123. Preparation of the $PdCl_2$ Complex of TADDOP, the Bis(diphenylphosphinite) of TADDOL: Use in Enantioselective 1,3-Diphenylallylations of Nucleophiles and Discussion of the Mechanism

by **Dieter Seebach***, **Edmée Devaquet**[1]), **Alexander Ernst**[1]), **Michiya Hayakawa**[2]), **Florian N. M. Kühnle**[3]), **W. Bernd Schweizer**, and **Beat Weber**[2])

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstrasse 16, CH–8092 Zürich

(28.VII.1995)

Reaction of the tartrate-derived diol (*R,R*)-α,α,α′,α′-tetraphenyl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (TADDOL) with chlorodiphenylphosphane gives a new bis(diphenylphosphanyl) ligand (TADDOP). The complex **4** formed with $PdCl_2$ has been crystallized and its structure determined by X-ray diffraction (*Fig. 1*). The complex is used for Pd-catalyzed enantioselective 1,3-diphenylallylations of various nucleophiles which give products with enantiomer ratios of up to 88:12 (*Scheme 2*). Crystallization procedures lead to the enantiomerically pure (> 99:1) product **11** derived from dimethyl malonate. The structure of the TADDOP complex **4** is compared with those of other transition-metal complexes containing chelating bis(diphenylphosphanyl) ligands (*Fig. 2*). A crystallographic data base search reveals that the structures of transition-metal complexes containing two Ph_2P groups (superpositions in *Fig. 3*) fall into one of two categories: one with approximate C_2 symmetry and the other with C_1 symmetry (20 and 19 examples, resp.). A mechanistic model is proposed which correlates the conformational chirality (δ or λ) of the four Ph groups' arrangement in such complexes with the topicity of nucleophile approach on Pd-bound *trans,trans*-1,3-diphenylallyl groups (*Scheme 3* and *Table*).

1. Introduction. – The α,α,α′,α′-tetraphenyl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol (**1**, TADDOL) and other analogous diols have been used for the generation of cyclic titanates and similar derivatives of Mg, Al, and Zr. These complexes of oxophilic metal centers were employed in catalytic and stoichiometric enantioselective transformations. Examples are the addition of dialkylzinc [1] [2] and of alkyl-Ti reagents [3] to aldehydes, the addition of *Grignard* reagents to ketones [4], the nucleophilic allylation of and the aldol addition to aldehydes [5], [2+2] and [4+2] cycloadditions and ene reactions with α,β-unsaturated *N*-acyl-oxazolidin-2-ones [6] and quinones [7], and many others [8]. In an effort to induce enantioselectivity in other types of reactions, we have prepared diamino analogs of **1** [9] for use in Li-enolate chemistry [10] and cyclic phosphonites [9] for use in transition-metal-catalyzed reactions such as the hydrosilylations of ketones [11]. Since bidentate ligands are normally more effective in influencing the course of transition-metal-mediated reactions [12–16] (see the extensive compilations in [17] and three review articles [18]), we also tried to prepare such ligands from TADDOL and test them in some typical reactions.

---

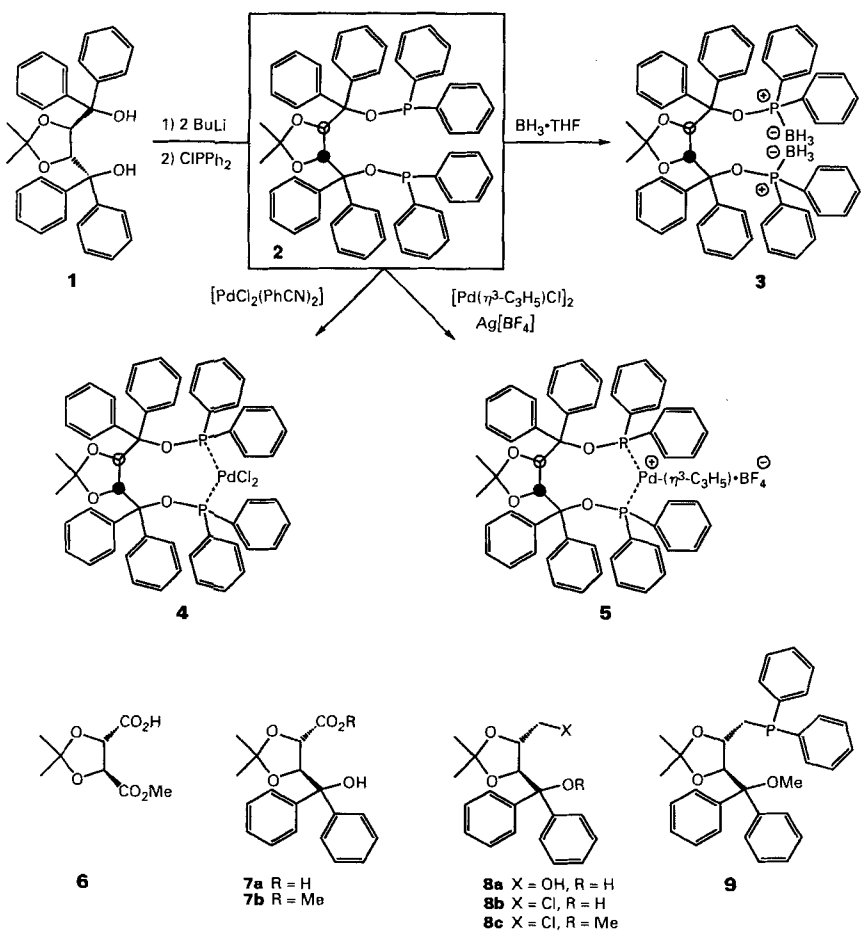
[1]) Part of the Master's Theses of *E. D.* (1993) and *A. E.* (1992/93), ETH-Zürich.

[2]) Part of the Ph. D. Theses No. 10352 and 10663 of *M. H.* (1993) and *B. W.* (1994), ETH-Zürich.

[3]) Part of the projected Ph. D. Thesis of *F.N.M.K.*

2. Preparative Results. – As for the preparation of *cyclic* phosphites and phosphonites of TADDOLs [9], we allowed the Li_2 alkoxide of **1** to react with the appropriate amount of the corresponding chlorophosphane to prepare a bis(phosphinite). Isolation of compound **2** (TADDOP) turned out to be difficult: it decomposed readily not only because of oxidation upon contact with air but also due to the fact that a rather stable carbocation is formed upon heterolytic fission of the C–OP bond (*cf.* the investigation of TADDOL-derived cations) [19]. Hence, we decided to trap the bidentate ligand **2** with BH_3, a procedure which had been found to be useful with other phosphorus derivatives [20]. Indeed, the bis-borane adduct **3** could be purified and fully characterized (see *Scheme 1*). On the other hand, removal of borane from this *Lewis* acid/*Lewis* base complex with Me_3N led to mixtures from which the free bis(phosphinite) could not be separated and isolated in pure form (it is unstable to attempted chromatography on SiO_2). We, there-

Scheme 1. *Preparation of the taddop Ligand* **2** *and of the Corresponding Pd Complexes* **4** *and* **5**. The unsymmetric ligand **9** and intermediates **6**–**8** in its preparation.



fore, trapped **2** *in situ* by evaporating the THF solvent in which it had been prepared, adding toluene and subsequently a solution of $[PdCl_2(NCPh)_2]$. Removal of the LiCl and recrystallization from CH_2Cl_2/pentane and then from benzene gave yellow crystals of the pure Pd complex **4** which was subsequently fully characterized; for an X-ray crystal-structure determination, see *Sect. 3*. Gram amounts of the complex **4** have been prepared at a time, and the compound turned out to be so stable that it can be stored and handled without precautions under atmospheric conditions. Similarly, the bis(phosphinite) **2** has been trapped with $[Pd(\eta^3\text{-allyl})Cl]_2$ to give the slightly less stable taddop complex **5** (*Scheme 1*) which was also fully characterized.

Remembering that the binaphthol-derived methoxyphosphine (mop) was employed successfully in certain enantioselective catalytic reactions [21], we also prepared the methyl ether **9** of a (diphenylphosphanyl)diphenylmethanol derived from the acetonide **6** of monomethyl tartrate (*Scheme 1*). Reaction of **6** [22] with excess phenyl *Grignard* reagent (→**7a**), esterification (→**7b**), $NaBH_4$ reduction (→**8a**), substitution of the primary OH group by Cl with CCl_4/PPh_3 (→**8b**), ether formation (→**8c**), and replacement of Cl by PPh_2 gave the MeO-substituted phosphane **9** in an overall yield of *ca.* 40%. This compound was quite stable in air, after it had been chromatographically purified in a glove box under an inert atmosphere; pure samples crystallize and have a sharp melting point (85–86°).

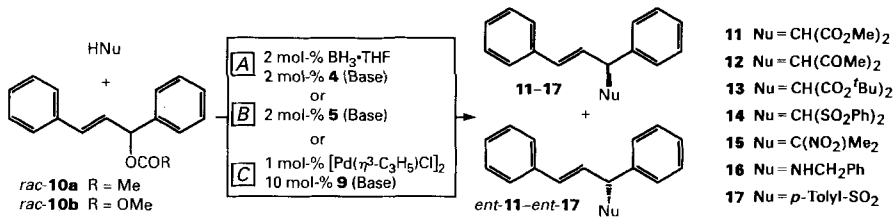
One of the standard reactions catalyzed by diphosphane complexes of Pd is the allylation of nucleophiles. We chose the 1,3-diphenylallyl acetate **10a** and the 1,3-diphenylallyl methyl carbonate **10b** which have been the subject of many investigations on enantioselective 1,3-diphenylallylations [23]. *Trost, Yamaguchi, Bosnich, Hayashi, Pregosin,* and their respective coworkers used diop [24], binapo [25], binap [26] [27], chiraphos [28], and bppf [29] [30] as bidentate P-ligands[4]) for allylations by esters of type **10**. We used the conditions specified as *A*, *B*, and *C* in *Scheme 2*[5]) for conversion of the 1,3-diphenylallyl esters **10** to the malonates **11** and **13**, to the diketone **12**, to the bis-sulfone **14**, the nitroalkane **15**, to the allylic amine **16** and to the allylic sulfone **17**. Except for the nitro compound **15**, all of these products have been previously described as racemic mixtures and/or in enantiomerically enriched form (for references, see *Exper. Part*). The enantiomer ratios (er) in the products were determined by NMR or HPLC methods, or, in one case, by optical comparison (see table in *Scheme 2*). The selectivities range from er 55:45 to 88:12; except with bis(phenylsulfonyl)methane and 2-nitropropane, the selectivities are ≥ 80:20. The absolute configurations of the major enantiomers are assigned (*R*) for the products **11**–**13** and (*S*) for **14**–**17**, the minor enantiomers being *ent*-**11**–*ent*-**17**. These assignments were made by comparison with literature data (for **11**, **12**, and **16**) and by analogy (for **13**–**15** and **17**). In the case of the dimethyl malonate **11**, we have shown that the *rac*-form can be removed by crystallization, and that an essentially enantiomerically pure sample may be subsequently prepared (*Scheme 2*). The comparison of the dimethyl-malonate 1,3-diphenylallylations using the

---

[4]) Abbreviations: binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; bppf = (*S*)-α-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethyl-dialkylamine; chiraphos = 2,3-bis(diphenylphosphino)butane, diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

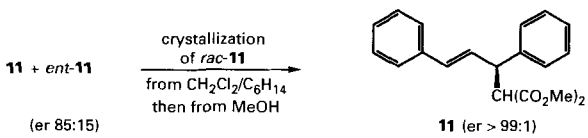
[5]) The frequently used *N*,*O*-bis(trimethylsilyl)acetamide (BSA) [25] did not give better results than NaH as a base.

Scheme 2. *Reactions of 1,3-Diphenylallyl Acetate or Methyl Carbonate with Various Nucleophiles in the Presence of the Pd Complexes* **4** *and* **5** *and of the Complex Formed from Allylpalladium Chloride and* **9**, *with Enantioselective Formation of the Products* **11**–**17**. Enantiomer enrichment of product **11** by crystallizing removal of the *rac*-form.



Allylic substrate	HNu	Base	Method	Reaction temp.	Reaction time	Product	Yield [%]	Enantiomer ratio, er
10a	$CH_2(CO_2Me)_2$	NaH	*A*	r.t.	15 h	(+)-(*R*)-**11**	72	88:12[a])
10b	$CH_2(CO_2Me)_2$	NaH	*A*	r.t.	15 h	(+)-(*R*)-**11**	79	86:14[a])
10a	$CH_2(CO_2Me)_2$	NaH	*B*	r.t.	15 h	(+)-(*R*)-**11**	95	82:18[a])
10a	$CH_2(CO_2Me)_2$	NaH	*C*	r.t.	14 h	(+)-(*R*)-**11**	> 95	80:20[a])
10b	$CH_2(COMe)_2$	NaH	*A*	110°	15 h	(−)-(*R*)-**12**	77	80:20[a])
10a	$CH_2(CO_2{}^tBu)_2$	NaH	*A*	r.t.	15 h	(+)-**13**	96	85:15[a])
10b	$CH_2(SO_2Ph)_2$	NaH	*A*	r.t.	20 h	(+)-**14**	52	55:45[b])
10a	$C(NO_2)Me_2$	NaOMe	*A*	r.t.	17 h	(+)-**15**	42	67:33[b])
10a	$PhCH_2NH_2$	–	*A*	40°	20 h	(+)-(*S*)-**16**	19	84:16[c])
10a	*p*-Tolyl–SO_2H[d])	[d])	*A*	r.t.	18 h	(+)-**17**	93	84:16[b])

[a]) Determined by ^{1}H-NMR spectroscopy, using [Eu(hfc)$_3$] (see *Exper. Part*).
[b]) Determined by HPLC analysis (column: *WHELK*, see *Exper. Part*).
[c]) $[\alpha]_D^{r.t.} = +17.6$ ($c = 1$, $CHCl_3$).
[d]) The sodium salt of *p*-tolyl-SO_2H was used.

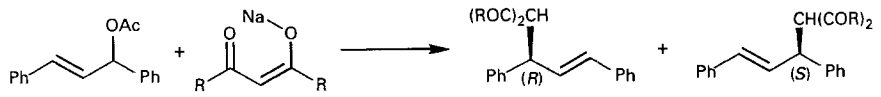


catalyst precursors **4** and **5** shows that there is no sizeable influence of chloride ions when left in the reaction mixture. Interestingly, the monodentate phosphane ligand **9** gives similar results in the enantioselective formation of **11**.

The new P-ligands **2** and **9** are thus performing only moderately well in the enantioselective Pd-catalyzed 1,3-diphenylallylation of nucleophiles (for a comparison of TADDOP (**2**) with other chelating ligands containing two P-atoms, see also discussion below and the *Table*).

3. Structural Studies. – In analogy to our previously reported work on TADDOL-mediated reactions [2], we hoped to gain information about the mechanism by elucidation of the catalyst's structure. Recrystallization of the Pd complex **4** from benzene yielded single crystals suitable for X-ray analysis. The asymmetric unit contains 2 molecules of **4** with slightly different conformations and 8 solvent molecules (*Fig. 1*). In both moieties, the Pd

Table. *Enantioselectivities in Pd-Catalyzed Allylations of Various Nucleophiles in the Presence of Chiral Phosphorous Derivatives.* For the ligand abbreviations, see *Footnote 4.* For the definition of δ and λ conformational chiralities, see the accompanying text and *Fig. 3.* Note that this table gives the absolute configuration of the ligands actually used, while all δ conformations are superimposed in *Fig. 3.*



Entry	Ligand	Conformation	Nucleophile	Yield [%]	(*R*)/(*S*)	Ref.
1	(*S,S*)-chiraphos	δ	$NaCH(CO_2Et)_2$	96	61:39	[28]
2	(*S,S*)-chiraphos	δ	$NaCH(CO_2Me)_2$	99	95:5	[31]
3	(*S,S*)-diop	λ	$NaCH(COMe)_2$	88	50:50	[32]
4	(*P*)-binap	δ	$NaCH(COMe)_2$	80	67:33	[33]
5	(*P*)-binap	δ	$NaCH(COMe)_2$	[a])	95:5	[26]
6	(*P*)-binapo	λ[b])	$NaCH(COMe)_2$	87	23:77	[25]
7	(*R*)-(*S*)-bppf–X (X=NMe_2)	λ	$NaCH(COMe)_2$	51	19:81	[32]
8	(*R*)-(*S*)-bppf–X (X=$NMe(CH_2)_2OH$)	λ	$NaCH(COMe)_2$	86	15:85	[32]
9	(*R*)-(*S*)-bppf–X (X=$NMeCH(CH_2OH)_2$)	λ	$NaCH(COMe)_2$	40	4:96	[32]
10	(*R*)-(*S*)-bppf–X (X=$NMeCH(CH_2OH)_2$)	λ	$NaCH(CO_2Me)_2$	98	26:74	[32]
11	(*R*)-(*S*)-bppf–X (X=$NMeC(CH_2OH)_3$)	λ	$NaCH(COMe)_2$	85	2:98	[35]
12	taddop	δ	$NaCH(CO_2Me)_2$	72	88:12	This paper

[a]) The yield was not indicated by the authors.

[b]) As there is no X-ray crystal structure of binapo published, the λ-conformation was assigned following a calculation using the TRIPOS force field in the Sybyl [34] program package.

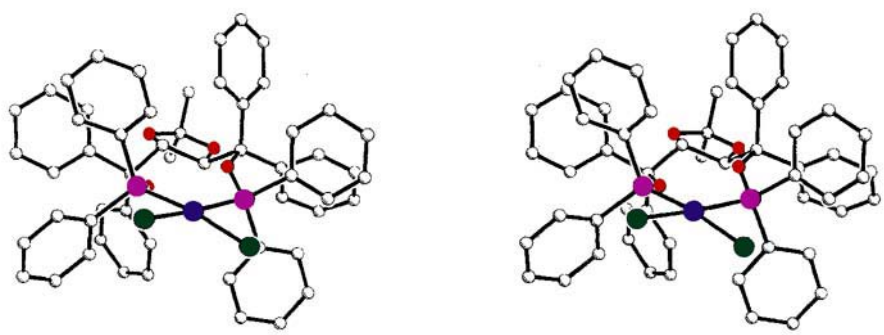


Fig. 1. *PLUTO Stereoview of the Pd complex* **4**. The H-atoms have been omitted for clarity. O-Atoms are indicated in red, P-atoms in purple, Cl-atoms in green, and the Pd-atom in blue.

cation is tetracoordinate with the chelating ligand **2** and two Cl^- anions in a typical square-planar geometry [36]. Only one of the two Cl-atoms deviates a little from this plane, and the Pd–Cl distances are equal within experimental error (2.33, 2.34, and 2.34, 2.36 Å in the two molecules). While the dioxolane ring is nearly planar, the nine-membered chelate ring has, like all nine-membered rings [37], a strongly puckered conforma-

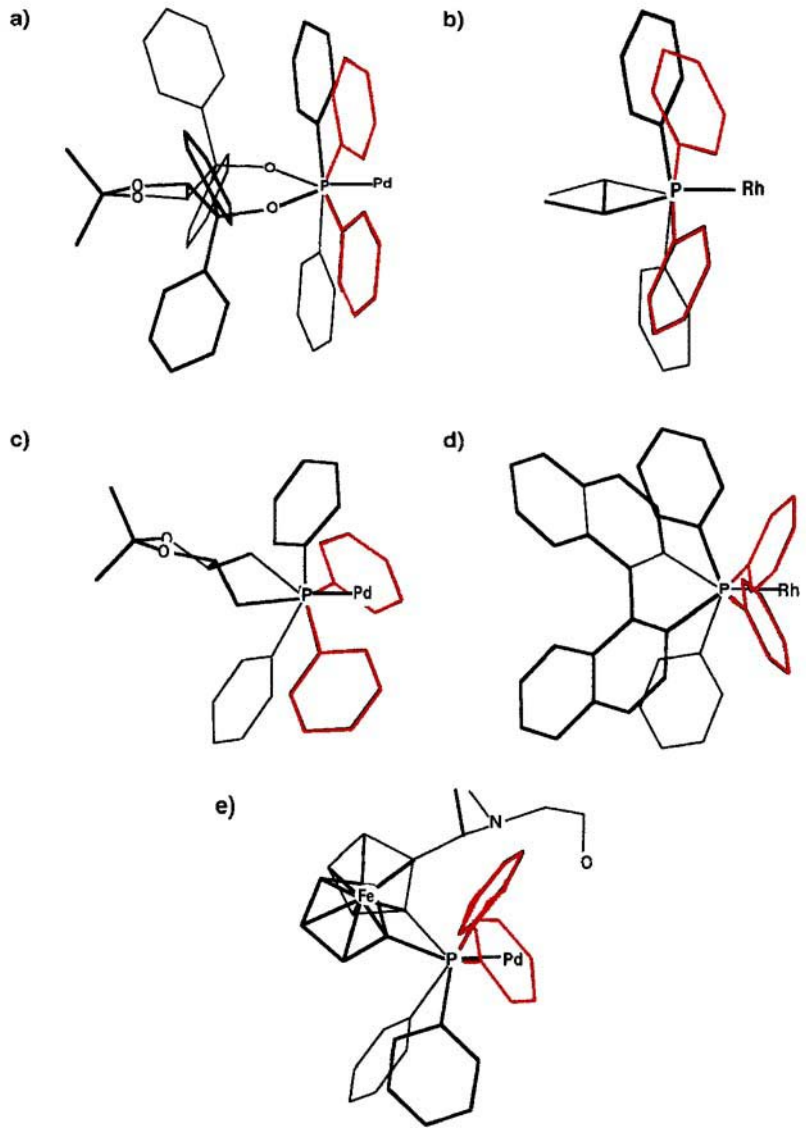


Fig. 2. *View along the P···P vector of some transition-metal complexes of bidentate Ph_2P ligands. a*) (*R*,*R*)-taddop, *b*) (*S*,*S*)-chiraphos (CUYYAW), *c*) (*S*,*S*)-diop (BICLOO), *d*) (*P*)-binap (BNAPRH), and *e*) (*R*)-(*S*)-bppf (JARSIE). The quasi-equatorial Ph groups are depicted in red (bold print of Ph in front). Note that the equatorial Ph groups are closer to the metal center than the axial ones. The CSD codes are given in parentheses.

tion. The H-atoms on the bridgeheads of the two rings are in axial positions, and this sets the stage for the positioning of the Ph substituents around the nine-membered ring. The two axial Ph groups in the moiety derived from TADDOL are antiperiplanar (*ap*) to these H-atoms, the equatorial Ph groups take an *ap* position with respect to the bond which is common to both rings. The two O-atoms of the nine-membered ring assume the positions of those CH_2 groups which are subject to the strongest transannular interaction within cyclononane itself. As the repulsive interactions between the lone pairs are much smaller, it is not surprising that the O···O distance (2.66 Å) is only slightly larger than those found in TADDOLs (2.60 Å) [2]. However, it is significantly smaller than in the spiro-titanium bis-TADDOLate (2.8 Å) [2] and in the dimethyl ether of TADDOL (**1**) (2.9 Å) [2]. Moving further around the ring, it can be seen that the O–P bonds are eclipsed (*syn-coplanar*) with the C–Ph bonds of the quasi-equatorial Ph groups. This local conformation positions the equatorial C–Ph group exactly between the two P–Ph groups (in a kind of staggered arrangement). Completing the ring by joining the two P-atoms with the Pd-atom, we arrive at a propeller-type positioning of the four P–Ph groups, two quasi-axial and two quasi-equatorial. The local chirality around the asymmetric C-atoms can be considered to be transferred through the ring conformation to the environment of the Pd-atom. This way, the characteristic λ-conformation of the (*R*,*R*)-TADDOL part (axial Ph group on the upper right and lower left side)[6]), generates a δ-arrangement around the P-atoms (axial Ph group on the upper left and lower right side)[7]).

A comparison of the structure of the taddop complex **4** with those of other transition-metal complexes of bidentate Ph_2P ligands is depicted in *Figs. 2* and *3*. A look along the P···P vector of **4** in *Fig. 2, a*, shows that the quasi-equatorial Ph groups are pushed towards the metal center, while the quasi-axial ones are at the rear. As pointed out before [2] [39], this structural feature is typical for complexes of the bidentate ligands with two Ph_2P groups (see the structures with nine-, seven-, and five-membered chelate rings in *Fig. 2*). When we compare almost 40 structures of complexes containing C_2-symmetrical bidentate $(Ph_2P)_2$ ligands found in the *Cambridge Crystallographic Data Base*, we notice that there are two distinct classes of structures: one, to which the TADDOP complex **4** belongs, has approximate C_2 symmetry of the chelate ring (*Fig. 3, a*; 20 cases), the other one has an arrangement of the Ph groups which deviates considerably from C_2 symmetry (*Fig. 3, b*; 19 cases). Whereas the left side of the superposition in this latter case still has quasi-equatorial and quasi-axial Ph groups, a distinction of equatorial and axial is no longer possible on the right side. Here, the P–metal–P plane approximately halves the angle between the two Ph–P bonds, so that this side might be called 'pseudo-symmetric'. There is a general tendency for the quasi-equatorial Ph groups to point towards the metal center, whereas the quasi-axial ones are farther away from it.

4. Mechanistic Discussion. – The reactivity and especially the regio- and stereoselectivity of catalytic transformations involving allylic Pd complexes with chelating Ph_2P ligands have been comprehensively discussed. In these discussions, an edge-on/face-on

---

[6]) The TADDOLate part of **4** has the very characteristic structure determined for dozens of TADDOL derivatives ([1f] [2] [6d] [19] [38], and references cited therein).

[7]) Note, that we use δ and λ referring to the position of the quasi-axial aryl groups (see Fig. 4 in [6d]), rather than referring to the puckering of the chelate ring.

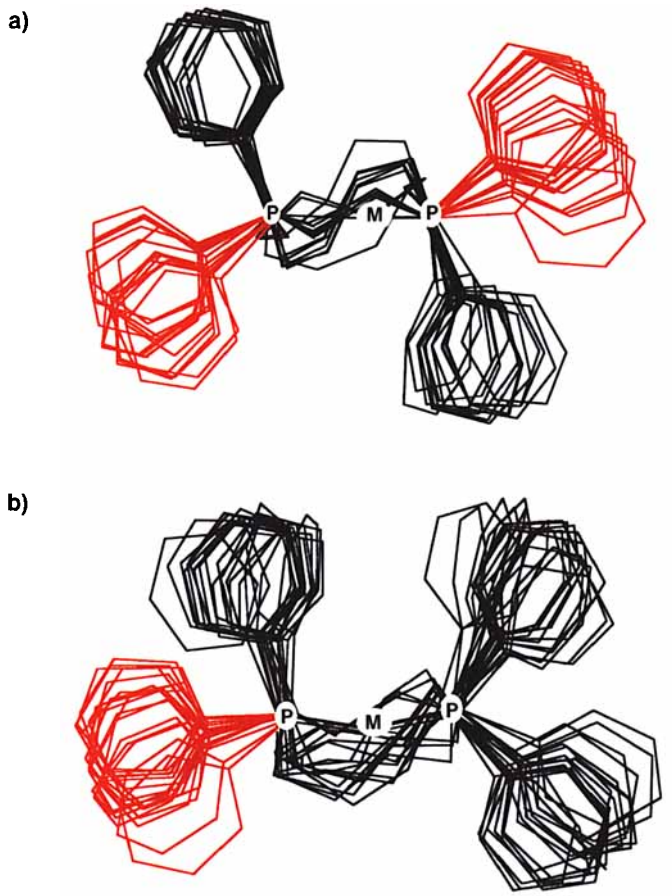
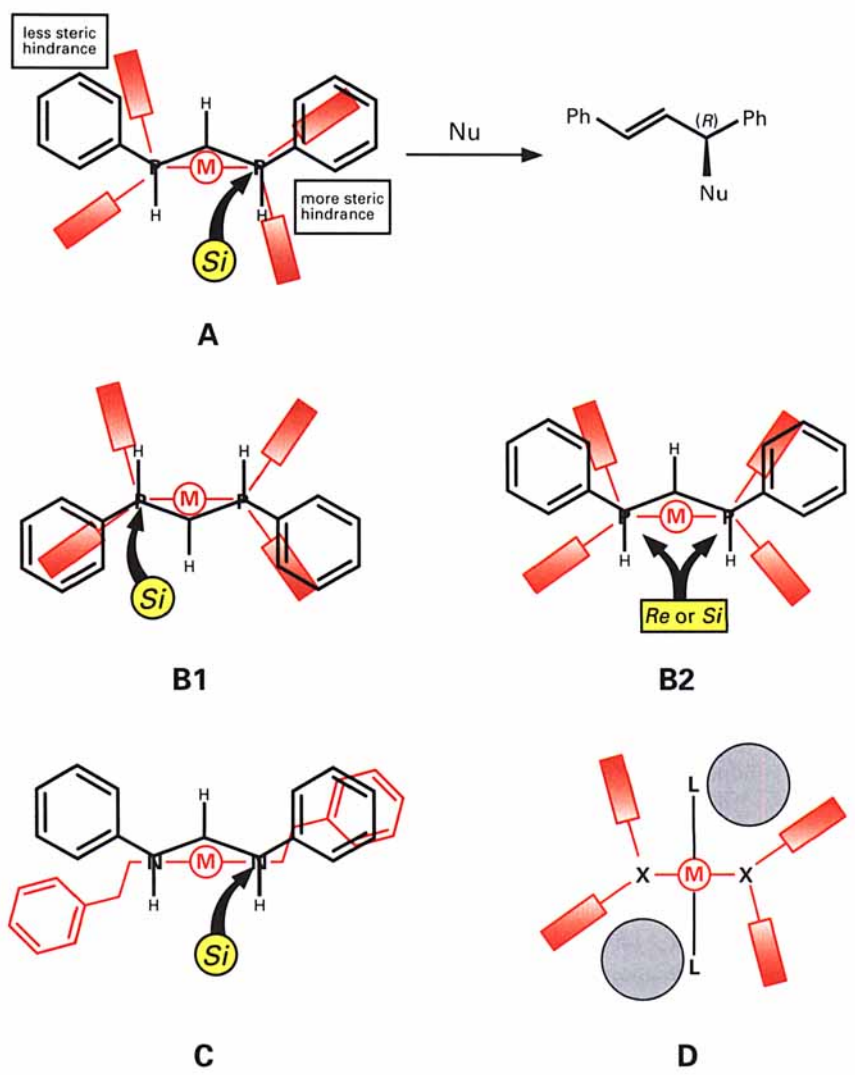


Fig. 3. a) *Superposition of 20 structures of transition-metal complexes of approximate C_2-symmetric bidentate diphenylphosphane ligands.* The structures are derivatives from the following basic skeletons (CSD codes in parentheses): norbornane (BAVSAS, CEJJEG, CUNKUR), cyclopentane and pyrrolidine (ALANPD, BUTWES, SACHIN), chiraphos (CUYYAW), biphenyl (JIPCAM, JUBVUX, GEDZAQ, JUBWAE, JUBWEI), binaphthol (BNAPRH, FALJOR, FUXSUM, LEGZOM, VIXZOR), ferrocene (one of *Hayashi*'s ligands, SEHLEW), and both TADDOP (**4**) structures. b) *Superposition of 19 transition-metal complexes of bidentate diphenylphosphane ligands, showing only C_1 symmetry.* diop (BEMGOP, BICLOO, CIPBNI, FICBIC, HOXLRH 2x, JUZLEV, VOFHON, VOJBEB, YAJPII, YAJPOO, YAJPUU, YAJRAC), η^6-arene complexes of Rh and Ru (GEDYUJ, JAPXAZ, SAZTAO, SAZTES), pyrrolidine (SOGBIZ, WAPBIY). The Ph groups, which are in quasi-equatorial positions are shown in red. For comparison with the (*R,R*)-taddop complex **4**, the structures are all shown in the δ-conformation. Some of them had to be inverted for that purpose. The best fit of the two P-atoms and of the metal atom was calculated.

effect ('*Knowles* effect' [40])[8]), a bite-angle effect [41], a ring-size effect ('chiral pocket' [25]), a pendant side-chain effect [32] [35] [42], and a *trans* or stereoelectronic effect [43–45] were proposed for rationalizing structure-selectivity correlations. Extensive use

[8]) In the superpositions of *Fig. 3*, we do not recognize a distinct preference for an axial edge-on *vs.* equatorial face-on arrangement.

Scheme 3. *Coordination of the* trans,trans-*1,3-Diphenylallyl Moiety with Various Pd Complexes or Metals with Higher Coordination Number*. The Ph groups of the chelating ligands in **A**, **B**, and **D** are symbolized as shaded, red rectangles; the presentation is not meant to indicate a particular conformation (such as edge-on/face-on orientation of the Ph groups!). **A**: Complex of *trans,trans*-1,3-diphenylallyl (black) with a C_2-symmetrical (Ph_2P) ligand. The difference in the steric hindrance is important. **B**: The two possible complexes of *trans,trans*-1,3-diphenylallyl (black) with a C_1-symmetrical (Ph_2P) ligand. The difference in the steric hindrance is less distinct than in **A**. **C**: Complex of *trans,trans*-1,3-diphenylallyl (black) with a C_2-symmetrical semicorrin ligand. As for **A**, the two Ph groups of the allyl moiety are subject to very different steric interactions. **D**: C_2-symmetrical ligand bound to a metal of tetrahedral coordination sphere. In this case, the steric interaction of the ligands L with the quasi-axial Ph groups is much larger than with the quasi-equatorial ones.



has been made of crystal-structure data (*cf. Figs. 2* and *3*, and [41–43] [45]), of NMR measurements [26] [39] [46–48], and of calculations [26] [46] [47]. It turns out that the outcome of the reactions is very sensitive to the conditions and to the actual structure of the allylic substrate.

When restricting the discussion to 1,3-diphenylallyl esters and to sodium malonate or acetyl acetonate (*Table*), we notice that, when the $(Ph_2P)_2$ ligands, which have a δ-arrangement of the axial Ph groups in the corresponding crystal and solution structures, are used, nucleophilic attack occurs from the *Si*-face of the diphenylallyl moiety ($\rightarrow$(*R*)-product), while the ligands giving rise to λ-arrangement in their transition metal complexes lead to preferential approach of the nucleophiles from the *Re*-face ($\rightarrow$(*S*)-product).

This experimental fact can be interpreted in terms of a steric-strain release effect. There is only one possible average geometry of the square-planar complex containing a C_2-symmetrical $(Ph_2P)_2$-chelated Pd and the C_{2v}-symmetrical *trans,trans*-1,3-diphenylallyl ligand (see **A** in *Scheme 3* and compare with *Fig. 3, a*). We notice that there is more steric interaction on the allylic C-atom of **A** which has the *Si*-face exposed such that nucleophilic attack on it will release more steric stain. With the C_1-symmetrical conformation of the chelate, there are two geometrically isomeric complexes (see **B1** and **B2** in *Scheme 3* and compare with *Fig. 2, b*). While *Si*-attack of a nucleophile in **B1** will still release more strain than *Re*-attack, the difference between the two allylic positions is smaller in **B2**[9])[10]).

The steric-strain release effect has been previously discussed, by consideration of an X-ray crystal-structure analysis and of extensive NMR measurements by *Pfaltz, Zehnder, Pregosin*, and their coworkers [45b], to interpret the stereochemical course of 1,3-diphenylallylations mediated by a C_2-symmetrical Pd-semicorrin complex (see **C** in *Scheme 3*).

Thus, a common structural feature of the $(Ph_2P)_2$ ligands and of the semicorrin ligands is likely to be responsible for the analogous stereochemical course of 1,3-diphenylallylations. The quasi-equatorial Ph groups (pointing towards the metal) in the Pd complexes and the substituents on the semicorrin system cause a similar bias for the higher reactivity of one of the heterotopic faces of the 1,3-diphenylallyl moiety. Similar conclusions were drawn by *Pregosin, Albinati*, and coworkers on the basis of NMR investigations [47].

In closing, it is worthwhile to point to the different factors governing the reactions of the square-planar, and of tetrahedral or trigonal bipyramidal transition-metal complexes containing ligands which provide quasi-axial and quasi-equatorial aryl groups in a λ- or δ-type arrangement (*cf.* **A** and **D** in *Scheme 3* and discussions in [1f] [2] [6d] [49] [50]). The axial aryl groups cause the bias in the latter, the equatorial ones in the former case.

We thank the *Stiftung Stipendien-Fonds der Chemischen Industrie*, Germany, for a scholarship granted to *F.N.M.K.* We gratefully acknowledge the assistance of *B. Brandenberg, M. Bolhalder* (NMR service), and Dr. *W. Amrein, R. Häfliger, O. Greter* (MS service). For the generous supply of THF (*BASF AG*, D–Ludwigshafen)

[9]) Actually, lower enantioselectivities are observed in Pd-catalyzed 1,3-diphenylallylations with diop [32] which belongs to the ligands forming C_1-symmetrical complexes as shown in *Fig. 3, b*.

[10]) The reaction, in which the unsymmetrical ligand **9** (with a Ph_2P and a MeO group) was employed, would have to be compared with reactions involving the mop ligand [43] and the likewise unsymmetrical ligands containing a N- and a Ph_2P-donor atom [44] [45].

and dimethyl tartrate (*Chemische Fabrik Uetikon*, CH–Uetikon), we thank the companies mentioned. Continuing support by *Sandoz Pharma AG*, Basel, is gratefully appreciated. We thank Prof. *P. S. Pregosin* for discussions on the subject of this paper and for sharing unpublished results [47] with us.

Experimental Part

General. Abbreviations: FC: flash chromatography; *GP*: general procedure. THF was distilled under Ar over K prior to use and transferred with syringes. The other solvents used in reactions were purchased from *Fluka* and stored over molecular sieves (4 Å). TADDOL (**1**) was synthesized according to [38]. BuLi was provided by *Chemmetall*, D–Frankfurt am Main, as a 1.5M soln. in hexane. $ClPPh_2$, $PdCl_2(PhCN)_2$ and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ were purchased from *Fluka*. All other chemicals are commercially available (*Fluka*) and were used without further purification. M.p.: open glass capillaries; *Büchi 510* or *SMP-20*. $[\alpha]_D$ at r.t. (*ca.* 20°); *Perkin-Elmer-241* polarimeter, *p.a.* solvents. IR: *Perkin-Elmer 298*; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian Gemini 200* (200 MHz (^1H), 50 MHz (^{13}C)), or *Bruker WM 300* (300 MHz (^1H), 75 MHz (^{13}C)); δ rel. to Me_4Si (= 0 ppm), *J* in Hz.

(4R,5R)-[2,2-Dimethyl-1,3-dioxolane-4,5-diylbis(diphenylmethyl)] Bis(diphenylphosphinite (P–B)borane) (**3**). BuLi (10.5 ml, 16.8 mmol, 1.6M hexane) was added *via* syringe at −78 to −70° to a soln. of TADDOL (**1**; 3.7 g, 7.9 mmol) in THF (40 ml). The resulting soln. was stirred at −78° for 15 min and then allowed to warm to r.t. After stirring for 1 h at r.t., the soln. was cooled to −78° and $ClP(Ph)_2$ (3.1 ml, 17 mmol) was added *via* syringe at −78 to −70°. The resulting yellow soln. was allowed to warm to r.t. and stirred for 3 h. At 0°, $BH_3 \cdot THF$ (16 ml, 16 mmol, 1.0M THF) was added. After stirring for 15 h at r.t., the soln. was diluted with Et_2O (60 ml), washed with H_2O (twice), dried (Na_2SO_4), and evaporated *in vacuo*. The residue was crystallized from Et_2O yielding **3** (4.1 g, 62%) as colorless crystals. M.p. 154°. $[\alpha]_D^{r.t.} = -88.9$ (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): 3100, 3060, 3020, 3010, 2390, 1440, 1230, 1210, 1200, 1110, 960. ^1H-NMR (400 MHz, $CDCl_3$): 7.52–7.17 (*m*, 4 arom. H); 7.13–7.00 (*m*, 6 arom. H); 5.21 (*s*, 2 CH); 0.96 (*s*, 2 Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.80; 138.75; 137.68; 135.39; 134.69; 133.77; 133.15; 131.99; 131.88; 131.45; 131.35; 130.74; 130.72; 130.54; 128.95; 128.02; 127.98; 127.88; 127.77; 127.20; 126.67; 106.83; 90.62; 81.65; 27.08. ^{31}P-NMR (162 MHz, $CDCl_3$): 101.4 (br. *s*). EI-MS: 427.2 (8.3), 368.2 (7.2), 265.2 (8.3), 241.2 (4.9), 201.1 (91), 186.1 (56), 167.1 (41), 108.1 (100), 77.1 (36), 51.0 (34). Anal. calc. for $C_{55}H_{54}O_4B_2P_2$: C 76.58, H 6.31; found: C 76.36, H 6.50.

Dichloro{(4R,5R)-[(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethyl)] Bis(diphenylphosphinite-P)}palladium(II) (**4**). BuLi (3.94 ml, 6.3 mmol, 1.6M hexane) was added *via* syringe at −78 to −70° to a soln. of **1** (1.4 g, 3.0 mmol) in THF (15 ml). The resulting soln. was stirred at −78° for 15 min and then allowed to warm to r.t. After stirring for 1 h at r.t., the soln. was cooled to −78°, and $ClP(Ph)_2$ (1.2 ml, 6.3 mmol) was added *via* syringe at −78 to −70°. The resulting yellow soln. was allowed to warm to r.t. and stirred for 3 h. The solvent was evaporated *in vacuo* and the residue stirred with toluene (15 ml) for 15 h. The slurry was filtered under Ar, and the soln. was added to $[PdCl_2(PhCN)_2]$ (1.2 g, 3.0 mmol) in toluene (150 ml). After 5 min, the resulting slurry was filtered through a *Celite* pad without an inert-gas atmosphere. Crystallization at −20° yielded **4** (1.5 g, 49%) as yellow crystals. From the mother liquor additional **4** (0.53 g, 16%) was isolated after addition of petroleum ether. An anal. pure sample was isolated after subsequent crystallization from CH_2Cl_2/pentane and benzene and careful drying (3 d, 10^{-5} bar). M.p. 135–136°. $[\alpha]_D^{r.t.} = -11.9$ (*c* = 0.62, $CHCl_3$). IR ($CDCl_3$): 3060, 2990, 1590, 1450, 1440, 1390, 1100, 990. ^1H-NMR (400 MHz, $CDCl_3$): 7.74 (*q*, *J* = 7.1, 5 arom. H); 7.59–7.56 (*m*, 5 arom. H); 7.44–7.31 (*m*, 10 arom. H); 7.27–7.12 (*m*, 10 arom. H); 6.89 (*t*, *J* = 7.8, 5 arom. H); 6.59 (br. *s*, 5 H); 4.68 (*s*, 2 H); 0.6 (*s*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.31; 139.03; 135.94; 135.78; 134.13; 134.01; 133.71; 132.05; 131.87; 131.79; 131.22; 129.03; 128.91; 128.36; 128.22; 127.97; 127.91; 127.85; 127.33; 127.24; 126.58; 125.29; 109.8; 93.1; 79.2; 26.9. ^{31}P-NMR (162 MHz, $CDCl_3$): 109.8(*s*). FAB-MS: 703.0 (5), 616.9 (5), 509.0 (38), 431.2 (63), 345.1 (36), 279.1 (27), 179.1 (100), 105.0 (60), 76.9 (29). Anal. calc. for $C_{55}H_{48}O_4P_2Cl_2Pd$: C 65.26, H 4.78; found: C 65.06, H 5.03.

(η³-Allyl){(4R,5R)-[(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethylene)] Bis(diphenylphosphinite-P)}palladium(II) Tetrafluoroborate (**5**). BuLi (1.3 ml, 2.1 mmol, 1.6M hexane) was added *via* syringe at −78 to −70° to a soln. of **1** (0.47 g, 1.0 mmol) in THF (5 ml). The resulting soln. was stirred at −78° for 15 min and then allowed to warm to r.t. After stirring for 1 h at r.t., the soln. was cooled to −78° and $ClP(Ph)_2$ (0.40 ml, 2.1 mmol) was added *via* syringe at −78 to −70°, the resulting yellow soln. was allowed to warm to r.t. At 0°, a soln. of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.19 ml, 0.53 mmol) in $CHCl_3$ (4 ml) was added. After stirring for 1 h at r.t., the solvent was evaporated *in vacuo*. The residue was suspended in toluene (10 ml) and filtered under Ar. $AgBF_4$ (2.3 ml, 1.6 mmol, 0.7M toluene) was added and stirring continued for 30 min. The resulting AgCl precipitate was removed by filtration, the filtrate washed with H_2O (three times), dried (Na_2SO_4), and the solvent evaporated *in vacuo*. The

remaining solid was crystallized from CH_2Cl_2/hexane yielding **5** (0.29 g, 27%) as yellow crystals. M.p. 145° (dec.). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.69–7.59 (*m*, 5 arom. H); 7.58–7.1 (*m*, 25 arom. H); 6.96–6.87 (*m*, 5 arom. H); 6.78–6.72 (*m*, 5 arom. H); 5.74–5.57 (*m*, CH(allyl), *meso*); 4.80 (*d*, J = 7.2, C*H*–CH); 4.72 (*d*, J = 7.2, C*H*–CH); 3.61–3.59 (*m*, CH(allyl), *syn*); 3.43–3.41 (*m*, CH(allyl), *syn*); 3.1–3.03 (*m*, CH(allyl), *anti*); 2.77–2.73 (*m*, CH(allyl), *anti*); 1.27 (*s*, Me); 0.6 (*s*, Me).

(4S,5S)-5-(Hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylic Acid (**7a**). A soln. of **6** [22] in THF (50 ml) was added to a soln. of PhMgBr (from Mg (8.8 g, 0.36 mol) and PhBr (37.8 ml, 0.36 mol)) in THF (340 ml) over 1 h. The temp. was kept at 20–30°. After stirring overnight, the dark soln. was quenched with ice (200 g) and acidified to pH ≈ 2 with aq. HCl (20%). The org. layer was extracted with Et_2O (500 ml), washed with brine (three times), dried (Na_2SO_4), and the solvent was evaporated *in vacuo*. The remaining oil was crystallized from AcOEt/hexane yielding **7a** (22.1 g, 67%) as a colorless solid, which was used in the next step without further purification. M.p. 140–150°. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.6–7.1 (*m*, 10 arom. H); 5.34 (*d*, J = 6.7, 1 H); 4.43 (*d*, J = 6.7, 1 H); 1.50 (*s*, Me); 1.45 (*s*, Me).

Methyl (4S,5S)-5-(Hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate (**7b**). At r.t., a suspension of **7a** (1.03 g, 3.14 mmol), MeI (0.30 ml, 4.8 mmol), Na_2CO_3 (0.50 g, 4.7 mmol), and DMF (10 ml) was stirred for 2 d. The mixture was then dissolved in Et_2O (80 ml), washed with H_2O (three times), dried (Na_2SO_4), and then the solvent was evaporated *in vacuo* to give **7b** (1.00 g, 93%) as a yellow powder, which was used in the next step without further purification. To obtain an anal. pure sample, **7b** was purified by FC (SiO_2, AcOEt/hexane 1:6). M.p. 111.5–112.5°. $[\alpha]_D^{r.t.} = -70.3$ (c = 1.5, $CHCl_3$). IR (KBr): 3580, 3005, 1755, 1500, 1460, 1390, 1280, 1260, 1220, 1170, 1075, 1050, 1020, 875, 760, 740, 700. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.6–7.2 (*m*, 10 arom. H); 5.37 (*d*, J = 7.2, H–C(5)); 4.41 (*d*, J = 7.2, H–C(4)); 3.33 (*s*, MeO); 3.14 (*s*, OH); 1.58 (*s*, Me–C(2)); 1.49 (*s*, Me–C(2)). Anal. calc. for $C_{20}H_{22}O_3$: C 70.16, H 6.48; found: C 69.94, H 6.48.

(4S,5R)-5-(Hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane-4-methanol (**8a**). $NaBH_4$ (15 g) was added to a soln. of **7b** (20.3 g, 59 mmol) in MeOH (300 ml). After stirring overnight, *ca.* 200 ml of the solvent was evaporated *in vacuo*, the residue was dissolved in Et_2O, washed with H_2O (three times), dried (Na_2SO_4), and then the solvent was evaporated *in vacuo* to give **8a** (17.7 g, 93%) as a colorless solid, which was used in the next step without further purification. To obtain an anal. pure sample **8a** was crystallized from Et_2O/hexane. M.p. 134.5–135°. $[\alpha]_D^{r.t.} = -107$ (c = 1, $CHCl_3$). IR (KBr): 3540, 3490, 3000, 2940, 1490, 1450, 1375, 1250, 1220, 1165, 1100, 1070, 990, 945, 920, 900, 860, 760, 700. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.6–7.2 (*m*, 10 arom. H); 4.90 (*d*, J = 8.4, H–C(4)); 4.12–4.07 (*m*, H–C(5)); 3.19 (*s*, OH); 3.08–3.0 (*m*, 1 H, CH_2); 2.4–2.3 (*m*, 1 H, CH_2); 1.81 (*s*, OH); 1.52 (*s*, Me); 1.46 (*s*, Me). Anal. calc. for $C_{19}H_{22}O_4$: C 72.59, H 7.05; found: C 72.74, H 7.28.

(4S,5S)-5-(Chlorodiphenylmethyl)-2,2-dimethyl-1,3-dioxolane-4-methanol (**8b**). A soln. of **8a** (0.70 g, 2.2 mmol) and PPh_3 (1.4 g, 5.3 mmol) in CCl_4 (3.5 ml) was stirred at 50° overnight. Additional PPh_3 (0.5 g, 1.9 mmol) was added to the resulting slurry, and stirring was continued for one day. The mixture was diluted with CH_2Cl_2 (20 ml) and hexane (80 ml), washed with H_2O (three times), dried (Na_2SO_4), and evaporated *in vacuo*. From the residue, **8b** (0.56 g, 79%) was isolated as a colorless solid by FC (hexane/Et_2O 8:1). M.p. 130–131°. An anal. pure sample was obtained by crystallization from Et_2O/hexane. M.p. 130–131°. $[\alpha]_D^{r.t.} = -32.2$ (c = 1.0, EtOH). IR ($CHCl_3$): 3570, 1600, 1490, 1450, 1380, 1370, 1070. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.6–7.2 (*m*, 10 arom. H); 4.92 (*d*, J = 8.0, H–C(5)); 4.28–4.21 (*ddd*, J = 8, 4.4, 2, H–C(4)); 3.13 (*s*, OH); 2.97 (*dd*, J = 12.2, 2, 1 H, CH_2); 2.22 (*dd*, J = 12.2, 4.4, 1 H, CH_2); 1.55 (*s*, Me); 1.46 (*s*, Me). Anal. calc. for $C_{19}H_{21}ClO_3$: C 69.26, H 6.68; found: C 69.35, H 6.59.

(4S,5S)-4-(Chloromethyl)-5-(methoxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane (**8c**). A soln. of **8b** (0.20 g, 0.70 mmol) in THF (1 ml) was added to a slurry of NaH (80 mg, dispersion in mineral oil *ca.* 60%) and THF (2 ml). After the gas evolution had ceased, MeI (0.13 ml, 2.1 mmol) was added and the mixture stirred overnight. The mixture was quenched with ice, the org. layer extracted with Et_2O, washed with H_2O, dried (Na_2SO_4), and the solvent evaporated *in vacuo*. FC (pentane/Et_2O 8:1) gave **8c** (0.24 g, 97%) as a colorless solid. An anal. pure sample was isolated after crystallization from Et_2O/hexane. M.p. 70–71°. $[\alpha]_D^{r.t.} = +10.1$ (c = 1.0, EtOH). IR ($CDCl_3$): 1655, 1600, 1490, 1445, 1380, 1370, 1080. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.5–7.2 (*m*, 10 arom. H); 4.86 (*d*, J = 8.2, H–C(5)); 4.11 (*ddd*, J = 8.2, 5.0, 2.3, H–C(4)); 3.35 (*dd*, J = 11.9, 2.3, 1 H, CH_2); 3.20 (*s*, MeO); 3.00 (*dd*, J = 11.9, 5.0, 1 H, CH_2); 1.52 (*s*, Me); 1.23 (*s*, Me). Anal. calc. for $C_{20}H_{23}ClO_3$: C 68.57, H 6.36; found: C 68.68, H 6.34.

(4S,5S)-4-[(Diphenylphosphanyl)methyl]-5-(methoxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane (**9**). BuLi (2.7 ml, 4.3 mmol, 1.6M hexane) was added under ice-cooling to a soln. of $HPPh_2$ (0.95 g, 5.1 mmol) in THF (7 ml) *via* syringe. After stirring for 30 min at r.t., a soln. of **8c** (1.04 g, 3.00 mmol) in THF (3 ml) was added to the orange soln., and stirring was continued overnight. The reaction was quenched with sat. NH_4Cl soln. under an inert-gas atmosphere, the org. layer extracted with Et_2O (three times 20 ml), and the solvent evaporated *in vacuo*. The residue was chromatographed (100 g SiO_2, 63–200 μm; toluene/hexane 1:1) in a glove box (the product-containing

fractions could be handled in the air) yielding **9** (1.35 g, 91%) as a colorless solid. An anal. pure sample was prepared by crystallization from CH_2Cl_2/hexane. M.p. 85–86°. $[\alpha]_D^{r.t.} = +93.4$ ($c = 0.92$, $CDCl_3$). IR (nujol mull): 1590, 1260, 1230, 1215, 1180, 1110, 1070, 1030, 900, 840, 745, 705. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.4–7.15 (*m*, 20 arom. H); 4.83 (*d*, $J = 8.0$, H–C(5)); 4.02–3.90 (*m*, H–C(4)); 3.14 (*s*, MeO); 2.15–2.05 (*m*, 1 H, CH_2); 2.0–1.88 (*m*, 1 H, CH_2); 1.43 (*s*, Me); 1.09 (*s*, Me). ^{31}P-NMR (121.5 MHz, $CDCl_3$): –21.73. FAB-MS: (499 (5), 498 (23), 497 (60)) ($[M + H]^+$), 496 (13), 481 (28), 467 (11), 466 (47), 465 (100), 464 (24). Anal. calc. for $C_{32}H_{33}CO_3P$: C 77.40, H 6.70; found: C 77.33, H 6.88.

Reactions of **10** *with Various Nucleophiles. General Procedure* (for conditions *A* and er values see *Scheme 2*). The Pd complex **4** (20 mg, 20 μmol) and the allylic substrate (1 mmol) were dissolved in THF (0.5 ml). The nucleophile (3 mmol in THF) was added and the mixture degassed with two freeze/thaw cycles. $BH_3 \cdot THF$ (20 μl, 20 μmol, 1.0M THF) was added and, after five additional freeze/thaw cycles, the reaction mixture stirred *in vacuo* as indicated in *Scheme 2*. The reaction mixture was poured into Et_2O, washed with sat. NH_4Cl soln. (twice), and H_2O (twice), dried ($MgSO_4$), and evaporated *in vacuo*. The product was isolated by FC.

Dimethyl 2-(1,3-Diphenylprop-2-enyl)malonate (**11**). According to the *GP*, **10a** (0.26 g) and dimethyl malonate (0.34 ml, deprotonated with NaH, dissolved in THF (12 ml)) gave, after FC (AcOEt/hexane 1:6), **11** (0.25 g, 79%) as a colorless solid. $[\alpha]_D^{r.t.} = +12.2$ ($c = 1.2$, EtOH). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.34–7.19 (*m*, 10 arom. H); 6.80 (*d*, $J = 15.8$, H–C(5)); 6.62–6.38 (*m*, H–C(4)); 4.27 (*dd*, $J = 10.8$, 8.1, H–C(3)); 3.95 (*d*, $J = 10.8$, H–C(2)); 3.70 (*s*, Me); 3.52 (*s*, Me). Determination of er: ^{1}H-NMR (200 MHz, C_6D_6; [Eu(hfc)$_3$]/**11** 8:5): separation of the MeO signal: 3.33 ppm → 3.62 and 3.57 ppm. For absolute configuration, see [33].

3-(1,3-Diphenylprop-2-enyl)pentane-2,4-dione (**12**). According to the *GP*, **10b** (0.28 g) and pentan-2,4-dione (0.31 ml, deprotonated with NaH, in THF (10 ml)) gave, after FC (AcOEt/hexane 1:6), **12** (0.23 g, 77%) as a colorless solid. $[\alpha]_D^{r.t.} = -12.0$ ($c = 1.0$, EtOH). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.36–7.18 (*m*, 10 arom. H); 6.43 (*d*, $J = 15.8$, H–C(6)); 6.25–6.17 (*m*, H–C(5)); 4.38–4.3 (*m*, H–C(3), H–C(4)); 2.25 (*s*, Me); 1.93 (*s*, Me). Determination of er: ^{1}H-NMR (200 MHz, C_6D_6; [Eu(hfc)$_3$]/**12** 2:1): separation of the MeO signal: 1.89 ppm → 4.17 and 4.13 ppm. For absolute configuration, see [32].

*Di(*tert*-butyl) 2-(1,3-Diphenylprop-2-enyl)malonate* (**13**). According to the *GP*, **10a** (0.25 g) and di(*tert*-butyl) malonate (0.67 ml, deprotonated with NaH, in THF (5 ml)) gave, after FC (AcOEt/hexane 1:6), **13** (0.44 g, 96%) as a colorless solid. $[\alpha]_D^{r.t.} = +9.0$ ($c = 1.0$, CH_2Cl_2). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.29–7.18 (*m*, 10 arom. H); 6.5–6.26 (*m*, H–C(4), H–C(5)); 4.2–4.09 (*m*, H–C(3)); 3.73 (*d*, $J = 10.9$, H–C(2)); 1.42 (*s*, *t*-Bu); 1.21 (*s*, *t*-Bu). Determination of er: ^{1}H-NMR (200 MHz, C_6D_6; [Eu(hfc)$_3$]/**13** 5:4): separation of the *t*-Bu signals: 1.34 ppm → 1.59 and 1.39 ppm. The (*R*)-configuration is assigned to **13** by analogy with the corresponding methyl ester **11**, which is the (+)-(*R*)-compound.

4,4-Bis(diphenylsulfonyl)-1,3-diphenylbut-1-ene (**14**). According to the *GP*, **10b** (0.28 g) and bis(phenylsulfonyl)methane (0.89 g, deprotonated with NaH in THF (5 ml)) gave, after FC (AcOEt/hexane 1:3), **14** (0.27 g, 52%) as a colorless solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.04–7.2 (*m*, 20 arom. H); 6.95 (*d*, $J = 15.4$, H–C(4)); 6.88 (*dd*, $J = 15.4$, 9.3, H–C(3)); 5.09 (*d*, $J = 2.4$, H–C(1)); 4.70 (*dd*, $J = 9.3$, 2.4, H–C(2)). Determination of er: HPLC: chiral column: *WHELK*®; detection: 254 nm UV detection; solvent: hexane/i-PrOH 4:1; flow rate: 1 ml/min; t_R: 42 and 54 min.

(S)-4-Methyl-4-nitro-1,3-diphenylpent-1-ene (**15**). According to the *GP*, **10a** (0.25 g) and 2-nitropropane (0.2 ml, deprotonated with NaOMe in MeOH (1.5 ml)) gave, after FC (Et_2O/hexane 1:20), **15** (0.12 g, 42%) as a colorless solid. $[\alpha]_D^{r.t.} = +22.4$ ($c = 1.0$, CH_2Cl_2). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.4–7.2 (*m*, 10 arom. H); 6.6–6.4 (*m*, H–C(1), H–C(2)); 4.17–4.09 (*m*, H–C(3)); 1.67 (*s*, Me); 1.54 (*s*, Me). Determination of er: HPLC: chiral column: *WHELK*®; detection: 254 nm UV detection; solvent: hexane/i-PrOH 200:1, flow rate: 0.5 ml/min; t_R: 35 and 38 min. The (*S*)-configuration is assigned to the major enantiomer by analogy with the products of known configuration in this series.

(S)-Benzyl(1,3-diphenylprop-1-enyl)amine (*S*)-**16**. According to the *GP*, **10a** (0.25 g) and benzylamine (0.16 ml, in THF (4 ml)) gave, after FC (AcOEt/hexane 1:10), **16** (64 mg, 19%) as a colorless solid. $[\alpha]_D^{r.t.} = +17.6$ ($c = 1.0$, $CDCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.47–7.16 (*m*, 15 arom. H); 6.59 (*d*, $J = 15.8$, H–C(3)); 6.31 (*dd*, $J = 15.8$, 7.4, H–C(2)); 4.40 (*d*, $J = 7.4$, H–C(1)); 3.83 (*d*, $J = 13.4$, PhC*H*); 3.76 (*d*, $J = 13.4$, PhC*H*); 1.7 (*s*, NH). Determination of er: $[\alpha]_D^{r.t.}$ (max) = –25.6 ($CHCl_3$), (*R*)-form. For abs. configuration, see [29a].

(S)-1,3-Diphenyl-3-(toluene-4-sulfonyl)prop-1-ene (**17**). According to the *GP*, **10a** (0.25 g) and 4-toluene-4-sulfinic acid/Na (0.53 g, in THF (5 ml)) gave, after FC (CH_2Cl_2/hexane 2:1), **17** (0.32 g, 93%) as a colorless solid. M.p. 138–139°. IR ($CHCl_3$): 3032, 1598, 1495, 1454, 1316, 1302, 1145, 1084, 963, 812, 625. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.56–7.2 (*m*, 14 arom. H); 6.63–6.5 (*m*, H–C(2), H–C(3)); 4.82 (*d*, $J = 7$, H–C(1)); 2.4 (*s*, Me). Determination of er: HPLC: chiral column: *WHELK*®; detection: 254 nm UV detection; solvent: hexane/

i-PrOH 4:1; flow rate: 1 ml/min; t_R: 18 and 23 min. The (*S*)-configuration is assigned to the major enantiomer by analogy with the products of known configuration in this series.

X-Ray Crystal-Structure Analysis of **4**. $C_{79}H_{72}Cl_2O_4P_2Pd$, colorless cube, 0.3 × 0.4 × 0.4 mm, monoclinic, space group $P2_1$, $a = 18.411$ Å, $b = 13.060$ Å, $c = 27.556$, $\beta = 91.92°$, $V = 6621.9$ Å^3, $Z = 4$, $\rho_{calc.} = 1.329$ g/cm^3, $2\theta_{max} = 50°$, MoK_α, $\lambda = 0.71073$ Å, $\omega/2\theta$ scan, $F(000) = 2752$, $T = 161$ K, 13513 refl. measured, 11408 independent refl. of which 9522 observed ($> 3\sigma(I)$), *Lorentzian* polarization correction was applied, soln. by *Patterson* method (SHELXS-86), full-matrix least-square refinement (SHELXL-93), 1345 parameters, H-atoms were added to the structure on idealized positions, final $R = 0.067$, $wR^2 = 0.1842$, rest electron density: max. 1.634 e/Å^3, min. −2.144 e/Å^3. The *Flack* parameter of the SHELXL-93 program gave the opposite of the shown chirality, but for chemical reasons and because of the relativily high R value, we decided to show in *Fig. 1* the absolute configuration derived from (*R*,*R*)-tartrate.

REFERENCES

[1] a) B. Schmidt, D. Seebach, *Angew. Chem.* **1991,** *103,* 100; *ibid. Int. Ed.* **1991,** *30,* 99; b) B. Schmidt. D. Seebach, *Angew. Chem.* **1991,** *103,* 1383; *ibid. Int. Ed.* **1991,** *30,* 1321; c) D. Seebach, L. Behrendt, D. Felix, *Angew. Chem.* **1991,** *103,* 991; *ibid. Int. Ed.* **1991,** *30,* 1008; d) J.L. v. d. Bussche-Hünnefeld, D. Seebach, *Tetrahedron* **1992,** *48,* 5719 [*Tetrahedron* Symposia-in-print No. 47 on 'Organotitanium Reagents in Organic Chemistry']; e) D. Seebach, A.K. Beck, B. Schmidt, Y.M. Wang, *Tetrahedron* **1994,** *50,* 4363 (*Tetrahedron* Symposia-in-Print No. 54 on 'Catalytic Asymmetric Addition Reactions'); f) Y.N. Ito, X. Ariza, A.K. Beck, A. Bohác, C. Ganter, R.E. Gawley, F.N.M. Kühnle, J. Tuleja, Y.M. Wang, D. Seebach, *Helv. Chim. Acta* **1994,** *77,* 2071.

[2] D. Seebach, D.A. Plattner, A.K. Beck, Y.M. Wang, D. Hunziker, W. Petter, *Helv. Chim. Acta* **1992,** *75,* 2171.

[3] B. Weber, D. Seebach, *Tetrahedron* **1994,** 50, 7473.

[4] B. Weber, D. Seebach, *Angew. Chem.* **1992,** *104,* 96; *ibid. Int. Ed.* **1992,** *31,* 84; B. Weber, D. Seebach, *Tetrahedron* **1994,** *50,* 6117 (*Tetrahedron* Symposia-in-Print No. 55 on 'Mechanistic Aspects of Polar Organometallic Chemistry').

[5] R.O. Duthaler, A. Hafner, *Chem. Rev.* **1992,** *92,* 807; A. Hafner, R.O. Duthaler, R. Marti, G. Rihs, P. Rothe-Streit, F. Schwarzenbach, *J. Am. Chem. Soc.* **1992,** *114,* 2321.

[6] a) K. Narasaka, *Synthesis* **1991,** 1; b) K. Narasaka, N. Iwasawa, in 'Organic Synthesis in Japan: Past, Present and Future', Ed. R. Noyori, Kagaku, Tokyo, 1992, pp. 283; c) K. Narasaka, N. Iwasawa, in 'Organic Synthesis: Theory and Applications', Ed. T. Hudicky, JAI, London, 1993, Vol. 2, pp. 93; d) D. Seebach, R. Dahinden, R.E. Marti, A.K. Beck, D.A. Plattner, F.N.M. Kühnle, *J. Org. Chem.* **1995,** *60,* 1788.

[7] T.A. Engler, M.A. Letavic, F. Takusagawa, *Tetrahedron Lett.* **1992,** *33,* 6731; T.A. Engler, M.A. Letavic, K.O. Lynch, Jr., F. Takusagawa, *J. Org. Chem.* **1994,** *59,* 1179; T.A. Engler, M.A. Letavic, J.P. Reddy, *J. Am. Chem. Soc.* **1991,** *113,* 5068.

[8] R. Dahinden, A.K. Beck, D. Seebach, in 'Encyclopedia of Reagents for Organic Synthesis', Ed.-in-Chief L.A. Paquette, John Wiley and Sons, Chichester, expected publication in 1995 (a copy of the manuscript may be requested from the correspondence author of the present paper); E.J. Corey, S.A. Rao, M.C. Noe, *J. Am. Chem. Soc.* **1994,** *116,* 9345; W. Adam, F. Prechtl, *Chem. Ber.* **1994,** *127,* 667; H. Schäfer, D. Seebach, *Tetrahedron* **1995,** *51,* 2305.

[9] D. Seebach, M. Hayakawa, J.-i. Sakaki, W.B. Schweizer, *Tetrahedron* **1993,** *49,* 1711 (*Tetrahedron* Symposia-in-Print No. 49 on 'Synthesis of Optically Active Compounds – Prospects for the 21st Century').

[10] E. Juaristi, A.K. Beck, J. Hansen, T. Matt, T. Mukhopadhyay, M. Simson, D. Seebach, *Synthesis* **1993,** 1271.

[11] J.-i. Sakaki, W.B. Schweizer, D. Seebach, *Helv. Chim. Acta* **1993,** *76,* 2654.

[12] B. Bosnich, Ed., Asymmetric Catalysis, NATO ASI Series E, No. 103, Martinus Nijhoff Publishers, 1986.

[13] R. Noyori, M. Kitamura, A. Pfaltz in 'Modern Synthetic Methods', Ed. R. Scheffold, Springer, Heidelberg, 1989, Vol. 5, pp. 155.

[14] S. Akutagawa, in 'Chirality in Industry', Eds. A.N. Collins, G.N. Sheldarke, and J. Crosby, John Wiley & Sons, Chichester, 1992, Chapt. 16–18, pp. 311.

[15] I. Ojima, 'Catalytic Asymmetric Synthesis', VCH, Weinheim, 1993.

[16] R. Noyori, 'Asymmetric Catalysis in Organic Synthesis', J. Wiley & Sons, New York, 1994.

[17] H. Brunner, W. Zettlmeier, 'Handbook of Enantioselective Catalysis', VCH, Weinheim, 1993.

[18] R.O. Duthaler, A. Hafner, *Chem. Rev.* **1992,** *92,* 807; M. Sawamura, Y. Ito, *ibid.* **1992,** *92,* 857; H.B. Kagan, O. Riant, *ibid.* **1992,** *92,* 1007.

[19] D. Seebach, P. B. Rheiner, A. K. Beck, F. N. M. Kühnle, B. Jaun, *Polish J. Chem.* **1994,** *68,* 2397.
[20] T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990,** *112,* 5244.
[21] Y. Uozumi, T. Hayashi, *J. Am. Chem. Soc.* **1991,** *113,* 9887; Y. Uozumi, S.-Y. Lee, T. Hayashi, *Tetrahedron Lett.* **1992,** *33,* 7185.
[22] J. A. Musnich, H. Rapoport, *J. Am. Chem. Soc.* **1978,** *100,* 4865.
[23] Review articles: O. Reiser, *Angew. Chem.* **1993,** *105,* 576; *ibid. Int. Ed.* **1993,** *32,* 547; C. G. Frost, J. Howarth, J. M. J. Williams, *Tetrahedron Asymm.* **1992,** *3,* 1089; S. A. Godleski, in 'Comprehensive Organic Synthesis', Ed. B. M. Trost, Pergamon, Oxford, 1991, Vol. 4, p. 585; B. M. Trost, *Angew. Chem.* **1989,** *101,* 1199; *ibid. Int. Ed.* **1989,** *28,* 1173; G. Consiglio, R. Waymouth, *Chem. Rev.* **1989,** *89,* 257; J. Tsuji, *Pure Appl. Chem.* **1986,** *58,* 869; J. Tsuji, in 'Organic Synthesis in Japan', Ed. R. Noyori, Kagaku Dozin, Tokyo, 1992, p. 487.
[24] B. M. Trost, T. J. Dietsche, *J. Am. Chem. Soc.* **1973,** *95,* 8200.
[25] B. M. Trost, D. J. Murphy, *Organometallics* **1985,** *4,* 1143.
[26] P. S. Pregosin, H. Rüegger, R. Salzmann, A. Albinati, F. Lianza, R. W. Kunz, *Organometallics* **1994,** *13,* 83.
[27] M. Yamaguchi, T. Shima, T. Yamaguchi, M. Hida, *Tetrahedron Lett.* **1990,** *35,* 5049.
[28] P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985,** *107,* 2033; P. B. Mackenzie, J. Whelan, B. Bosnich, *ibid.* **1985,** *107,* 2046.
[29] a) T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Am. Chem. Soc.* **1989,** *111,* 6301, *cf.* the ferrocenyl diphosphine ligands with different substitution pattern and Ph_2P/Cy_2P units used by Togni et al. [30]; b) T. Hayashi, in 'Ferrocenes' Eds. A. Togni and T. Hayashi, VCH, Weinheim, 1995, pp. 105.
[30] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994,** *116,* 4062.
[31] M. Yamaguchi, T. Shima, T. Yamagishi, M. Hida, *Tetrahedron Asymm.* **1991,** *2,* 663.
[32] T. Hayashi, A. Yamamoto, T. Hagihara, Y. Ito, *Tetrahedron Lett.* **1986,** *27,* 191.
[33] M. Yamaguchi, T. Shima, T. Yamagishi, M. Hida, *Tetrahedron Lett.* **1990,** *31,* 5049.
[34] SYBYL, TRIPOS Associates, Inc. a subsidiary of Evans & Sutherland, St. Louis, Missouri 63144, USA.
[35] T. Hayashi, *Pure Appl. Chem.* **1988,** *60,* 7.
[36] N. N. Greenwood, A. Earnshaw, 'Chemie der Elemente', 1st edn., VCH, Weinheim, 1988, pp. 1472.
[37] J. Dale, 'Stereochemie und Konformationsanalyse', VCH, Weinheim, 1978, pp. 171; R. F. Bryan, J. D. Dunitz, *Helv. Chim. Acta* **1960,** *43,* 3.
[38] A. K. Beck, B. Bastani, D. A. Plattner, W. Petter, D. Seebach, H. Braunschweiger, P. Gysi, L. LaVecchia, *Chimia* **1991,** *45,* 238.
[39] P. S. Pregosin, H. Rüegger, R. Salzmann, A. Albinati, F. Lianza, R. W. Kunz, *Organometallics* **1994,** *13,* 5040.
[40] W. S. Knowles, B. D. Vineyard, M. J. Sabacky, B. R. Stults, *Fundam. Res. Homogenous Catal.* **1978,** *3,* 537; K. E. Koenig, M. J. Sabacky, G. L. Bachman, W. C. Christofel, H. D. Barnstorff, R. B. Friedman, W. S. Knowles, B. R. Stults, B. D. Vineyard, D. J. Weinkauff, *Ann. N. Y. Acad. Sci.* **1980,** *333,* 16; W. S. Knowles, *Acc. Chem. Res.* **1983,** *16,* 106.
[41] T. Hayashi, A. Ohno, S.-j. Lu, Y. Matsumoto, E. Fukuyo, K. Yanaga, *J. Am. Chem. Soc.* **1994,** *116,* 4221.
[42] T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Am. Chem. Soc.* **1989,** *111,* 6301.
[43] T. Hayashi, H. Iwamura, Y. Uozumi, Y. Matsumoto, F. Ozawa, *Synthesis* **1994,** 526; T. Hayashi, *J. Synth. Org. Chem. Jpn.* **1994,** *52,* 900.
[44] J. Sprinz, M. Kiefer, G. Helmchen, *Tetrahedron Lett.* **1994,** *35,* 1523.
[45] a) A. Pfaltz, *Acc. Chem. Res.* **1993,** *26,* 339; b) P. von Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rüegger, P. S. Pregosin, *Helv. Chim. Acta* **1995,** *78,* 265.
[46] J. S. Giovannetti, C. M. Kelly, C. R. Landis, *J. Am. Chem. Soc.* **1993,** *115,* 4040.
[47] P. Barbaro, P. S. Pregosin, R. Salzmann, A. Albinati, R. Kunz, *Organometallics,* in press.
[48] P. S. Pregosin, R. Salzmann, *Magn. Reson. Chem.* **1994,** *32,* 128.
[49] C. Haase, C. R. Sarko, M. DiMare, *J. Org. Chem.* **1995,** *60,* 1777.
[50] K. V. Gothelf, R. G. Hazell, K. A. Jørgensen, *J. Am. Chem. Soc.* **1995,** *117,* 4435.