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Coordination Chemistry Reviews
178–180 (1998) 755–770

COORDINATION CHEMISTRY REVIEWS

Synthetic approaches to chiral phosphetanes

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Received 30 October 1997; accepted 5 May 1998

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Abstract

Studies concerning the design of chiral ligands based on the phosphetane structural motif are presented. Homochiral phosphetanes are easily accessible from the reactions of suitable olefins with chiral dichlorophosphines, which are readily prepared from chiral pool precursors such as menthol and pinene. Alternatively, C-chiral phosphetanes can be obtained from primary phosphines and derivatives of optically pure 1,3-diols.

The chemistry of 1-menthyl-2,2,3,3-tetramethyl-substituted phosphetane derivatives has been studied in some detail. The parent phosphetane oxide undergoes highly selective transformations which afford diastereomerically pure α-substituted phosphetanes. This flexible methodology allows significant modification of the phosphorus environment, the introduction of selected functional groups or additional chiral centers, and the formation of symmetrical and nonsymmetrical bidentate phosphines. Preliminary investigations of phosphetanes as ligands in enantioselective organometallic catalysis have been performed with P-chiral monodentate derivatives in various palladium-catalyzed reactions.

Keywords: Asymmetric catalysis; Phosphetanes; Transition metals

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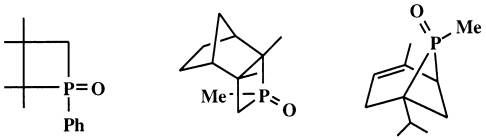
0010-8545/98/$ – see front matter
PII S0010-8545(98)00149-0

1. Introduction

Cyclic chiral phosphines should have useful properties as ligands in transition-metal assisted asymmetric catalysis because their restricted conformational flexibility should enhance the efficiency of the chiral transfer during the catalytic process. The most impressive demonstration of this effect can be seen in the work of Burk and coworkers, who have developed processes employing phospholane-based chiral ligands [1–10].

Apart from this noteworthy exception, chiral phosphines having a phosphorus atom incorporated into a monocyclic structure have not attracted particular attention. Six-membered and larger rings have been considered periodically [11–14], but no systematic studies of their synthesis and properties have been reported. Recently, chiral phosphiranes have also been prepared [15,16], but their applications in organometallic catalysis are likely to be restricted by the low stability associated with their highly strained three-membered rings. In the field of chiral phosphetanes, only the optically active phosphetane oxides **1**–**3** have been mentioned briefly [17–19].



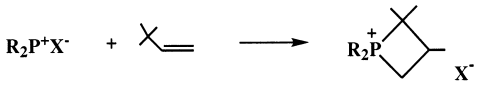
1 **2** **3**

This account summarizes our efforts to develop phosphetane chemistry into a useful foundation for chiral ligand design.

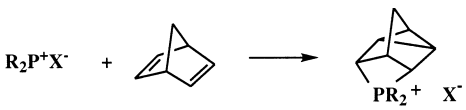
2. Synthetic routes to the phosphetane ring

The principal syntheses of phosphetane rings involve the addition of phosphenium ions to suitable unsaturated substrates (Eqs. (1) and (2)) [20–23], heteroatom exchange reactions using titanacyclobutanes (Eq. (3)) [24,25] and the direct cyclisation of 1,3-dihalides with suitable phosphorus containing derivatives (Eqs. (4) and (5)) [26–28].

The oldest method, which employs the reaction of phosphorus chlorides with highly



(1)



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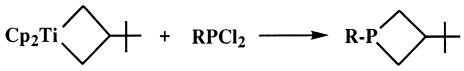

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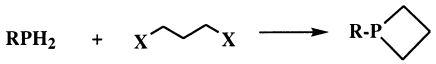

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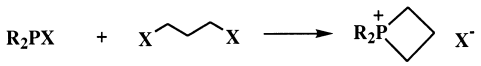
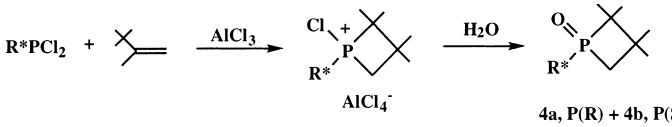


(5)

substituted olefins in the presence of aluminum trichloride (Eq. (1)), was introduced by McBride et al. [20]. Subsequently, it has found extensive use as the source of starting materials for systematic studies of the structural, NMR and chemical properties of trivalent phosphetanes, their oxides and phosphonium salts [29].

The same approach can be adapted to provide a convenient synthesis of chiral phosphetane oxides from optically pure dichlorophosphines (Eq. (6) [30,31].



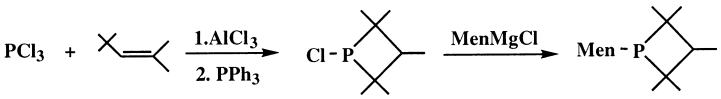
(6)

R*P =	*l*-Menthyl (Men)	(1S)-Myrtanyl	(1R)-Isopinocampheyl	(1S)-Bornyl	(1R)-Fenchyl
yield	65 %	60 %	40%	50 %	30 %
isomer ratios	1 : 1	1 : 1	8 : 2	6 : 4	9 : 1

"Chiral pool" substrates, such as menthol, pinene and their derivatives are readily accessible starting materials for the preparation of the necessary dichlorophosphines. A subsequent reaction of these dichlorophosphines with 2,3,3-trimethyl-1-butene in the presence of aluminum trichloride affords the corresponding phosphetane oxides **4**, as mixtures of two epimers having opposite configurations at phosphorus. Yields and isomer ratios are highly dependent upon the nature of the chiral auxiliary. Significant diastereoselectivities and moderate yields are obtained from isopinocampheyl and fenchyldichlorophosphine. Conversely, P-menthylphosphetane oxide is obtained in good yield as a 1:1 mixture of the two isomers. Despite the lack of diastereoselectivity during the formation of the four-membered ring, the two epimers of the P-menthylphosphetane oxide are easily separated and can be obtained in pure form by fractional crystallization. Because of the large scale availability of menthyl-

dichlorophosphine [32] and the straightforward separation of the two isomers of the product, the synthesis of **4a**,**b**, with R* = *l*-menthyl, is the most practical approach to chiral phosphetane oxides via McBride's method.

Alternatively, P-menthyl substituted phosphetanes can be obtained by chlorine displacement from a preformed P-chlorophosphetane, as shown in Eq. (7) [30].

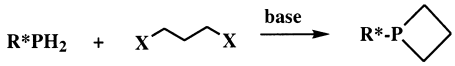


cis isomer, 32% yield (7)

Thus, McBride's method provides a very efficient synthesis of chiral phosphetanes. However, the choice of substituents at carbon in the four-membered ring is restricted because the presence of at least three methyl groups is almost imposed by the reaction mechanism.

Greater flexibility during the building of chiral phosphetanes can be achieved by the reaction of primary phosphines with 1,3-difunctional electrophiles (Eq. (4)) [26,27].

This strategy allows access to two different classes of chiral phosphetanes (Eqs. (8) and (9)). In the first (Eq. (8)), a chiral auxiliary is attached to the phosphorus atom of a primary phosphine which reacts with an achiral electrophile. In the second (Eq. (9)), an optically pure difunctional electrophile reacts with an achiral phosphine to afford a C-chiral phosphetane.



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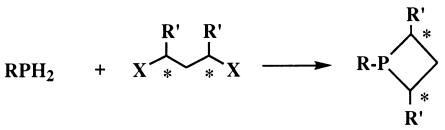
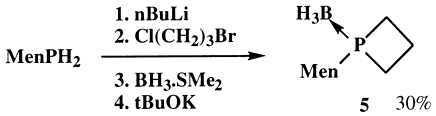


(9)

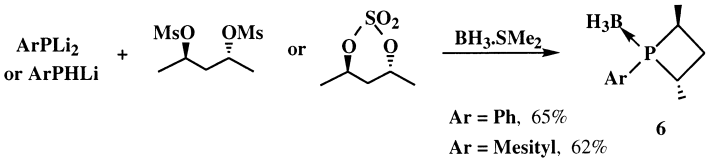
The first approach is illustrated in Eq. (10): reaction of *l*-menthylphosphine with 1-bromo-3-chloropropane gives a C-unsubstituted phosphetane (as its borane complex **5**) in moderate yield [33].



5 30% (10)

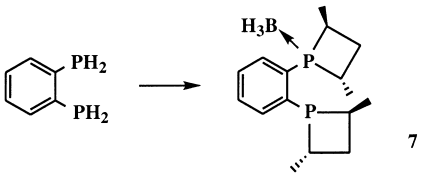
The second approach is typified by Eq. (9), which is simply an extension of the well-known synthesis of chiral phospholanes from 1,4-diol derivatives [2,3]. Here, the reaction of (R,R)-2,4-pentanediol dimesylate or cyclic sulfate with lithiated

phosphines affords a stereospecific route to (S,S)-2,4-dimethylphosphetanes **6** (Eq. (11)) [34,35].



(11)

Complexation to borane increases the stability of the phosphetane moiety and eliminates the possibility of aerial oxidation during the purification steps. The same strategy has been applied to the synthesis of **7**. This compound is the four-membered analogue of Me-DuPHOS, prepared by Burk and coworkers [3].

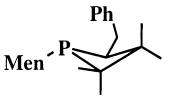


(12)

Under optimized conditions, **7** can be recovered in 45% yield. Other chiral diols can also be used as starting materials.

The synthetic approaches to chiral phosphetane moieties described above produce either phosphetane oxides or borane complexes. In both cases, the corresponding trivalent phosphetanes can be easily recovered. Respectively, reduction of the oxides by $HSiCl_3$–Et_3N and deboration by phosphine–amine exchange reactions with dabco produce the desired phosphetanes under mild conditions, with total retention of stereochemistry at phosphorus [30,34].

Concerning P-chiral trivalent phosphetanes, it can be emphasized that the activation energy for racemisation at phosphorus is supposed to be significantly increased by its inclusion into the strained four-membered ring [36]. Acyclic phosphines have half-lives of about 3–4 h at 135 °C, but the α-benzyl-substituted phosphetane **8**



8

remains unchanged after heating for 48 h at 135 °C in a sealed NMR tube.This will probably be a key feature in the use of P-chiral phosphetanes as chiral ligands for organometallic catalysis.

3. Elaboration of the phosphetane scaffold

Eqs. (6), (8) and (9) provide the basis for building the four-membered ring of chiral phosphetanes. The last method affords phosphetanes **6** and **7**, whose properties in enantioselective catalysis should be easily predicted because of their similarity to well-known chiral phospholanes. Optimization of chiral induction from these phosphetanes should be possible through structural modifications: these may be incorporated by variation of the chiral diols used as starting materials.

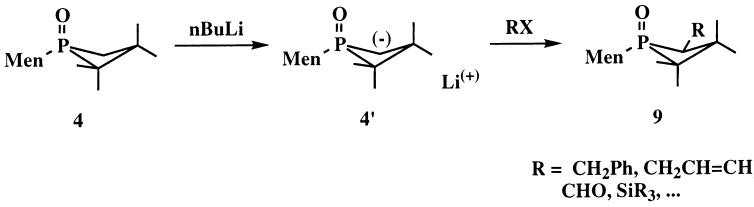
The P-chiral phosphetanes **4′** have a more unusual structure, so the prediction of their uses and the precise factors which influence their ability to induce enantioselectivity is more difficult. In this context, it is desirable to develop a simple and flexible method which allows structural elaboration of the phosphetane moiety, thus permitting the structural features of the ligand to be matched to the specific requirements of any given catalytic reaction. This has been achieved by metalation–substitution reactions at the α-CH_2 group of phosphetane oxide **4** (R* = Men) and subsequent transformations.

The phosphorus-stabilized carbanion **4′** reacts stereospecifically with activated alkyl halides [30], chlorosilanes [37], dimethylformamide [38] and other electrophiles to afford the α-substituted phosphetane oxides **9** in an optically pure form (Eq. (13)).

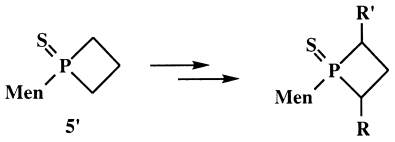
Functionalization at the ring carbon has been performed separately on both epimers of the menthylphosphetane oxides **4a** and **4b** (R* = *l*-menthyl). Invariably, the incoming R substituent takes up an equatorial position, *trans* to the menthyl group. This is probably because of sterical constraints in the hindered four-membered ring.

The high selectivity of the reactions outlined in Eq. (13) offers a straightforward access to families of structurally related phosphetanes. This allows their properties as ligands to be examined as a function of steric and electronic changes in the environment about phosphorus. Furthermore, the C-unsubstituted phosphetane **5**, which has two α-CH_2 groups, should permit more sophisticated functionalization. The stereochemistry of the metalation–substitution reactions of both intracyclic α-carbon atoms in the corresponding sulfide **5′** has been examined (Eq. (14)) [33]. The diastereoselectivity is sufficiently high to allow a useful preparation of α,α′-disubstituted chiral phosphetane sulfides.

These α-substitution reactions provide the means to vary the steric environment



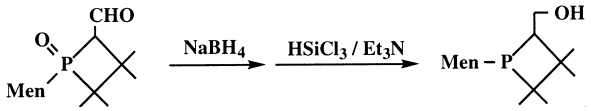
(13)



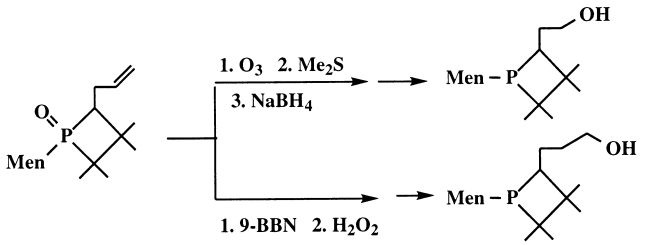
(14)

about phosphorus and to introduce additional functional groups, chiral centers or coordination sites, either directly or via successive transformations. A number of modified phosphetanes are discussed below.

One class, phosphetanes bearing an hydroxyl group at a three, four or five-bond distance from phosphorus, have been prepared as shown in Eqs. (15) and (16) [39].



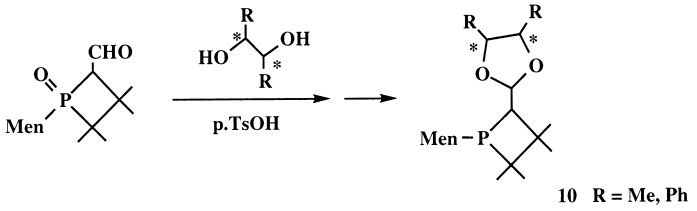
(15)



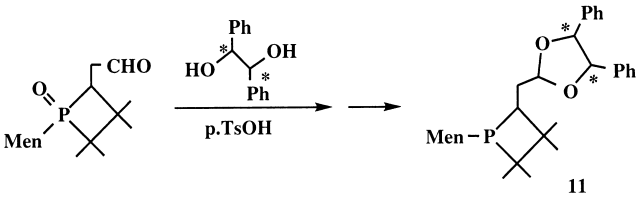
(16)

The interest in hydroxyl-substituted phosphetanes reflects the recent trend in ligand design towards functionalized phosphines which are capable of establishing secondary interactions between the functional group and the reacting substrates. These interactions reduce the degree of configurational freedom in the complexes and facilitate the stereochemical control of various catalytic reactions [40]. Notably, the hydroxyl group has been targeted because of its ability to form hydrogen bonds to nucleophilic reagents in palladium-catalysed allylic alkylations [41,42].

Supplementary chiral centers can be added to the phosphetane skeleton by the incorporation of chiral dioxolane units, as shown in Eqs. (17) and (18) [37,43].



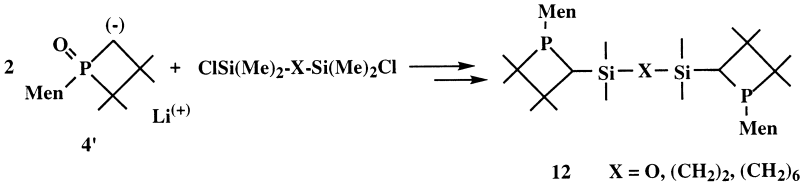
(17)



(18)

Four epimers of phosphetanes **10** and **11** are obtained separately by reacting the optically pure diols with the two discrete epimers of the formylphosphetane starting materials. Compounds **10** and **11** have multiple chirality: in addition to the menthyl group, chiral centres of known absolute configuration are present at the phosphorus atom, the intracyclic α-carbon and the two dioxolane carbons. An appropriate selection of relative configuration at the various chiral centers allows an optimization of chiral induction from these phosphetane ligands (see Section 5).

Various chelating bidentate ligands are also accessible from **4**, either by connecting two phosphetane units or by combining phosphetane and PPh_2 functionalities. Bridged diphosphetanes have been prepared by reacting the anionic species **4′** with bifunctional chlorosilanes, e.g. 1,3-dichloro-tetramethyldisiloxane, 1,2-bis(chlorodimethylsilyl)ethane or 1,6-bis(chlorodimethylsilyl)hexane (Eq. (19)) [37].

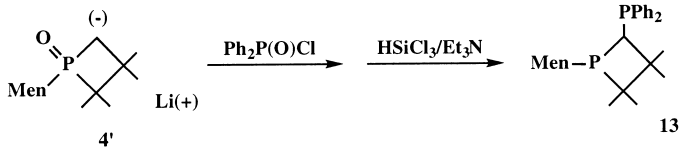


(19)

A single isomer is obtained for each phosphetane **12**.

Reaction of organic dihalides such as α,α′-dibromoxylenes with **4′** failed to produce the corresponding *bis*-phosphetane ligands. The high reactivity and excellent diastereoselectivity of the chlorosilanes make them the reagents of choice for such transformations.

Starting from **4**, unsymmetrical bidentate ligands can be obtained in several ways. Examples are given in Eqs. (20) and (21). Anion **4′** reacts with diphenylphosphinyl chloride to afford an intermediate dioxide whose reduction gives the 1,1-diphosphine **13** [44].



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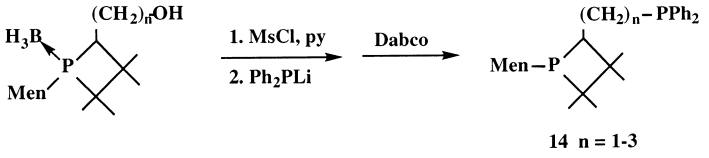


(21)

Eq. (21) shows the conversion of various hydroxy-phosphetanes issued from **4**, into diphosphines by reaction of the corresponding mesylates with lithium diphenylphosphides [39].

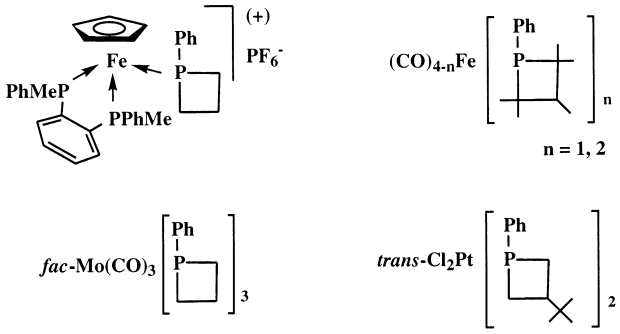
Potentially, the phosphetane-based bidentate phosphines **12**–**14** are precursors to a series of chelated transition-metal complexes having a wide range of bite angles and ring sizes. These range from highly constrained four-membered rings in **13** to very large thirteen-membered rings for **12** when $X=(CH_2)_6$. We will discuss their coordination chemistry below.

4. Phosphetane–transition metal complexes

The coordination chemistry of phosphetanes has been developed very little. Only in the recent literature have iron [45–47], molybdenum [26,27] and platinum [25] complexes been described (Scheme 1). None of these derivatives has ever been tested as a catalyst.

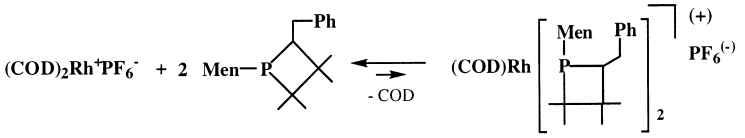
According to Ref. [25], the structural and NMR features of the platinum complex suggest that 3-*t*-butyl-1-phenylphosphetane behaves as an hindered ligand with a weak *trans* influence and poor π-acceptor character. The same features have been observed in studies of the behaviour of P-menthyl-substituted phosphetanes toward transition metals. The coordination chemistry of these chiral phosphetanes with respect to potential rhodium, iridium, palladium and ruthenium catalyst precursors has been examined.

The monodentate P-menthyl phosphetanes serve as poor ligands towards rhodium(I) in its cationic *bis*(cyclooctadiene) complex. The *cis-bis*(phosphine)rhod-



Scheme 1.

ium complex **15** can be detected by ^{31}P NMR spectroscopy in the reaction mixture given in Eq. (22), but a left-side-shifted equilibrium with free phosphetane is established. The steric hindrance about the phosphetane may be a major drawback in this case, given that the analogous iridium complex **16** [38] and the *trans*-rhodium complex **17** [39] are easily accessible, stable compounds.



(22)

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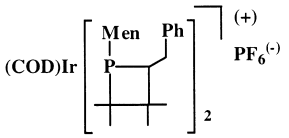

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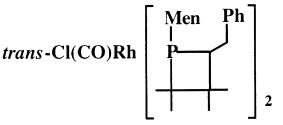
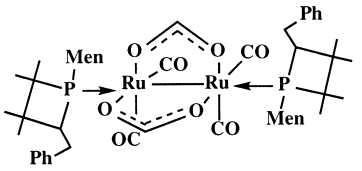


17

In complex **17**, the electron-withdrawing effect of the CO ligand complements the σ-donor ability of the phosphetane, which may explain the increased stability of the complex. The strong donor character of these trialkyl-substituted phosphines is revealed by the low value of the infrared carbonyl stretching frequency at 1951 cm^{-1}.

In the reaction with ruthenium complexes, monodentate phosphetanes do not deplace the COD or the chloride ligands from the [(2-methylallyl)$_2$Ru(COD)] and [(*p*-cymene)$RuCl_2$]$_2$ complexes, respectively, under the usual reaction conditions. However, the bimetallic ruthenium complex **18** [39] is easily obtained from $Ru_3(CO)_{12}$ according to published procedures [48].



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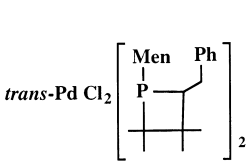
Monodentate phosphetane ligands are well suited to the formation of palladium complexes, as shown by the isolation of several *trans*-$PdCl_2L_2$, (allyl)PdCl(L) and cationic (allyl)$PdL_2^+PF_6^-$ derivatives (L = phosphetane). X-ray diffraction studies of **19** [38] and **20** [43] have been performed.These compounds have been used as precursors for various catalytic reactions (Section 5).

The chelating ability of bidentate phosphetane-based ligands increases the stability of their complexes, most notably in the case of rhodium derivatives. Even the 1,1-diphosphine **13** readily gives the chelated cationic rhodium complex **21**, whose stability is not affected by the severe geometric constraints of the bicyclic structure having two fused four-membered rings [44].The same 1,1-diphosphine **13** has a



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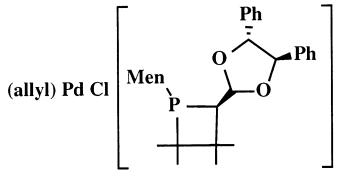

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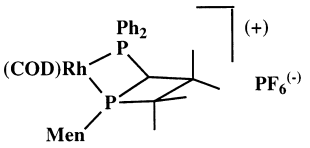

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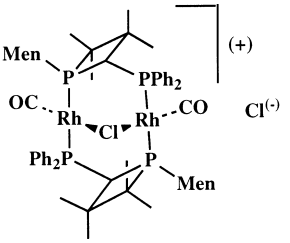
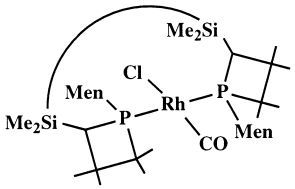


22

second use in the building of binuclear complexes such as the "A-frame" rhodium derivative **22**. Here, the metal centres are kept in close proximity and are potentially able to react cooperatively in stoichiometric or catalytic systems [49–51].

Potentially, the symmetrical *bis*-phosphetanes **12** are chelating ligands, but *cis*-coordination of the two phosphorus atoms to the same metal is prevented by steric hindrance about the highly substituted four-membered rings. *Trans*-coordination becomes possible when the two phosphetane units are connected by a sufficiently long bridging chain. This is the case for **12** when $X=(CH_2)_6$. The *trans*-chelated



23 ⌒ = $(CH_2)_6$

rhodium complex **23** has been characterized by X-ray crystallography [37].The pioneering work of Ito and coworkers on the TRAP series of *bis*-ferrocenyl based ligands [52–55] suggests that *trans*-chelating chiral diphosphines such as **12** might be applicable to asymmetric catalysis. With these ligands, a coordination site of the catalytically active species will either be masked or only accessible to very small reagents. Thus, the catalytic properties, reaction mechanisms and stereoselectivity in their complexes should be significantly modified.

In summary, monodentate, P-menthyl-substituted phosphetanes are generally effective ligands for late transition metals such as palladium, but their rhodium and ruthenium complexes are sometimes rather labile species. A wider range of organo-

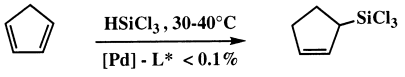
metallic complexes is accessible with bidentate phosphetane-based ligands. Such complexes include 1,1-diphosphine and *trans*-chelated derivatives, whose structural features are quite unusual amongst homochiral ligands. The potential of these complexes as catalysts in transition metal-assisted asymmetric synthesis is clearly open to investigation.

5. Catalytic properties

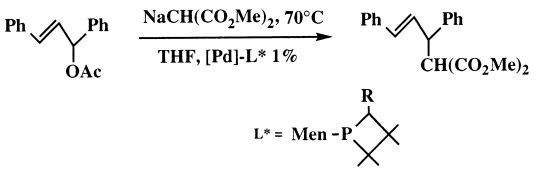
This section concerns the use of the P-menthylphosphetanes derived from **4**, R* = *l*-menthyl, as chiral auxiliaries in transition-metal mediated asymmetric catalysis.

The P-menthylphosphetanes above are highly hindered, P-chiral, electron-rich and for the most part, monodentate phosphines. As such, they belong to a class of chiral ligands which has been comparatively infrequently used in asymmetric catalysis, but which should have some potential within specific areas. It seems likely that the four-membered ring of these phosphines will exert a positive influence on stereochemical control, due to its restricted conformational freedom. However, its compatibility with various catalytic processes and its influence upon their outcome are difficult to predict. Thus, exploratory studies on the applications of phosphetanes to organometallic catalysis have been instigated.

Monodentate phosphetanes appear to be acceptable ligands for various palladium-catalysed reactions. Olefin hydrosilylation and allylic nucleophilic substitutions have been considered to date (Eqs. (23) and (24) and Table 1).



(23)

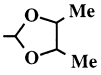
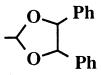


(24)

Olefin hydrosilylation reactions have been performed using trichlorosilane and the usual model substrates, i.e. cyclopentadiene (Eq. (23)) and styrene [56,38]. The highest catalytic activity is observed with a 1:1 phosphetane-to-palladium molar ratio, and significant inhibition by excess phosphine ligand has been observed. This confirms previous assumptions of 1:1 phosphine–palladium complexes as intermediates, and is consistent with the widespread use of monodentate ligands in these hydrosilylation reactions [57,58].

Phosphetane-assisted hydrosilylations of styrene generally show poor enantiomeric excesses (<30%), but e.e.s of 65% and 72% (S enantiomer) are obtained when cyclopentadiene is hydrosilylated in a system containing the phosphetane-dioxolanes 10a, R = Me [P(R)C(R,R,R) epimer] and 10b, R = Ph [P(R)C(R,R,R) epimer], respectively. Although unsatisfactory, the 72% e.e. is competitive with the values of

Table 1
Selected results on Pd-catalysed reactions

L[a]				Hydrosilylation (Eq. (23))	Allylic substit. (Eq. (24))
R	Configurations				
	P	α-C	C,C	e.e. (config.)	e.e. (config.)
CH_2Ph	R	S		54(S)	
	S	R		16 (S)	
10a 	R	R	R,R	65(S)	43(R)
	R	R	S,S	57(S)	
	S	S	R,R	10 S)	
	S	S	S,S	11(R)	
10b 	R	R	R,R	72(S)	82(R)/91(R)*
	R	R	S,S		65(R)
	S	S	R,R		0
	S	S	S,S		24(R)

[a]Under improved experimental conditions.

between 70 and 80% which are given by $iPrCH(NHSO_2CF_3)CH_2PPh_2$ [59] and MOP-phen [60], the most effective phosphines known at present.

Certain other catalytic reactions require, or at least prefer, the use of monodentate phosphine ligands for either the generation of the catalytically active species, or the control of selectivity [61–67]. The use of phosphetanes in such reactions is envisaged.

P-menthylphosphetanes have also been tested in the palladium-catalysed allylic nucleophilic substitution of 1,3-diphenylpropenyl acetate (Eq. (24)) [43]. The electron-rich nature of these phosphines induces only a moderate activation of the allyl–palladium complexes towards nucleophiles. Nonetheless, the observed catalytic activity is satisfactory. The enantiomeric excesses in this reaction, as well as in hydrosilylations, are highly dependent upon the structural features of the phosphetane ligand. Both the nature of the R substituent and the relative configurations of the various chiral centers, including phosphorus, play a major role in stereochemical control (see Table 1). For example, the four epimers of the phosphetane-dioxolane gave very different results, with e.e. rising from 0% for the P(S)C(S,R,R) to 82% for the P(R)C(R,R,R) epimer, under the same reaction conditions. An e.e. of 91% was obtained subsequently after some experimental optimization. Thus, although chirality is an attribute of the molecule as a whole, it appears that individual chiral centers can act either in opposition or in a cooperative manner [68–70] with respect to chiral induction. For instance, an R configuration at phosphorus associated with the *l*-menthyl moiety affords usually the higher enantioselectivity for each pair of epimeric phosphetanes.

The preliminary catalytic tests above indicate that phosphetane **10b**

[P(R)C(R,R,R) epimer] is the most efficient ligand for both hydrosilylation and allylic substitution reactions. The precise nature of the catalyst and the potential involvement of the dioxolane oxygen atoms in the coordination sphere of palladium remain open questions. Further investigations and the extension of this work to other catalytic reactions are in progress.

A few experiments to evaluate the potential of phosphetane ligands in rhodium mediated olefin-hydrogenation reactions have been performed. Monodentate P-menthyl substituted phosphetanes show low catalytic activity and poor enantioselectivity in standard hydrogenations of dehydroaminoacids. To some extent, this is consistent with the observed lability of their rhodium complexes. Consistently, the bidentate phosphetane-PPh_2 ligands **13** and **14**, whose rhodium complexes are markedly more stable, show acceptable catalytic activity. Moderate enantiomeric excesses, up to 75%, have been obtained in unoptimized tests. The best chiral inductions were afforded by phosphetane **14** ($n=1$) which forms a rather rigid five-membered ring upon chelation to the metal [39]. It may be possible to exploit the combination of two sterically and electronically different phosphorus fragments in further applications of this ligand [71].

6. Conclusion

This review shows that chiral phosphetanes are easily accessible in enantiomerically pure form. Highly selective reactions allow simple modifications to their structural features, whilst retaining the four-membered ring motif. Thus, phosphetanes represent a new structural unit for building chiral mono and bidentate ligands for selected transition-metal mediated asymmetric synthesis. Given that their development is still in its early stages, a considerable amount of work remains to be done in this area.

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