*)-[3-(Trimethylsilyloxy)cyclohex-2-enyl]ferrocenylphenylphosphine-borane (15e). To a solution of (*R*)-ferrocenylphenylphosphine-borane **7d** (60 mg, 0.19 mmol, 1 equiv., 87% ee) in 2 mL of toluene at -90 °C was added a solution of *n*-BuLi (0.09 mL, 0.21 mmol, 1.1 equiv). The temperature was stirred until -80 °C and after 30 minutes, bromo(trimethyl)silane **10c** (30 μL, 0.23 mmol, 1.2 equiv) was added at -90 °C. The reaction mixture was stirred during 3 hours from -90 °C up to -60 °C, and a solution of cyclohexenone **13c** (37 μL, 0.39 mmol) in 0.5 mL of THF was added. The reaction mixture was then allowed to warm up at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **15e** as a yellowish uncrystallized mixture of two diastereosiomers in 1:1 ratio (0.07 g, 75% yield). R_f = 0.89 (dichloromethane/ethyl acetate 98:2); $[\alpha]_D^{25}$ = -68.0 (c 2, $CHCl_3$) 87% ee uncorrected. ^{1}H NMR (300 MHz, C_6D_6): δ 0.00 (s, 4.5H, SiMe$_3$); 0.12 (s, 4.5H, SiMe$_3$); 1.05-1.39 (m, 2H, CH$_2$); 0.90-2.20 (m, 3H, BH$_3$); 1.41-1.57 (m, 1H, CH$_2$); 1.57-1.70 (m, 1H, CH$_2$); 1.71-1.97 (m, 2H, CH$_2$); 2.79-2.85 (m, 1H, CHP); 3.77 (s, 2.5H, Fc); 3.81 (s, 2.5H, Fc); 4.00 (sl, 3H, Fc); 4.58 (d, *J* = 7.81 Hz, 0.5H, Fc); 4.67 (s, 0.5H, CH=); 4.74 (s, 0.5H, CH=); 4.78 (d, *J* = 7.8 Hz, 0.5H, Fc); 6.85-7.05 (m, 3H, Ph); 7.65-7.90 (m, 2H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ 0.4 (s, SiMe$_3$); 0.6 (s, SiMe$_3$); 22.4 (d, J_{PC} = 4.4 Hz, CH$_2$); 22.6 (d, J_{PC} = 4.8 Hz, CH$_2$); 23.7 (s, CH$_2$); 23.9 (s, CH$_2$); 30.0 (m, CH$_2$); 35.8 (d, J_{PC} = 18.6 Hz, CHP); 36.8 (d, J_{PC} = 18.7 Hz, CHP); 69.6 (d, J_{PC} = 61.1 Hz, Fc); 69.6 (d, J_{PC} = 59.6 Hz, Fc); 70.1(s, Fc); 70.2 (s, Fc); 71.0 (m, Fc); 71.1 (d, J_{PC} = 8.1 Hz, Fc); 71.2 (d, J_{PC} = 8.3 Hz, Fc); 71.8 (d, J_{PC} = 5.9 Hz, Fc); 72.1 (d, J_{PC} = 6.1 Hz, Fc); 74.5 (d, J_{PC} = 14.7 Hz, Fc); 75.1 (d, J_{PC} = 14.4 Hz, Fc); 100.3 (d, J_{PC} = 1.5 Hz, CH=); 100.8 (d, J_{PC} = 2.7 Hz, CH=); 128.3 (d, J_{PC} = 10.3 Hz, Ph); 128.4 (d, J_{PC} = 9.5 Hz, CH_{Ph}); 129.6 (d, J_{PC} = 53.3 Hz, Ph); 130.1 (d, J_{PC} = 51.7 Hz, Ph); 131.1 (d, J_{PC} = 2.3 Hz, Ph); 131.2 (d, J_{PC} = 2.2 Hz, Ph); 133.0 (d, J_{PC} = 8.3 Hz, Ph); 133.4 (d, J_{PC}

= 8.1 Hz, Ph); 154.2 (d, J_{PC} = 2.7 Hz, =CH-O); 154.4 (d, J_{PC} = 3.2 Hz, =CH-O). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +33.7 (m). HRMS (ESI-Q-TOF) calcd for $C_{25}H_{34}BFeOPSiNa$ $[M+Na]^+$: 499.14561, found 499.14140. FTIR (neat): 3057, 3005, 2938, 2385, 2348, 1657, 1369, 1252, 1198, 1174, 904, 844, 748. The enantiomeric (87% ee) and diasteromeric purities (1:1) was determined by HPLC on Chiralcel OK column using a mixture hexane/*i*-propanol 97:3 as eluent, flow 1 mL/min., λ = 254 nm., T = 30 °C. The retention times for the stereoisomers were t_1 = 11.8, $t_{1'}$ = 15.2, t_2 = 13.7 and $t_{2'}$ = 25.4 minutes, respectively.[48]

(±)-[3-(Trimethylsilyloxy)cyclohex-2-enyl]diphenylphosphine (16). To a solution of [3-(trimethylsilyloxy)cyclohex-2-enyl](diphenyl)phosphine-borane **15c** (1.47 g, 4.0 mmol) in 10 mL of degassed toluene was added at room temperature under stirring, a solution of DABCO (0.8 g, 8.0 mmol) in 10 mL of toluene. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **16** as a colorless uncrystallized compound (1.41 g, 100% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.03 (s, 9H, $SiMe_3$); 1.70 (m, 2H, CH_2); 1.95 (m, 2H, CH_2); 2.35 (m, 2H, CH_2); 3.09 (m, 1H, CH-P); 4.56 (m, 1H, CH=CO); 7.24-7.33 (m, 6H, Ph); 7.40-7.53 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 0.2 (s, $SiMe_3$); 21.6 (d, J_{PC} = 9.8 Hz, CH_2); 25.6 (d, J_{PC} = 17.3 Hz, CH_2); 29.8 (d, J_{PC} = 2.2 Hz, CH_2); 33.1 (d, J_{PC} = 21.1 Hz, CH_2-P); 103.6 (d, J_{PC} = 7.5 Hz, CH=CO); 128.6 (d, J_{PC} = 3.0 Hz, C-aryl); 130.3 (d, J_{PC} = 2.3 Hz, C-aryl); 133.6 (d, J_{PC} = 8.3 Hz, C-aryl); 137.9 (d, J_{PC} = 17.4 Hz, C-aryl); 152.2 (d, J_{PC} = 8.2 Hz, CO). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -6.2 (s). ^{29}Si NMR (99.4 MHz, C_6D_6): δ +16.2. MS (ESI) m/z (relative intensity %): 282 [M-$SiMe_3$, 100].

Methyl 3-[(boranato)diphenylphosphino]propenoate (18).[49] To a solution of diphenyl(trimethyl)silylphosphine-borane **11a** (0.32 g, 1.19 mmol) in 10 mL of THF was added a solution of methyl propiolate **13d** (0.11 mL, 1.2 mmol) in 4 mL of THF under inert atmosphere at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford **18** as a colorless uncrystallized compound. (0.19 g, 56% yield). R_f = 0,76 (toluene/pentane 80:20). ^{1}H NMR (300 MHz, C_6D_6): δ 0.90-2.20 (br, 3H, BH_3); 3.25 (s, 3H, OMe); 6.79 (dd, 1H, *J* = 16.7 Hz, *J* = 16.6 Hz, CH); 7.60 (dd, 1H, *J* = 10 Hz, *J* = 16.7 Hz, CH); 6.89-7.01 (m, 6H, Ph); 7.46-7.53 (m, 4H, Ph). ^{13}C NMR (75.4 MHz, C_6D_6): δ 50.2 (OMe); 127.7 (d, J_{PC} = 9.9 Hz, C-aryl); 130.1 (d, J_{PC} = 2.2 Hz, C-aryl); 131.5 (d, J_{PC} = 9.9 Hz, C-aryl); 135.5 (d, J_{PC} = 45.2 Hz, PCH=); 136.0 (d, J_{PC} = 3.9 Hz, C=C); 163.0 (d, *J* = 19.5 Hz, CO). ^{31}P NMR (121.4 MHz, C_6D_6): δ +14.9 (dl, $^1J_{PB}$ = 62 Hz). HRMS (ESI-Q-TOF) calcd for $C_{16}H_{18}BO_2PNa$ $[M+Na]^+$: 307.1032, found: 307.1023.

(±)-1-Phenyl-3,4-bis[(boranato)diphenylphosphino]pyrrolidine-2,5-dione (19a).

To a solution of diphenylphosphine-borane **7a** (R^1, R^2 = Ph) (182 mg, 0.91 mmol, 2.2 equiv) in 4 mL of toluene was added at -78 °C a solution of *n*-BuLi (0.36 mL, 0.91 mmol, 2.2 equiv). After 30 minutes stirring, bromo(trimethyl)silane **10c** (0.13 mL, 0.99 mmol, 2.4 equiv) was added. After stirring 2 hours at -78 °C, a solution of 2,3-dichloromaleimide **13e** (0.10 g, 0.41 mmol) in 0.5 mL of THF was added and the reaction mixture was then allowed to warm up at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum and

the residue was purified by chromatography on silica gel to afford the compound **19a** as a white solid (0.20 g, 86% yield). R_f = 0.75 (dichloromethane/pentane 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.50-1.50 (br, 6H, BH_3); 4.32-4.41 (AB, *J* = 11.1 Hz, 2H, CH); 6.86-6.92 (m, 2H, Ph-N); 7.29-7.35 (m, 3H, Ph-N); 7.40-7.62 (m, 12H, Ph); 7.75-7.86 (m, 8H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 40.8 (d, J_{PC} = 25.7 Hz, CHP); 125.1 (d, *J* = 55.9 Hz, C-aryl); 126.6 (s, C-aryl); 128.9 (s, C-aryl); 129.1 (s, C-aryl), 129.1 (d, J_{PC} = 9.1 Hz, C-aryl); 129.3 (d, J_{PC} = 9.1 Hz, C-aryl); 131.1 (s, C-aryl, Ph-N); 132.4 (d, J_{PC} = 12.8 Hz, C-aryl); 133.2 (d, J_{PC} = 9.1 Hz, C-aryl); 133.4 (d, J_{PC} = 9.1 Hz, C-aryl); 170.6 (s, C=O). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +29.6 (sl). HRMS (ESI-Q-TOF) calcd for $C_{34}H_{33}B_2P_2NO_2Na$ $[M+Na]^+$: 594.2070, found: 594.2091. FTIR (neat): 3058, 2950, 2392, 2349, 1713, 1497, 1436, 1378, 1192, 1105, 1060, 1028, 737, 689. An additional fraction was isolated as a colorless uncrystallized product that corresponds to the compound **20a** (27 mg, 11% yield).

(±)-1-Benzyl-3,4-bis[(boranato)diphenylphosphino]pyrrolidine-2,5-dione (19b).

To a solution of 2,3-dibromomaleimide **13f** (0.142 g, 0.41 mmol) in 10 mL of THF under inert atmosphere was added at -78 °C a solution of diphenyl(trimethylsilyl)phosphine-borane **11a** (0.215 g, 0.83 mmol) in 10 mL of THF. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford the compound **19b** as a colorless uncrystallized compound (0.12 g, 50% yield). R_f = 0.73 (dichloromethane/pentane 80:20). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.50-1.50 (br, 6H, BH_3); 4.26-4.32 (AB, *J* = 12.0 Hz, 2H, CH); 4.34 (s, 2H, CH_2Ph); 7.09-7.99 (m, 25H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 40.6 (d, J_{PC} = 27.2 Hz, C-P); 43.6 (s, CH_2Ph); 125.2 (d, *J* = 55.8 Hz, C-aryl); 127.9 (s, C-aryl); 128.5 (s, C-aryl); 128.8 (d, J_{PC} = 10.6 Hz, C-aryl); 129.1 (d, J_{PC} = 10.6 Hz, C-aryl); 129.6 (s, C-aryl); 132.2 (d, J_{PC} = 12.1 Hz, C-aryl); 133.0 (d, J_{PC} = 9.8 Hz, C-aryl); 133.3 (d, J_{PC} = 9.8 Hz, C-aryl); 134.4 (s, C-aryl); 171.6 (s, C=O). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +28.9 (sl). HRMS (ESI-Q-TOF) calcd for $C_{35}H_{35}B_2P_2NO_2Na$ $[M+Na]^+$: 608.2227, found: 608.2248.

1-Phenyl-3-[(boranato)diphenylphosphino]-4-(diphenylphosphino)pyrrole-2,5-dione (20a).

To a solution of 2,3-dichloromaleimide **13e** (0.10 g, 0.41 mmol) in 5 mL of diethylether under inert atmosphere was added at 0 °C a solution of diphenyl(trimethylsilyl)phosphine-borane **11a** (0.215 g, 0.83 mmol) in 5 mL of diethylether. After 16 hours stirring the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford the compound **20a** as a colorless uncrystallized compound (0.08 g, 35% yield). R_f = 0.20 (pentane/ethyl acetate 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00-2.00 (br, 3H, BH_3); 7.23-7.26 (m, 2H, Ph); 7.30-7.39 (m, 15H, Ph); 7.44 (td, *J* = 3.0 Hz, *J* = 6.0 Hz, 3H, Ph); 7.53 (td, *J* = 3.0 Hz, *J* = 6.0 Hz, 2H, Ph); 7.81-7.86 (m, 3H, Ph). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 125.8 (s, C-aryl); 127.3 (d, J_{PC} = 48.5 Hz, C-aryl); 127.9 (s, C-aryl); 128.5 (d, J_{PC} = 7.3 Hz, C-aryl); 128.6 (d, J_{PC} = 3.6 Hz, C-aryl); 128.9 (d, J_{PC} = 5.0 Hz, C-aryl); 129.0 (s, C-aryl); 129.4 (s, C-aryl); 131.2 (s, C-aryl); 131.9 (d, J_{PC} = 2.7 Hz, C-aryl); 132.9 (d, J_{PC} = 9.7 Hz, C-aryl); 133.4 (d, J_{PC} = 9.7 Hz, C-aryl); 133.8 (s, C-aryl); 134.0 (s, C-aryl); 134.1 (d, J_{PC} = 9.7 Hz, C-aryl); 155.1 (dd, J_{PC} = 49.8 Hz, *J* = 4.8 Hz, C-P); 166.2 (m, C=O). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +13.3 (sl), -28.3 (s). HRMS (ESI-Q-TOF) calcd for $C_{34}H_{28}BP_2NO_2Na$ $[M+Na]^+$: 578.1580, found: 578.1573. FTIR

(neat): 3054, 2925, 2855, 2409, 2363, 1712, 1500, 1483, 1434, 1373, 1100, 1052, 1027, 738, 688.

1-Benzyl-3-[(boranato)diphenylphosphino]-4-(diphenylphosphino)pyrrole-2,5-dione (20b). To a solution of diphenylphosphine borane **7a** (R^1,R^2 = Ph) (182 mg, 0.91 mmol, 2.2 equiv.) in 4 mL of toluene was added at -78°C a solution of *n*-BuLi (0.36 mL, 0.91 mmol, 2.2 equiv.). After 30 minutes, bromo(trimethyl)silane **10c** (0.13 mL, 0.99 mmol, 2.4 equiv.) was then added. After 2 hours stirring at -78°C, a solution of 2,3-dibromomaleimide **13f** (0.142 g, 0.41 mmol) in 0.5 mL of THF was added. The reaction mixture was then allowed to warm up at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford the compound **20b** as a solid (0.225 g, 96% yield). R_f = 0.75 (dichloromethane/pentane 80:20). Mp = 208°C; ^{1}H NMR (300 MHz, $CDCl_3$); δ 0.50-1.50 (br, 3H, BH_3); 4.56 (s, 2H, CH_2Ph); 7.19-7.84 (m, 25H, Ph). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 42.5 (s, CH_2Ph); 125.3 (d, J = 55.8 Hz, C-P); 126.9 (d, J = 57.6 Hz, C-P); 127.8 (s, C-aryl); 128.5 (s, C-aryl); 128.9 (d, J_{P-C} = 10.6 Hz, C-aryl); 129.1 (d, J_{P-C} = 10.6 Hz, C-aryl); 129.6 (s, C-aryl); 131.7 (d, J = 1.6 Hz); 132.3 (d, J_{PC} = 12.1 Hz, C-aryl); 133.0 (d, J_{PC} = 9.8 Hz, C-aryl); 133.3 (d, J_{PC} = 9.8 Hz, C-aryl); 134.4 (s, C-aryl); 167.1 (d, J_{PC} = 8.1 Hz, C=O). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ +12.8 (sl); -28.2 (s). HRMS (ESI-Q-TOF) calcd for $C_{35}H_{30}BP_2NO_2Na$ $[M+Na]^+$: 592.1737; found: 592.1727. FTIR (neat): 3057, 2929, 2394, 2349, 1705, 1434, 1389, 1337, 1102, 1052, 737, 690.

2-Chloro-3-(diphenylphosphino)quinoxaline (21).[50] To a solution of diphenyl phosphine-borane **7a** (R^1,R^2 = Ph) (182 mg, 0.91 mmol, 2.2 equiv.) in 4 mL of toluene was added at -78°C a solution of *n*-BuLi (0.36 mL, 0.91 mmol, 2,2 equiv.). After 30 minutes, bromo(trimethyl)silane **10c** (0.13 mL, 0.99 mmol, 2.4 equiv.) was added. After 2 hours stirring at -78°C, a solution of 2,3-dichloroquinoxaline **13g** (0.08 g, 0.41 mmol) in 0.5 mL of THF was added. The reaction mixture was then allowed to warm up at room temperature. After 16 hours stirring, the reaction mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel to afford the compound **21** as a white solid (0.15 g, 46% yield). R_f = 0.77 (dichloromethane/pentane 80:20). Mp = 128°C; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.38-7.49 (10H, H-arom); 7.69-7.86 (m, 2H); 7.92 (dd, J = 4.8 Hz, J = 0.9 Hz, 1H); 8.15 (dd, J = 4.8 Hz, J =0.9 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 128.1 (s, C-aryl); 128.6 (d, J_{PC} = 7.6 Hz, C-aryl); 128.8 (d, J_{PC} = 10.6 Hz C-aryl); 129.6 (d, J_{PC} = 7.6 Hz, C-aryl); 129.9 (s, C-aryl); 131.0 (s, C-aryl); 131.3 (s, C-aryl); 133.7 (d, J_{PC} = 10.6 Hz, C-aryl); 133.9 (d, J_{PC} = 7.6 Hz, C-aryl); 134.7 (d, J_{PC} = 20.4 Hz, C-aryl); 141.0 (s, C-aryl); 141.6 (s, C-aryl); 150.6 (d, J_{PC} = 34.7 Hz, C-aryl); 159.4 (d, J_{PC} = 16.6 Hz, C-aryl). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -2.6 (s). HRMS (ESI-Q-TOF) calcd for $C_{20}H_{14}ClN_2PNa$ $[M+Na]^+$: 371.0475, found: 371.0484 and for $C_{20}H_{14}ClN_2OPNa$ $[M+O+Na]^+$: 387.0424, found: 387.0439.

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