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Influence of structural changes in ferrocene phosphane aminophosphane ligands on their catalytic activity

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ABSTRACT

New phosphane aminophosphane ligands based on [3]ferrocenophane skeleton were synthesized using a direct double lithiation followed by phosphanylation. Influence of ligand structure on catalytic performance was evaluated by performing a series of Pd-catalyzed allylic substitution on different substrates. Enantioselectivities up to 55% ee were obtained with bridged ligand compared to 33% ee with analogous non-bridged BoPhoz ligand.

1. Introduction

Transition metal complexes with chiral ferrocene ligands represent an important class of enantioselective catalysts [1]. Ferrocene scaffold is, for its interesting stereochemical properties, an attractive and often used design motive. Numerous enantioselective transformations are successfully catalyzed by chiral ferrocene diphosphanes [2–4], amino phosphanes [5] as well as other types of ligands [6–10].

Ferrocenes with carbon-bridged cyclopentadienyl rings, ferrocenophanes, are interesting subgroup of ferrocene derivatives [11]. Although many ferrocenophane derivatives are known, only compounds having three and five carbon bridge were used as ligands for asymmetric catalysis. Weissensteiner described several [3]ferrocenophane phosphane ligands which were applied in Pt-catalyzed carbonylation [12], and Rh-catalyzed hydrogenations of olefins [13]. In Pd-catalyzed allylic alkylation, diphosphane ligands were active (up to 70% ee) but aminophosphane **1** produced racemic allylation product [14]. This observation stimulated us to prepare modified [3]ferrocenophane aminophosphane ligand **2** with increased chelate ring size due to inserted methylene group between phosphorus and cyclopentadienyl ring. Palladium complexes with ligand **2** were useful catalysts for allylic substitution (up to 86% ee) [15]. Erker prepared [3]ferrocenophane diphosphanes of different type which were efficient in Rh-catalyzed hydrogenations [16]. We have also recently showed that [5] ferrocenophane phosphanes are interesting ligands for Pd-catalyzed allylic substitution, Rh-catalyzed hydrogenation and Cu-catalyzed conjugate addition of Et_2Zn [17,18] (see Fig. 1).

We hypothesized that another way to improve ligand **1** and to gain further information on effects of structural changes on catalytic performance of ligands of this type could be preparation of phosphano aminophophane **3**. Such compounds would also be bridged analogs to well-known BoPhoz ligands [19]. In this paper, we present synthesis of this new type of ligands along with results of comparative study of their catalytic performance.

2. Results and discussion

The ligand synthesis starts from ketone **4**. The stereogenic center was introduced by reductive amination of oxo group using (*S*)-phenylethylamine and $NaBH_4$. The resulting diastereoisomeric amines were separated by flash chromatography and (*S*,*S*)-diastereoisomer was then reductively methylated using formaldehyde and $NaBH_4$ to form tertiary amine **5** [20]. To remove 2-phenylethyl group, amine **5** was subjected to hydrogenolysis with Pd/C in formic acid. This reaction produced *N*-methylated amine **6** in 80% yield (Scheme 1).

At the beginning we planned to use dimethylamino derivative **1** for diastereoselective *ortho*-lithiation and subsequently transform it to *N*-monomethyl compound for introduction of second phosphane group. However this approach failed, the desired nucleophilic substitution on α-carbon to Cp-ring could not be performed, presumably, because of large steric hindrance. Therefore, we looked for alternatives.

Diastereoselective *ortho*-metallation, particularly lithiation, is the main method for introduction of planar chirality in ferrocene

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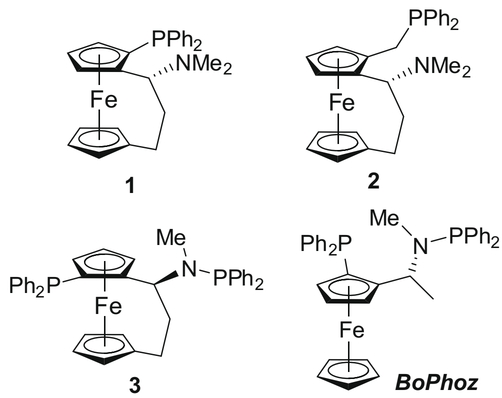
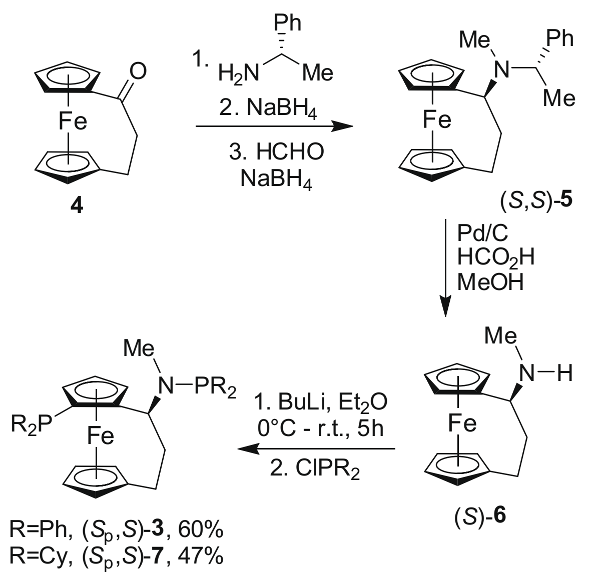


Fig. 1. Aminophosphane Ferrocene and Ferrocenophane ligands.



Scheme 1.

derivatives [21,22]. Most often nitrogen containing substituents, such as amines [23,24], oxazolines [25,26], imidazolines [27] were used as *ortho*-directing groups. Several other functionalities such as acetal [28], sulfoxide [29] and oxazaphospholidine-oxide [30] were also described as suitable directing groups. However, examples of proton containing groups as *ortho*-directing substituents are scarce. Interestingly, lithiation of Boc-protected amine led to introduction of lithium to unfunctionalized Cp-ring [31], Recently, direct *ortho*-lithiation of free ferrocenyl alcohols was also described [32]. We envisaged that it would be of high value if amine **6** could be directly and diastreoselectively lithiated with added benefit of one-pot introduction of desired phosphane group also on nitrogen upon reaction with appropriate electrophile. Treating amine **6** with 2.5 equiv. of BuLi and subsequent reaction with chlorodiphenylphosphane led indeed to formation of phosphane **3** in 60% yield after a rapid flash chromatography and crystallization. Proton and phosphorus NMR spectra of the crude reaction mixture revealed that d.r. is 99:1. Similarly, reaction with chlorodicyclohexylphosphane resulted in formation of phosphane **7** in 47% yield (Scheme 1). Noteworthy is also the fact that lithiation of analogous non-bridged derivative led to a complicated mixture of compounds.

We were not able to produce crystals suitable for X-ray analysis from phosphanes **3** or **7**. However, NOESY NMR experiments confirmed that a relative configuration of planar stereogenic unit is S_p. Fig. 2 depicts major NOE interactions and NOESY spectrum of phosphane **3**. Configuration of chiral carbon was established previously [33].

As a benchmark C–C bond forming reaction we chose Pd-catalyzed allylic alkylation. Symmetrical substrates, 1,3-diphenylpropenyl acetate (**8**) and cyclohexenyl acetate (**10**) were reacted with C-anion generated from dimethyl malonate under catalysis of in situ formed Pd-complex of chiral ligands (Scheme 2). For comparison, reaction was performed also with BoPhoz ligand, which was prepared according to known procedures [19]. We chose (*R*,*R*)-configuration of BoPhoz ligand so that it matches relative configuration of bridged derivatives **3** and **7**.

Product of allylic substitution, diester **9**, was obtained under various conditions in good yields but with only mediocre enantioselectivity. Influence of several parameters, including solvent, temperature and base was investigated. Noteworthy is effect of base and palladium source on enantioselectivity. The highest enantioselectivity (55% ee) was obtained with ligand **3** using Pd_2dba_3 as a source of palladium. Under same conditions, BoPhoz ligand afforded product **9** with only 20% ee, but the reaction was faster. Using $[Pd(allyl)Cl]_2$ the difference in enantioselectivity is smaller (40% and 33% ee, respectively). Cyclic derivative **10** seems as a more difficult substrate for ligand **3**, even though diester **11**

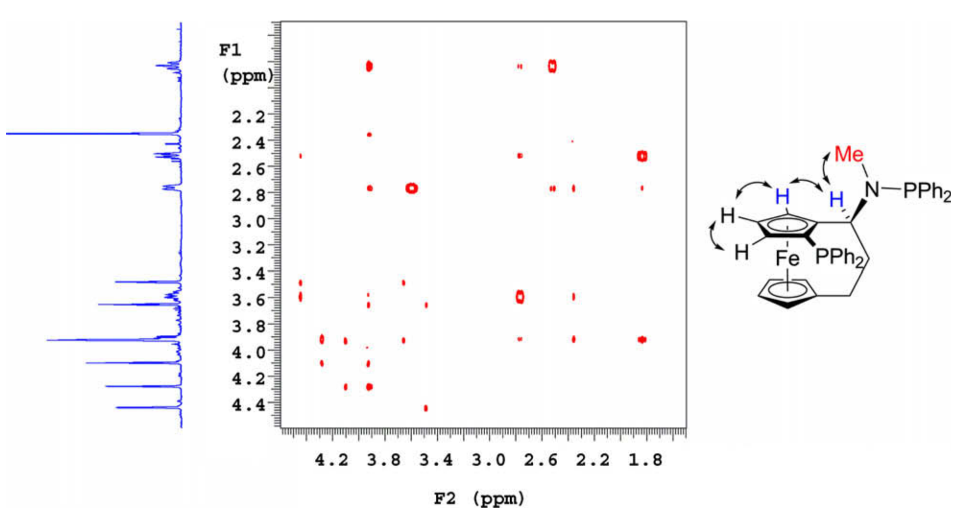
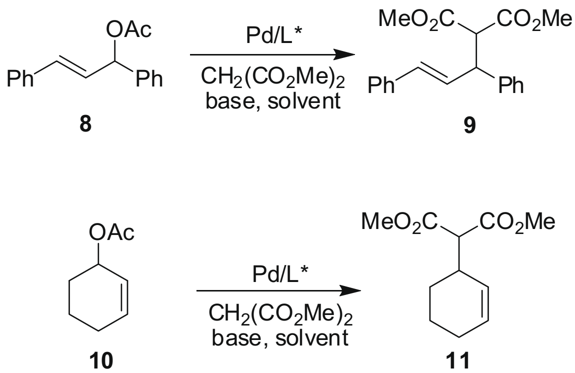


Fig. 2. NOESY spectrum of ligand 3.



Scheme 2.

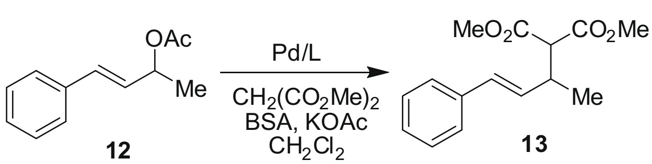
Table 1
Pd-Catalyzed allylic alkylation of symmetrical substrates **8** and **10**.

Substrate	Ligand	[Pd]	Base	Solvent	Time (h)	Isolated yield (%)	ee (%)[a]
8	3	$[Pd(allyl)Cl]_2$	BSA/KOAc	CH_2Cl_2	21	86	40 (*S*)
8	3	$[Pd(allyl)Cl]_2$	BSA/KOAc	Toluene	24	97	12 (*S*)
8	3	$[Pd(allyl)Cl]_2$	BSA/KOAc	THF	24	52	34 (*S*)
8	3	$[Pd(allyl)Cl]_2$	Et_2Zn	THF	24	40	34 (*S*)
8	3	$[Pd(allyl)Cl]_2$	BSA/KOAc	CH_2Cl_2	24	19	44 (*S*)[b]
8	3[c]	$[Pd(allyl)Cl]_2$	BSA/KOAc	CH_2Cl_2	3.5	98	35 (*S*)
8	3	$Pd_2dba_3 \cdot CHCl_3$	BSA/KOAc	CH_2Cl_2	21	80	55 (*S*)
8	3	$Pd_2dba_3 \cdot CHCl_3$	BSA/LiOAc	CH_2Cl_2	21	77	30 (*S*)
8	3	$Pd_2dba_3 \cdot CHCl_3$	Cs_2CO_3	CH_2Cl_2	48	95	0
8	7	$[Pd(allyl)Cl]_2$	BSA/KOAc	CH_2Cl_2	19	84	10 (*S*)
8	BoPhoz	$[Pd(allyl)Cl]_2$	BSA/KOAc	CH_2Cl_2	3	96	33 (*R*)
8	BoPhoz	$Pd_2dba_3 \cdot CHCl_3$	BSA/KOAc	CH_2Cl_2	5	81	20 (*R*)
10	3	$[Pd(allyl)Cl]_2$	BSA/KOAc	CH_2Cl_2	4	70	4 (*S*)[d]
10	BoPhoz	$[Pd(allyl)Cl]_2$	BSA/KOAc	CH_2Cl_2	1	80	20 (*R*)[d]

[a] Determined by HPLC on Daicel Chiralpak AD-H column.
[b] Reaction performed at −25 °C.
[c] 5 mol% of ligand.
[d] Determined by NMR using chiral shift reagent tris{3-(heptafluoropropylhydroxymethylene)-*d*-camphorato}europium(III).

was obtained in reasonable yield (70%), enantioselectivity was only small (4% ee). Interestingly, with BoPhoz ligand diester **11** was obtained with 20% ee. Results of Pd-catalyzed allylic substitutions are summarized in Table 1.

We were also interested whether unsymmetrical acetate **12** would undergo enantioselective allylic substitution (Scheme 3). Both ligand **3** and BoPhoz afforded solely product **13** in good yields



Scheme 3.

Table 2
Pd-catalyzed allylic substitution on unsymmetrical acetate **12**.

Substrate	Ligand	[Pd]	Time (h)	Isolated yield (%)	ee (%)[a]
12	3	$[Pd(allyl)Cl]_2$	26	54	6
12	3	$Pd_2dba_3 \cdot CHCl_3$	26	66	0
12	BoPhoz	$[Pd(allyl)Cl]_2$	26	69	1
12	BoPhoz	$Pd_2dba_3 \cdot CHCl_3$	26	71	0

[a] Determined by HPLC on Daicel Chiralpak AD-H column.

and without any regioisomer in position 1. However, in all cases, diester **13** was produced with very low enantioselectivity (6% ee) or as a racemate (Table 2).

Data of catalytic experiments suggest that introduction of carbon bridge into BoPhoz ligand has a positive effect on ligand performance in Pd-catalyzed allylic substitution.

3. Conclusions

We developed efficient method for preparation of phosphane aminophosphane ferrocenophane derivatives by one-pot double lithiation of carbon and nitrogen followed by reaction with chlorophosphanes. We believe that this procedure could be useful for preparation of new chiral ferrocene derivatives. Although ferrocenophane ligands are only moderately selective in Pd-catalyzed allylic substitution of acyclic 1,3-diphenylpropenyl acetate (up to 55% ee), this enantioselectivity is higher than that of BoPhoz ligand for this substrate (33% ee).

4. Experimental

General: All reactions were carried out in inert atmosphere of N_2 or Ar. The solvents were purified by standard methods. Reactions with organometallic reagents were carried out using standard Schlenk techniques. NMR spectra were recorded on Varian Mercury plus instrument (300 MHz for ^1H, 75 MHz for ^{13}C and 121.5 MHz for ^{31}P) and Varian Inova instrument (600 MHz for ^1H). Chemical shifts (δ) are given in ppm relative to tetramethylsilane for ^1H NMR, relative to residual solvent peak for ^{13}C NMR and relative to H_3PO_4 as external standard for ^{31}P NMR. Specific optical rotations were measured on Perkin–Elmer instrument and are given in deg cm^{-3} g^{-1} dm^{-1}. Flash chromatography was performed on Merck silica gel 60. Thin-layer chromatography was performed on Merck TLC-plates silica gel 60, F-254. Enantiomeric excesses were determined by HPLC on Chiralpak AD-H (Daicel Chemical Industries) column using hexane/*i*-PrOH = 9:1 as a mobile phase and detection with UV-detector at 254 nm. Mass spectra were recorded on Waters Premium QTOF instrument. Compound **5** have been prepared according to literature procedure [20].

4.1. Preparation of (S)-1,1′-(1-methylamino-propanediyl)ferrocene (6)

Palladium on charcoal (10% Pd, 148 mg) was, under nitrogen atmosphere, suspended in HCOOH/MeOH mixture (1:20, 9 mL) and amine **5** (500 mg, 1.39 mmol) in HCOOH/MeOH mixture (1:20, 16 mL) was added into this solution. The resulting mixture was stirred at r.t. for 2 h. Then it was passed through Celite and solvent was evaporated in vacuum. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc = 3:1) to give amine **7** (304 mg, 80%) as orange crystals. ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (bs, 1H, NH), 1.90–2.02 (m, 1H, CH_2), 2.10–2.17 (m, 2H, CH_2), 2.33–2.40 (m, 1H, CH), 2.38 (s, 3H, Me^N), 3.03–3.07 (dd, 1H, *J* = 7.2, 5.3 Hz, CH^N), 3.96–3.98 (m, 1H, CH^{Cp}), 4.03–4.10 (m, 6H, CH^{Cp}), 4.23–4.24 (m, 1H, CH^{Cp}).

The NMR data were identical to literature values [34].

*4.2. Preparation of (S,S$_p$)-1-diphenylphosphanyl-2,1′-[N-diphenylphosphino-1-metylaminopropanediyl]ferrocene (**3**)*

Amine **6** (483 mg, 1.79 mmol) was dissolved in anhydrous Et_2O (5 mL). The solution was cooled in an ice bath and BuLi (1.6 M in hexane, 0.8 mL, 1.28 mmol) was added. The resulting mixture was stirred for 5 h and temperature was allowed to rise to r.t during this time. Then the reaction mixture was cooled again in the ice bath and $ClPPh_2$ (0.25 mL, 1.39 mmol) was added. The mixture was stirred overnight (0 °C – r.t.). Saturated $NaHCO_3$ solution. (5 mL) was added and phases were separated. Organic layer was washed with water, dried (Na_2SO_4) and concentrated. Flash chromatography (SiO_2, hexane/EtOAc/Et_3N = 66:33:1) followed by crystallization from hot *i*PrOH afforded pure phosphane **3** (686 mg, 60%) as a yellow solid. M.p. 62–65 °C. $[\alpha]_D = -199.2$ (c = 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 2.03–2.11 (m, 1H, CH_2), 2.15 (d, 3H, J = 3.9 Hz, Me^N), 2.67 (m, 2H, CH_2), 3.37–3.50 (m, 1H, CH_2), 3.40–3.41(m, 1H, CH^{Cp}), 3.77(dt, 1H, J = 1.3, 2.3 Hz, CH^{Cp}), 3.81–3.93 (m, 2H, CH^{Cp}, CH^N), 4.14 (td, 1H, J = 1.4, 2.5 Hz, CH^{Cp}), 4.24 (td, 1H, J = 1.4, 2.5 Hz, CH^{Cp}), 4.40–4.42 (m, 1H, CH ^{Cp}), 4.43–4.45 (m, 1H, CH^{Cp}), 7.06–7.36 (m, 18H, CH^{Ph}), 7.48–7.55 (m, 2H, CH^{Ph}). ^1H NMR (600 MHz, C_6D_6) δ 1.82 (t, 1H, J = 13.3 Hz, CH_2), 2.34 (d, 3H, J(H-P) = 3.6 Hz, Me^N), 2.51 (dt, 1H, J = 3.24, 14.4 Hz, CH_2), 2.74–2.78 (m, 1H, CH_2), 3.48 (dd, 1H, J = 2.4, 3.6 Hz, CH^{Cp}), 3.54–3.62 (m, 1H, CH_2), 3.65 (dt, 1H, J = 1.3, 2.4 Hz, CH^{Cp}), 3.89–3.92 (m, 3H, CH^N, CH^{Cp}), 4.09 (dt, 1H, J = 0.6, 2.5 Hz, CH^{Cp}), 4.27 (td, 1H, J = 1.6, 3.2 Hz, CH^{Cp}), 4.44 (m, 1H, CH^{Cp}), 6.94–7.00 (m, 3H, CH^{Ph}), 7.03–7.08 (m, 6H, CH^{Ph}), 7.08–7.14 (m, 3H, CH^{Ph}), 7.25–7.28 (m, 2H, CH^{Ph}), 7.34–7.36 (m, 2H,CH^{Ph}), 7.38–7.41 (m, 2H, CH^{Ph}), 7.56–7.59 (m, 2H, CH^{Ph}). ^{13}C NMR (75 MHz, C_6D_6) δ 21.2 (s, CH_2), 34.9 (t, J(C-P) = 8.3 Hz, Me^N), 40.4 (dd, J(C-P) = 12.0, 16.4 Hz, CH_2), 67.7 (s, CH^{Cp}), 68.0 (d, J(C-P) = 33.6 Hz, CH^N), 70.5 (s, CH^{Cp}), 71.1 (s, CH^{Cp}), 72.1 (s, 2xCH^{Cp}), 74.2 (d, J(C-P) = 16.5 Hz, Cq^{Cp},), 75.5 (d, J(C-P) = 4.6 Hz CH^{Cp}), 76.9 (d, J(C-P) = 5.4 Hz, CH^{Cp}), 89.2 (s, Cq^{Cp}), 89.4 (dd, J(C-P) = 22.7, 5.84 Hz, Cq^{Cp},), 127.9, 128.2, 128.5, 129.0 (s, 12 × CH^{Ph}, overlap with C_6D_6), 132.2 (d, J(C-P) = 19.2 Hz, CH^{Ph}), 132.9 (d, J(C-P) = 17.8 Hz, CH^{Ph}), 133.2 (d, J(C-P) = 20.8 Hz, CH^{Ph}), 135.9 (d, J(C-P) = 21.7 Hz, CH^{Ph}), 139.3 (d, J(C-P) = 9.4 Hz, CH^{Ph}), 139.4 (d, J(C-P) = 4.9 Hz, Cq^{Ph}), 139.6 (d, J(C-P) = 8.8 Hz, Cq^{Ph}), 141.7 (d, J(C-P) = 9.9 Hz, Cq^{Ph}). ^{31}P (121 MHz, $CDCl_3$) δ −20.2 (d, J = 4.7 Hz), 60.7 (d, J = 4.7 Hz). ESI HRMS Calc. for $C_{38}H_{35}FeNP_2Na$ $[M+Na]^+$ 646.1461; found: 646.1407.

*4.3. Preparation of (S,S$_p$)-1-dicyclohexylphosphanyl-2,1′-[N-dicyclohexylphosphino-1-metylaminopropanediyl]ferrocene (**7**)*

Amine **6** (270 mg, 1.0 mmol) was dissolved in anhydrous Et_2O (3 mL). The solution was cooled in an ice bath and BuLi (1.6 M in hexane, 0.8 mL, 1.28 mmol) was added. The resulting mixture was stirred for 5 h and temperature was allowed to rise to r.t during this time. Then the reaction mixture was cooled again in the ice bath and $ClPCy_2$ (0.62 mL, 2.7 mmol) was added. The mixture was stirred overnight (0 °C – r.t.). Saturated $NaHCO_3$ soln. (5 mL) was added and phases were separated. Organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated. Flash chromatography (SiO_2, hexane/EtOAc/Et_3 N = 66:33:1) followed by crystallization from hot EtOH afforded pure phosphane **7** (302 mg, 47%) as a yellow solid. M.p.: 150–152 °C. $[\alpha]_D = -72.2$ (c = 0.5, CH_2Cl_2). ^1H NMR (300 MHz, C_6D_6) δ 1.12–1.56 (m, 22H, Cy), 1.60–2.00 (m, 22H, Cy), 2.34–2.41 (m, 1H, CH_2), 2.42–2.55 (m, 2H, CH_2), 2.81(s, 3H, Me^N), 3.20–3.35(m, 1H, CH_2), 3.84 (m, 1H, CH^{Cp}), 3.95 (m, 2H, CH^{Cp}), 4.00– 4.09 (m, 2H, CH^{Cp}, CH^N), 4.09–4.11 (m, 1H, CH^{Cp}), 4.20 (m, 1H, CH^{Cp}), 4.35 (m, 1H, CH^{Cp}). ^{13}C NMR (75 MHz, C_6D_6) δ 27.0 (d, J(C-P) = 10.96 Hz, CH_2), 27.1 (d, J(C-P) = 7.9 Hz, CH_2), 27.5 (d, J(C-P) = 2.36 Hz, CH_2), 27.67(d, J(C-P) = 5.4 Hz, CH_2), 27.71 (d, J(C-P) = 17.7 Hz, CH_2), 27.75(s, 2xCH_2), 27.8 (d, J(C-P) = 7.8 Hz, CH_2), 28.2 (d, J(C-P) = 13.4 Hz, CH_2), 28.8 (d, J(C-P) = 12.0 Hz, CH_2), 29.4 (d, J(C-P) = 7.0 Hz, CH_2), 30.0 (d, J(C-P) = 6.3 Hz, CH_2), 30.20 (s, 2 × CH_2), 30.23 (d, J(C-P) = 5.1 Hz, CH_2), 30.4 (d, J(C-P) = 9.2 Hz, CH_2), 30.9 (d, J(C-P) = 9.0 Hz, CH_2), 32.9 (d, J(C-P) = 16.7 Hz, CH_2), 33.8 (d, J(C-P) = 21.9 Hz, CH_2), 34.2 (bs, Me^N), 36.10 (d, J(C-P) = 17.1 Hz, CH^{cy}), 38.7 (d, J(C-P) = 15.0 Hz, CH^{cy}), 36.13 (dd, J(C-P) = 16.2, 68.1 Hz, CH^N), 39.1 (d, J(C-P) = 8.8 Hz, CH_2), 39.2 (d, J(C-P) = 8.7 Hz, CH_2), 67.5 (s, CH^{Cp}), 70.0 (s, CH^{Cp}), 71.0 (s, CH^{Cp}), 71.6 (d, J(C-P) = 2.2 Hz, CH^{Cp}), 71.8 (s, CH^{Cp}), 72.9 (d, J(C-P) = 3.8 Hz, CH^{Cp}), 76.0 (d, J(C-P) = 4.8 Hz, CH^{Cp}), 78.5 (d, J(C-P) = 25 Hz, Cq^{Cp}), 87.6 (dd, J(C-P) = 22.0, 3.3 Hz, Cq^{Cp}), 89.5 (s, Cq^{Cp}). ^{31}P NMR (121 MHz, $CDCl_3$) δ −13.6 (s), 80.4 (bs). ESI HRMS Calc. for $C_{38}H_{60}FeNP_2$ $[M+H]^+$ 648.3519; found 648.4038.

*4.4. General procedure for allylic substitution of acetates **8**, **10** and **12***

Ligand (0.02 mmol) and $[Pd(allyl)Cl]_2$ or $Pd_2dba_3.CHCl_3$ (0.01 mmol) were dissolved in CH_2Cl_2 (3 mL) and stirred for 20 min. This solution was added to a solution of substrate (1 mmol) in CH_2Cl_2 (2 mL). Then bis(trimethylsilyl)acetamide (2 mmol), dimethylmalonate (2 mmol) and KOAc (0.05 mmol) were added in this order. The resulting solution was stirred at r.t. and monitored by TLC (SiO_2, hexane/EtOAc 4:1). When all starting material was consumed, saturated aq. NH_4Cl solution (3 mL) and *t*BuOMe were added and layers were separated. Organic layer was washed with brine (10 mL), dried (Na_2SO_4) and concentrated. Flash chromatography (SiO_2, hexane/EtOAc = 9:1) of the crude mixture afforded pure allylation product.

*4.5. Dimethyl 2-(1,3-diphenylallyl)malonate (**9**) [35]*

^1H NMR (300 MHz, $CDCl_3$) δ 3.52 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.95 (d, J = 10.9 Hz, 1H, CH), 4.27 (dd, J = 10.9, 8.5 Hz, 1H, CH), 6.32 (dd, J = 15.7, 8.5 Hz, 1H, CH), 6.48 (d, J = 15.7 Hz, 1H, CH), 7.17–7.35 (m, 10H, Ph). HPLC (AD-H, hexane/*i*-PrOH 90:10, 0.75 mL/min, 254 nm) t_R = 14.13 min (R), t_R = 19.08 min (S), 55% ee $[\alpha]_D = -3.9$ (1.01, $CHCl_3$).

*4.6. Dimethyl 2-(cyclohex-2-enyl)malonate (**11**) [36]*

^1H NMR (300 MHz, $CDCl_3$) δ 1.31–1.43 (m, 1H, CH), 1.49–1.84 (m, 3H, CH_2), 1.96–2.03 (m, 2H, CH_2), 2.86–2.96 (m, 1H, CH_2), 3.74 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.29 (d, J = 9.5 Hz, 1H, CH), 5.50–5.55 (m, 1H, CH), 5.75–5.81 (m, 1H, CH).

*4.7. Dimethyl 2-(4-phenylbut-3-en-2-yl)malonate (**13**) [35]*

^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, 3H, J = 6.8 Hz, CH_3), 3.08–3.19 (m, 1H, CH), 3.40 (d, J = 8.9 Hz, 1H, CH), 3.67 (s, 3H, OMe), 3.75 (s, 3H, OMe), 6.12 (dd, J = 15.8, 8.5 Hz, 1H, CH), 6.46 (d, J = 15.8 Hz, 1H, CH), 7.18–7.35 (m, 5H, Ph). HPLC (OD-H, hexane/*i*-PrOH 99:1, 0.5 mL/min, 254 nm) t_R = 19.38 min, t_R = 21.46 min.

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