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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 15 (2004) 2139–2150

TETRAHEDRON: ASYMMETRY REPORT NUMBER 68

Cationic Rh-bisphosphine-diolefin complexes as precatalysts for enantioselective catalysis—what information do single crystal structures contain regarding product chirality?

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Received 23 April 2004; revised 24 May 2004; accepted 9 June 2004

Abstract—For all five-membered Rh-bisphosphine-diolefin complexes of the type $[Rh(PP)(diolefin)]^+$ as precursors for enanatioselective catalysis in the Cambridge Structural Database both the bite angle and the rotation of the diolefin are compiled and discussed, in relation to the product configuration. The bite angles are narrowly distributed and do not lead to a correlation with the product configuration. Additionally, it is not possible to discern a clear relation between the direction of rotation of the diolefin in the precatalyst and the product configuration.

Contents

1. Introduction

Particular attention in research is paid to strategies for the rational control of the selectivity of enantioselective catalysis, and a substantial part of this effort deals with the development of new ligands and catalyst systems.[1] Applications are not restricted to the academic area, as the large scale synthesis of metolachlor demonstrates.[2]

As enantioselectivity inducing ligands chelating phosphines are undoubtedly dominate. Chirality transfer from the ligand via the metal of the catalyst to the desired molecule has been widely investigated, especially for the asymmetric hydrogenation with chiral 1,2-bis(diphenylphosphino)ethane derivatives, supported by detailed conformational analyses of diolefin complexes as precatalysts.[3] The five-membered ring chelate with the transition metal is present in the λ- or δ-conformation. The orientation of the phenyl groups resulting from the favoured conformation leads to a chiral array around the transition metal, which finally affects the complexed prochiral olefin (Fig. 1). Independent on the kind of chirality in the ligand and the size of the

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doi:10.1016/j.tetasy.2004.06.036

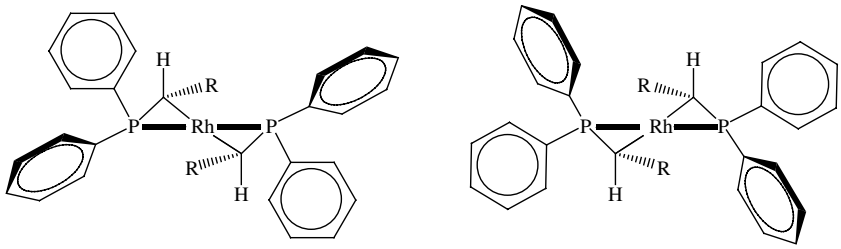


Figure 1. Ligand backbone conformation for 1,2-bis(diphenylphosphino)ethane derivatives.

chelate ring, the situation in different types of ligands is basically analogous.

A substantial feature of published X-ray structures of cationic bisphosphine-diolefin complexes of the general type $[Rh(PP)(diolefin)]^+$ is that deviations from the expected square-planar structure emerge that is the centroids of the double bonds (C_M), the phosphorus atoms of the bisphosphine and the rhodium as central atom are not in the same plane.

Already in 1977, from X-ray analyses of [Rh(CHIRAPHOS)(COD)]ClO_4 (CHIRAPHOS = 2,3-bis(diphenylphosphino)butane, COD = (*ZZ*)-cycloocta-1,5-diene) it could be shown that characteristic distortions towards a tetrahedral geometry occur.[4] Consequently, the diolefin can either adopt in clockwise twist (Fig. 2, right) or anticlockwise twist (Fig. 2, left).

Kyba and Davis et al. developed the idea that 'the forces, which cause this nonideal diene orientation, be they steric or electronic, presumably would be those, which would lead to enantioface differentiation in a prochiral olefin.' At the same time, a correlation between the direction of rotation of the diolefin and the chirality of the phosphine ligand was suspected.[6] For ligands of the DuPHOS type it could be shown that a clockwise twist orientation of the diolefin in the precatalyst obviously leads to (*S*)- and an anticlockwise twist orientation to (*R*)-amino acid derivatives in asymmetric hydrogenation.[7] Following these ideas one would expect that for a given chiral ligand the direction of rotation of the diolefin does not depend on the diolefin itself.

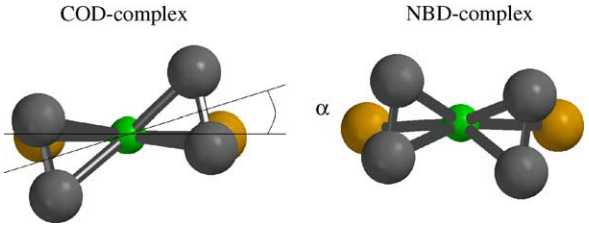


Figure 2. Tetrahedral distortion of the ideal square-planar arrangement for [Rh(SKEWPHOS)(diolefin)]BF_4 from the direction of the diolefin.[5] (From the ligands only the double bonds of the diolefin [COD and NBD (NBD = norborna-2,5-diene), respectively], and the phosphorus atoms of the phosphine ligand are shown.)

However, the X-ray analyses of the diolefin complexes with the ligands Et-DuPHOS (1,2-bis(2,5-diethylphospholano)benzene),[8] SKEWPHOS (2,4-bis-(diphenylphosphino)pentane)[5] and CYC-PROPRAPHOS ((*S*)-2,3-O,N-bis(diphenylphosphino)-1-(naphthoxy)-2-hydroxy-3-cyclohexylaminopropane),[9] respectively, show that COD and NBD exhibit opposite directions of rotation (see Fig. 1 for SKEWPHOS). A very interesting example is the X-ray analysis of η^2,η^2-1,5-cyclooctadiene-1(*S*),2(*S*)-cyclopentane-1,2-diylbis(dicyclohexylphosphine)-rhodium(I) trifluoromethanesulfonate containing two cations in the asymmetric unit. For the COD a clockwise twist orientation (21.5°) is observed for one cation, for the second one present in the same asymmetric unit one finds the opposite anticlockwise twist orientation (17.4°) of the diolefin! In both cases the ligand backbone has a δ-conformation.[10] The causes of such unusual behaviour are unclear, but they could originate from the cyclohexyl residues. However, possible influences of packing effects should not be underestimated.[11]

A characteristic feature for phosphine ligands is the so-called bite angle.[12] It was recently reported that changes in the ligand backbone—replacement of the 1,2-phenylene bridge in Me-DuPHOS with maleic anhydride—on the one hand alter the bite angle of the complex and on the other hand influence the enantioselectivity of the asymmetric hydrogenation.[13]

Herein for all five-membered Rh-bisphosphine–diolefin complexes of the type $[Rh(PP)(diolefin)]^+$ in the Cambridge Structural Database (CSD version 5.25; 11. 2003) with complete atom positions both the bite angle and the rotation of the diolefin are compiled and discussed.

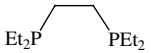
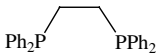
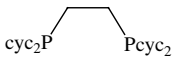
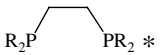
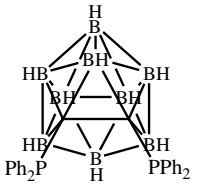
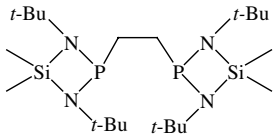
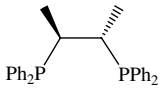
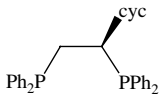
2. Results and discussion

In Table 1 the data of 29 different structures from the Cambridge Structural Database as well as data of eight further X-ray analyses that are prepared within the framework of this paper are listed. Because there is more than one cation in the asymmetric unit for several compounds there are 50 crystal structures altogether.[14]

2.1. Bisphosphine coordination

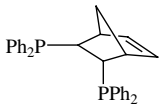
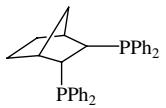
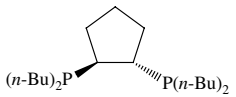
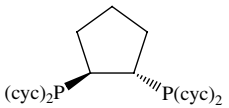
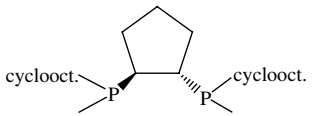
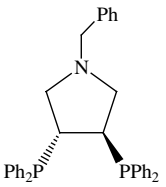
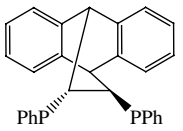
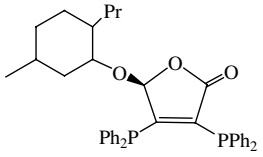
The bite angle on average lies at 84.3° for all structures considered and varies in a narrow range, independent of

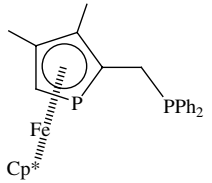
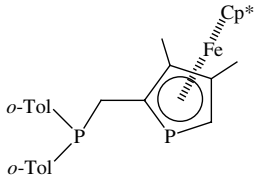
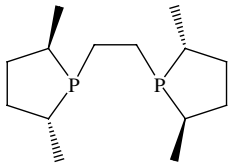
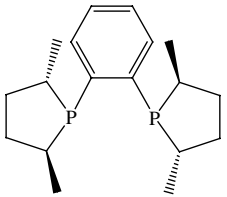
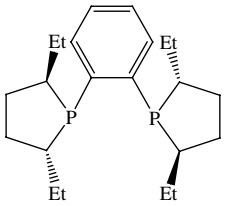
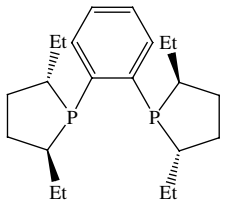
Table 1. Selected structural data for five-membered ring chelates of the type [Rh(PP)(diolefin)]$^+$ (distances in angstrom, angles in degree)[15]

No	Ligand	CSD chiral., conformat.	Diolefin anion	P–Rh	C–Rh first bond	C–Rh second bond	Centroid-Rh	P–Rh–PC_M–Rh–C_M	C_M–Rh–P	P–Rh–P/C_M–Rh–C_M	Lit.
1		—	COD	2.281	2.242	2.254	2.140	83.9	95.6	0.7	
		—, —	BF_4	2.283	2.255	2.263	2.148	85.2	95.3	—	Ref. 16
2		—	COD	2.291	2.238	2.250	2.137	83.2	96.6	8.3	This work
		—, —	BF_4	2.267	2.236	2.238	2.129	85.2	95.2	Clockwise	Ref. 17
		—	NBD	2.290	2.207	2.237	2.116	83.9	106.0	1.3	This work
3		—, —	BF_4	2.268	2.207	2.209	2.099	69.4	100.7	—	Ref. 17
4		XEMXUI	COD	2.308	2.233	2.252	2.132	83.7	96.6	8.0	
		—, —	BF_4	2.300	2.229	2.241	2.127	85.4	94.7	Clockwise	Ref. 18
		XEMXOC	NBD	2.308	2.195	2.217	2.097	85.0	102.9	8.5	
5		—, —	BF_4	2.309	2.200	2.209	2.096	69.3	103.2	Anticlockwise	Ref. 18
6		MOFFOC	COD	2.273	2.204	2.276	2.127	82.4	97.1	13.1	
		—, —	$B(Ph)_4$	2.272	2.224	2.263	2.140	86.2	95.5	Clockwise	Ref. 19
7		TOMHUY I[20]	COD	2.289	2.309	2.319	2.199	85.3	95.9	10.4	
		—, —	Boran	2.284	2.240	2.262	2.145	85.4	94.2	—	Ref. 21
		TOMHUY II	COD	=	2.218	2.263	2.133	=	94.9	12.8	
		—, —	Boran	=	2.290	2.293	2.203	86.7	94.2	—	Ref. 21
8		LUNHIL	COD	2.247	2.302	2.304	2.204	87.4	94.5	2.8	
		—, —	BF_4	2.252	2.301	2.312	2.211	83.2	94.9	Clockwise	Ref. 22
9		OCPBRH	COD	2.275	2.242	2.247	2.138	83.8	95.8	9.1	
		(*S*,*S*), δ	ClO_4	2.266	2.237	2.248	2.137	85.2	95.8	Anticlockwise	Ref. 4
		—	COD	2.280	2.228	2.241	2.129	83.8	96.1	9.8	This work
10		(*S*,*S*), δ	BF_4	2.285	2.225	2.242	2.128	85.6	95.1	Anticlockwise	Ref. 17
		PNOBRH 01 A	NBD	2.286	2.031	2.139	2.004	83.5	101.9	4.4	
		(*R*), λ	ClO_4	2.283	2.269	2.283	2.190	70.3	104.4	Clockwise	Ref. 23
11		PNOBRH 01 B	NBD	2.283	2.113	2.161	2.014	84.8	101.7	5.8	
		(*R*), λ	ClO_4	2.291	2.131	2.248	2.089	69.7	103.4	Clockwise	Ref. 23
		PNOBRH 02	NBD	2.286	2.189	2.195	2.082	84.2	98.9	5.2	
		(*R*), λ	ClO_4	2.323	2.236	2.249	2.134	69.7	107.3	Clockwise	Ref. 23

(*continued on next page*)

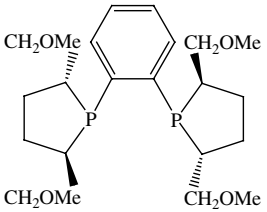
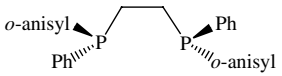
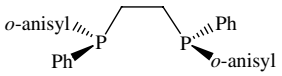
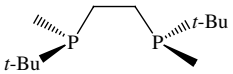
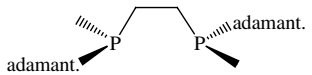
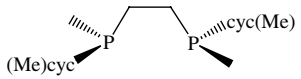
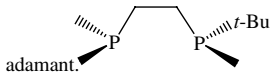
Table 1 (*continued*)

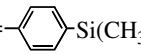
No	Ligand	CSD chiral., conformat.	Diolefin anion	P–Rh	C–Rh first bond	C–Rh second bond	Centroid-Rh	P–Rh–PC_M–Rh–C_M	C_M–Rh–P	P–Rh–P/C_M–Rh–C_M	Lit.
12		BAVSAS (*S*,*S*), δ	NBD ClO^4	2.321 2.320	2.183 2.208	2.195 2.212	2.081 2.101	86.4 70.4	101.1 102.3	4.7 Anticlockwise	Ref. 6a
13		CEJJEG (*R*,*R*), λ	NBD ClO_4	2.325 2.323	2.189 2.205	2.201 2.218	2.084 2.102	86.3 70.6	101.1 102.0	3.3 Clockwise	Ref. 6b
14		CIQJER A (*S*,*S*), δ CIQJER B (*S*,*S*), δ	COD CF_3SO_3 COD CF_3SO_3	2.311 2.308 2.313 2.303	2.228 2.246 2.244 2.240	2.247 2.261 2.250 2.253	2.130 2.150 2.146 2.145	84.5 85.3 84.6 85.6	95.0 95.7 95.6 94.9	7.8 Anticlockwise 9.3 Anticlockwise	Ref. 10 Ref. 10
15		CIQJIV A (*S*,*S*), δ CIQJIV B (*S*,*S*), δ	COD CF_3SO_3 COD CF_3SO_3	2.332 2.330 2.327 2.331	2.204 2.295 2.231 2.208	2.213 2.222 2.246 2.255	2.099 2.154 2.133 2.119	84.9 85.1 86.2 84.5	94.7 97.5 95.7 97.1	17.4 Anticlockwise 21.5 Clockwise	Ref. 10 Ref. 10
16		CIQJOB (*S*,*S*), δ	COD CF_3SO_3	2.305 2.316	2.217 2.228	2.226 2.238	2.116 2.135	84.3 84.4	95.5 95.8	1.4 Anticlockwise	Ref. 10
17		SACHIN (*R*,*R*), λ	COD BF_4	2.316 2.285	2.226 2.214	2.245 2.235	2.133 2.120	84.6 85.6	96.3 93.5	2.9 Anticlockwise	Ref. 24
18		YERKIP 01 (*R*,*R*), λ	COD BF_4	2.311 2.287	2.235 2.257	2.247 2.260	2.132 2.150	85.2 85.8	94.9 94.2	4.1 Clockwise	Ref. 25
19		VAZDUV A, (5*S*), — VAZDUV B (5*S*), —	COD PF_6 COD PF_6	2.290 2.277 2.276 2.279	2.227 2.247 2.260 2.258	2.243 2.254 2.275 2.327	2.127 2.132 2.162 2.191	85.3 86.8 86.4 85.1	94.5 93.3 93.4 95.3	3.8 Clockwise 5.3 Anticlockwise	Ref. 26 Ref. 26

20		OCOVUX (R_p), —	COD PF_6	2.254 2.302	2.225 2.188	2.240 2.199	2.126 2.084	80.2 86.6	101.0 94.4	16.9 Clockwise	Ref. 27
21		NERGEW (S_p), —	COD ClO_4	2.224 2.313	2.202 2.203	2.239 2.247	2.123 2.113	82.3 86.3	96.6 96.0	17.4 Clockwise	Ref. 28
22		JEWZOA (*R*,*R*), δ	COD SbF_6	2.259 2.276	2.209 2.211	2.267 2.273	2.134 2.140	83.3 85.1	97.2 97.3	19.4 Anticlockwise	Ref. 29
23		HASWAZ (*S*,*S*), —	COD SbF_6	2.263 2.273	2.235 2.214	2.269 2.259	2.145 2.130	84.7 84.8	96.4 96.6	17.8 Clockwise	Ref. 30
24		—	COD	2.278	2.206	2.280	2.115	84.7	96.4	16.4	This work
		(*S*,*S*), —	BF_4	2.268	2.214	2.257	2.133	85.0	96.0	Clockwise	Ref. 17
25		TUVBUH (*S*,*S*), —	NBD BF_4	2.265 2.275	2.205 2.223	2.228 2.232	2.106 2.120	84.6 69.1	103.7 102.8	8.8 Clockwise	Ref. 31
26		QIXDIK (*R*,*R*), —	COD BF_4	2.291 2.262	2.236 2.223	2.297 2.243	2.166 2.098	85.3 85.0	98.3 94.8	21.1 Anticlockwise	Ref. 8
27		MOQVIX A (*R*,*R*), —	COD BARF	2.239 2.275	2.157 2.235	2.352 2.243	2.155 2.128	85.4 84.0	97.9 96.4	21.8 Anticlockwise	Ref. 32
		MOQVIX B (*R*,*R*), —	COD BARF	2.268 2.276	2.139 2.238	2.217 2.280	2.068 2.155	85.2 87.0	95.1 96.9	22.6 Anticlockwise	Ref. 32
28		QIXDEG A (*S*,*S*), —	NBD BF_4	2.297 2.275	2.243 2.199	2.250 2.211	2.140 2.099	84.5 68.9	103.8 103.0	6.1 Anticlockwise	Ref. 8
		QIXDEG B (*S*,*S*), —	NBD BF_4	2.288 2.277	2.222 2.145	2.254 2.230	2.131 2.085	84.7 69.1	104.7 103.0	15.0 Anticlockwise	Ref. 8

(*continued on next page*)

Table 1 (*continued*)

No	Ligand	CSD chiral., conformat.	Diolefin anion	P–Rh	C–Rh first bond	C–Rh second bond	Centroid-Rh	P–Rh–PC_M–Rh–C_M	C_M–Rh–P	P–Rh–P/C_M–Rh–C_M	Lit.
29		CACNAW	COD	2.285	2.207	2.283	2.139	84.4	97.7	21.8	Ref. 33
		(*R*,*R*), —	BF_4	2.265	2.210	2.250	2.123	85.8		Clockwise	
30		—	NBD	2.270	2.231	2.245	2.133	84.5	104.8	22.2	Ref. 34
		(*R*,*R*), —	BF_4	2.258	2.173	2.200	2.076	69.6	102.9	Clockwise	
31		SULMUH A	NBD	2.312	2.224	2.240	2.130	83.6	106.0	3.3	
		(*R*,*R*), δ	PF_6	2.273	2.164	2.191	2.069	69.3	101.1	Anticlockwise	Ref. 35
		SULMUH B	NBD	2.291	2.227	2.236	2.126	84.4	102.8	6.1	
		(*R*,*R*), δ	PF_6	2.292	2.193	2.229	2.101	70.0	103.0	Clockwise	Ref. 35
		SULMUH C	NBD	2.290	2.204	2.232	2.106	83.9	103.5	7.5	
		(*R*,*R*), δ	PF_6	2.284	2.181	2.209	2.092	69.7	102.5	Clockwise	Ref. 35
32		—	COD	2.282	2.218	2.250	2.128	82.7	104.8	9.5	This work
		(*R*,*R*), λ	BF_4	2.280	2.210	2.239	2.115	85.7	102.9	Clockwise	Ref. 17
33		—	NBD	2.295	2.209	2.213	2.104	83.8	102.8	3.4	This work
		(*S*,*S*), δ	BF_4	2.300	2.204	2.222	2.103	69.5	103.8	3.4	Ref. 17
34		NIFRID	NBD	2.314	2.216	2.220	2.111	83.3	104.0	3.9	
		(*R*,*R*), λ	BF_4	2.299	2.200	2.221	2.101	69.3	103.5	Clockwise	Ref. 36
35		QIXFAE A	NBD	2.296	2.199	2.204	2.088	83.8	101.2	8.6	
		(*R*,*R*), λ	BF_4	2.302	2.230	2.235	2.124	71.2	103.9	Clockwise	Ref. 37
		QIXFAE B	NBD	2.303	2.213	2.220	2.109	83.3	103.4	7.9	
		(*R*,*R*), λ	BF_4	2.304	2.194	2.218	2.098	69.6	104.0	Clockwise	Ref. 37
		QIXFAE C	NBD	2.309	2.226	2.236	2.126	83.6	105.4	9.3	
		(*R*,*R*), λ	BF_4	2.293	2.211	2.216	2.098	69.2	102.3	Clockwise	Ref. 37
36		QIXFEI	NBD	2.305	2.214	2.227	2.113	83.0	105.9	7.0	
		(*R*,*R*), λ	BF_4	2.302	2.184	2.225	2.096	70.1	101.2	Clockwise	Ref. 37
37		MIQSAG 01 A	NBD	2.309	2.198	2.207	2.096	82.9	100.1	10.4	
		(*R*,*R*), λ	BF_4	2.317	2.213	2.232	2.109	70.0	107.1	Clockwise	Ref. 38
		MIQSAG 01 B	NBD	2.296	2.246	2.257	2.141	83.8	103.3	9.1	
		(*R*,*R*), λ	BF_4	2.301	2.255	2.269	2.152	69.6	103.8	Clockwise	Ref. 38

*: R=  $Si(CH_3)_2CH_2CH_2C_6F_{13}$.

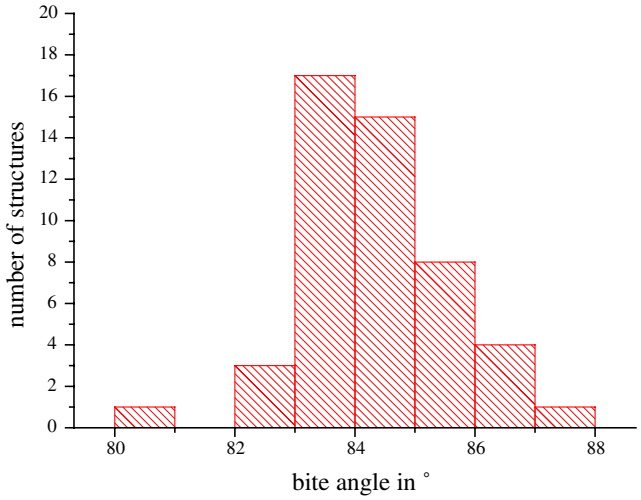


Figure 3. Distribution of bite angles as a function of the number of structures according to Table 1.

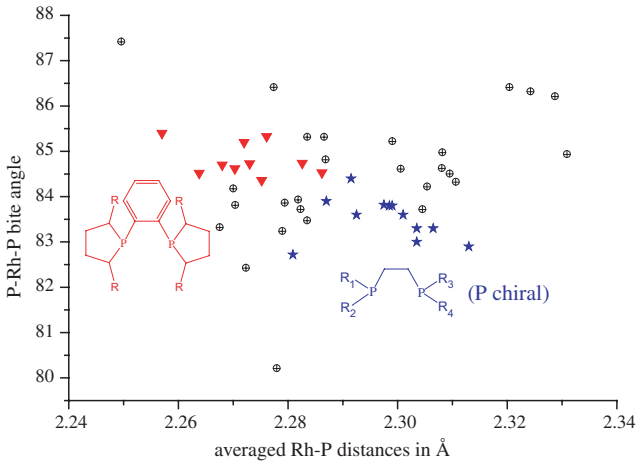


Figure 4. Bite angles as a function of the each averaged Rh–P bond lengths.

whether the complex is chiral or achiral. Figure 3 illustrates the distribution as a bar diagram. The smallest bite angle shows η^2,η^2-cycloocta-1,5-diene-2-(diphenylphosphinomethyl)-1′,2′,3,3′,4,4′,5′-heptamethyl-1-phosphaferrocene-P,P′-rhodium(I) hexafluorophosphate (OCOFUX) with 80.2°, the largest one η^4-cyclo-octadiene-1,2-bis (1,3-di-*t*-butyl-4,4-dimethyl-1,3-diaza-2-phospha-4-siletidin-2-yl)ethane-rhodium(I) tetrafluoroborate (LUNHIL) with 87.4°.

The distances Rh–P for all listed complexes lie in a narrow range between 2.224 and 2.332 Å, the mean value is 2.290 Å. While both of the Rh–P bonds in complexes containing C_2-symmetric ligands essentially have the same length, a few complexes with C_1-symmetric ligands sometimes show distinctly varying bond lengths. Most marked is this difference for the planar chiral η^2,η^2-cycloocta-1,5-diene-2-(di-*o*-tolylphosphinomethyl)-3,4-dimethyl-1-phosphaferrocene-P,P′-rhodium perchlorate (NERGEW), with an sp^3 and an sp^2 hybridized phosphorus atom in the ligand. The complex provides an efficient catalyst for the enantioselective isomerization of allylic alcohols.

No reasonable correlation between the bite angle and each averaged Rh–P bond length can be recognized (Fig. 4). However, for specific classes of ligands 'islands' emerge.

In Table 2 bite angles for all known X-ray structures of DuPHOS type ligands are compiled. Independent of three different anions, on the diolefins COD and NBD as well as on other η-coordinating ligands such as benzene and toluene, respectively, a mean value of 84.7° results with a very narrow distribution; the variance is not higher than for examples with several cations in the asymmetric unit. On the other hand, it could be shown that for a few other complexes from Table 2 the enantioselectivities of asymmetric hydrogenations can be very different even with almost equal bite angles.[33] Therefore, it does not seem to be reasonable to associate differences in the enantioselectivity to differences in the bite angle.

Table 2. Bite angle for structures with ligands of the DuPHOS type

Complex	Bite angle (deg)	Literature
[Rh(Me-DuPHOS)(COD)]SbF_6	84.7	Ref. 30
[Rh(Me-DuPHOS)(COD)]BF_4	84.7	Ref. 17
[Rh(Me-DuPHOS)(NBD)]BF_4	84.6	Ref. 31
[Rh(Me-DuPHOS)(toluene)]BF_4	84.9	Ref. 39
[Rh(Et-DuPHOS)(COD)]BF_4	85.3	Ref. 8
[Rh(Et-DuPHOS)(NBD)]BF_4	84.5/84.7	Ref. 8
[Rh(Et-DuPHOS)(COD)]BARF	85.4/85.2	Ref. 32
[Rh(Et-DuPHOS)(benzene)]BF_4	84.5	Ref. 39
[Rh(BASPHOS)(COD)]BF_4	84.4	Ref. 33
[Rh(BASPHOS)(NBD)]BF_4	84.5	Ref. 34

2.2. Diolefin coordination

In terms of the rhodium–diolefin bonds one can summarize the following: Only a few structures (e.g., OCPBRH) exhibit similar distances for all four C-atoms. In general, unequal bond lengths for the particular Rh–C distances (compare e.g., the DuPHOS derivatives) certainly correlate with deviations from the ideal square-planar structure discussed below.

The dependence of the C_M–Rh–C_M angle over all four values averaged Rh–C bond lengths for COD and NBD, respectively, is represented in Figure 5 for all complexes from Table 1. As expected the angles for a diolefin hardly vary and the smaller NBD shows a smaller C_M–Rh–C_M angle than COD. Moreover, Figure 5 indicates over which ranges the average lengths of the Rh–C bonds vary. On average the bond lengths in NBD complexes are shorter. Nevertheless, an overlapping sector for COD and NBD complexes can clearly be seen. In other words, in spite of significant differences of the C_M–Rh–C_M angle a few COD and NBD complexes show the same average Rh–C bond lengths.[40]

As already mentioned, most crystal structures show a deviation from the ideal square-planar arrangement. A more detailed consideration of the present structures shows that there are also other deviations from the

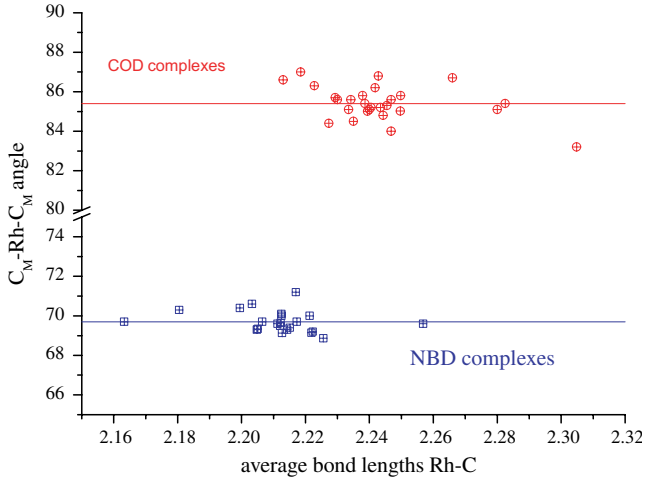


Figure 5. Average Rh–C bond lengths for the diolefins as a function of the C_M–Rh–C_M angle. (The parallel line to the *x*-axis correspond to the averaged C_M–Rh–C_M angle; 85.4° for COD and 69.7° for NBD complexes, respectively.)

square-planar structure occurring than the tetrahedral distortion. If one defines the ideal square-planar arrangement according to Figure 6 as the *x*/*y* plane with rhodium in the point of origin, the tetragonal distortion corresponds to the rotation of the diolefin around the *y*-axis. The similarly possible rotation around the *x*-axis results in a square-pyramidal arrangement with the rhodium atom at the top of the pyramid.[41] To conclude, a rotation of the diolefin around the *z*-axis is also imaginable, it leads to a situation in which the two P–Rh–C_M angles become dissimilar. All three disturbances influence and depend on each other. Thus, without the expenditure of trigonometric considerations there is no simple quantification possible, nonetheless the tetrahedral distortion is generally the most remarkable one and is therefore considered exclusively in the following discussion.

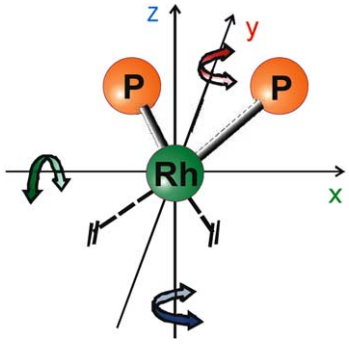


Figure 6. Square-planar [Rh(PP)(diolefin)]$^+$ complex in the *x*/*y*-plane, rhodium in the point of origin.

This tetrahedral distortion, a 'twist' of the diolefin, is generally explained by steric demands of the phosphine ligand. Comparison of the angle of the tetrahedral distortion for the normal compound of the 1,2-bis(phosphino)ethane with three different residues defined in Figure 2, entries 1, 2 and 4 in Table 1, confirms this assumption. The angle enclosed by the planes P–Rh–P and C_M–Rh–C_M, respectively, increases for the COD complexes, according to the steric demand of the functional groups, from ethyl (0.7°) to phenyl (8°) and cyclohexyl (8°), respectively.

Considering the ligands Me-BPE and Me-DuPHOS as examples, Burk et al. discussed distances between relevant C-atoms of the diolefin and the C-atoms of the chiral ligand from X-ray structures.[30] To estimate the presumed steric gain resulting from the rotation of the diolefin we were interested in the comparison to the ideal square-planar structure. Using the program Spartan[42] we traced back the distortion around the rhodium as the centre of rotation to the square-planar structure to obtain these distances at least qualitatively.

Because this simple procedure is only reasonable, if the chiral ligand is not influenced in its geometry, for these mediations we considered only to Me-DuPHOS whose ligand backbone is considered to be fixed. The spatially shortest distances for the X-ray structure of [Rh(Me-DuPHOS)COD]BF_4 (no 24 from Table 1) are shown on the left in Figure 7. The shortest distances between COD and Me-DuPHOS are firstly the distances to the methyl substituents at the phospholane ring and secondly the opposing distance to the asymmetric centre result.[43] Comparison with the 'virtual' square-planar structure, central picture in Figure 7, reveals distinctly shorter distances for all examined lengths. Thus, the practically observed rotation of COD leads to a lesser steric demand. If one increases the angle α greater than that observed in the X-ray structure, the steric pressure would continue decreasing, but the overlapping of relevant orbitals for the binding of the ligand to the rhodium atom would become more unfavourable. Obviously, the tetrahedral distortion in the observed

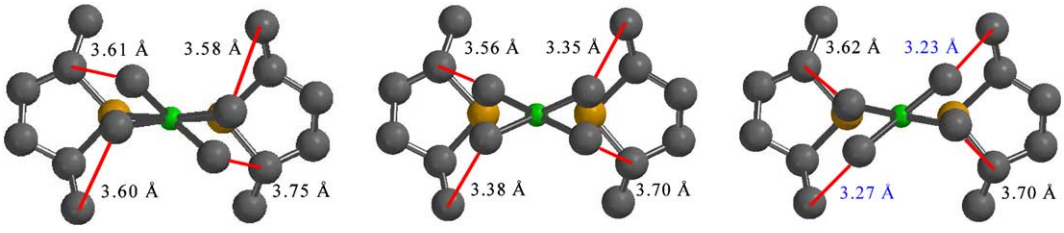


Figure 7. Each shortest C–C distances between COD and Me-DuPHOS (–) for [Rh(Me-DuPHOS)COD]BF_4. (Left: X-ray structure with clockwise twist arrangement of COD, centre: square-planar arrangement (Spartan), right: anticlockwise twist arrangement (Spartan)).

structures forms an optimum between mutual steric avoidance of the ligands and the binding of these ligands to the central atom, in as far as packing effects can be neglected. However, this simple view does not explain the direction of the rotation of the diolefins. To answer this question we turned the diolefin in the above-mentioned way beyond the square-planar structure by the same amount as observed in the original structure but in the opposite direction, right in Figure 7. Surprisingly, the distances of the methyl groups on the phospholane rings pointing to the diolefin again decrease in relation to the 'square-planar' arrangement, and therefore become sterically less favourable. Accordingly, the direction of rotation of the diolefin is clearly understood and obviously not random.

Entirely analogous considerations result for the NBD complex of Me-DuPHOS (no 25 from Table 1; TUVBUH). The only difference to the COD complex is the fact that the values of the shortest distances between NBD and the phospholane ligand are higher. In other words, the NBD has to rotate less to achieve a similar steric relief as the COD complex. Thus, the tetrahedral distortion for NBD complexes should always be smaller than for the analogous COD complexes.[44] In published structures of COD and NBD complexes with seven-membered ring chelates this expectation is confirmed.[9,45]

In this context it may be noted that the rate constants for the hydrogenation of the diolefins COD and NBD, respectively, systematically differ as well. The NBD complex in all observed systems is hydrogenated remarkably faster, which is especially marked for five-membered ring chelates.[8,46] A higher tetrahedral distortion possibly results in a hindrance of the oxidative addition of hydrogen from the axial position, because an optimal orbital overlapping seems to be restricted.

As already mentioned in the introduction, in the literature a correlation between the direction of rotation and the chirality of the product for asymmetric hydrogenations is assumed. Therefore, below for each listed structure in Table 1, the directions of rotation are analyzed.

For ligands containing phenyl substituents on the phosphorus atom an anticlockwise twist orientation of the diolefin for the δ-conformation but a clockwise twist orientation for the λ-conformation is expected following Figure 1, because of steric reasons. Examination of Table 1 shows[47] that almost all the complexes employed as hydrogenation catalysts that contain ligands with stereogenic C-atoms in the ethylene bridge come up to expectations: the δ-conformation shows the anticlockwise twist orientation of the diolefin while the λ-conformation leads to a clockwise twist.[48] Only DEGUPHOS® (SACHIN) is exceptional. The (*R*,*R*)-Me-BPE (JEWZOA) shows the typical anticlockwise twist orientation of the diolefin linked to the δ-conformation and thus presents the connection to the phenyl bridged DuPHOS derivatives. Except for [Rh(Et-DuPHOS)NBD]$^+$ (QIXDEG) all the (*R*,*R*)-derivatives principally show the anticlockwise twist orientation and the (*S*,*S*)-derivatives the clockwise twist for the diolefin. (Note the apparent inversion at the BASPHOS complexes caused by the change of priority in the CIP rules.) Finally, even the P-chiral complexes (entries 31–37)—except SULMUH[47]—show the typical clockwise twist orientation of the diolefin for the λ-conformation and the anticlockwise twist orientation for the δ-conformation.

Summarizing this aspect, the theory already mentioned in literature can be confirmed for the vast majority of the X-ray structures, in which the λ-conformation and the appropriate (*S*,*S*)-enantiomers of the DuPHOS-ligands, respectively, leads to a clockwise twist orientation, but in contrast the δ-conformation to an anticlockwise twist orientation of the diolefin.

The complexation of the prochiral substrates of interest repeated within the framework of the catalytic cycle underlies analogous steric conditions as the binding of the diolefins. In that case it would be reasonable to consider known catalyst–substrate complexes with reference to the arrangement of the prochiral olefin at the bisphosphine–rhodium complex in more detail.

Following the fundamental work of Halpern, Landis and Brown, the minor substrate complex leads to the main product because of its high reactivity.[49,50] An important support of this major–minor concept (antilock and key, respectively), are two X-ray structures of major substrate complexes.[49a,e] However in the case of a chiral P/S ligand it has very recently been shown that the major substrate complex leads to the major product. Thus the major–minor concept appears not to be generally valid.[51]

We succeeded in crystallizing a further catalyst–substrate complex with a DOPA derivative: [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl-propenoat)]BF_4 (Fig. 8). By analogy to the known examples the substrate is bound to the rhodium centre via the amide oxygen as well as the double bond of the olefin. The asymmetric hydrogenation in MeOH at 25 °C under normal pressure with (*S*,*S*)-DIPAMP as

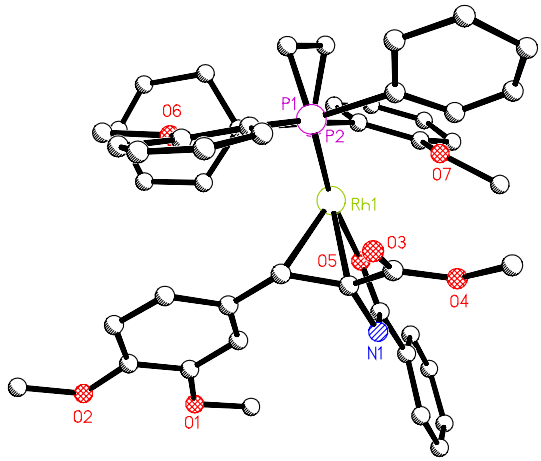


Figure 8. X-ray structure of [Rh((*S*,*S*)-DIPAMP)((*Z*)-2-benzoylamino-3-(3,4-dimethoxyphenyl)-methyl-propenoat)]BF_4.[17]

Table 3. Data from X-ray structures of catalyst–substrate complexes

Ligand	Conformation	Direction of olefin rotation	Bite angle (deg)	Substrate/product chirality from the substrate complex	P–Rh–P/C_M–Rh–C_M
(*S*,*S*)-CHIRAPHOS[52]	δ	Anticlockwise	83.1	EAC (*S*)	18.8°
(*R*,*R*)-DIPAMP	λ	Clockwise	83.1	MPAA (*R*)	30.2°
(*S*,*S*)-DIPAMP[17]	δ	Anticlockwise	83.3	DOPA-derivative (*S*)	21.4°

the chiral ligand leads to an enantiomeric excess of 98.2 % in favour of the (*R*)-configured hydrogenation product. On the other hand the formal addition of hydrogen to the isolated intermediate shown in Figure 8 results in the (*S*)-enantiomer! Hence, this system again acts as expected from the major–minor concept.

In Table 3 relevant data of known catalyst–substrate complexes with prochiral olefins are compiled. Contrary to the diolefin complexes the double bonds are not arranged perpendicularly to the O–(amide)–Rh–C_M plane. As expected, clear tetrahedral distortion can be seen as deviations from the ideal square-planar structure.

The correlation found for the diolefin complexes between conformation and direction of rotation of the now prochiral olefin is confirmed; δ- and anticlockwise twist as well as λ-conformation and clockwise twist belong together. Surprisingly, all the structures compiled in Table 1 concern the major substrate structures, which do not lead to the excess enantiomer! Moreover it may be remarked, that the conformation of the substrate complexes as well as the chirality of the product originating from the same substrate complexes is opposite to the λ/δ rule in all the three cases. Regarding this empirical rule the λ-conformation leads to the (*S*)-product and the δ-conformation to the (*R*)-product.[53]

However, it cannot be predicted with certainty, which direction of rotation is to be expected for the actually interesting diastereomeric minor substrate complexes. If they show the same direction of rotation as the major substrate complexes a correlation between sense of rotation and product chirality is not reasonable. Even if the sense of rotation was contrary to the major substrate complexes, a model for the hydrogenation to correlate the sense of rotation of the diolefin and the configuration of the product would be necessary! Still, one cannot assume that for single catalyst/substrate systems the as proved seen major–minor concept has a generally valid character.[54]

Accordingly, one could understand that each one of the crystal structures by Imamoto et al. (entries 34–37 in Table 1) showing clockwise twist arrangement of the diolefin does not lead to the (*S*)-amino acid derivatives as expected from the theory proposed.[7]

3. Conclusion

Both the bite angle and the direction of rotation of the diolefins have been analyzed for 37 different X-ray structures with 50 cations of five-membered ring chelates of the general type $[Rh(PP)(diolefin)]^+$, which provide precatalysts for enantioselective catalyses such as the asymmetric hydrogenation.

The bite angle is narrowly distributed and does not correlate with the product configuration. For the coordination of the diolefin it could be shown that, besides other possible influences, tetrahedral distortions from the expected ideal square-planar arrangement predominate. Regarding the resulting direction of rotation it could be confirmed that steric demands of the phosphine ligand lead to a clockwise twist and an anticlockwise twist orientation of the diolefin, respectively. Most of the structures show that the δ-conformation and the appropriate (*R*,*R*)-DuPHOS derivatives, respectively, lead to an anticlockwise twist orientation of the diolefin while a λ-conformation leads to a clockwise twist. In fact, known major catalyst–substrate complexes show analogous behaviour but do not lead to the excess enantiomer in asymmetric hydrogenations. Hence, a clear relation between the direction of rotation of the diolefin in the precatalyst and the product configuration cannot be found.

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