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Helical Triskelion Monophosphites as Ligands in Asymmetric Catalysis

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Abstract: Members of a new family of chiral triskelion P ligands, namely helical C_3-symmetric monophosphites $P(OR)_3$, have been prepared in two steps by monoacylation of (*R*)- or (*S*)-1,1′-binaphthyl-2,2′-diol (BINOL) or diphenol using a carboxylic acid chloride followed by PCl_3 phosphorylation. The most sterically hindered member of these monophosphites, derived from the compound accessible by monoacylation of BINOL using adamantane carboxylic acid chloride, has been characterized by X-ray crystallography and NMR spectroscopy as a single well-defined compound. It exists exclusively in the syn conformation, with a propeller-like (twisted) geometry resulting in helicity. Upon utilization of (*R*)- or (*S*)-BINOL in the two-step synthesis, the helicity proves to be *P* or *M*, respectively. When used as ligands in the Rh-catalyzed asymmetric hydrogenation of prochiral homoallylic alcohols, these bulky helical ligands lead to respectable enantioselectivities (79−98% ee). In contrast, the less sterically congested and more flexible BINOL-derived phenyl analogue exists in several conformeric forms, even in the crystal, and this leads to poor enantioselectivity in the model reactions (ee = 32%). For the purpose of structural comparison, the analogous monophosphites derived from diphenol were also prepared and characterized. These compounds, again in contrast to the BINOL-derived adamantyl derivatives, occur in several different conformeric states.

Introduction

The design of novel chiral ligands for application in asymmetric transition-metal-catalyzed reactions continues to be a field of intense interest.[1] The ligands reported to date are characterized by central, axial, or planar chirality or combinations thereof. Helical or screwlike ligands are sometimes viewed as a special chirality class,[2−5] but it should be noted that they can be assigned to either axial or planar chirality, the *P* and *M* designations then being replaced by *S* and *R*, respectively.[2] Irrespective of the nomenclature, screwlike ligand systems for use in transition-metal catalysis have been reported. For example, chiral 2,15-bis(diphenylphosphino)hexahelicene (PHelix) was prepared in the *P* and *M* helical forms, which were used as ligands in Rh-catalyzed olefin hydrogenation (up to 39% ee)[3a] and Pd-catalyzed kinetic resolution of chiral allylic acetates (98% ee at 40% conversion).[3b] Along a completely different line, special polypeptides derived from chiral phosphino amino acids were shown to adopt a helical secondary structure, and their use as bidentate ligands in Rh-catalyzed olefin hydrogenation resulted in moderate enantioselectivity (ee up to 37%).[4] The idea of helical polymers originating from achiral monomers harboring N or P ligands and their use in Pd-catalyzed asymmetric allylic substitution (ee up to 60%) constitutes a different concept.[5] Helical polymers with side chains bearing Ru complexes composed of centrally chiral amino alcohols, which have been used as catalysts in Noyori-type asymmetric ketone reduction (ee up to 36%), have also been devised.[6]

A different potential source of helicity is the use of appropriate chiral C_3-symmetric ligands.[7] This class of compounds can have very diverse structural features, and in fact they may or may not be helical. If they are characterized by screw- or twistlike geometries, they can be considered as helical. For

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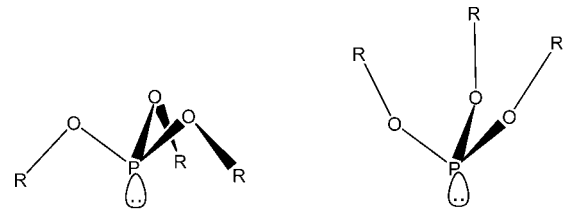
10.1021/ja809297a CCC: $40.75

example, Bolm and Sharpless[8] have reported the synthesis of a helical C_3-symmetric phospha[2.2.2]cyclophane, but rapid interconversion of the *P* and *M* enantiomeric forms due to the fluxional behavior prohibits their use in asymmetric transition-metal catalysis. This relates to the early work of Mislow[9] on propeller-like compounds such as bulky triarylmethanes, a research area which has been extended by other groups.[10] If fluxional compounds of this kind contain additional configurationally stable elements of central, axial, or planar chirality, any dynamic process that regards the sense of the helicity results in rapid diastereoisomerization. A number of chiral and possibly helical C_3-symmetric ligands harboring additional central or axial chirality have been described,[7,11] although in many cases the issue of diastereoisomerism was not addressed. Such ligands can be mono-, bi-, or tridentate. Some researchers have used the term *triskelion* to denote ligands, metal complexes, or receptors that possess threefold rotational symmetry; they may be chiral or achiral.[12] Double-helical D_3-symmetric triskelion metal complexes also deserve mention.[13] In a different approach to asymmetric catalysis, chiral Lewis acids with helical character have been described,[14] as in the case of a 1,1′-binaphthyl-2,2′-diol (BINOL)-derived boron compound.[14a]

Scheme 1. Two Conformeric Forms of Phosphites $P(OR)_3$



Here we focus on a special class of triskelion compounds, namely, configurationally stable helical C_3-symmetric monodentate phosphites $P(OR)_3$, as chiral ligands in transition-metal catalysis. Phosphites derived from centrally chiral alcohols ROH have been prepared and used as ligands previously,[1,15] but the possibility of diastereomeric forms due to potential helicity was not considered, probably because the researchers did not view the compounds as being so bulky that helical conformers might be locked in.[16] Before our approach to this problem is presented, it is important to point out that such compounds may exist in two basically different conformeric forms, which we denote as syn or anti according to Scheme 1. In the syn conformer, the first C atoms (C_α) in the R groups of $P(OR)_3$ are on the same side of the P atom as the phosphorus lone pair, while in the anti conformer, they reside on the opposite side.[17] Of course, within each series, as for example in the case of the syn compounds, a subset of further conformers is possible, depending upon the nature of the R groups.

In the absence of chirality in the R groups, these monophosphites can become chiral if they adopt a helical (twist) form, giving rise to *P* or *M* helicity, as illustrated in Scheme 2. However, unless such propeller-type compounds are locked in the *P* or *M* form in some way that makes enantiomerization no longer possible, they cannot be expected to be of any use as ligands in asymmetric transition-metal catalysis.

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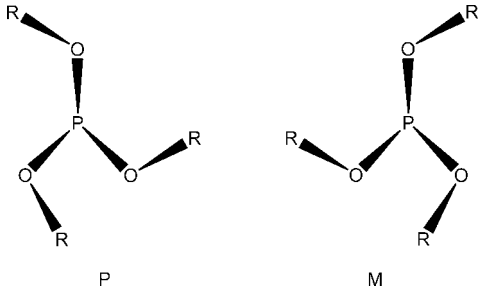
(15) For example, see: (a) Stolmàr, M.; Floriani, C.; Gervasio, G.; Viterbo, D. *J. Chem. Soc., Dalton Trans.* **1997**, 1119–1121.

(16) One of the simplest organic species characterized by helicity is the helical conformer of *n*-butane,[2b] but this is obviously a fluxional system.

(17) We define the C_α atom of the R moiety as the direction of R. It should be noted that in the case of bulky R groups, the rest of the group can be positioned either on the same side of the P atom as the lone pair or on the opposite side; this can lead to confusion. Moreover, conformers other than the all-syn or all-anti ones are in principle possible, although we have no direct evidence of their existence in the present systems.

Scheme 2. *P* and *M* Enantiomers of Triskelion Monophosphites $P(OR)_3$

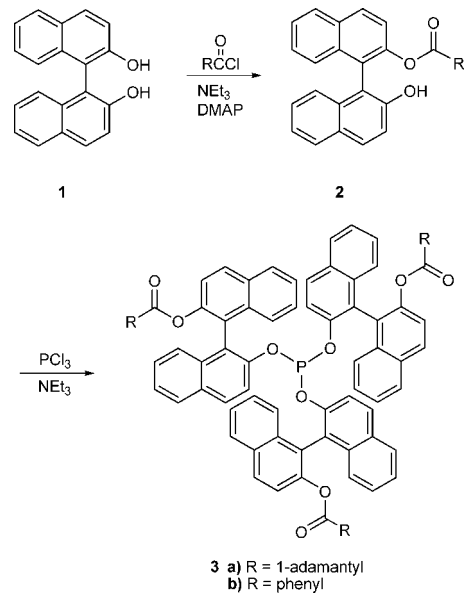


The challenge is to choose appropriate alkoxy groups in the monophosphites $P(OR)_3$ that are not only characterized by configurationally stable central, axial, or planar chirality but also able to lock in one of the diastereoisomeric helical conformers, *P* or *M*, thereby preventing the formation of an undesired mixture of rapidly interconverting diastereoisomers. Inspired by the work of Mislow,[9,10a] we have devised a simple approach for achieving this goal by designing and synthesizing appropriately bulky monophosphites $P(OR)_3$. We also show that such monodentate phosphites are respectable ligands in the Rh-catalyzed hydrogenation of prochiral homoallylic alcohols, which are considered to be a "difficult" class of olefins for such asymmetric transformations.[18] This extends the class of presently known chiral monodentate P ligands[1g,19,20] by a new family.

Results and Discussion

Synthesis and Characterization of the Ligands. We envisioned a straightforward two-step synthesis of chiral monophosphites **3** starting from commercially available (*R*)- or (*S*)-BINOL (**1**) (Scheme 3). BINOL in either enantiomeric form is currently one of the cheapest chiral auxiliaries, and it has been used in the synthesis of many other (nonhelical) monodentate P ligands, including monophosphites,[1g,19,20] and in a multitude of other applications.[21] Our approach was to incorporate the very bulky adamantyl group into ligand **3a**, hoping that this would induce helicity. Moreover, we conjectured that the three alkoxy residues at phosphorus would be "locked" into a screwlike orientation, so only one helical diastereoisomeric conformer, either the *P* or the *M* form, would result. Consideration of simple molecular models of **3a** suggested that this may be the case. MM calculations were performed, but these were not conclusive. It was even more difficult to predict the preferred geometry of the less sterically demanding phenyl analogue **3b** because of its greater flexibility. Compound **3b** was nevertheless included in this study for the purpose of comparison.

Scheme 3. Synthesis of Chiral Triskelion Phosphites



The syntheses of **3a** and **3b,** in either the *S*,*S*,*S* or the enantiomeric *R*,*R*,*R* forms (with respect to BINOL), proved to be trivial, all steps proceeding with essentially quantitative conversion (>95% yields). The NMR spectra of the enantiomeric ligand (*R*,*R*,*R*)-**3a** were identical to those of (*S*,*S*,*S*)-**3a**. In order to address the question of conformeric states, we first studied the ^{1}H, ^{13}C, and ^{31}P NMR spectra of (*S*,*S*,*S*)-**3a** at various temperatures between 23 and −78 °C. In all cases, just one set of signals was observed (except for a trace of an unidentified impurity), consistent with the presence of a single species. It needs to be pointed out that a single set of NMR signals would also be observed if two or more species were in sufficiently rapid exchange with each other. In that case, the chemical shifts would be weighted averages of the contributing species. However, it is reasonable to expect that unless the barrier to exchange is very low, the onset of broadening would be observed at low temperature for signals where the exchanging nucleii have widely differing chemical shifts. Close inspection of the spectra of **3a** revealed no such preferential broadening of any signals at any temperature studied and that the relative heights and widths of all of the signals remained nearly the same. No indication of dynamic behavior involving two or more species was thus observed. This strongly suggests the occurrence of a single conformer. It was, however, not possible to conclude whether the syn or the anti conformer was adopted or to say anything about the potential helicity. We therefore turned to X-ray crystallography.

Ligands **3a** and **3b** can easily be crystallized, but in the case of **3b**, the presence of dichloromethane was necessary to obtain satisfactory crystals. The crystal structure determination of (*S*,*S*,*S*)-**3a** shows that it does in fact adopt a helical triskelion structure in the syn conformation (Figure 1). Inspection of the van der Waals structure indicates that there is little room for conformational change, so the molecule appears to be locked into one conformation. It should be noted that the P−O bond is not the only rotatable single bond and therefore potential chiral element in the backbone chain; the others are O1−C2, C1−C11, C12−O2, O2−C21, and C21−C22. Of these, the chirality of

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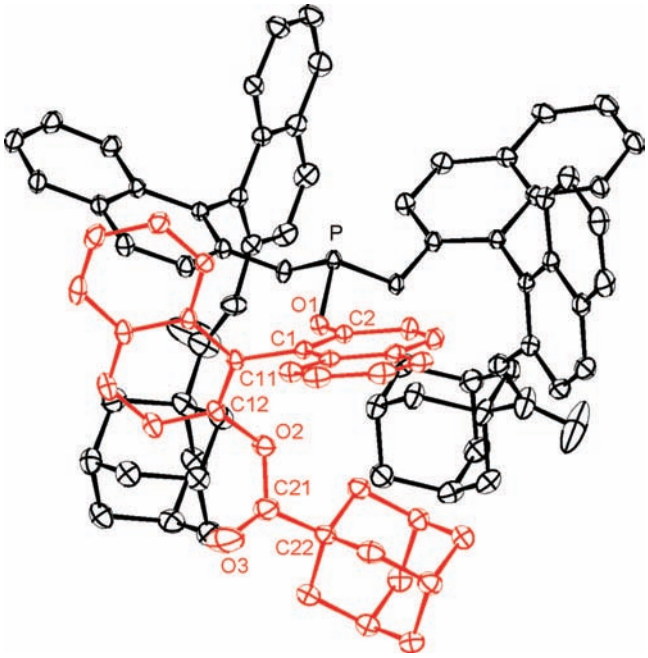

Figure 1. Crystal structure of *syn*-(*S*,*S*,*S*)-**3a** having *M* helicity (an exact threefold axis of symmetry passes through the phosphorus atom and its lone pair). Selected torsion angles along the backbone (deg): (phosphorus lone pair)−P−O1−C2, −38.9(2); P−O1−C2−C1, 126.4(2); O1−C2−C1−C11, 2.57(2); C2−C1−C11−C12, 68.0(2); C1−C11−C12−O2, −7.2(2); C11−C12−O2−C21, −133.7(3); C12−O2−C21−C22, −174.8(3).

C1−C11 is fixed by the handedness of the binaphthyl employed, and the others are induced by the bulky binaphthyl and adamantyl moieties and the close proximity of the other chains. Since this conformeric form appears to be relatively rigid, we can use the (phosphorus lone pair)−P−O−C dihedral angle to designate the diastereoisomer. Accordingly, the (lone pair)−P−O−C torsion angle is −38.9(2)° (− synclinal). Taking the lone pair on phosphorus as the reference according to Prelog,[22] we assign the helicity of (*S*,*S*,*S*)-**3a** as *M*.

In order to illuminate the unique structural features of (*S*,*S*,*S*)-**3a** more extensively, a space-filling representation was generated (Figure 2). The top view clearly reveals the helical triskelion nature of the ligand, while the bottom view shows that the three bulky adamantyl groups are closely packed, an effect that helps to lock the compound into a screwlike conformation. It is worth noting here that the distance between the centroids of the adamantyl groups [6.37(1) Å] is comparable to the shortest distance between adamantane molecules in the solid form of the parent compound [6.48(1) Å].[23]

In further characterization, the circular dichroism (CD) spectra of (*R*,*R*,*R*)- and (*S*,*S*,*S*)-**3a** were measured in CH_2Cl_2 (Figure 3). In order to establish whether the induced chirality brought about by the helical geometry has an effect on the circular dichroism, the CD spectrum of the (*S*)-configurated BINOL-derived isopropylphosphite **4** was likewise recorded for the purpose of comparison (Figure 4). Compounds (*R*,*R*,*R*)-**3a** and (*S*,*S*,*S*)-**3a** display a broad absorption centered at 290 nm, which is absent in the simple ligand **4**. Although these data do not allow a distinction between the syn and anti conformers, they do show that an additional element of chirality has been introduced into compound **3a**, in agreement with the propeller-like triskelion structure derived from the X-ray data.

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We then turned to the characterization of the less sterically encumbered ligand **3b**. Whereas the crystal structure of the adamantyl analogue (*S*,*S*,*S*)-**3a** shows the presence of just one species, the crystal of the phenyl derivative (*S*,*S*,*S*)-**3b** contains two crystallographically independent, almost identical phosphite moieties, each exhibiting a threefold axis of symmetry and having disordered PO_3 units (see the Supporting Information); these are shown in red and black in Figure 5. The two independent moieties differ only slightly in their conformations (the root-mean-square difference in the torsion angles along the backbone is 17°), despite their different crystal environments. The disorder of the PO_3 units indicates that for each of the two independent moieties, there are two conformers of *syn*-(*S*,*S*,*S*)-**3b** in the crystal that are present in approximately the same amounts. Interestingly, for one of these conformers, the (phosphorus lone pair)−P1A−O1A−C torsion angle is 44.2(3)° (+ synclinal), indicating *P* helicity, whereas in the case of the other conformer, the (phosphorus lone pair)−P1B−O1B−C torsion angle is −48.4(3)° (− synclinal), indicating *M* helicity. In contrast to the adamantane analogue, the ligands in **3b**, which contain the smaller phenyl group, can apparently flip from one side of the phosphorus lone pair to the other; the stereochemical integrity of the binaphthyl group is, of course, maintained. These results show that the presence of the bulky adamantyl group in **3a** is crucial for locking the molecule into one helical form.

In order to understand more fully the influence of the chirality of the binaphthyl group on the nature of the conformers of **3a**, we prepared the analogous chiral but racemic phosphite **7** derived from diphenol (**5**) (Scheme 4). It is well-known that compounds of the type **5** or monophosphites derived therefrom are axially chiral but not configurationally stable because of rapid rotation about the central C−C bond connecting the two phenyl groups (tropos compounds).[1g,24] Such rapid interconversion can also be expected to occur in the phosphite **7**, which in addition is also less sterically shielded than the binaphthyl-derived analogue **3a**.

Compound **7** crystallized, but the crystals were consistently of poor quality. Therefore, we prepared its oxide **8** (Scheme 4), which crystallized well with dichloromethane solute in the crystal. The results of the crystal structure analysis are shown in Figure 6 (the dichloromethane solute has been omitted for clarity). The compound crystallizes as a racemate, with both enantiomers in the unit cell. This is consistent with the expected ready interconversion between the two enantiomers, even though the R group is the bulky 1-adamantyl residue. These observations support our previous expectation regarding the relative bulkiness of **3a** versus **7**. It is worth noting that the torsion angles along the three crystallographically independent backbones in **8** are very similar (root-mean-square deviation: 6.7°) and that they are also very similar to those in **3a** (root-mean-square

(24) For examples of ligands composed of fluxional (tropos) diphenol-derived entities and configurationally stable axially chiral moieties,[1g] see: (a) Reetz, M. T.; Neugebauer, T. *Angew. Chem.* **1999**, *111*, 134−137; Reetz, M. T.; Neugebauer, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 179−181. (b) Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem.* **1999**, *111*, 517−519; Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 495−497. (c) Pàmies, O.; Net, G.; Ruiz, A.; Claver, C. *Tetrahedron: Asymmetry* **1999**, *10*, 2007–2014. (d) Bolm, C.; Beckmann, O. *Chirality* **2000**, *12*, 523–525. (e) Alexakis, A.; Rosset, S.; Allamand, J.; March, S.; Guillen, F.; Benhaim, C. *Synlett* **2001**, 1375–1379. (f) Zalubovskis, R.; Bouet, A.; Fjellander, E.; Constant, S.; Linder, D.; Fischer, A.; Lacour, J.; Privalov, T.; Moberg, C. *J. Am. Chem. Soc.* **2008**, *130*, 1845–1855. (g) Becker, J. J.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 9478–9479.

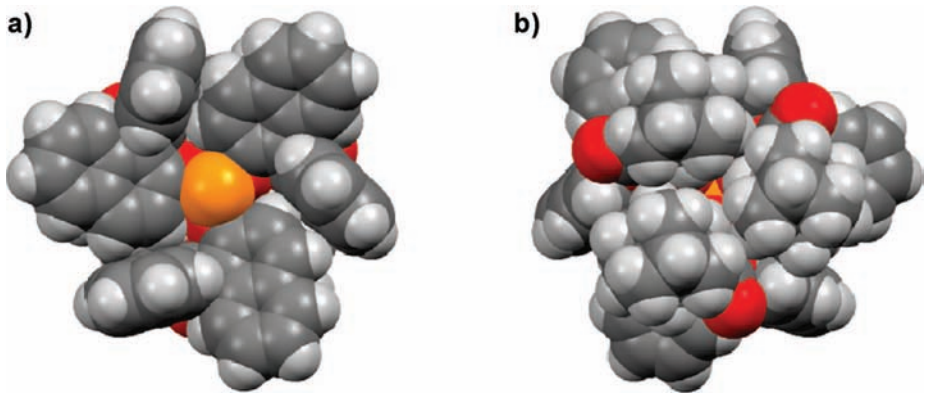


Figure 2. Space-filling views of the crystal structure of (*S*,*S*,*S*)-**3a** along the exact threefold axis of symmetry of the molecule from (a) above and (b) below. Color code: P (orange); O (red); C (gray); H (white).

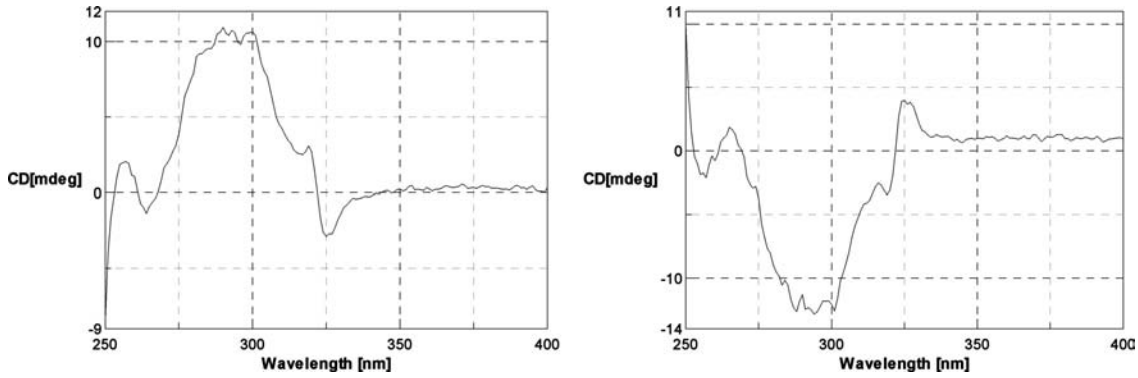


Figure 3. CD spectra of (*R*,*R*,*R*)-**3a** and (*S*,*S*,*S*)-**3a**.

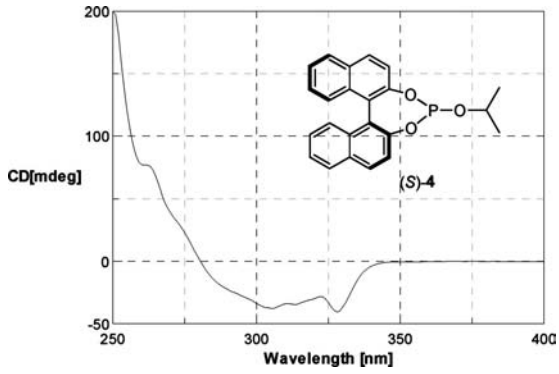


Figure 4. CD spectrum of (*S*)-**4**

deviation: 18°), indicating that the observed geometry is a preferred conformation.

Characterization of Rh Complexes. The unambiguous characterization of the Rh complexes of the ligands, even of **3a**, proved to be difficult, especially since crystals suitable for X-ray structural analyses could not be obtained. In contrast to conventional BINOL-derived monophosphites or monophosphoramidites, (L), which are known to react with $Rh(COD)_2BF_4$ to afford metal complexes bearing two such ligands, $Rh(L)_2(COD)BF_4$,[1g,19,20] models suggested that the use of the very bulky monophosphite **3a** allows only one ligand to be coordinated to rhodium as a result of steric factors, as in the case of certain other sterically encumbered monodentate P ligands.[20,25] Indeed, upon reaction of either 1 or 2 equiv of (*R*,*R*,*R*)-**3a** with $Rh(COD)_2OTf$, a single species was found that could be assigned to Rh((*R*,*R*,*R*)-**3a**)(COD)OTf. The evidence was derived from the integrals of the ^1H, ^{13}C, and ^{31}P NMR spectra and from the MALDI mass spectrum (parent peak at 1583).

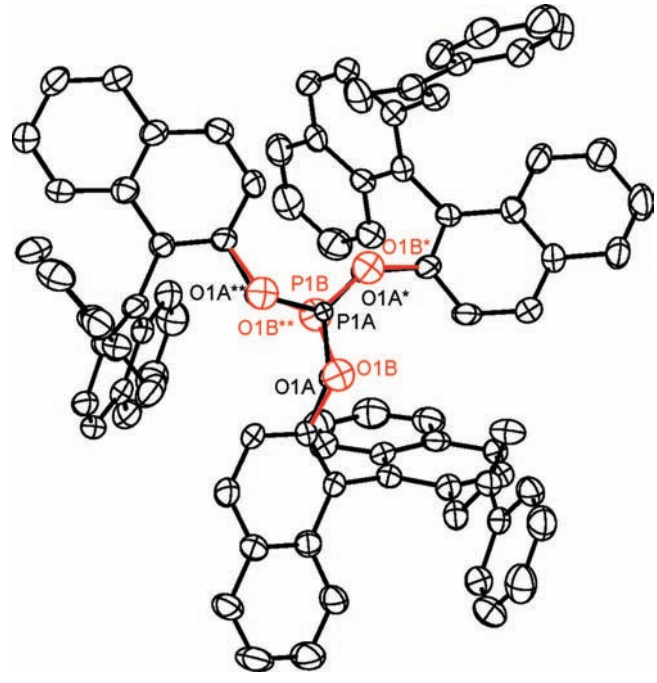
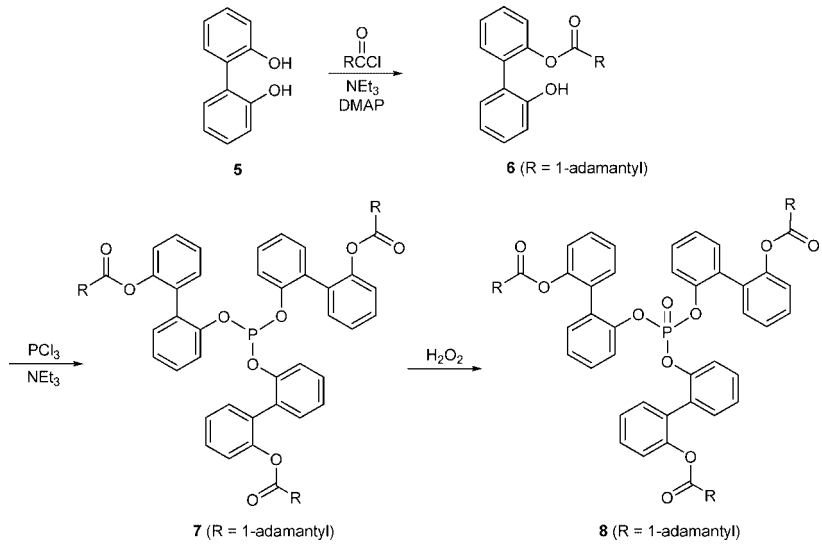


Figure 5. Crystal structure of (*S*,*S*,*S*)-**3b**, showing one of the two almost identical, crystallographically independent molecules in the unit cell (an exact threefold axis of symmetry passes through the phosphorus atoms P1A and P1B). The PO_3 unit is disordered over two positions with half-occupancy (red and black), showing the presence of two different conformers. Hydrogen atoms and solute dichloromethane have been removed for clarity.

Scheme 4. Synthesis of the Diphenol-Derived Phosphite **7** and Its Oxide **8**

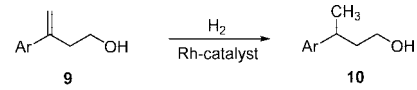


The NMR spectra show the presence of one major species in addition to a minor component. Unfortunately, it was not possible to make any unambiguous assignments of the details of the structure.

We speculated that the carbonyl function of **3a** might also coordinate to Rh and therefore recorded the IR spectra of the ligand (*R*,*R*,*R*)-**3a** and the corresponding Rh complex. No significant shift in the carbonyl stretch frequency (1720 cm^{-1}) was observed, suggesting that intramolecular coordination of the carbonyl function with Rh does not occur.

Use of Helical Triskelion Phosphites as Ligands in Asymmetric Hydrogenation. We examined the use of the helical phosphites **3a** and **3b** as ligands in the Rh-catalyzed asymmetric hydrogenation of homoallylic alcohols **9** to form alcohols **10** (Scheme 5). Very few cases of successful asymmetric hydrogenation of compounds of this type are known: the reported

Scheme 5. Asymmetric Rh-Catalyzed Hydrogenation of Homoallylic Alcohols **9** (Rh salt/**3a**/**9** = 1:2:50; 1.3 bar H_2; 24 h)



9 **10**

a) Ar = C_6H_5
b) Ar = 2-MeC_4H_4
c) Ar = 3-MeC_6H_4
d) Ar = 4-MeC_4H_4
e) Ar = 4-$MeOC_6H_4$
f) Ar = 4-*n*-BuC_6H_4
g) Ar = 4-*i*-PrC_6H_4
h) Ar = 4-*t*-BuC_6H_4
i) Ar = 4-FC_6H_4
j) Ar = 4-ClC_6H_4
k) Ar = 3,4-$Me_2C_6H_3$
l) Ar = 3,4-$MeO_2C_6H_3$
m) Ar = 3,5-$Me_2C_6H_3$
n) Ar = 2-naphthyl

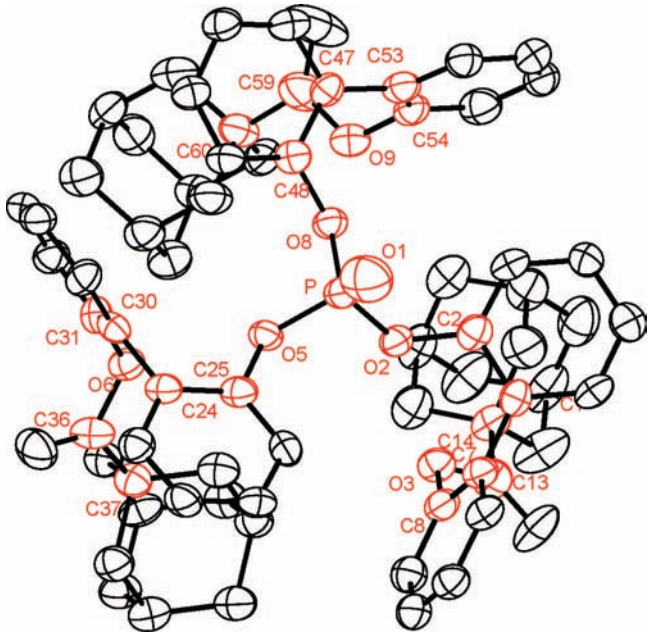


Figure 6. Crystal structure of oxide **8**/tris(dichloromethane) solute, with its almost exact threefold axis of symmetry despite its asymmetric crystal environment (the phosphite backbones are shown in red; the root-mean-square deviation of the torsion angles along the backbones is 6.7°).

examples involve homogeraniol (92% ee)[18a] and more highly substituted substrates (0−85% ee)[18b] with Ru−BINAP complexes as chiral catalysts at a H_2 pressure of 100 bar.

Table 1 shows that good to excellent enantioselectivities of 79−98% ee were obtained when the bulky ligand **3a** was used. Although it was not rigorously proven, the hydroxy function of substrates **9** may coordinate to the metal. Evidence comes from the result of the hydrogenation of 2-phenylbutene lacking a hydroxyl function, in which case essentially no enantioselectivity was observed (ee ≈ 3%). In contrast to the respectable performance of ligand **3a** in the hydrogenation of olefins **9**, the use of the phenyl derivative **3b** led to poor enantioselectivity (entry 2, Table 1). This may be due to the difference in steric bulk of the two monophosphite ligands and/or diastereoisomerization of the phenyl derivative **3b**, leading to the presence of the two different helicities. We did not screen the whole collection of commercially available chiral bidentate ligands,

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Table 1. Asymmetric Rh-Catalyzed Hydrogenation of Olefins **9** Using Helical Monophosphites **3a** and **3b** as Ligands (Rh salt/**3a**/**9** = 1:2:50; 1.3 bar H_2; 24 h)[a]

entry	ligand	Rh salt	substrate	solvent	temp (°C)	ee (%)[b]
1	**3a**	$Rh(COD)_2OTf$	**9a**	toluene	23	88
2	**3b**	$Rh(NBD)BF_4$	**9a**	CH_2Cl_2	23	32
3	**3a**	$Rh(COD)_2OTf$	**9b**	toluene	23	79
4	**3a**	$Rh(COD)_2OTf$	**9c**	toluene	23	94
5	**3a**	$Rh(COD)_2OTf$	**9d**	toluene	23	94
6	**3a**	$Rh(COD)_2OTf$	**9e**	toluene	23	94
7	**3a**	$Rh(COD)_2OTf$	**9f**	CH_2Cl_2	23	97
8	**3a**	$Rh(COD)_2OTf$	**9g**	toluene	40	92
9	**3a**	$Rh(COD)_2OTf$	**9h**	toluene	40	96
10	**3a**	$Rh(COD)_2OTf$	**9i**	CH_2Cl_2	23	87
11	**3a**	$Rh(COD)_2OTf$	**9j**	CH_2Cl_2	23	94
12	**3a**	$Rh(COD)_2OTf$	**9k**	toluene	40	92
13	**3a**	$Rh(COD)_2OTf$	**9l**	toluene	40	96
14	**3a**	$Rh(COD)_2OTf$	**9m**	toluene	23	98
15	**3a**	$Rh(COD)_2OTf$	**9n**	toluene	40	96

[a] The use of (*R*)-BINOL in the synthesis of ligands **3a** and **3b** led to (*R*)-configurated products **10** when these ligands were used in the Rh-catalyzed hydrogenation of olefins **9**. Abbreviations: COD, 1,5-cyclooctadiene; NBD, norbornadiene; OTf, triflate. [b] Conversion was ≥99% in all cases.

but when BINAP was used as the ligand in the Rh-catalyzed hydrogenation of olefin **9a**, an ee value of only 6% was obtained.

Conclusions

We have designed, prepared, and characterized by NMR spectroscopy, CD, and X-ray crystallography the first configurationally stable helical monophosphite **3a** having a triskelion structure in which the sense of helicity does not interconvert by the rapid equilibration $P \rightleftarrows M$. The screwlike compound is derived from axially chiral (*R*)- or (*S*)-BINOL and sterically encumbered adamantane carboxylic acid. Significantly, the ligand exists solely as the syn conformer and in the *P* or *M* helical form, depending upon the absolute configuration of the BINOL used in the synthesis. Thus, (*R*,*R*,*R*)-**3a** exists solely in the *P* helical form, whereas (*S*,*S*,*S*)-**3a** has *M* helicity. In the case of the likewise BINOL-derived but less sterically demanding phenyl derivative (*S*,*S*,*S*)-**3b**, X-ray crystallographic analysis showed the occurrence of two distinctly different diastereoisomeric syn conformers with *P* and *M* helicities, respectively, in the unit cell. This indicates that the substituents of phosphite **3b** can rotate freely.

The helical C_3-symmetric ligands **3a** and **3b** coordinate to Rh in a 1:1 manner as shown by NMR spectroscopy, as is the case with other highly sterically encumbered P ligands,[20,25] but so far we have not been able to obtain crystals of the Rh complex that are suitable for unambiguous X-ray structural analysis. The efficiency of the two structurally related ligands in the Rh-catalyzed asymmetric hydrogenation of homoallylic alcohols **9** differs dramatically: whereas the adamantyl derivative **3a** results in respectable enantioselectivities (79−98% ee), compound **3b** is a poor ligand for these "difficult" transformations (32% ee). This may be due to the ability of the ligand **3b** to diastereoisomerize rapidly, leading to the presence of the *P* and *M* conformers and thereby imparting very different steric environments at the transition metal (Rh) in the respective transition states of hydrogenation. Since the two-step synthesis of phosphites of the type **3** is straightforward, it should be easy to extend the series to include other bulky chiral alcohols as building blocks. Such helical P ligands may prove to be interesting candidates for various types of transition-metal-catalyzed transformations.

Acknowledgment. We thank the Fonds der Chemischen Industrie for generous support. Helpful discussions with Günter Helmchen regarding the assignment of *P* and *M* helicity in the present system are gratefully acknowledged.

Supporting Information Available: X-ray data and experimental protocols for the synthesis of ligands **3a**, **3b**, **7**, and **8**, homoallylic alcohols **9**, and the hydrogenation products **10**; NMR and MS characterization data for these compounds; and crystallographic data (excluding structure factors) for the structures (*S*,*S*,*S*)-**3a**, (*S*,*S*,*S*)-**3b**, (*R*,*R*,*R*)-**3a**, and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data has also been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication nos. CCDC 673480−673483. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44 1223/336−033; e-mail: deposit@ccdc.cam.ac.uk) or via http://www.ccdc.cam.ac.uk/data_request/cif.

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