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Stereospecific stilbene formation from β-hydroxy-α,β-diphenylethylphosphoranes. Mechanistic proposals based upon stereochemistry

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Abstract—All four diastereomers of β-hydroxy-α,β-diphenylethylspirophosphoranes bearing two Martin ligands were prepared from a P–H (equatorial) spirophosphorane. Treatment of these phosphoranes with *t*-BuOK or *t*-BuONa at low temperature (ca. −40°C) led to the formation of stilbene with complete stereospecificity. In half of the cases the reaction proceeded quantitatively, whereas the other half gave rise to retro-aldol reaction with the formation of varying amounts of benzaldehyde and benzylphosphorane. A kinetic examination revealed that of the four the quantitatively proceeding reaction that gives *cis*-stilbene was the fastest. Based on the experimental observations, a mechanistic rationale for the previously reported Wittig-type reaction of exceptionally high *Z*-selectivity using an ethoxycarbonylmethylspirophosphorane is presented. © 2002 Published by Elsevier Science Ltd.

1. Introduction

The Wittig reaction and its variant, the Horner–Wadsworth–Emmons (HWE) reaction are exceptionally useful reactions for regioselectively and often stereoselectively introducing unsaturation with the accompaniment of carbon–carbon bond formation.[1] It is generally assumed that both of these groups of reagents undergo olefin formation via 10-P-5 phosphorane intermediates. We[2] and others[3–5] have found yet another group of phosphorus compounds, 10-P-5 phosphoranes, that are already hypervalent to begin with can also serve as olefination reagents, thus providing another example of the utility of hypervalent compounds for organic transformations.[6] As for the limited examples on Wittig type reactions involving 10-P-5 phosphoranes of 'stabilized ylide' and 'semi-stabilized ylide' type, those with dative P–N bonds such as **1**[4] and **2**[5] have the tendency to give high *E*-selectivity, whereas neutral phosphoranes such as **3**[3] and **4**[2] show a completely opposite trend favoring *Z*-olefins.

We have found that by the use of spirophosphorane **4** bearing Martin ligands,[7] extremely high *Z*-selectivities, typically *Z*:*E*=95:5 or better could be achieved with an ester[2b] (**4a**) or amide[2d] (**4b**) group as the electron-withdrawing group regardless of whether the reacting aldehyde was aromatic or aliphatic. Also found was that **4c**, which bears a cyano[2d] group, is effective for aliphatic aldehydes though not for aromatic aldehydes. These compounds are additions to a rather limited list of reagents that give rise to the thermodynamically less stable *Z*-olefins with high selectivity.[8] Mechanistically, we assumed for **4a** that the reaction involved hexacoordinated intermediates, which have one bond more than the ordinary pentacoordinated Wittig-type reaction intermediate, and that the high *Z*-selectivity was a consequence of the initial aldehyde addition reaction being the rate determining step and the relative rate of the reverse reaction (retro-aldol reaction) being slow. The retro-aldol pathway has been established to be the cause for the high *E*-selectivity often observed in ordinary HWE reactions using reagents bearing electron-withdrawing groups (**7a**).[9] As for the assumption of hexacoordination, such intermediates could not be observed under the reaction conditions for **4a**. However, the quantitative formation of persisting hexacoordinated phosphates upon deprotonation of **5** has provided strong evidence for the intermediacy of such species in general for this system.[2a,10]

In order to gain evidence on the slow retro-aldol process, we attempted to prepare **13** and carry out stereochemical examinations similar to those previously carried out on **7a**.[9] However, this could not be achieved, so instead, we decided to look into the closest analogs, i.e. 'semi-stabilized' type

Keywords: hypervalent; phosphorane; pentacoordinated; hexacoordinated; Wittig reaction; stereospecific; mechanism.

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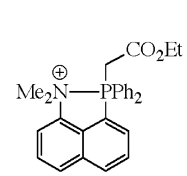

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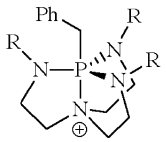

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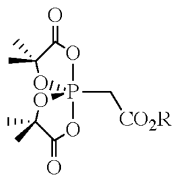

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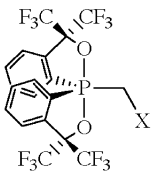
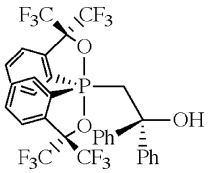


4a: X = CO_2R
4b: X = $CONR_2$
4c: X = CN



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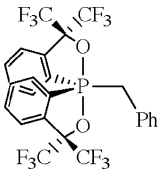

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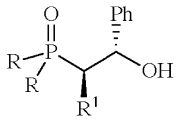
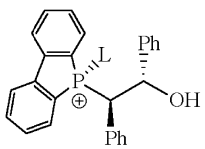
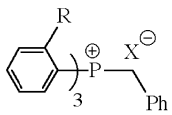


7a: R = MeO, R^1 = CO_2Me
7b: R = MeO, R^1 = Ph
7c: R = Ph, R^1 = Ph



8a: L = Me
8b: L = O^-



9a: R = $MeOCH_2O$, X= Br
9b: R = H, X = I

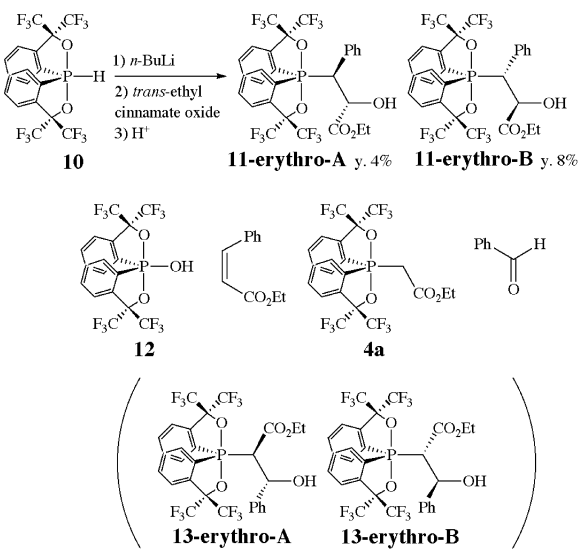
reagents, **6**. Thus, we prepared all four diastereomers of β-hydroxy-α,β-diphenylethylspirophosphoranes **14** bearing two Martin ligands and preliminarily reported that olefin is formed with high stereospecificity upon treatment of these compounds with sodium or potassium bases.[2c] In mechanistic studies involving analogous HWE reagents, it has been found that treatment of erythro β-hydroxy-α,β-diphenylethylphosphonates (**7b**)[11] and -phosphine oxides (**7c**)[12] with strong base lead to high percentages of the thermodynamically more favorable *E*-olefin and/or benzylphosphonates (or benzylphosphine oxides). The formation of the *E*-olefins was appropriately rationalized to have arisen via retro-aldol reaction, ensuing recombination to give the corresponding threo isomer, and consequent breakdown of the adduct into the observed products. Although there is a difference in reactivity between ordinary 'stabilized' and 'semi-stabilized' type HWE reagents, the predominance of *E*-olefin formation is much alike. Exceptions to the *E*-selectivities have come about by utilizing of the 'ring effect'.[13] The reactions of **8a**[14] and **8b**[15] were found to give *Z*-stilbene, exclusively or nearly so. Unlike **7a** and **7b**, which could be prepared from HWE reagent and aldehyde in an ordinary manner, preparation of **8a** and **8b** required the use of epoxides. Thus, with semi-stabilized HWE reagents that use aldehyde as the reactant, it is rather difficult to obtain *Z*-olefins with high selectivity and the only satisfactory methods that have been reported utilize the Wittig reaction with modifications either in the reagent (**9a**)[16] or reaction conditions (**9b**).[17] Herein, we provide a full account of the preliminarily reported results along with a mechanistic rationale based upon a kinetic examination of the olefination step.

2. Results and discussions

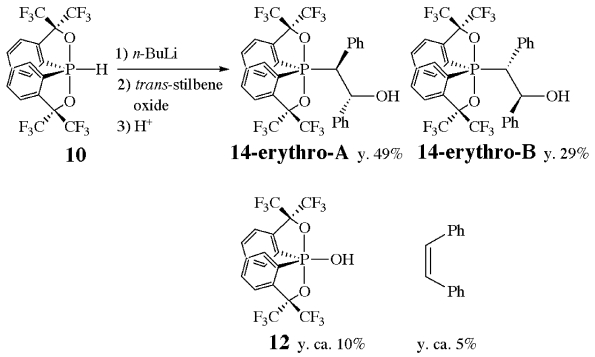
2.1. Preparation and structural determination of all four diastereomeric β-hydroxy-α,β-diphenylethylspiro-phosphoranes

Since our initial objective was to gain insight to the mechanism of the reaction of **4a**, we commenced our investigation by attempting to isolate the aldehyde adduct of **4a** by using metals such as Mg^{2+} which have proven effective for systems such as **7**.[9] However, the desired adducts **13** could not be obtained. We reasoned that this was because of the low reactivity of the Mg^{2+} enolate of **4a**. We next turned our attention to the reaction of the Mg^{2+} salt of the phosphoranide from **10**[18,19] (**10-Mg**$^{2+}$) with a suitable epoxide. However, no reaction occurred upon using ethyl *trans*-3-phenyloxiranecarboxylate as the epoxide. With no alternatives left, we reacted **10-Li**$^+$ with the epoxide. No desired **13-erythro-A** or **13-erythro-B** could be found in the mixture. Obtained was a complex mixture and the only isolable phosphorane species were **11-erythro-A** (4%) and **11-erthyro-B** (8%) along with hydroxide **12** and a small amount of ethyl *cis*-cinnamate (Scheme 1). The stereochemical identity of **11-erythro-B** was determined by X-ray analysis (see Section 4.4) and that of **11-erythro-A** in analogy with **14** (vide infra). Here, **11-erythro-A** and **11-erthyro-B** could be viewed as intermediates in the Wittig-type reaction of **6**, a semi-stabilized ylide type reagent and the fact that these compounds could be isolated implied that intermediates for semi-stabilized reagents are not as prone to decomposition as those for stabilized ylide reagents such as **4**, and thus would be more easy to handle. To simplify matters for further investigations, we decided to examine analogs of **7** or **8**, which give rise to symmetric stilbene.

The preparation of three of the four possible diastereomeric β-hydroxyethylspirophosphoranes was carried out by treating **10-Li**$^+$ with stilbene oxide at rt in THF. Reaction with *trans*-stilbene oxide yielded a pair of *anti* diastereomers, **14-erythro-A** ($S_P^*S^*R^*$[20]; y. 49%) and **14-erythro-B** ($S_P^*R^*S^*$; y. 29%), along with a small amount of P–OH phosphorane



Scheme 1.



Scheme 2.

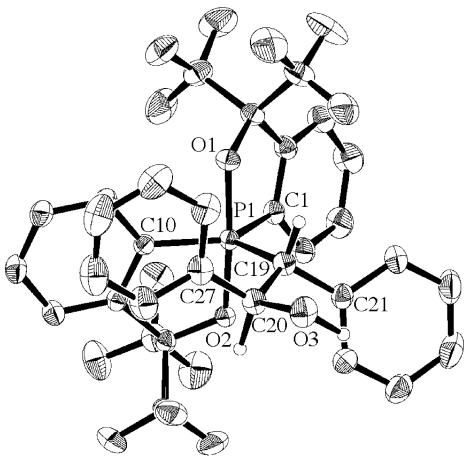
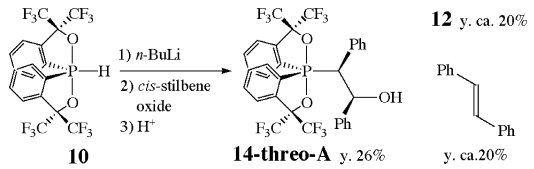


Figure 1. The ORTEP drawing of **14-erythro-B** showing the thermal ellipsoids at the 30% probability level. All the hydrogens other than C19-*H19*, C20-*H20* and O3-*H3* have been omitted for clarity.

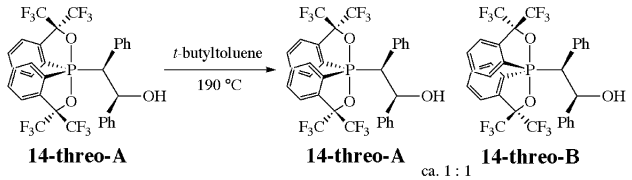


Scheme 3.

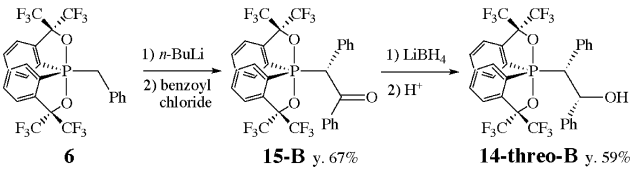
12 (y. ca. 5%) and *cis*-stilbene (y. ca. 10%), the latter two of which are products of overreaction (Scheme 2). The relative stereochemistry of **14-erythro-B** was established by X-ray structural analysis (Fig. 1).

On the other hand, the reaction of **10-Li**$^+$ with *cis*-stilbene oxide (Scheme 3) gave **14-threo-A** ($S_P^*S^*S^*$; y. 26%) as the only isolable adduct, together with *trans*-stilbene (y. ca. 20%) and oxide **12** (y. ca. 20%).

The remaining diastereomer **14-threo-B** ($S_P^*R^*R^*$) was obtained as a diastereomeric mixture with **14-threo-A** (**14-threo-A**–**14-threo-B**=5:2) upon heating **14-threo-A** in *t*-butyltoluene at 190°C for 11 days via pseudorotation upon the phosphorus atom (Scheme 4). No olefination to stilbene and **12** or reverse reaction to benzaldehyde and benzyl-spirophosphorane **6** could be observed under the rather



Scheme 4.



Scheme 5.

harsh conditions, thus indicating that the β-hydroxyethyl-phosphoranes are sturdy as long as they are not deprotonated.

Since **14-threo-B** could not be obtained in an efficient manner, an alternative method was sought. The reaction of **6** with *n*-BuLi followed by the treatment with benzoyl chloride furnished **15-B** ($S_P^*R^*$) as the sole adduct (Scheme 5). The relative stereochemistry for this compound was also established by X-ray analysis (Fig. 2). Reduction of this compound with $LiBH_4$ was also found to be stereo-selective, giving only the desired diastereomer **14-threo-B** (Scheme 5).

Other than the furnished isomer, the reduction could have given rise to the side-chain β-carbon epimer **14-erythro-B**, the diastereomer established by X-ray analysis. As it was not, chemical correlation allowed the assignment of the stereochemistry of **14-threo-B** to be $S_P^*R^*R^*$ as shown and it followed that the stereochemistry of **14-threo-A** was $S_P^*S^*S^*$. That left **14-erythro-A** with the remaining $S_P^*S^*R^*$ configuration, thus permitting the establishment of the relative stereochemistries of all four stereoisomers.

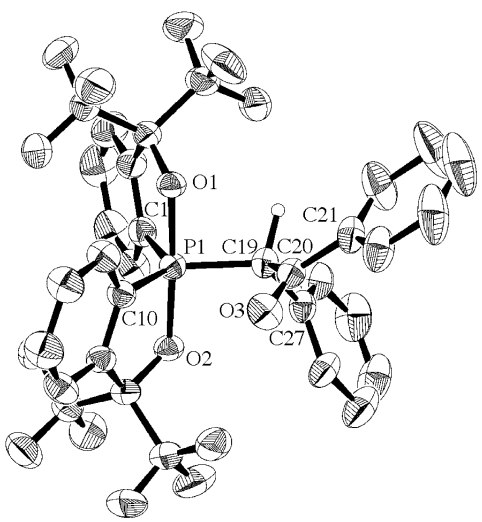
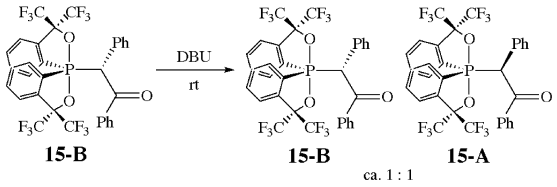
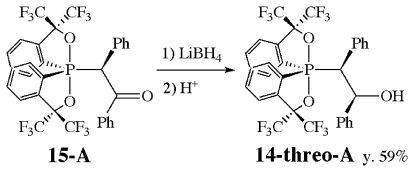


Figure 2. The ORTEP drawing of **15-B** showing the thermal ellipsoids at the 30% probability level. All the hydrogens other than C19-*H19* have been omitted for clarity.



Scheme 6.



Scheme 7.

Incidentally, treating **15-B** with DBU at rt for 2 days resulted in a ca. 1:1 mixture of **15-B** and its side-chain α-carbon epimer **15-A** ($S_P^*S^*$) (Scheme 6), and as expected, reduction of **15-A** similarly with $LiBH_4$ resulted in the exclusive formation of **14-threo-A** (Scheme 7).

2.2. Rationalization of the stereoselective transformations

For the reaction of the phosphoranide **10-Li**$^+$ with *trans*-stilbene oxide (Scheme 2), since both the oxide and phosphorane **10** are racemic, not much of a differentiation was expected, and accordingly a diastereomeric mixture was obtained. There is an apparent selectivity of **14-erythro-A**–**14-erythro-B**=2:1, however, it is the latter of these two, which gives olefin at a higher rate (vide infra). Thus, the observed ratio could just be a consequence of advanced decomposition of the latter adduct **14-erythro-B**.

cis-Stilbene oxide on the other hand is *meso* and the occurrence of selective reaction is possible as observed here (Scheme 3). The observed selectivity can be rationalized by assuming that phosphoranide **10-Li**$^+$ is high in TBP character. This is not unreasonable because in an antimony analog with Sb in the place of P and Et_4N^+ in the place of Li^+ in **10-Li**$^+$, we have established approximate TBP structure by X-ray analysis.[21] Upon reaction, bulky substituents upon an electrophile are expected to be oriented away from the apical bond since its bond angle is nearly 180° whereas the corresponding angle involving equatorial bonds have an angle of about 120°. Thus, in the transition state, the substituent of primary hindrance, the bulky phenyl group directly attached to the carbon that undergoes S_N2 reaction is expected to have its C(phenyl)–C(epoxide) bond in the equatorial plane as shown in the drawings in Figure 3.

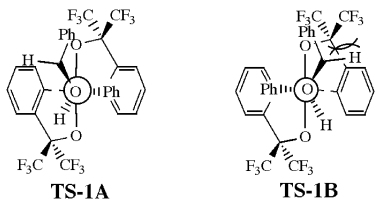


Figure 3. Plausible transition states of the reaction of phosphoranide **10-Li**$^+$ (generated from **10**) with *cis*-stilbene oxide.

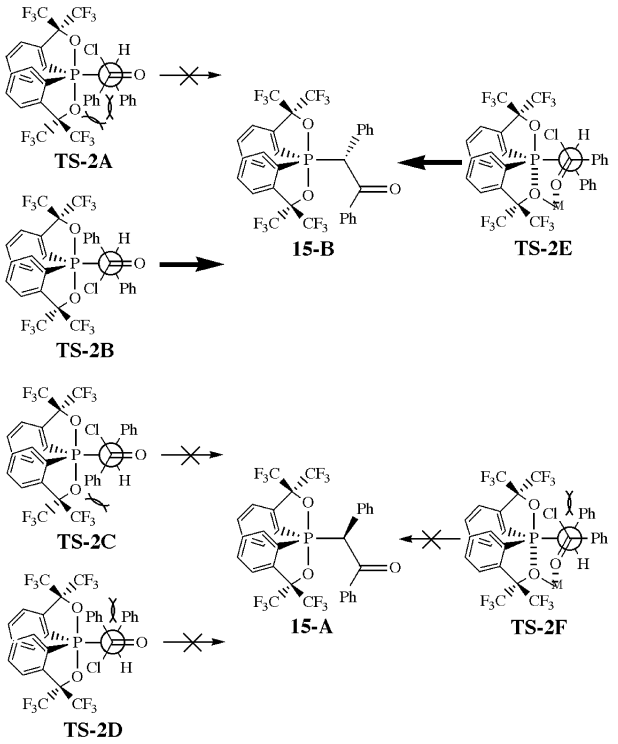


Figure 4. Plausible transition states of the reaction of the benzyl anion **6-Li**$^+$ (generated from **6**) with benzoyl chloride.

Of the two transition states, **TS-1A** has the remaining epoxide carbon in the open space between the two bidentates whereas in **TS-1B** there is repulsion between this epoxide carbon and a CF_3 group facing it. Thus, **A** should be more favored and this coincides with the actual results. As in the **14-erythro** case, there was the possibility that **14-threo-B** was not observed due to decomposition. However, **14-threo-A** has been found to decompose faster than **14-threo-B** (vide infra) so the predominance of **14-threo-A** as a primary reaction product does not change.

For the benzoylation reaction (Scheme 5), if we can assume that chelation is not involved, the approach of the nucleophilic phosphorus species would be expected to occur with the bulky phosphorus moiety *anti* to the carbonyl oxygen as depicted in Figure 4. In that case four modes of attack (**TS-2A** to **TS-2D**) can be envisioned and of the four, three will experience either repulsion between the two phenyl groups (size order Ph>Cl>O) or between the phenyl group of the acid chloride and a CF_3 group of the phosphorus part, leaving **TS-2B** as the most likely candidate to account for the observed selectivity. We cannot strictly disregard chelation or electrostatic interactions. If these were in effect, it would be more appropriate to coordinate the metal to an oxygen atom of the apical bond and to have the carbonyl oxygen in the coordinating sphere of the metal as described for the reaction of **4a** and aldehyde in the presence of base (Scheme 12). Of the two plausible transition states (**TS-2E** and **TS-2F**), **TS-2E**, which is less prone to steric hindrance, is sufficient for explaining the observed selectivity.

The reduction processes (Schemes 5 and 7) are rather straightforward. As shown in Figure 5, the stereochemistry

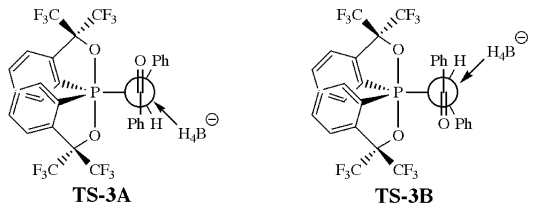
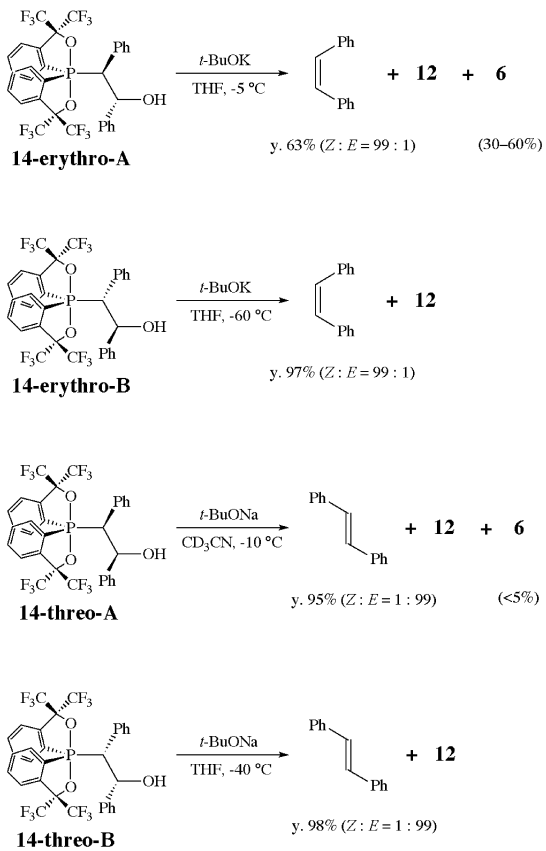


Figure 5. Felkin–Anh models for the reaction of $LiBH_4$ with **15-A** (**TS-3A**) and **15-B** (**TS-3B**).

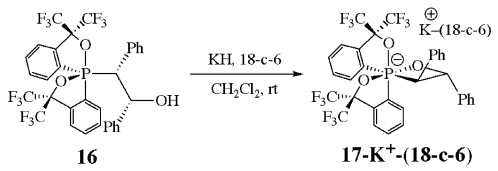
is consistent with Felkin–Anh selectivity. Similar threo selectivity (ca. 9:1) has been observed for the reduction of β-ketophosphine oxides.[22]

2.3. Olefin formation reactions

As anticipated, treatment of **14** with *n*-BuLi resulted in slow and rather complex reactions for all four diastereomers. Upon using NaH, *t*-BuONa or *t*-BuOK, **14-erythro-B** and **14-threo-B** quantitatively and stereospecifically furnished *cis* and *trans* stilbenes, respectively (Scheme 8). **14-erythro-A** and **14-threo-A** also furnished *cis* and *trans* stilbenes, respectively, with nearly complete selectivity. However, varying amounts of retro-aldol product, **6** were also found to form depending upon reaction conditions. While the total amount of **6** formation for the latter was less than 5% and practically negligible in some instances, the amount of **6** was 30–60% for the former, which gives rise to *cis*-stilbene. The fact that all four diastereomers of **14** gave rise to olefinic product at temperatures as low as −40°C is in remarkable contrast with hexacoordinated phosphate **17**



Scheme 8.



Scheme 9.

which was prepared from *anti*-apicophilic[23] phosphorane **16** (Scheme 9).[23d] Compound **17-K$^+$-18-c-6** was found to be stable at rt and required heating for the formation of olefin.

2.4. Kinetic examination of the olefin formation process

The fact that the product distribution differed among diastereomers implied that there was a difference in the rate of olefin formation. Thus, we decided to carry out rate measurements on the olefination process at −40°C using *t*-BuONa as base. Since it was found that *t*-BuONa could not deprotonate **6**, and the addition of aldehyde to **6-M$^+$** was very slow, the formation of **6-M$^+$** via retro-aldol reaction at low temperature could be assumed to irreversibly give **6** upon protonation by *t*-BuOH. This irreversibility allowed us to apply first order kinetics.

For **14-erythro-A**, the rate of **6** formation was also measured. The reaction of *cis*-stilbene-forming **14-erythro-B** was fastest and the measurement had to be carried out at −60°C. As listed in Table 1, the order of olefin formation was **14-erythro-B**>**14-threo-B**>**14-threo-A**>**14-erythro-A**. At this temperature, for **14-erythro-A**, the retro reaction was found to be almost twice as fast as the olefin formation reaction. Kinetic parameters for the reaction of **14-threo-B** were calculated to be $\Delta H^{\neq}=12.6\pm0.8$ kcal mol^{-1} and $\Delta S^{\neq}=-23.0\pm3.2$ eu (−60 to −40°C). For **17-K$^+$-18-c-6**, the entropy value was found to be near zero. The large negative entropy value here indicates that although the reactant is already in a hexacoordinated state, even higher order is required for formation of olefin. This could be due either to solvation of the countercation to localize charge and weaken the bonds about the phosphorus atom or to orientation of the phenyl rings to conformations, which facilitate bond cleavage. The fact that the presence of **18-c-6** facilitated the reaction of **17** supports the former assumption on bond weakening.

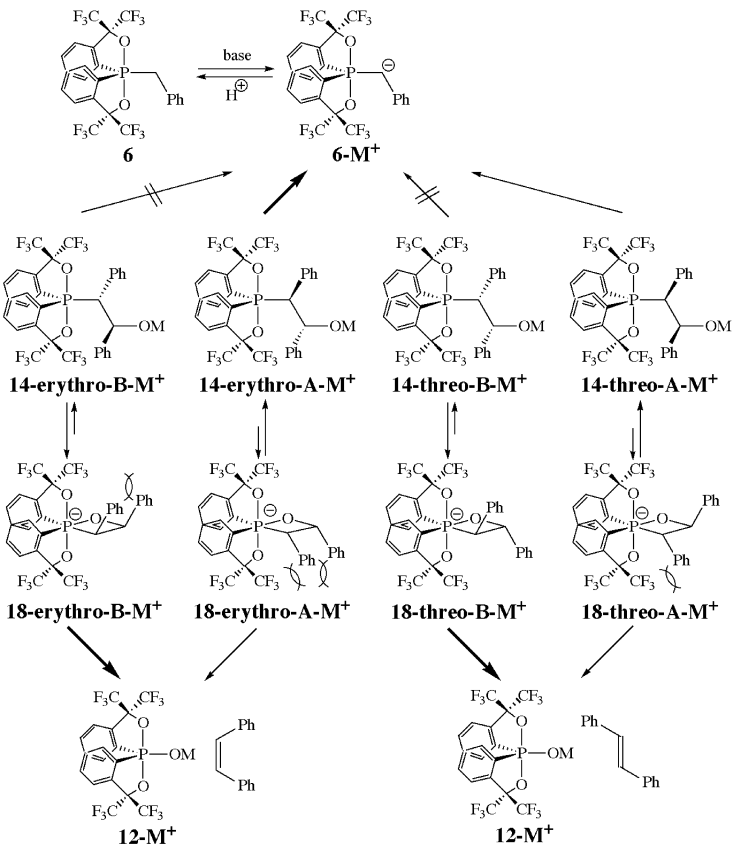
2.5. Attempted observation of hexacoordinated intermediates

In order to determine whether hexacoordinated species are actually involved in the reaction, all four diastereomers of

Table 1. Reaction rates

Substrate	Temperature (°C)	k (s^{-1})
14-erythro-B	−60	$(1.44\pm0.03)\times10^{-4}$
14-threo-B	−50	$(1.90\pm0.03)\times10^{-5}$
	−40	$(7.58\pm0.14)\times10^{-4}$
	−30	$(2.02\pm0.07)\times10^{-4}$
14-threo-A	−40	$(1.05\pm0.03)\times10^{-4}$
14-erythro-A	−40	$(1.21\pm0.02)\times10^{-5}$
	−40	[a] $(2.05\pm0.03)\times10^{-5}$

[a] Denotes **6** formation reaction.



Scheme 10.

14 were first treated with *n*-BuLi in THF at rt only to provide ^{31}P NMR signals assignable to pentacoordinated species. Upon lowering the temperature to −30°C, however, the solution containing **14-threo-B** showed a sharp signal (δ_P (THF) −112) attributable to a hexacoordinated species in a 4:1 ratio with a pentacoordinated species. Furthermore, the sodium salt of **14-threo-B** (**14-threo-B-Na**$^+$) formed upon treatment with *t*-BuONa at −60°C lead to complete conversion to the hexacoordinated species (δ_P (THF) −112) while **14-erythro-B** (**14-erythro-B-Na**$^+$) newly gave rise to a hexacoordinated species (δ_P (THF) −110 (br)) (ca. 1:1) at the same temperature. The 1:1 ratio did not change upon progression of the olefin forming process, thus indicating that the 1:1 ratio was the equilibrium ratio between the pentacoordinated sodium alkoxide of **14-erythro-B** and a hexacoordinated species at the specified temperature and that equilibration is faster than olefin formation. Only pentacoordinated species could be observed for **14-erythro-A** and **14-threo-A**.

2.6. Mechanistic rationalization of the decomposition of the four diastereomers

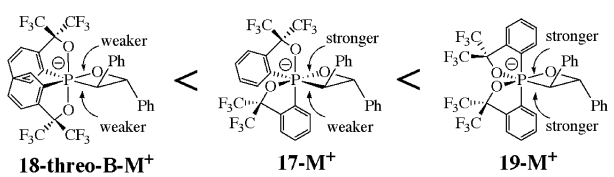
The phosphoranes that gave rise to hexacoordinated species incidentally were the ones that showed no sign of reverse reaction to generate aldehyde. This implied that facility to take on hexacoordinated structure was related to ease in olefin formation. A mechanistic rationale of the decomposition reaction of **14** based on observations is rather straightforward as shown in Scheme 10. Deprotonation of **14** gives rise to **14-M**$^+$. Without configurational change upon the phosphorus atom, ring closure with P–O bond formation occurs to give hexacoordinated species **18**. Stereomutation upon the phosphorus atom prior to olefin formation can be disregarded since stereomutation of similar hexacoordinated phosphates have been determined to be rather slow even at rt with K^+ or Na^+ as the countercation[2a] while the actually observed olefin formation temperature here is well below 0°C. Thus, olefin formation could be regarded to occur directly from these species, and stereochemical interpretations require only to consider these configurations. The common feature between **14-erythro-B-M**$^+$ and **14-threo-B-M**$^+$, which show no sign of reverse reaction, is that CF_3-α-phenyl interaction is minimized in their ring closed hexacoordinated isomers **18-erythro-B-M**$^+$ and **18-threo-B-M**$^+$, respectively. This absence of repulsive interaction would be expected to facilitate ring closure and is in good accord with ^{31}P NMR observations. In **14-erythro-B-M**$^+$, 1,2-interaction between the phenyl groups becomes operative upon ring closure and this serves as an unfavorable factor for ring-closure compared with **14-threo-B-M**$^+$ and this is reflected in the fact that the portion of the hexacoordinated isomer is larger for **14-threo-B-M**$^+$ than **14-erythro-B-M**$^+$. The fact that hexacoordinated species could not be observed for **14-erythro-A-M**$^+$ and **14-threo-A-M**$^+$ indicates that repulsion between CF_3 and the α-phenyl is quite severe. The fact that all the X-ray structures, i.e., **11-erythro-B**, **14-erythro-B**, and **15-B**, showed the α-phenyl group and the closest (upper) CF_3 groups to be farthest apart also is a good indication that such interaction is highly unfavorable. In the case of **14-erythro-A-M**$^+$, in addition to the CF_3-α-phenyl interaction,

1,2-phenyl interaction disfavors ring closure and this is reflected in the fact that the ratio of reverse reaction is highest for this species. Although hexacoordinated species are ordinarily expected to be less stable than pentacoordinated species, the use of the unique Martin ligand system makes the pentacoordinated metal alkoxide less stable than the hexacoordinated species, in which charge delocalization by the coordination of the oxygen atom seems to have overcome the instability caused by the formation of higher coordination. Thus, for **14-erythro-M**$^+$ and **14-threo-A-M**$^+$, it can be said that the favored ring closure has been inhibited by steric reasons. As for the formation of olefin, the formation of the hexacoordinated species becomes a prerequisite, and although this is more favorable for **14-threo-B**, the hexacoordinated species **18-threo-B** formed from **14-threo-B-M**$^+$ is stereochemically stable and other than the weakness of the P–C bond in this species there are no other driving forces to help accelerate olefin formation. On the other hand, in **18-erythro-B**, the 1,2-phenyl eclipse interaction not only serves to facilitate ring opening back to **14-erythro-B-M**$^+$, but can also serve as a buttress effect to facilitate P–C bond dissociation. Thus, for **14-erythro-B-M**$^+$, the delicate balance in steric hindrance works as an advantage and as a result olefin formation becomes fastest for this substrate. Thus, in the reaction of **4a-M**$^+$[2b] or **6-M**$^+$[23d] with aldehydes, whether or not the retro-aldol reaction occurs is highly dependent upon which adduct among **14-M**$^+$ is formed.

The fact that hexacoordinated phosphates assumed here, in which two carbon atoms are situated *trans* to the two ligating atoms (oxygen and carbon) of the oxaphosphetane ring as represented by **18-threo-B-M**$^+$, are less stable than **17-M**$^+$ in which one oxygen atom has become *trans* to the oxygen atom of the 4-membered ring indicates that *trans* influence is highly related to the stability of the hexacoordinated phosphates bearing an oxaphosphetane ring. In other words, **17** which has a better *trans* group (oxygen) is more reluctant to undergo decomposition to olefin. Thus, we can further anticipate that if we were able to obtain an isomer in which two oxygen atoms are *trans* to the atoms of the oxaphosphetane ring, it would be even more unwilling to produce olefin (Scheme 11). This thermodynamic propensity is also consistent with **5-M**$^+$ undergoing quantitative rearrangement to a species analogous to **19-M**$^+$ (differing only in the position of the phenyl groups on the phosphetane ring) under equilibration conditions.[2a]

2.7. Rationalization of the selectivity observed in the reaction of 4a

The reaction between aldehydes and reagent **4a-M**$^+$[2b] or **6-M**$^+$[23d] has been found to require temperatures as high as 0°C or more. On the other hand, the olefin formation process

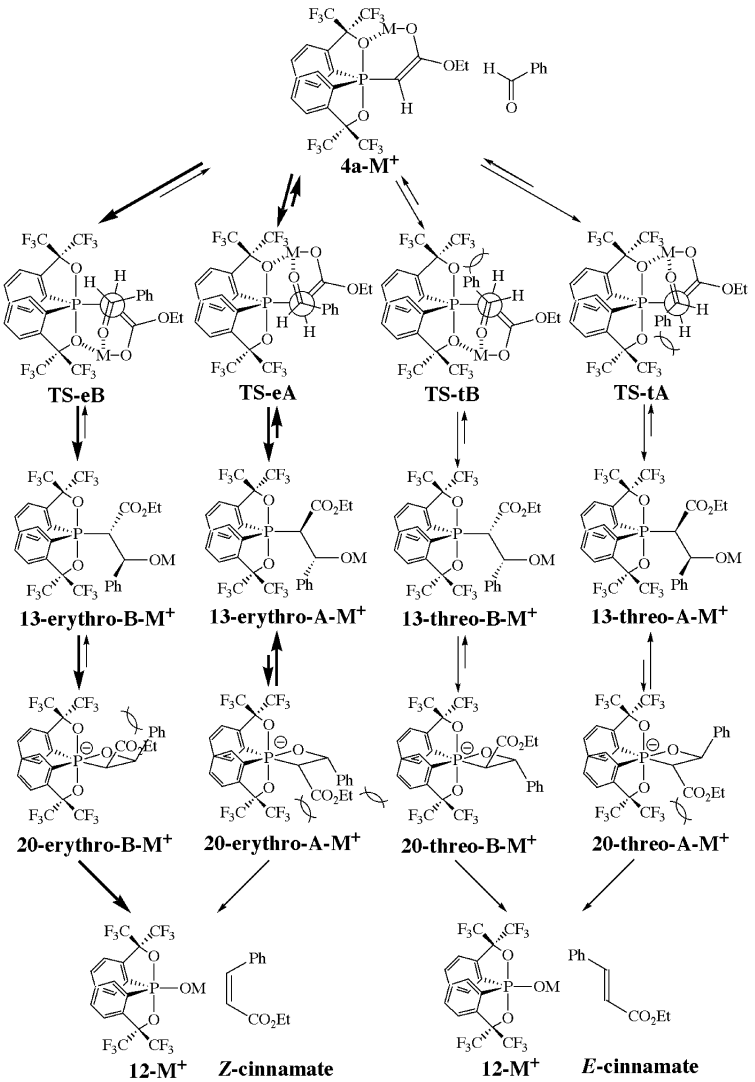


Scheme 11.

from **14** was found to proceed at temperatures as low as −40°C. Olefin formation from **13** is expected to be even faster. Therefore, it is not unreasonable to say that the rate determining step for the olefin forming reaction of both **4a-M**$^+$[2b] and **6-M**$^+$[23d] is definitely the initial addition step. This is in contrast to HWE reactions where the rates of the initial aldehyde addition and olefin furnishing decomposition are regarded to be comparable.[1] The reasons for the diverse behavior of the phosphoranes here would be because of the lower rate of retro-aldol reaction resulting from the lower thermodynamical acidity of phosphoranes in general, and the steric hindrance exerted by the extra coordination, as previously assumed.[2b]

Although direct verification of the mechanism of the reaction of **4a** could not be carried out, the stereochemical results gained here provide useful information. Thus, consideration of the order of olefin formation rate and ^{31}P NMR observations enables us to make minor revisions of our tentative rationale on the mechanism involving **4a**, which did not take the stereochemistry upon the chiral (but in this case not optically active) phosphorus atom in consideration.[2b] Enolate **4a-M**$^+$ formed upon deprotonation of **4a** probably has the OM group and the phosphorus moiety on the same side of the double bond due to either chelation or electrostatic attraction between the metal and an oxygen atom of an apical bond (Scheme 12). The incoming aldehyde should also be involved in the interaction as shown in the transition state drawings. Calculations involving HWE reagents also favor similar spacial arrangement with attractive interaction between the enolate metal, the phosphoryl oxygen atom and the aldehyde oxygen.[24] Comparing the four plausible transition states which involve metal–oxygen interaction, **TS-tB** and **TS-tA** are clearly unfavorable due to severe steric interaction between the phenyl group of the aldehyde and the phosphorus moiety of the reagent. Of the remaining two transition states, it is rather difficult to say which is more favorable. Actually, it would not matter which is preferred since both lead to the *Z*-olefin. Since interaction between a CF_3 group and the metal in **TS-eB** is projected to be unfavorable, it could be that **TS-eA** is more likely as the kinetically favored transition state. In that case, analogy from isomers of **18** would make **20-erythro-A-M**$^+$ extremely unfavorable, and both olefin formation and retro-aldol reaction would be assumed to occur. Upon regeneration of aldehyde and P enolate via this path, primary equilibration would be between **13-erythro-B-M**$^+$ and **13-erythro-A-M**$^+$, and since the product olefin could be formed via **13-erythro-B-M**$^+$ with no obstacles, secondary equilibration involving **13-threo-B-M**$^+$ and **13-threo-A-M**$^+$ need not be operative, thus accounting for the observed high *Z*-selectivity. This again is in contrast to HWE reactions which have to consider *E*-olefin precursors corresponding to **13-threo-B-M**$^+$ and **13-threo-A-M**$^+$ in pre-equilibrations.

The reaction of **6-K**$^+$ with benzaldehyde was found to be considerably less selective (*Z*:*E*=80:20) compared with the reaction of **4-K**$^+$ (*Z*:*E*=98:2). Thus, since the retro-aldol reaction is suppressed, similar considerations would lead to the conclusion that unlike the reaction of **4-M**$^+$, the initial addition of aldehyde to **6-M**$^+$ is not very selective and



Scheme 12.

either **14-threo-B-M**$^+$ or **14-threo-A-M**$^+$ is formed along with one or two of the precursors to *Z*-stilbene.

3. Conclusion

In summary, we have found that all four diastereomers of β-hydroxy-α,β-diphenylethylspirophosphoranes bearing Martin ligands lead to the formation of stilbene with complete stereospecificity upon treatment with *t*-BuOK or *t*-BuONa at low temperature (ca. −40°C). In half of the cases the reaction proceeded quantitatively, whereas the other half gave rise to retro-aldol reaction side reactions and formation of varying amounts of aldehyde and benzylspirophosphorane. A kinetic examination revealed that of the four, the quantitatively proceeding reaction that gives *cis*-stilbene was the fastest. The reason for the high specificity can be attributed to the low acidity of the benzyl hydrogen and to low reactivity of the benzyl anion once generated due to the sterically hindered environment in its vicinity. These factors combine to disfavor retro-aldol reaction and even in cases where retro reaction does proceed, recombination of aldehyde and benzyl anion is suppressed and this serves to maintain the selectivity due to a faster protonation reaction. Although reverse reactions are expected to be more facile for **4a** because of the stability of the anion generated from it, the mechanistic results for **14** allow for a rational plausible mechanism for the reaction of **4a**.

4. Experimental

4.1. General procedures

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm from residual chloroform-*d* (δ=7.26). ^{13}C NMR chemical shifts (δ) are given in ppm from chloroform-*d* (δ=77.0). ^{19}F NMR chemical shifts (δ) are given in ppm from external $CFCl_3$. ^{31}P NMR chemical shifts (δ) are given in ppm from external 85% H_3PO_4. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer.

All reactions were carried out under N_2. THF was freshly distilled from Na-benzophenone. Ethanol was distilled from magnesium. All other solvents were distilled from CaH_2. Preparative thin layer chromatography was carried out on plates of Merck silica gel 60 GF_{254}.

4.1.1. (S_P^*,1S^*,2R^*)-1-(2-Ethoxycarbonyl-2-hydroxy-1-phenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (11-erythro-A) and (S_P^*,1R^*,2S^*)-1-(2-ethoxycarbonyl-2-hydroxy-1-phenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (11-erythro-B). To P–H (equatorial) phosphorane **10** (214 mg, 0.415 mmol) in THF (5 mL) was added *n*-BuLi (0.27 mL, 0.427 mol) at 0°C. To this solution was added ethyl *trans*-3-phenyloxiranecarboxylate (72.0 mg, 0.374 mmol) in THF (2 mL) and the resulting mixture was stirred at rt for 11 h. The solution was quenched with 1 M HCl, extracted with Et_2O and the combined organic solvents were washed with water and brine. This was followed by drying over anhydrous $MgSO_4$ and concentration in vacuo. Separation of the residue on TLC (hexane–Et_2O=3:1) followed by recrystallization (hexane–CH_2Cl_2) gave **11-erythro-A** (10.8 mg, 4%) and **11-erythro-B** (23.5 mg, 8%). **11-erythro-A**: mp 211.5–212.5°C (dec); ^{1}H NMR ($CDCl_3$) δ 8.04–7.99 (m, 2H), 7.75–7.64 (m, 6H), 7.17–7.01 (m, 5H), 4.81 (s, 1H), 4.25 (d, J=7.3 Hz, 1H), 4.21–4.12 (m, 1H), 4.01–3.95 (m, 1H), 2.35 (s, 1H), 0.89 (t, J=7.3 Hz, 3H); ^{31}P NMR ($CDCl_3$) δ −21.2. Anal. calcd for $C_{29}H_{21}F_{12}O_5P$: C, 49.17; H, 2.99. Found: C, 49.13; H, 2.78. **11-erythro-B**: mp 156–157°C (dec); ^{1}H NMR ($CDCl_3$) δ 8.26–8.21 (m, 2H), 7.72–7.61 (m, 6H), 7.21–7.00 (m, 5H), 5.34 (dd, J=3.4 Hz, $^2J_{PH}$=7.4 Hz, 1H), 4.16 (dd, J=3.4 Hz, $^2J_{PH}$=23.4 Hz, 1H), 3.96–3.89 (m, 2H), 0.89 (t, J=7.3 Hz, 3H); ^{31}P NMR ($CDCl_3$) δ −25.0. Anal. calcd for $C_{29}H_{21}F_{12}O_5P$: C, 49.17; H, 2.99. Found: C, 49.10; H, 2.77.

4.1.2. (S_P^*,1S^*,2R^*)-1-(2-Hydroxy-1,2-diphenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (14-erythro-A) and (S_P^*,1R^*,2S^*)-1-(2-hydroxy-1,2-diphenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (14-erythro-B). To P–H (equatorial) phosphorane **10** (196 mg, 0.380 mmol) in THF (2 mL) was added *n*-BuLi (0.25 mL, 0.408 mol) at 0°C. To this solution was added *trans*- stilbene oxide (75.0 mg, 0.382 mmol) in THF (2 mL) and the resulting mixture was stirred at rt for 5 h. The solution was quenched with water, extracted with Et_2O and the combined organic solvents were washed with water and brine. This was followed by drying over anhydrous $MgSO_4$ and concentration in vacuo. Separation of the residue on TLC (hexane–benzene=2:1) followed by recrystallization (hexane–CH_2Cl_2) gave **14-erythro-A** (132.6 mg, 49%) and **14-erythro-B** (78.2 mg, 29%). **14-erythro-A**: mp 200.5–201.5°C (dec); ^{1}H NMR ($CDCl_3$) δ 7.60–7.08 (m, 18H), 5.36 (d, J=10.3 Hz, 1H), 4.29 (dd, J=10.3 Hz, $^2J_{PH}$=19.5 Hz, 1H), 1.83 (s, 1H); ^{19}F NMR ($CDCl_3$) δ −71.9 (q, $^4J_{FF}$=10.1 Hz, 6F), −73.3 (q, $^4J_{FF}$=10.1 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ −21.9. Anal. calcd for $C_{32}H_{21}F_{12}O_3P$: C, 53.95; H, 2.97. Found: C, 54.12; H, 2.87. **14-erythro-B**: mp 203.5–204.5°C (dec); ^{1}H NMR ($CDCl_3$) δ 7.62–7.05 (m, 18H), 5.31 (dd, J=10.3 Hz, $^2J_{PH}$=4.9 Hz, 1H), 4.47 (dd, J=10.3 Hz, $^2J_{PH}$=16.1 Hz, 1H), 1.90 (s, 1H); ^{19}F NMR ($CDCl_3$) δ −73.4 (q, $^4J_{FF}$=10.1 Hz, 6F), −74.6 (q, $^4J_{FF}$=10.1 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ −23.5. Anal. calcd for $C_{32}H_{21}F_{12}O_3P$: C, 53.95; H, 2.97. Found: C, 54.04; H, 2.91.

4.1.3. (S_P^*,1S^*,2S^*)-1-(2-Hydroxy-1,2-diphenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (14-threo-A). To P–H (equatorial) phosphorane **10** (201 mg, 0.389 mmol) in THF (2 mL) was added *n*-BuLi (0.27 mL, 0.421 mol) at 0°C. To this solution was added *cis*-stilbene oxide (86.9 mg, 0.443 mmol) in THF (2 mL) and the resulting mixture was stirred at rt for 5 h. The solution was quenched with water, extracted with Et_2O and the combined organic solvents were washed with water and brine. This was followed by drying over anhydrous $MgSO_4$ and concentration in vacuo. Separation of the residue on TLC (hexane–Et_2O=9:1) followed by recrystallization (hexane–CH_2Cl_2) gave **14-threo-A** (72.1 mg, 26%). Mp 196–197°C (dec); ^{1}H NMR ($CDCl_3$) δ 8.03 (br s, 2H), 7.75–7.54 (m, 6H), 7.02–6.59 (m, 10H), 5.27 (dd, J=10.3 Hz, $^2J_{PH}$=8.3 Hz, 1H), 4.02 (dd, J=10.3 Hz, $^2J_{PH}$=17.1 Hz, 1H), 3.72 (s, 1H); ^{19}F NMR ($CDCl_3$) δ −73.7 (br s, 6F), −74.5 (br s, 6F); ^{31}P NMR ($CDCl_3$) δ −19.3. Anal. calcd for $C_{32}H_{21}F_{12}O_3P$: C, 53.95; H, 2.97. Found: C, 54.00; H, 2.88.

4.1.4. (S_P^*,1R^*)-1-(2-Oxo-1,2-diphenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (15-B). To benzylphosphorane **6** (1.00 g, 1.65 mmol) in THF (5 mL) was added *n*-BuLi (1.10 mL, 1.74 mol) at 0°C. After stirring at rt for 5 m, benzoyl chloride (0.200 mL, 1.72 mmol) was added and the resulting mixture was stirred overnight. The solution was quenched with water, extracted with Et_2O and the combined organic solvents were washed with water and brine. This was followed by drying over anhydrous $MgSO_4$ and concentration in vacuo. Separation of the residue on TLC (hexane–benzene=1:1) followed by recrystallization (hexane–CH_2Cl_2) gave **15-B** (958 mg, 82%). Mp 160–161°C; ^{1}H NMR ($CDCl_3$) δ 8.17–8.12 (m, 2H), 7.76–7.19 (m, 14H), 6.97–6.95 (m, 2H), 5.91 (d, $^2J_{PH}$=18.6 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −73.9 (q, $^4J_{FF}$=10.0 Hz, 6F), −74.4 (q, $^4J_{FF}$=10.0 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ −25.2. Anal. calcd for $C_{32}H_{19}F_{12}O_3P$: C, 54.10; H, 2.70. Found: C, 53.98; H, 2.49.

4.1.5. (S_P^*,1S^*)-1-(2-Oxo-1,2-diphenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (15-A). A mixture of phosphorane **15-B** (300 mg, 0.422 mmol) and DBU (0.13 mL, 0.85 mmol) in Et_2O (3 mL) was stirred at rt for 52 h. After removal of solvent, the residue was separated on TLC (hexane–benzene=1:1) followed by recrystallization (hexane–CH_2Cl_2) to give **15-A** (111 mg, 37%). Mp 189–190°C; ^{1}H NMR ($CDCl_3$) δ 7.70–7.12 (m, 18H), 5.91 (d, $^2J_{PH}$=26.9 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −73.5 (q, $^4J_{FF}$=9.8 Hz, 6F), −74.6 (q, $^4J_{FF}$=9.8 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ −24.3. Anal. calcd for $C_{32}H_{19}F_{12}O_3P$: C, 54.10; H, 2.70. Found: C, 54.08; H, 2.53.

4.1.6. (S_P^*,1R^*,2R^*)-1-(2-Hydroxy-1,2-diphenylethyl)-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1λ^5-benzoxaphosphole] (14-threo-B). A mixture of phosphorane

15-B (30 mg, 0.042 mmol) and $LiBH_4$ (3.0 mg, 0.138 mmol) in THF (3.5 mL) was stirred at rt for 20 h. The solution was quenched with water, extracted with Et_2O and the combined organic solvents were washed with water and brine. This was followed by drying over anhydrous $MgSO_4$ and concentration in vacuo. Separation of the residue on TLC (hexane–benzene=1:1) followed by recrystallization (hexane–CH_2Cl_2) gave **14-threo-B** (24.1 mg, 80%). Mp 165–165.5°C (dec); ^1H NMR ($CDCl_3$) δ 8.08 (br s, 2H), 7.68–6.93 (m, 16H), 5.29 (ddd, J=11.2, 4.9 Hz, $^2J_{PH}$=11.2 Hz, 1H), 4.33 (dd, J=11.2 Hz, $^2J_{PH}$=13.2 Hz, 1H), 1.82 (d, J=4.9 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −73.6 (q, $^4J_{FF}$=8.5 Hz, 6F), −74.2 (q, $^4J_{FF}$= 8.5 Hz, 6F); ^{31}P NMR ($CDCl_3$) δ −19.1. Anal. calcd for $C_{32}H_{21}F_{12}O_3P$: C, 53.95; H, 2.97. Found: C, 54.04; H, 2.91.

4.2. General procedure for the olefination reaction

To a mixture of **14** and an excess of *t*-BuOK (or *t*-BuONa) was added a specified solvent at −78°C. After stirring at a specified temperature, the solution was worked up and the residue was separated on TLC (hexane) to give the products.

4.3. Kinetic measurements of the olefin formation process

Phosphorane **14** (ca. 10 mg) and *t*-BuONa (2 equiv.) were placed in NMR tubes and flushed with N_2. To the tubes was added freshly distilled solvent (0.5–0.6 mL) at liquid N_2 temperature, and the tubes were then sealed under N_2 while contents were still frozen. The decomposition reactions were monitored by measuring ^{19}F NMR spectra in a variable temperature mode, and the specified temperatures were maintained throughout each set of measurements (error within ±1°C). The data were analyzed by assuming irreversible first-order kinetics using the equation $\ln(c_0/c) = kT$, in which c_0=concentration of reactant at t=0, c= concentration of reactant at arbitrary intervals.

4.4. Supplementary material

ORTEP drawing of **11-erythro-B** and crystallographic data on **11-erythro-B**, **14-erythro-B**, and **15-B**.

Acknowledgements

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