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Conjugate phosphination of cyclic and acyclic acceptors using Rh(I)–phosphine or Rh(I)–carbene complexes. Probing the mechanism with chirality at the silicon atom or the phosphorus atom of the Si–P reagent

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ABSTRACT

The Rh(I)-catalyzed conjugate phosphinyl transfer from an Si–P reagent to an electron-deficient acceptor requires individual protocols for cyclic and acyclic α,β-unsaturated carbonyls and carboxyls. While 1,4-addition to cyclic acceptors is catalyzed by a Rh(I)–phosphine complex, a Rh(I)–carbene complex is needed to promote conjugate phosphination of acyclic acceptors. General procedures for both systems are reported. Aside from monophosphine-derived Si–P reagents as phosphinide sources, dppe- as well as dppp-derived reagent having two Si–P units do also participate in this reaction. The mechanism of this Rh(I)-catalyzed activation of the Si–P reagent is still under debate. Control experiments with enantiopure silicon-stereogenic and racemic phosphorus-stereogenic Si–P reagents support a catalysis commencing with transmetalation rather than oxidative addition. Preparation and full characterization data of the Si–P compounds used in this investigation is included.

1. Introduction

Transmetalation of a carbon nucleophile from a main group element to a transition metal is one of the common principles in catalysis to generate C–TM metal bonds (TM=transition metal) for subsequent C–C bond formation.[1] In contrast to oxidative addition, the oxidation state of the transition metal remains unchanged. Among the prominent examples of transmetalation-based catalysis are the Suzuki–Miyaura cross-coupling reaction[2] (generation of a C(sp^2)–Pd(II) complex) and the Hayashi–Miyaura conjugate addition reaction[3] (generation of a C(sp^2)–Rh(I) complex). In both transition metal-catalyzed processes, the carbon nucleophile is released from boron, usually a boronic acid. The latter Rh(I) catalysis is however not limited to the conjugate transfer of carbon nucleophiles. After Rh(I)-catalyzed activation of B–B[4] and Si–B[5] bonds through transmetalation, the thus-formed nucleophilic boron as well as silicon complexes also undergo conjugate C–B and (asymmetric) C–Si bond formation, respectively. Aside from boron-based precursors, we were recently able to further extend the scope of interelement linkages to Si–P reagents for the 1,4-addition of nucleophilic phosphorus.[6] We assume that all these Rh(I) catalyses are likely to share the basic mechanistic steps. We also note that an identical mechanism of action might apply to closely related Pd(II)-catalyzed conjugate addition of carbon[7] as well as phosphorus[8] nucleophiles.

Hayashi et al. established the mechanism of the Rh(I)-catalyzed 1,4-addition of boronic acids.[9] Our approach to interelement bond activation was guided by that, and we proposed a tentative mechanism for the Rh(I)-catalyzed 1,4-addition of phosphorus nucleophiles to electron-deficient α,β-unsaturated carbonyl compounds (Scheme 1).[6] The active catalyst is the Rh(I)–OH complex **A**, formed from a Rh(I) pre-catalyst in basic aqueous media. The catalysis then commences with coordination of the Si–P reagent **B** to **A** (**A**→**C**). In complex **C**, the slightly Lewis acidic silicon atom is located in close proximity to the Lewis basic oxygen (the hydroxy group might even be deprotonated). Intramolecular attack of the oxygen at silicon then results in net transmetalation to afford the phosphinide transfer complex **E** along with silanol **D** (**C**→**E**). The α,β-unsaturated acceptor **F** is then captured by **E**, and conjugate phosphinyl transfer yields Rh(I) enolate **G** (**E**→**G**). Its hydrolysis completes the catalytic cycle, releasing adduct **H** (**G**→**H**) and regenerating catalytically active **A**.

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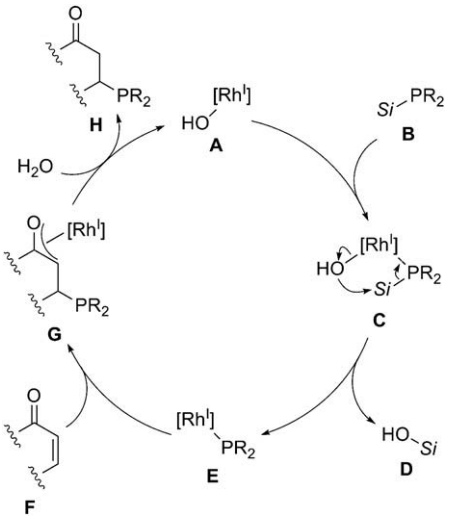


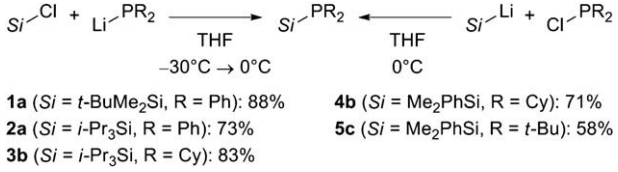
Scheme 1. Tentative catalytic cycle of conjugate phosphinyl transfer.

In this full account, we summarize our efforts toward the Rh(I)-catalyzed conjugate transfer of Ph_2P, Cy_2P, and t-Bu_2P groups from Si–P reagents[10] on cyclic[6] and acyclic acceptors.[11,12] We also provide sound mechanistic evidence for the debated transmetalation pathway.[13]

2. Results and discussion

2.1. Preparation of Si–P reagents

Si–P reagents had been employed as phosphinyl group sources in the past, and there are a few protocols available. We accessed silylphosphines **1**–**3** according to a procedure reported by Hayashi et al. (left, Scheme 2).[14] While high chemical yields were obtained for t-$BuMe_2Si$–Cl and i-Pr_3Si–Cl as electrophiles, the related preparation of **4**–**5** using Me_2PhSi–Cl bearing an aryl group at the silicon atom failed. Quantitative formation of Me_2PhSi–$SiPhMe_2$ indicated a lithium–chlorine exchange at the silicon atom. Introducing the silicon unit as the nucleophilic component resulted in the formation of the desired silylphosphines **4**–**5** in good yields (right, Scheme 2). The molecular structure of **3b** was secured by X-ray analysis (Fig. 1).



Scheme 2. Preparation of silylphosphines **1**–**5**.

Encouraged by our findings in the Rh(I)-catalyzed 1,4-addition of simple silylphosphines to cyclic α,β-unsaturated ketones,[6] we envisioned novel bridged bis(silylphosphines) **8**–**10** as an interesting entry into bisphosphine ligand structures. For this, bidentate phosphines dppe (**6**) and dppp (**7**) were reductively metalated with elementary lithium and then trapped with the corresponding chlorosilane,[15] furnishing bridged bis(silylphosphines) **8**–**10** in high overall yields yet as an isomeric mixture (dr=50:50) of *meso*- and *rac*-**8**–**10**.

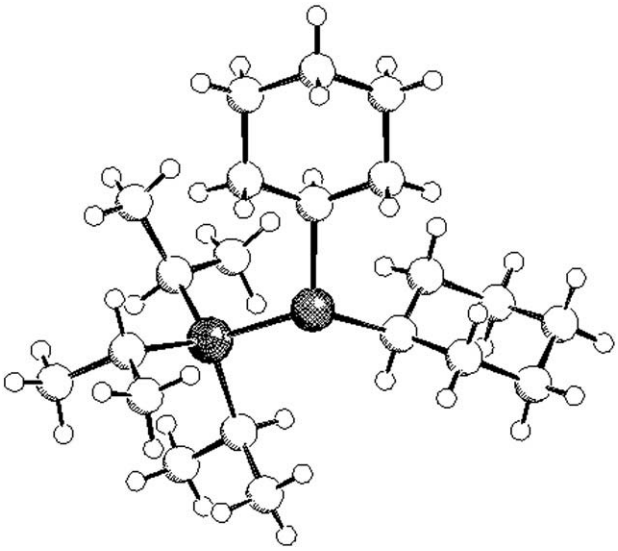
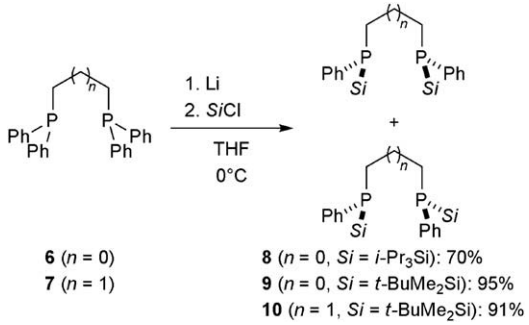


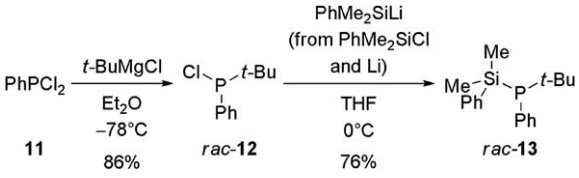
Figure 1. Molecular structure of silylphosphine **3b**.



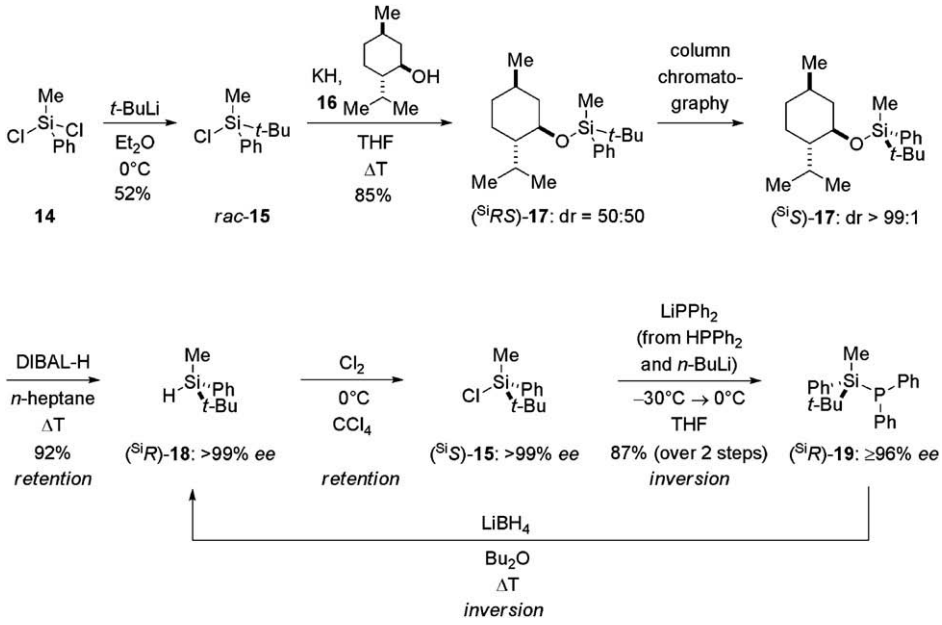
Scheme 3. Preparation of bridged bis(silylphosphines) **8**–**10**.

The phosphorus-stereogenic silylphosphine *rac*-**13** was prepared from *rac*-**12**[16] (Scheme 4) analogous to our reported protocol (right, Scheme 2).[6]

We decided to make silicon-stereogenic (^{Si}R)-**19** in highly enantioenriched form by conventional resolution of diastereomeric menthyl ethers[17] followed by stereospecific substitutions at the silicon atom (Scheme 5). Treatment of dichloromethylphenylsilane (**14**) with *tert*-butyllithium afforded chlorosilane *rac*-**15** in moderate yield (**14**→*rac*-**15**). Using (−)-menthol (**16**) as the chiral auxiliary in the resolution, its potassium salt was reacted with *rac*-**15** to give (^{Si}SR)-**17** as a mixture of diastereomers (dr=50:50); (^{Si}S)-**17** was obtained in diastereomerically pure form after several cycles of flash chromatography on silica gel (*rac*-**15**→(^{Si}SR)-**17**→(^{Si}S)-**17**). Stereospecific, racemization-free reduction with DIBAL–H[18] provided silane (^{Si}R)-**18**[19] in excellent yield and a perfect enantiomeric excess of >99% ((^{Si}S)-**17**→(^{Si}R)-**18**). Subsequent chlorination of (^{Si}R)-**18** using a saturated solution of Cl_2 in CCl_4 furnished chlorosilane (^{Si}S)-**15** ((^{Si}R)-**18**→(^{Si}S)-**15**).[18] (^{Si}S)-**15** was directly converted into desired (^{Si}R)-**19** with lithium diphenylphosphide ((^{Si}S)-**15**→(^{Si}R)-**19**). Both



Scheme 4. Preparation of phosphorus-stereogenic silylphosphine *rac*-**13**.



Scheme 5. Preparation of silicon-stereogenic silylphosphine (^{Si}R)-**19**.

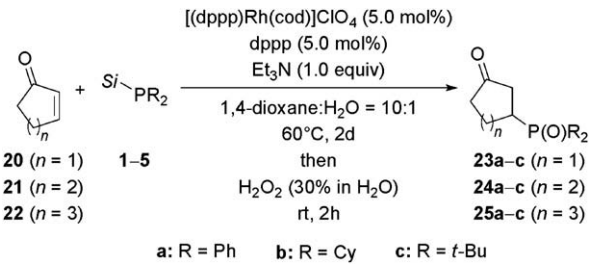
the stereochemical course of this final nucleophilic displacement and the enantiomeric excess of (^{Si}R)-**19** were unequivocally determined by HPLC analysis after known enantiospecific reduction with $LiBH_4$ ((^{Si}R)-**19**→(^{Si}R)-**18**).[20]

2.2. Phosphinyl transfer to cyclic acceptors catalyzed by a Rh(I)–phosphine complex

On the basis of the assumed mechanistic analogy of the conjugate transfer of carbon,[9] boron,[4] silicon,[5] and phosphorus nucleophiles, we chose conditions similar to those reported for the Rh(I)-catalyzed 1,4-addition of boronic acids. A series of control experiments showed that both the presence of a base and the absence of strongly coordinating counter ions were crucial for success.[6] We were pleased to find that the combination of cationic Rh(I) complex [(dppp)Rh(cod)]ClO_4 and an equimolar amount of the free ligand dppp in the presence of Et_3N as base promoted the desired 1,4-addition (Scheme 6 and Table 1).

Due to oxygen-sensitivity in solution, we decided to oxidize the intermediate trivalent phosphine adduct prior to purification (phosphinyl→phosphinoyl oxidation), which afforded the corresponding phosphine oxides **23**–**25**. Protection by sulfurization with S_8 to give related phosphine sulfides was also possible.

After identification of a suitable catalyst system,[6] we tested a few representative α,β-unsaturated cyclic ketones **20**–**22** using several phosphinide sources (Table 1). The PPh_2 group transfer



Scheme 6. Conjugate phosphinyl transfer to α,β-unsaturated cyclic ketones using a Rh(I)–phosphine complex (see Table 1 for details).

using **1a** proceeded in high yields (73–89%, entries 1–3), slightly better than with **2a** (60–76%, entries 4–6). Transfer of a PCy_2 group worked equally well with **3b** (79–92%, entries 7–9) and **4b** (64–89%, entries 10–12). Even **5c** with an electron-rich P*t*-Bu_2 group participated with moderate yields (48–58%, entries 13–15).

Unfortunately, extension of the substrate scope using less reactive acyclic α,β-unsaturated acceptors failed under these reaction conditions. This prompted us to seek a new Rh(I)–ligand combination, which would promote the conjugate phosphination of acyclic electron-deficient alkenes (cf. Section 2.4 and Ref. 8).

2.3. Rh(I)-catalyzed twofold phosphination using bridged bis(silylphosphines)

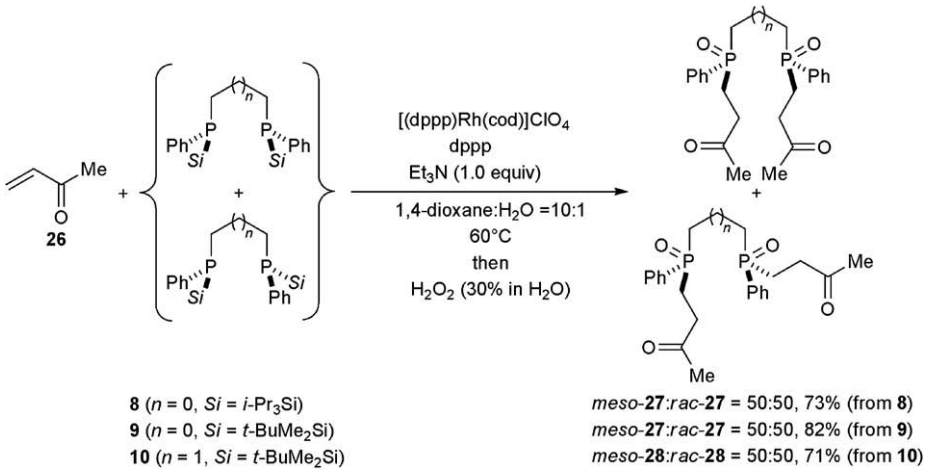
Attracted by the remarkably facile preparation of bridged bis(silylphosphines) **8**–**10** (Scheme 3), we briefly explored the possibility of twofold conjugate additions as an access to bidentate phosphine ligand motifs (Scheme 7). To limit the number of

Table 1
Conjugate phosphinyl transfer to cyclic acceptors **20**–**22**[a]

Entry	Si–PR_2	Acceptor	Product	Yield[b] (%)
1	**1a**	**20** (n=1)	**23a**	88
2	**1a**	**21** (n=2)	**24a**	73
3	**1a**	**22** (n=3)	**25a**	89
4	**2a**	**20** (n=1)	**23a**	72
5	**2a**	**21** (n=2)	**24a**	60
6	**2a**	**22** (n=3)	**25a**	76
7	**3b**	**20** (n=1)	**23b**	79
8	**3b**	**21** (n=2)	**24b**	87
9	**3b**	**22** (n=3)	**25b**	92
10	**4b**	**20** (n=1)	**23b**	64
11	**4b**	**21** (n=2)	**24b**	84
12	**4b**	**22** (n=3)	**25b**	89
13	**5c**	**20** (n=1)	**23c**	48
14	**5c**	**21** (n=2)	**24c**	55
15	**5c**	**22** (n=3)	**25c**	58

[a] Reactions were conducted using [(dppp)Rh(cod)]ClO_4 (5.0 mol %), dppp (5.0 mol %), Et_3N (1.0 equiv), and silylphosphine **1**–**5** (2.5 equiv) in 1,4-dioxane:H_2O=10:1 at 60 °C for 2 days.

[b] Isolated yield of analytically pure phosphine oxide after flash chromatography on silica gel.



Scheme 7. Rh(I)-catalyzed conjugate phosphination using bridged bis(silylphosphines) **8–10**.

diastereomers formed, we confined ourselves to using methyl vinyl ketone (**26**) as the simplest acceptor possible. We note that, in contrast to acyclic β-substituted α,β-unsaturated carbonyls and carboxyls, β-unsubstituted systems do react in the presence of our Rh(I)–dppp catalyst.[13] We were delighted to isolate the products **27** and **28**, respectively, in excellent chemical yields albeit as a mixture of *meso* and *rac* diastereomers, which were separated by flash chromatography on silica gel (Scheme 7). As expected, cyclic **20**–**22** do react in good yields as well.

2.4. Phosphinyl transfer to acyclic acceptors catalyzed by a Rh(I)–carbene complex

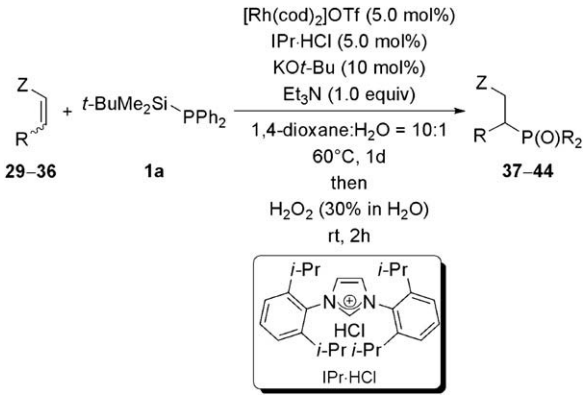
In an effort to also make acyclic acceptors susceptible for the phosphinyl transfer, we screened a number of phosphine ligands with little or no success. To our surprise, typical *N*-heterocyclic carbene ligands brought about the formation of more reactive Rh(I)–carbene complexes, which facilitated the desired 1,4-addition. For example, $[Rh(cod)_2]OTf$ (5.0 mol %), IPr·HCl (5.0 mol %), and KO*t*-Bu (10 mol %) were used to generate the active catalyst, which then effectively promoted C–P bond formation in the presence of Et_3N (Scheme 8).

A number of *Z*- and *E*-configured α,β-unsaturated active esters **29**–**31**,[21] ketones **32**–**33**, imides **34**, diesters **35**, and nitroalkene **36** were included in our survey (Fig. 2). *Z*-configured acceptors were accessed by Lindlar reduction.[5b]

As summarized in Table 2, all electron-deficient acceptors generally gave good chemical yields. We made a number of observations, which agree with data obtained in the related Pd(II)-catalyzed phosphination:[8] (1) α,β-unsaturated carboxyls are intrinsically less reactive than carbonyl compounds, which is why non-activated carboxyls do not react at all.[21] Gratifyingly, phosphinyl transfer to activated **29**–**31** proceeded in decent yields (entries 1–5). (2) Isolated yields were invariably higher for *Z* than for *E*-configured precursors. (3) α,β-unsaturated imides **34** extended the scope (entries 9 and 10), later allowing for auxiliary-based, diastereoselective variants.[22] (4) Both fumaric (*E*-**35**) and maleic ester (*Z*-**35**) reacted cleanly (entries 11 and 12).

2.5. Mechanistic insight using silicon- and phosphorus-stereogenic Si–P reagents as stereochemical probes

As outlined in the introduction (Section 1), we believe that the Si–P bond is cleaved by transmetalation (**A**→**C**→**E**, Scheme 1), and that there is no change of the oxidation state of the Rh(I) catalyst. Conversely, Hayashi et al. had proposed an alternative Rh(I)/Rh(III) cycle involving an oxidative addition of the Si–P bond to Rh(I).[13] To clarify this situation, we envisaged probing the Si–P bond activation step with an enantiopure silicon-stereogenic Si*–P reagent, an unconventional strategy that had assisted us in other mechanistic investigations in the past.[23] Analysis of the level of stereoselection in the stereoselectivity-determining 1,4-addition itself (**F**→**G**) would then reveal the true nature of the nucleophilic phosphinyl



Scheme 8. Conjugate phosphinyl transfer to acyclic acceptors (see Table 2 for details).

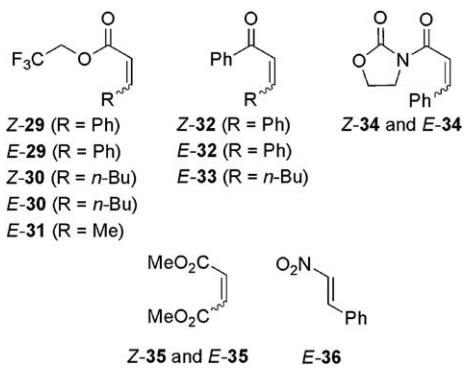
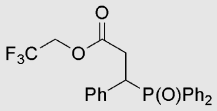
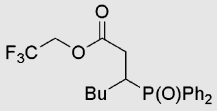
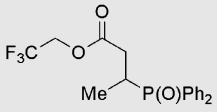
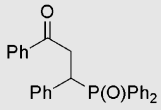
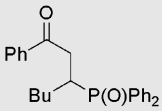
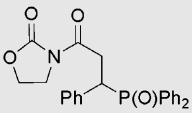
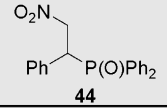
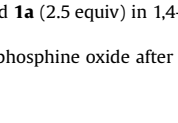


Figure 2. Acyclic *Z*- and *E*-configured α,β-unsaturated acceptors investigated in this study.

Table 2
Conjugate phosphinyl transfer to acyclic acceptors[a]

Entry	Acceptor	Product	Yield[b] (%)
1	*Z*-**29**		65
2	*E*-**29**	**37**	37
3	*Z*-**30**		63
4	*E*-**30**	**38**	54
5	*E*-**31**		88
6	*Z*-**32**	**39**	86
7	*Z*-**32**		65
8	*E*-**33**	**40**	83
9	*Z*-**34**		73
10	*E*-**34**	**41**	70
11	*Z*-**35**		95
12	*E*-**35**	**42**	77
13	*E*-**36**		75
		43	
			
		44	

[a] Reactions were conducted using $[Rh(cod)_2]OTf$ (5.0 mol %), IPr·HCl (5.0 mol %), KO*t*-Bu (10 mol %), Et_3N (1.0 equiv), and **1a** (2.5 equiv) in 1,4-dioxane:H_2O=10:1 at 60 °C for 1 day.
[b] Isolated yield of analytically pure phosphine oxide after flash chromatography on silica gel.

transfer complex **E** (Scheme 1). For comparison, we also tested a racemic phosphorus-stereogenic Si–P* reagent.

Our line of thought is further illustrated with two pairs of possible Rh(I) and Rh(III) intermediates, all of which are hypothetical phosphinyl transfer complexes (Fig. 3). Use of a Si*–P reagent will enable to distinguish between the transmetalation and the oxidative addition pathways. While the former will produce achiral Rh(I) complex **E**, the latter will form chiral Rh(III) complex ^{Si}**E***, and stereoinduction in the subsequent conjugate addition step might only be seen if silicon-stereogenic Rh(III) complex is operative. Performing the same experiment with the Si–P* is not expressive since both transmetalation and oxidative addition yield chiral complexes, Rh(I) complex **E*** and Rh(III) complex ^{P}**E***.

For these purposes, we had prepared silicon-stereogenic (^{Si}*R*)-**19** (≥96% ee) in almost enantiomerically pure form (Scheme 5) and phosphorus-stereogenic *rac*-**13** (Scheme 4). In the decisive

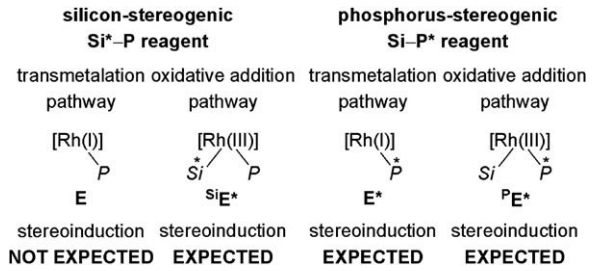
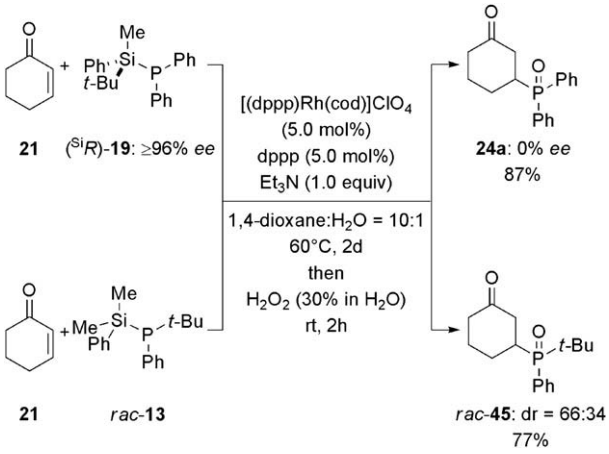


Figure 3. Possible scenarios after transmetalation or oxidative addition.



Scheme 9. Chirality at the silicon and the phosphorus atoms as stereochemical probes in the 1,4-addition.

experiment, (^{Si}*R*)-**19** was processed following our standard protocol with the Rh(I)–phosphine combination for cyclic model substrate **21** (**21**→**24a**, Scheme 9). As expected for a transmetalation pathway, absolutely no stereoinduction (0% ee) was detected. This outcome clearly substantiates that the silicon moiety is released from the catalytic cycle (**D**, Scheme 1) rather than being coordinated to the catalyst. Oxidative addition is therefore unlikely.

Under identical reaction conditions, *rac*-**13** performed well in the 1,4-addition but diastereoselectivity (dr=66:34) was somewhat disappointing (**21**→*rac*-**45**, Scheme 9). The asymmetrically substituted phosphorus atom is directly involved in the stereochemistry-determining C–P bond formation, which is why one might have expected higher stereocontrol.[24]

3. Summary

In summary, we developed an efficient methodology for the Rh(I)-catalyzed conjugate phosphination of α,β-unsaturated electron-deficient carbonyls and carboxyls. Cyclic acceptors react in the presence of a Rh(I)–phosphine catalyst while acyclic acceptors require a Rh(I)–carbene complex as catalyst. The debated mechanism of action, transmetalation versus oxidative addition, was probed with a silicon-stereogenic Si*–P reagent. The absence of any stereoinduction using a chiral phosphinide source strongly indicated a transmetalation pathway. Extension of this methodology to the development of enantioselective and substrate-controlled variants are the focus of our current work.

4. Experimental

4.1. General information

Reagents obtained from commercial suppliers were used without further purification unless otherwise noted. Racemic

tert-butylchlorophenylphosphine (*rac*-**12**)[16] and racemic *tert*-butylchloromethylphenylsilane (*rac*-**15**)[25] were prepared according to reported procedures. All reactions were performed in flame-dried glassware under a static pressure of argon. Liquids and solutions were transferred with syringes or double-ended needles; 1,4-dioxane was purified following a standard procedure, both 1,4-dioxane and H_2O were thoroughly degassed prior to use. Et_3N was distilled from CaH_2 and stored at 4 °C under exclusion of air. Technical grade solvents for extraction or flash chromatography (cyclohexane, *tert*-butyl methyl ether, ethyl acetate, CH_2Cl_2, and methanol) were distilled before use. Analytical thin layer chromatography was performed on silica gel 60 F_{254} glass plates by Merck and flash chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) by Merck. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker AM 300, AM 400, and DRX 500 instruments. Chemical shifts are reported in ppm with the solvent reference as the internal standard (δ=7.26 ppm for ^1H NMR and δ=77.1 ppm for ^{13}C NMR). Chemical shifts for $^{31}P\{^1H\}$ NMR are reported downfield in ppm relative to external standard 85% H_3PO_4 (δ=0.0 ppm). Infrared spectra were recorded on a Digilab Excalibur Series FTS 4000 spectrophotometer. Enantiomeric ratios were determined by analytical HPLC analysis on an Agilent 1200 Series with a chiral stationary phase using Daicel Chiralpak IC as well as Daicel Chiralcel OJ-H columns (*n*-heptane–*i*-PrOH solvent mixtures). Optical rotations were measured on a Perkin Elmer 341 polarimeter. High resolution mass spectrometry (HRMS) and electron spray ionization mass spectrometry (ESI-MS) were performed by the Analytic Department at the Organisch-Chemisches Institut, Universität Münster.

Full experimental data for silylphosphines **3**–**5** (Scheme 2) and cyclic β-phosphinoyl ketones **23**–**25** (Table 1) are reported in the Electronic Supplementary Data of Ref. 6. For full experimental data of acyclic β-phosphinoyl compounds **40**–**44** (Table 2), see Ref. 8.

4.2. Typical procedure for the preparation of bridged bis[(triorganosilyl)phosphines] *meso*-/*rac*-8–10

To a large excess (~10 equiv) of freshly cut lithium wire (activated with Me_3SiCl) in THF (30 mL), a solution of dppe (**6**, 2.00 g, 5.02 mmol, 1.00 equiv) or dppp (**7**, 2.07 g, 5.02 mmol, 1.00 equiv) and THF (20 mL) was added with a syringe pump over a period of 2 h at 0 °C. The reaction mixture was maintained at 0 °C for 18 h and successively sonicated for an additional hour. To separate the reaction mixture from unreacted lithium metal, the supernatant was transferred to another Schlenk flask via a double-ended cannula. To this solution, the corresponding chlorosilane (4.06 g, 21.1 mmol, 4.20 equiv) was added at 0 °C with a syringe pump over a period of 2 h. The addition was accompanied by a color change and precipitation of lithium chloride. The reaction mixture was allowed to warm to room temperature and subsequently heated at reflux for further 30 min. After evaporation of the solvents, the residue was purified via Kugelrohr distillation.

4.2.1. *meso*-/*rac*-1,2-Bis[(triisopropylsilyl)phenylphosphino]ethane (*meso*-/*rac*-***8***)

Colorless oil; yield: 70%. 6×10^{-6} mbar at 280 °C oven temperature. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, *J*=7.2 Hz, 18H), 0.96 (d, *J*=7.2 Hz, 18H), 1.10 (m, 6H), 1.89 (m, 2H), 2.51 (m, 2H), 7.11–7.26 (m, 6H), 7.32–7.48 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7, 12.6 (d, J_{C-P}=4.5 Hz), 18.5, 19.1 (d, J_{C-P}=7.8 Hz), 127.0, 127.1, 128.5, 132.9, 133.2, 133.5, 134.7, 135.0 ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −73.6, −74.8 ppm. IR (ATR): 1441 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{56}P_2Si_2$ (558.91): C, 68.77; H, 10.10. Found: C, 68.54; H, 10.01.

4.2.2. *meso*-/*rac*-1,2-Bis[(tert-butyldimethylsilyl)phenylphosphino]ethane (*meso*-/*rac*-***9***)

Pale yellowish oil; yield: 95%. 1×10^{-5} mbar at 250 °C oven temperature. ^1H NMR (400 MHz, $CDCl_3$): δ −0.19 (d, *J*=5.9 Hz, 6H), 0.03 (d, *J*=6.3 Hz, 6H), 0.85 (s, 9H), 0.89 (s, 9H), 1.81 (m, 2H), 2.31 (m, 2H), 7.18–7.38 (m, 8H), 7.40–7.48 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ −7.1, −6.3, 18.4 (d, J_{C-P}=11.5 Hz), 19.8 (d, J_{C-P}=19.8 Hz), 25.6, 27.0, 127.4 (d, J_{C-P}=9.2 Hz), 128.0 (d, J_{C-P}=4.3 Hz), 128.1 (d, J_{C-P}=5.2 Hz), 133.2 (d, J_{C-P}=9.4 Hz), 133.4 (d, J_{C-P}=3.0 Hz), 133.6 (d, J_{C-P}=9.4 Hz), 134.5 (d, J_{C-P}=14.4 Hz), 135.0 (d, J_{C-P}=10.4 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −79.5, −81.4 ppm. IR (ATR): 1437 (s) cm^{-1}. Anal. Calcd for $C_{26}H_{44}P_2Si_2$ (474.75): C, 65.78; H, 9.84. Found: C, 65.52; H, 9.84.

4.2.3. *meso*-/*rac*-1,3-Bis[(tert-butyldimethylsilyl)phenylphosphino]propane (*meso*-/*rac*-***10***)

Pale yellowish oil; yield: 91%. 2×10^{-5} mbar at 250 °C oven temperature. ^1H NMR (300 MHz, $CDCl_3$): δ −0.17 (d, *J*=2.7 Hz, 3H), −0.15 (d, *J*=2.7 Hz, 3H), 0.05 (d, *J*=3.0 Hz, 3H), 0.09 (d, *J*=3.0 Hz, 3H), 0.89 (s, 9H), 0.91 (s, 9H), 1.61–1.88 (m, 4H), 2.22–2.48 (m, 2H), 7.18–7.30 (m, 6H), 7.33–7.44 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −7.3, −7.2, −6.3, −6.2, 18.5 (d, J_{C-P}=12.1 Hz), 21.5 (d, J_{C-P}=13.1 Hz), 21.9 (d, J_{C-P}=13.7 Hz), 27.1, 27.2, 27.4, 28.0, 127.1, 127.2, 127.9 (d, J_{C-P}=7.5 Hz), 128.0 (d, J_{C-P}=7.5 Hz), 133.2, 133.4, 135.2 (d, J_{C-P}=18.2 Hz), 135.5 (d, J_{C-P}=18.2 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −88.5, −89.5 ppm. IR (ATR): 1466 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{46}P_2Si_2$ (488.26): C, 66.35; H, 9.45. Found: C, 66.44; H, 9.61.

4.3. *rac*-(Dimethylphenylsilyl)-*tert*-butylphenylphosphine (*rac*-13)

To a large excess (~10 equiv) of freshly cut lithium wire (activated with Me_3SiCl) in THF (30 mL), chlorodimethylphenylsilane (4.25 g, 25.9 mmol, 1.00 equiv) was added in one portion at room temperature. The reaction mixture was maintained at −13 °C for 18 h (dark red coloration indicated formation of the corresponding lithium compound). The mixture was allowed to warm to 0 °C and was sonicated for an additional hour. To separate the solution of the lithium reagent from unreacted lithium metal, the supernatant was transferred to a dropping funnel connected to a Schlenk flask via a double-ended cannula. Prior to slow addition (2 h) of the lithium reagent at 0 °C, the Schlenk flask was charged with *tert*-butylchlorophenylphosphine (*rac*-**12**, 5.00 g, 25.9 mmol, 1.00 equiv) and *n*-hexane (60 mL). The addition was accompanied by a color change and precipitation of lithium chloride. The reaction mixture was allowed to warm to room temperature and was maintained at this temperature for another 2 h. After evaporation of the solvents, the residue was purified via Kugelrohr distillation (5×10^{-1} mbar at 225 °C oven temperature) yielding *rac*-**13** (5.67 g, 76%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 3H), 0.70 (s, 3H), 1.14 (d, *J*=12.6 Hz, 9H), 7.31–7.42 (m, 6H), 7.49–7.59 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.9, 0.9, 24.5 (d, J_{C-P}=16.5 Hz), 29.7 (d, J_{C-P}=13.0 Hz), 127.4 (d, J_{C-P}=7.4 Hz), 127.7, 128.0 (d, J_{C-P}=5.9 Hz), 128.3 (d, J_{C-P}=6.2 Hz), 129.2, 132.9, 133.8, 135.5 (d, J_{C-P}=16.2 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −5.4 ppm. IR (ATR): 1445 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{25}PSi$ (300.45): C, 71.96; H, 8.39. Found: C, 71.79; H, 8.31.

4.4. (^{Si}*RS*)-*tert*-Butyl-(−)-menthoxymethylphenylsilane ((^{Si}*RS*)-17)

A solution of (−)-menthol (**16**, 7.03 g, 45.0 mmol, 1.50 equiv, >99% ee) in THF (30 mL) was added to a suspension of oil-free potassium hydride (1.81 g, 45.0 mmol, 1.50 equiv) in THF (20 mL) at 0 °C. For complete deprotonation, the mixture was heated at reflux for 3 h. After cooling to room temperature, the mixture was treated with racemic chlorosilane *rac*-**15** (6.36 g, 30.0 mmol, 1.00 equiv) in

THF (50 mL). Heating at reflux for 16 h was followed by cooling to ambient temperature, quenching with H_2O (100 mL) and neutralization (pH=7) with 2 M HCl. The organic layer was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (4×60 mL). The combined organic layers were washed with brine (70 mL), dried ($MgSO_4$), filtered and the volatiles were evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel with cyclohexane as eluent affording the title compound (^{Si}RS)-**17** (8.47 g, 85%, dr=50:50) as a colorless oil. After repeated flash chromatography, (^{Si}S)-**17** (4.11 g, 41%, dr>99:1) was separated as colorless oil. R_f=0.35 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.43 (s, 3H), 0.65 (d, J=6.6 Hz, 3H), 0.74–0.83 (m, 2H), 0.87 (d, J=6.6 Hz, 3H), 0.90 (d, J=7.1 Hz, 3H), 0.92 (s, 9H), 1.02 (m, 1H), 1.21 (m, 1H), 1.29 (m, 1H), 1.55–1.65 (m, 2H), 1.88 (m, 1H), 2.36 (qqd, J=2.5, 7.0, 7.0 Hz, 1H), 3.51 (ddd, J=4.5, 10.2, 10.2 Hz, 1H), 7.33–7.42 (m, 3H), 7.57–7.61 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.2, 15.8, 18.6, 21.4, 22.4, 22.6, 25.1, 26.1, 31.6, 34.5, 45.4, 50.5, 72.9, 127.3, 129.1, 134.6, 136.6 ppm. IR (ATR): 1110 (s) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{36}OSiNa$ ([M+Na]$^+$): 355.2428. Found: 355.2435.

4.5. (^{Si}R)-*tert*-Butylmethylphenylsilane ((^{Si}R)-18)

A 100 mL Schlenk flask equipped with a magnetic stirring bar and a reflux condenser was charged with (^{Si}S)-**17** (1.86 g, 5.60 mmol, 1.00 equiv, dr>99:1) and *n*-heptane (30 mL). DIBAL–H (1.0 M in *n*-hexane, 22.4 mL, 22.4 mmol, 4.00 equiv) was added and the reaction mixture was subsequently heated at reflux for 20 h. The reaction mixture was quenched at ambient temperature by careful addition of H_2O (60 mL) followed by neutralization (pH=7) with 2 M HCl. The organic layer was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (4×50 mL). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$), filtered and the volatiles were evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel with cyclohexane as eluent, furnishing highly enantiomerically enriched silane (^{Si}R)-**18** (916 mg, 92%, >99% ee) as a colorless oil. HPLC (Daicel Chiracel OJ-H column, column temperature 12 °C, solvent *n*-heptane:*i*-PrOH 99:1, flow rate 0.7 mL min^{-1}): t_R=5.23 min for (^{Si}S)-**18** (minor enantiomer) and t_R=6.27 min for (^{Si}R)-**18** (major enantiomer). R_f=0.70 (cyclohexane). $[\alpha]_D^{20}$ −25.6 (*c* 0.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.36 (d, J=3.7 Hz, 3H), 0.96 (s, 9H), 4.16 (q, J=3.7 Hz, 1H), 7.34–7.42 (m, 3H), 7.52–7.57 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ −8.5, 16.6, 26.8, 127.6, 129.2, 135.1, 135.5 ppm. IR (ATR): 2111 (s) cm^{-1}. HRMS (EI) calculated for $C_{11}H_{18}Si$ ([M]$^+$):178.1172. Found: 178.1178.

4.6. (^{Si}R)-(*tert*-Butylmethylphenylsilyl)diphenylphosphine ((^{Si}R)-19)

A saturated solution of Cl_2 in CCl_4 (6.0 mL) was added to a solution of (^{Si}R)-**18** (916 mg, 5.14 mmol, 1.00 equiv) in CCl_4 (5.0 mL) at 0 °C until the pale yellow color persisted. After 10 min, the reaction mixture was purged with argon. Evaporation of the solvent under reduced pressure provided chlorosilane (^{Si}S)-**15** as a colorless oil, which was used without further purification. Simultaneously, a 50 ml-Schlenk flask charged with diphenylphosphine (960 mg, 5.14 mmol, 1.00 equiv) in THF (20 mL) was cooled to −30 °C and *n*-butyllithium (1.6 M in hexane, 3.21 ml, 5.14 mmol, 1.00 equiv) was added dropwise. The resulting red solution was allowed to warm to room temperature and stirred for another hour. After cooling to 0 °C, a solution of freshly prepared (^{Si}S)-**15** and THF (5 mL) was slowly added. The reaction mixture was heated at reflux for 1 h. After evaporation of the solvents, the residue was purified via Kugelrohr distillation (4×10^{-1} mbar at 220 °C oven temperature), affording (^{Si}R)-**19** as a pale yellowish, highly viscous oil (1.62 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47 (d, J=1.8 Hz, 3H), 0.80 (d, J_{C-P}=0.7 Hz, 9H), 7.01–7.10 (m, 5H), 7.30–7.41 (m, 6H), 7.66–7.71 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ −8.6 (d, J_{C-P}=1.9 Hz), 19.7 (d, J_{C-P}=11.4 Hz), 27.5 (d, J_{C-P}=2.9 Hz), 126.4, 127.7, 127.9 (d, J_{C-P}=6.3 Hz), 128.4, 128.7, 129.2 132.6 (d, J_{C-P}=14.5 Hz), 134.2 (d, J_{C-P}=11.8 Hz), 135.5 (d, J_{C-P}=6.0 Hz), 136.1 (d, J_{C-P}=12.8 Hz), 136.5 (d, J_{C-P}=16.5 Hz), 136.8 (d, J_{C-P}=20.1 Hz) ppm.[31] P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −64.7 ppm. IR (ATR): 1441 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{27}PSi$ (362.16): C, 76.20; H, 7.51. Found: C, 76.50; H, 7.59.

4.7. General procedure for the Rh(I)-catalyzed 1,4-addition using bridged bis(silylphosphines) *meso*-/*rac*-8–10

Under argon atmosphere, a Schlenk tube equipped with a magnetic stirring bar is charged with methyl vinyl ketone (**26**, 1.0 equiv) dissolved in deoxygenated 1,4-dioxane:H_2O=10:1 (approximately 0.5 M based on substrate). After addition of [(dppp)Rh(cod)]ClO_4 (5.0 mol %) and dppp (5.0 mol %), Et_3N (1.0 equiv) and silylphosphine *meso*-/*rac*-**8**–**10** (0.51 equiv) are successively added. The reaction mixture is maintained at 60 °C for 2 days. The reaction mixture is cooled to room temperature and is directly oxidized with H_2O_2 (30%, 2.0 equiv). After additional stirring for 4 h, H_2O and aqueous $FeSO_4$ (0.5 M) are added. The organic layer is separated and the aqueous phase is extracted with *tert*-butyl methyl ether (3×). The combined organic phases are dried ($MgSO_4$) and the volatiles are removed under reduced pressure. Purification by flash column chromatography on silica gel (CH_2Cl_2–methanol) provides phosphine oxides **27** and **28**.

4.7.1. meso- and rac-4-({2-[(3-Oxobutyl)phenylphosphinoyl]-ethyl}phenylphosphinoyl)butan-2-one (meso- and rac-27)

meso-**27**:[26] pale yellow solid; yield: 37% (from **8**), 42% (from **9**); R_f=0.24 (CH_2Cl_2–methanol 50:1). Mp 120–121 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.87 (m, 2H), 2.03 (s, 6H), 2.08 (m, 2H), 2.11–2.21 (m, 4H), 2.41 (m, 2H), 2.73 (m, 2H), 7.47–7.59 (m, 6H), 7.61–7.67 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7 (d, J_{C-P}=32.2 Hz), 23.6 (d, J_{C-P}=35.5 Hz), 29.5, 34.8, 128.9 (d, J_{C-P}=5.7 Hz), 129.0 (d, J_{C-P}=5.6 Hz), 129.4, 130.4 (d, J_{C-P}=4.6 Hz), 130.5 (d, J_{C-P}=4.6 Hz), 130.7, 131.9, 132.2, 205.6 (d, J_{C-P}=6.2 Hz) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 41.1 ppm. IR (ATR): 1704 (s) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{28}O_4P_2Na$ ([M+Na]$^+$): 441.1355. Found: 441.1352.

rac-**27**:[26] pale yellow solid; yield: 36% (from **8**), 40% (from **9**); R_f=0.18 (CH_2Cl_2–methanol 50:1). Mp 120–121 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.84 (m, 2H), 2.08 (s, 6H), 2.12 (m, 2H), 2.20–2.36 (m, 4H), 2.49 (m, 2H), 2.81 (m, 2H), 7.41–7.46 (m, 4H), 7.50–7.57 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5 (d, J_{C-P}=29.3 Hz), 23.4 (d, J_{C-P}=35.5 Hz), 29.6, 34.9, 128.8 (d, J_{C-P}=5.7 Hz), 128.9 (d, J_{C-P}=6.0 Hz), 129.6, 130.3 (d, J_{C-P}=4.5 Hz), 130.4 (d, J_{C-P}=4.5 Hz), 130.9, 132.2, 132.4, 205.7 (d, J_{C-P}=6.1 Hz) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 40.9 ppm. IR (ATR): 1712 (s) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{28}O_4P_2Na$ ([M+Na]$^+$): 441.1355. Found: 441.1354.

4.7.2. meso- and rac-4-({2-[(3-Oxobutyl)phenylphosphinoyl]-propyl}phenylphosphinoyl)butan-2-one (meso- and rac-28)

meso-**28**:[26] pale yellow oil; yield: 36%. R_f=0.18 (CH_2Cl_2–methanol 25:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.69 (m, 2H), 1.88–2.00 (m, 4H), 2.01 (s, 6H), 2.04–2.24 (m, 4H), 2.39 (m, 2H), 2.72 (m, 2H), 7.32–7.61 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.7 (d, J_{C-P}=26.2 Hz), 28.9, 30.0 (d, J_{C-P}=11.9 Hz), 30.9 (d, J_{C-P}=11.9 Hz), 34.7 (d, J_{C-P}=2.8 Hz), 128.8 (d, J_{C-P}=5.8 Hz), 131.1, 131.3 (d, J_{C-P}=19.0 Hz), 131.9 (d, J_{C-P}=2.5 Hz), 206.0 (d, J_{C-P}=12.3 Hz) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 41.0 ppm. IR (ATR): 1710 (s) cm^{-1}. HRMS (ESI) calculated for $C_{23}H_{30}O_4P_2H$ ([M+H]$^+$): 433.1698. Found: 433.1691.

rac-**28**:[26] pale yellow oil; yield: 35%. R_f=0.13 (CH_2Cl_2–methanol 25:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (m, 2H), 1.77–2.01 (m, 4H), 2.03 (s, 6H), 2.04–2.22 (m, 4H), 2.36 (m, 2H), 2.80 (m, 2H), 7.36–7.67 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.8 (d, J_{C-P}=26.1 Hz),

29.5, 29.8 (d, J_{C-P}=11.4 Hz), 30.7 (d, J_{C-P}=11.4 Hz), 34.8 (d, J_{C-P}=2.4 Hz), 128.7 (d, J_{C-P}=5.7 Hz), 130.3, 131.4 (d, J_{C-P}=19.2 Hz), 131.8 (d, J_{C-P}=2.5 Hz), 206.1 (d, J_{C-P}=12.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 40.7 ppm. IR (ATR): 1712 (s) cm^{-1}. HRMS (ESI) calculated for $C_{23}H_{30}O_4P_2H$ ($[M+H]^+$): 433.1698. Found: 433.1689.

4.8. General procedure for the Rh(I)-catalyzed 1,4-addition of α,β-unsaturated acyclic acceptors

In a flame-dried Schlenk tube equipped with a magnetic stirring bar, $[Rh(cod)_2]OTf$ (5.0 mol %), IPr·HCl (5.0 mol %) and KO*t*-Bu (10 mol %) are dissolved in 1,4-dioxane (0.2 M based on substrate) and stirred for 30 min at room temperature. The acyclic α,β-unsaturated acceptor (1.0 equiv), Et_3N (1.0 equiv), silylphosphine **1a** (2.5 equiv), and H_2O (0.02 M based on substrate) are added in this order. The mixture is maintained at 60 °C for 16 h. The reaction mixture is cooled to room temperature and is directly oxidized with H_2O_2 (30%, 2.0 equiv). After additional stirring for 2 h, H_2O and aqueous $FeSO_4$ (0.5 M) are added. The organic layer is separated and the aqueous phase is extracted with *tert*-butyl methyl ether (3×). The combined organic phases are dried ($MgSO_4$) and the volatiles are removed under reduced pressure. The residue is purified by flash chromatography on silica gel (cyclohexane–ethyl acetate), yielding phosphine oxides **37–44**.[8]

4.8.1. 3-Diphenylphosphinoyl-3-phenylpropionic acid 2,2,2-trifluoroethyl ester (*37*)

White solid; yield: 65% (from *Z*-**29**), 37% (from *E*-**29**); R_f=0.56 (cyclohexane–ethyl acetate 1:3). Mp 175 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 3.01 (ddd, *J*=3.7, 8.7, 16.7 Hz, 1H), 3.22 (ddd, *J*=6.8, 11.3, 16.7 Hz, 1H), 4.04 (ddd, *J*=3.7, 8.4, 11.3 Hz, 1H), 4.23 (m, 2H), 7.11–7.30 (m, 7H), 7.33–7.40 (m, 3H), 7.51–7.62 (m, 3H), 7.89–7.99 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.5, 42.9 (d, J_{C-P}=65.8 Hz), 60.5 (q, J_{C-F}=36.7 Hz), 122.6 (q, J_{C-F}=279 Hz), 127.5 (d, J_{C-P}=2.4 Hz), 128.1 (d, J_{C-P}=11.9 Hz), 128.4 (d, J_{C-P}=1.9 Hz), 128.9 (d, J_{C-P}=11.2 Hz), 129.5 (d, J_{C-P}=5.2 Hz), 130.4 (d, J_{C-P}=7.4 Hz), 131.1 (d, J_{C-P}=9.1 Hz), 131.3 (d, J_{C-P}=1.5 Hz), 131.4 (d, J_{C-P}=8.9 Hz), 131.6 (d, J_{C-P}=3.1 Hz), 132.2 (d, J_{C-P}=2.8 Hz), 134.4 (d, J_{C-P}=5.5 Hz), 169.8 (d, J_{C-P}=17.6 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 32.0 ppm. IR (ATR): 1754 (s) (C=O) cm^{-1}. Anal. Calcd for $C_{23}H_{20}F_3O_3P$ (432.11): C, 63.89; H, 4.66. Found: C, 63.82; H, 4.62.

4.8.2. 3-Diphenylphosphinoylheptanoic acid 2,2,2-trifluoroethyl ester (*38*)

Colorless oil; yield: 63% (from *Z*-**30**), 54% (from *E*-**30**); R_f=0.66 (cyclohexane–ethyl acetate 1:4). ^1H NMR (400 MHz, $CDCl_3$): δ 0.75 (t, *J*=7.1 Hz, 3H), 1.10–1.39 (m, 4H), 1.54 (m, 1H), 1.67 (m, 1H), 2.58 (ddd, *J*=7.9, 9.4, 17.2 Hz, 1H), 2.78 (ddd, *J*=4.6, 14.6, 17.2 Hz, 1H), 2.94 (m, 1H), 4.19 (dq, *J*=8.3, 12.7 Hz, 1H), 4.39 (dq, *J*=8.3, 12.7 Hz, 1H), 7.42–7.55 (m, 6H), 7.77–7.85 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 22.4, 28.0 (d, J_{C-P}=1.7 Hz), 29.4 (d, J_{C-P}=10.0 Hz), 32.3, 33.8 (d, J_{C-P}=72.1 Hz), 60.5 (q, J_{C-F}=37.1 Hz), 122.6 (q, J_{C-F}=280 Hz), 128.7 (d, J_{C-P}=11.7 Hz), 130.8 (d, J_{C-P}=9.0 Hz), 130.9 (d, J_{C-P}=8.9 Hz), 131.0, 131.1 (d, J_{C-P}=8.9 Hz), 131.8 (d, J_{C-P}=6.8 Hz), 131.9 (d, J_{C-P}=2.8 Hz), 132.0, 171.0 (d, J_{C-P}=13.2 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 36.1 ppm. IR (ATR): 1756 (s) (C=O) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{24}O_3F_3PNa$ ($[M+Na]^+$): 435.1307. Found: 435.1307.

4.8.3. 3-Diphenylphosphinoylbutyric acid 2,2,2-trifluoroethyl ester (*39*)

White solid; yield: 88%; R_f=0.32 (cyclohexane–ethyl acetate 1:3). Mp 90 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (dd, *J*=7.2, 16.1 Hz, 3H), 2.57 (ddd, *J*=6.4, 10.7, 16.7 Hz, 1H), 2.76 (ddd, *J*=3.4, 9.9, 16.7 Hz, 1H), 2.90 (m, 1H), 4.42 (m, 2H), 7.47–7.59 (m, 6H), 7.79–7.87 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.8 (d, J_{C-P}=2.7 Hz), 29.2 (d, J_{C-P}=73.9 Hz), 33.9, 60.4 (q, J_{C-F}=36.0 Hz), 122.7 (d, J_{C-F}=275 Hz), 128.7 (d, J_{C-P}=11.4 Hz), 128.8 (d, J_{C-P}=11.5 Hz), 130.6 (d, J_{C-P}=25.5 Hz), 131.0 (d, J_{C-P}=6.8 Hz), 131.1 (d, J_{C-P}=6.6 Hz), 131.6 (d, J_{C-P}=24.4 Hz), 131.9 (d, J_{C-P}=2.7 Hz), 132.0 (d, J_{C-P}=2.9 Hz), 170.5 (d, J_{C-P}=17.7 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 35.3 ppm. IR (ATR): 1758 (s) (C=O) cm^{-1}. Anal. Calcd for $C_{18}H_{18}F_3O_3P$ (370.09): C, 58.38; H, 4.90. Found: C, 58.45; H, 4.83.

4.9. *rac*-3-(*tert*-Butylphenylphosphinoyl)cyclohexanone (*rac*-45)

A Schlenk tube equipped with a magnetic stirring bar was charged with **21** (38.8 mg, 0.415 mmol, 1.00 equiv) dissolved in deoxygenated 1,4-dioxane: H_2O=10:1 (approximately 0.5 M based on substrate). After addition of $[(dppp)Rh(cod)]ClO_4$ (15.0 mg, 0.021 mmol, 5.0 mol %) and dppp (8.6 mg, 0.021 mmol, 5.0 mol %), Et_3N (58 μL, 41.9 mg, 0.415 mmol, 1.00 equiv) and silylphosphine *rac*-**13** (249 mg, 0.830 mmol, 2.50 equiv) were successively added. The reaction mixture was maintained at 60 °C for 2 days. The reaction mixture was cooled to room temperature and directly oxidized with H_2O_2 (30%, 85 μL, 0.830 mmol 2.00 equiv). After additional stirring for 4 h, H_2O (1 mL) and aqueous $FeSO_4$ (1 mL) were added. The organic layer was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3×2 mL). The combined organic phases were dried ($MgSO_4$) and the volatiles were removed in vacuo. Purification by flash column chromatography on silica gel (ethyl acetate) provided phosphine oxide *rac*-**45** as a mixture of diastereomers (88.9 mg, 77%, dr=66:34) as a white solid. R_f=0.13 (CH_2Cl_2–methanol 50:1). Mp 77 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.13 (d, *J*=14.5 Hz, 6H), 1.17 (d, *J*=14.5 Hz, 9H), 1.48–1.87 (m, 2H), 1.95–2.18 (m, 4H), 2.22–2.42 (m, 5H), 2.44–2.94 (m, 4H), 7.41–7.51 (m, 5H), 7.61–7.72 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 24.6, 25.7, 25.8, 26.1 (d, J_{C-P}=14.2 Hz), 26.6 (d, J_{C-P}=13.8 Hz), 33.5 (d, J_{C-P}=65.4 Hz), 33.6 (d, J_{C-P}=65.6 Hz), 35.6 (d, J_{C-P}=61.0 Hz), 35.8 (d, J_{C-P}=60.7 Hz), 40.4 (d, J_{C-P}=3.6 Hz), 40.8 (d, J_{C-P}=3.2 Hz), 40.9, 41.0, 128.4 (d, J_{C-P}=10.1 Hz), 128.5 (d, J_{C-P}=10.5 Hz), 129.3 (d, J_{C-P}=25.4 Hz), 130.0 (d, J_{C-P}=25.6 Hz), 131.2 (d, J_{C-P}=7.4 Hz), 131.3 (d, J_{C-P}=7.3 Hz), 131.5 (d, J_{C-P}=2.4 Hz), 131.6 (d, J_{C-P}=2.4 Hz), 209.9 (d, J_{C-P}=12.8 Hz), 210.0 (d, J_{C-P}=12.3 Hz) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 48.5,48.7 ppm. IR (ATR): 1702 (s) cm^{-1}. HRMS (ESI) calculated for $C_{16}H_{23}O_2PNa$ ($[M+Na]^+$): 301.1328. Found: 301.1319.

4.10. X-ray data

4.10.1. General information

Data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[27a] absorption correction Denzo,[27b] structure solution SHELXS-97,[27c] structure refinement SHELXL-97,[27d] graphics SCHAKAL (Universität Freiburg, **1997**).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC-718494 (**3b**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

4.10.2. X-ray crystal structure analysis for *3b*

Formula $C_{21}H_{43}PSi$, *M*=354.61, colorless crystal 0.60×0.50×0.45 mm, *a*=9.6011(2), *b*=10.5024(2), *c*=11.6826(3) Å, α=81.600 (1), β=81.620(1), γ=75.210(1)°, *V*=1119.50(4) $Å^3$, ρ_{calcd}=1.052 g cm^{-3}, μ=1.566 mm^{-1}, empirical absorption correction ($0.453 \le T \le 0.539$), *Z*=2, triclinic, space group *P*1bar (No. 2), λ=1.54178 Å, *T*=223(2) K, ω and φ scans, 12,250 reflections collected

($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ]=0.60 Å^{-1}, 3899 independent (R_{int}=0.040) and 3781 observed reflections [$I \geq 2\ \sigma(I)$], 214 refined parameters, R=0.043, wR^2=0.115, max (min) residual electron density 0.47 (−0.21) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

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