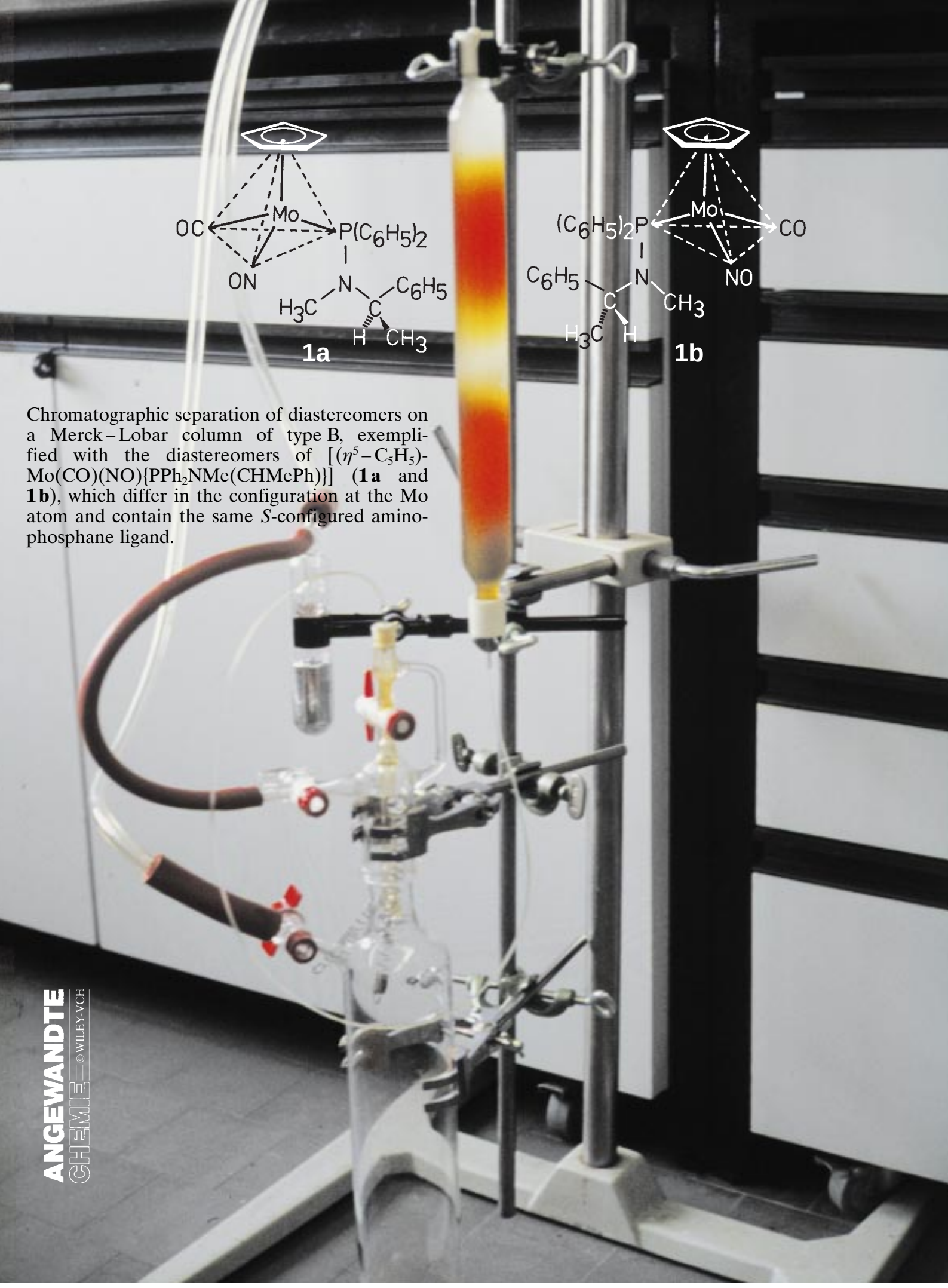

Chromatographic separation of diastereomers on a Merck–Lobar column of type B, exemplified with the diastereomers of $[(\eta^5-C_5H_5)$-Mo(CO)(NO){$PPh_2NMe(CHMePh)$}] (**1a** and **1b**), which differ in the configuration at the Mo atom and contain the same *S*-configured aminophosphane ligand.

Optically Active Organometallic Compounds of Transition Elements with Chiral Metal Atoms

Henri Brunner*

Dedicated to Professor Helmut Werner on the occasion of this 65th birthday

Chemistry is stereochemistry. In transition metal chemistry the optically active tris-chelating complexes, which have been known since the beginning of this century, were supplemented over the last thirty years by organometallic half-sandwich complexes of three- and four-legged piano-stool structure whose metal atom is stereogenic ("chiral transition metal atoms"). A few of the new optically active compounds proved to be configurationally stable at the metal atom even at higher temperatures. These complexes have been tools in the elucidation of the spatial course of follow-up reactions, as shown in the 1930s by Hughes and Ingold for nucleophilic substitution at a carbon atom. There is still much to do in this area. Some of the other new optically active compounds are configurationally labile at the metal and racemize or epimerize in solution. In these cases the mechanism of the change of configuration at the metal atom and the resulting intermediates can be investigated. Complexes that are configurationally stable at the metal atom could be used as optically active auxiliaries in organic synthesis. An example is the enolate chemistry of the commercially available compounds (+)- and (−)-[(η^5-C_5H_5)Fe(CO)(PPh_3)(COMe)]. Chiral metal atoms also play a role in enantioselective catalysis. The metal centers often become stereogenic in the catalytic cycle of metal-catalyzed reactions. Their chirality usually disappears upon product cleavage in the final reductive elimination of the cycle. However, it is regained in the next catalytic cycle. Control of the metal chirality during the catalysis has not yet been possible, although the use of half-sandwich complexes with chiral centers in enantioselective catalysis is beginning to show up.

Keywords: asymmetric catalysis · chirality · coordination chemistry · optical activity · reaction mechanisms

1. Introduction

Organometallic chemistry of the transition metals is intermediate between inorganic and organic chemistry, and is characterized by a manifold of structures and a multitude of reaction possibilities. Typical of a field matured by intense research for decades, transition metal chemistry today deals with subtle problems and effects, in particular with respect to the synthesis of organic compounds and catalysis of organic reactions. While the chemistry of metal carbonyl complexes developed mainly during the first half of our century, initiated with the discovery of tetracarbonylnickel by Ludwig Mond more than 100 years ago, the starting signal for modern transition metal chemistry was the discovery and structural elucidation of ferrocene in the early 1950s. It was followed by the golden period of preparative transition metal chemistry, in which many of the basic compound types were found which still today are used as starting materials. This was the situation of transition metal chemistry in the 1960s, when I chose as the topic for my Habilitation the preparation of optically active transition metal compounds in which a tetrahedrally coordinated transition metal M is surrounded by four different ligands L^1, L^2, L^3, and L^4 (Figure 1).[1]

A simple chiral anion which derives from tetrahedral $[NiCl_4]^{2-}$ would be $[NiFClBrI]^{2-}$. Nobody would try to resolve a racemate of this anion, because rapid ligand exchange

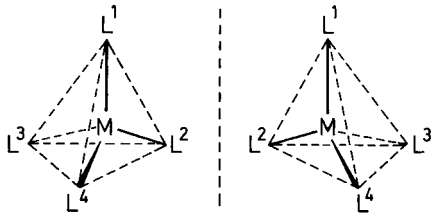

Figure 1. Image and mirror image of a transition metal complex with four different ligands.

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reactions would not only quickly interconvert image and mirror image, but symmetrization reactions would form all possible mixed species including the pure tetrahalo complexes from $[NiF_4]^{2-}$ to $[NiI_4]^{2-}$. In contrast, analogous organometallic compounds are kinetically inert, because the ligands are bound strongly to the metal atoms by the combination of σ-donor and π-acceptor bonds. Synthesis and ligand exchange reactions generally are slow, they can be controlled and planned, and there is an arsenal of methods in synthetic organometallic chemistry that is comparable to that in organic chemistry and allows specific transformations. Transition metal compounds are mainly low-spin complexes in which the metal atoms adopt a noble gas configuration. They are diamagnetic, and therefore, besides X-ray structure analysis, NMR spectroscopy is available as an efficient method of investigation.

2. Image – Mirror Image Isomerism

Image – mirror image isomerism of the asymmetric carbon atom has dominated stereochemistry since its discovery by van't Hoff and LeBel in 1874.[2, 3] Also tetrahedral compounds of other main group elements, for example silicon, with four different substituents have been obtained in optically active form. The first reports on the resolution of racemates of silicon compounds appeared already at the beginning of this century.[4] However, the field was investigated systematically only in the 1950s by L. H. Sommer and then R. J. P. Corriu et al.[5–7] Resolution of tetrahedral compounds with four different substituents was extented to the higher elements of the carbon group (Group 14) and to the elements of the nitrogen group (Group 15). Today even optically active compounds with bismuth carrying four different substituents are known.[8, 9]

Especially important are chiral compounds of the main group elements in which one of the "substituents" is a free electron pair. In the ammonia derivatives $NR^1R^2R^3$ these pseudotetrahedral compounds are notoriously configurationally labile because of inversion of the nitrogen atom through the plane of the substituents.[10] In the corresponding phosphanes $PR^1R^2R^3$, however, the process of pyramidal inversion is so slow, that they can be prepared in optically active form (Horner phosphanes).[11] Also other classes of pseudotetrahedral compounds such as sulfoxides $S(O)R^1R^2$ show high configurational stability.

Phosphanes are variable ligands in organometallic complexes, for example in hydrogenation reactions with rhodium catalysts of the Wilkinson type. Optically active phosphanes with a chiral phosphorus atom already played a role in the beginnings of enantioselective hydrogenation in 1968.[12, 13] The chelating ligand 1,2-ethanediylbis[(2-methoxyphenyl)-phenylphosphane] (dipamp), which contains two chiral phosphorus atoms, was introduced in the 1970s into the industrial production of L-dopa, a drug used against Parkinson's disease (Monsanto amino acid process).[14]

Image – mirror image isomerism in the series of transition metals is dominated by the octahedral tris-chelating type, which after the asymmetric carbon atom is the next important element of chirality.[15, 16] Metal tris-chelates with three identical symmetric ligands, for example $[Co(en)_3]X_3$, are not asymmetric. They belong to the point group D_3, and contain a C_3 and three C_2 axes, but no symmetry plane, no inversion center, and no higher improper axis, which would remove chirality. $[Co(en)_2(NH_3)Cl]Cl_2$ was the first octahedral complex to be prepared in optically active form by A. Werner in 1911.[17] Until the end of the 1960s, however, no optically active compounds existed in which a transition metal M was surrounded by four different ligands L^1, L^2, L^3, and L^4.

In this review, the term "optically active" is used to distinguish between dextro- and levorotatory isomers. "Stereogenic" is used when the number of isomers and isomeric possibilities are discussed, whereas "asymmetric" is used when symmetry characteristics are important. The term "chiral", whose use in the literature is not uniform, incorporates both optically active and stereogenic, since formulations such as "chiral metal atom", "chiral-at-metal", and "chiral-at-iron", etc. have meanwhile become accepted terminology.

3. The First Optically Active Transition Metal Compounds with Four Different Substituents

Thirty years ago, the first resolution of a transition metal complex with four different substituents was achieved with the manganese complex **1** (Scheme 1).[18, 19] In the cation of this complex the manganese atom is surrounded by a cyclopentadienyl, a carbonyl, a nitrosyl, and a triphenylphosphane ligand. It can be obtained in two steps from the commercially available compound $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$, and is formed as

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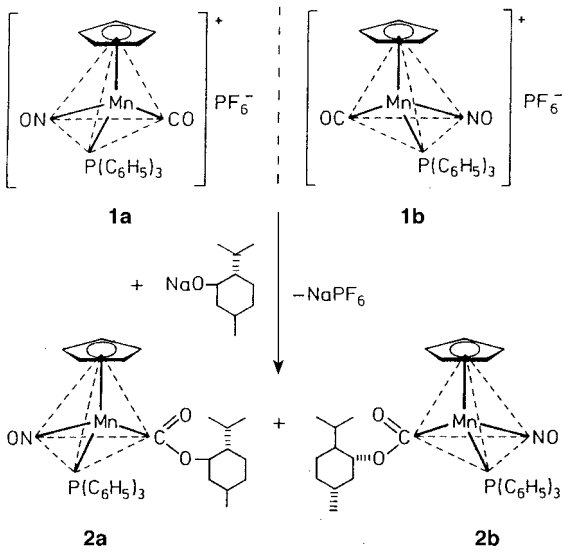
Henri Brunner, born in 1935, studied chemistry at the Universität München, Germany, where he received his Diplom in 1960. He completed his dissertation in the research group of Professor E. O. Fischer in 1963. After a one-year postdoc at the University of California, Los Angeles, with Professor H. D. Kaesz, he finished his Habilitation at the Technische Universität München. In 1971 he accepted a position at the Institut für Anorganische Chemie at the Universität Regensburg, where he is still working. His areas of research are the stereochemistry of organometallic complexes and reactions, enantioselective catalysis, and the investigation of platinum complexes in cancer chemotherapy. He has received many awards and fellowships, including the German – French Alexander von Humboldt Award in 1993, the Max Planck Research Award for International Cooperation in 1997, and the Horst Pracejus Award of the German Chemical Society in 1999.

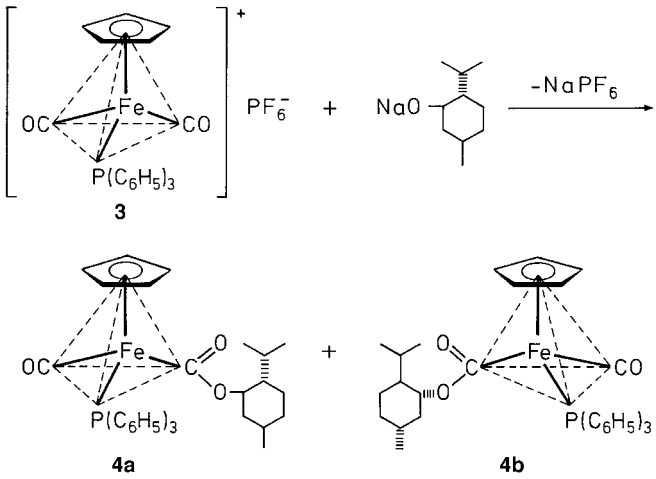


Scheme 1. Complexes **2a** and **2b**, the first optically active transition metal complexes with four different ligands.

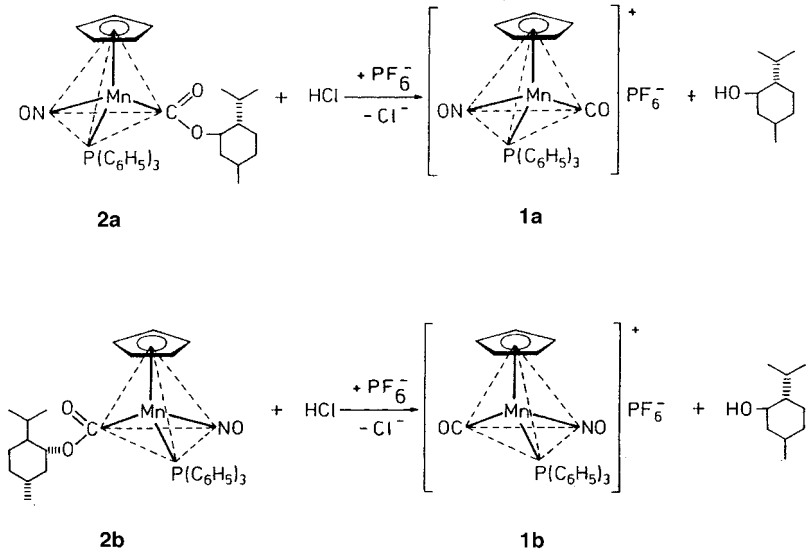
the racemate **1a**/**1b**.[20–23] To convert the pair of enantiomers **1a**/**1b** into a pair of diastereomers, it is allowed to react with the sodium derivative of the optically active alcohol (1*R*,3*R*,4*S*)-menthol. The mentholate ion adds to the carbon atom of the carbonyl ligand in the cationic starting material. The neutral "esters" **2a**/**2b** are formed, which differ only in the configuration of the manganese atom. The two diastereomers can be separated on the basis of their solubility differences. The $(+)_{579}$ diastereomer dissolves in petroleum ether, whereas the $(-)_{579}$ diastereomer is only sparingly soluble in this solvent.[18]

To complete the resolution the optically active auxiliary has to be removed from the separated diastereomers. This occurs upon bubbling of HCl through solutions of **2a** and **2b** in benzene. In this reaction the $C-O_{menthyl}$ bond is cleaved. Menthol is formed, and the ester group is retransformed into the carbonyl group of the starting cation. The counterion is first Cl^-; it is then replaced by PF_6^- (Scheme 2).[19] Starting from the $(+)_{579}$ diastereomer **2a** the $(+)_{579}$ PF_6^- salt **1a** is formed, while the $(-)_{579}$ diastereomer **2b** is transformed into the $(-)_{579}$ PF_6^- salt **1b**.[19] The diastereomers **2a** and **2b** contain four asymmetric centers each, the asymmetric manganese atom and three asymmetric carbon atoms in the menthyl part of the molecule. After removal of menthol the stereogenic manganese atom is the only source of chirality in complexes **1a** and **1b**. The optical rotations of the two enantiomers have opposite signs and, within the limits of error, the same magnitude.[18, 19, 24]

The addition of mentholate ions to form diastereomers which only differ in the metal configuration is confined to cationic carbonyl complexes. Whereas the cationic manganese complexes in Scheme 1 are enantiomers, the cation in the complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3]PF_6$ (**3**)[25] is prochiral. It contains a symmetry plane which passes through the cyclopentadienyl ligand, the triphenylphosphane ligand, and the iron atom and bisects the angle between the two carbonyl groups. It is on addition of the mentholate ion that the iron atom becomes an asymmetric center (Scheme 3). The attack



Scheme 3. Transformation of the prochiral complex **3** into the two diastereomers **4a** and **4b** with the help of menthol.

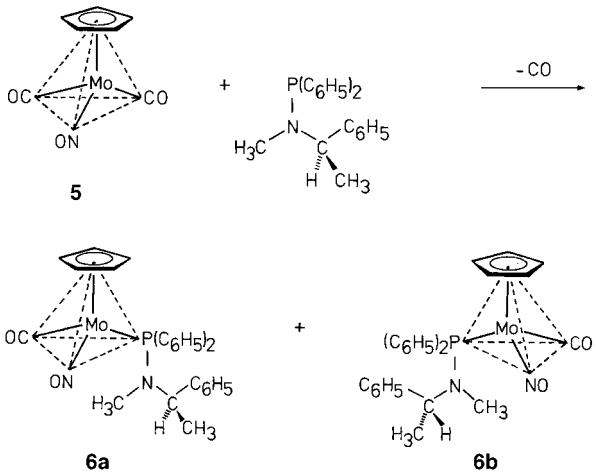


Scheme 2. Formation of the enantiomers **1a** and **1b** from the diastereomers **2a** and **2b**.

on the two enantiotopic carbonyl groups results in the two diastereomers **4a** and **4b** with opposite configuration at the iron atom. As with **2a** and **2b**, **4a** and **4b** can be separated on the basis of solubility differences.[26, 27] However, an acid cleavage of the ester groups as in the case of **2** would lead to a loss of chirality and stereogenicity at the iron atom.[27]

Phosphanes are excellent ligands for organometallic compounds. Therefore, optically active phosphanes should be universally suitable for the production of diastereomeric complexes which only differ in the metal configuration. Aminophosphanes of the type (*R*)-Ph_2P–NH(CHMePh) and (*S*)-Ph_2P–NMe(CHMePh) can easily be prepared from Ph_2PCl and the corresponding optically active amines.[28, 29] In terms of size and

electronic effect, they resemble the standard ligand triphenylphosphane.[30] The anisotropy beams which are connected with their phenyl groups usually cause the diastereomeric metal complexes to differ in their ^{1}H NMR spectra. In these cases the diastereomer ratio can be determined by integration of suitable signals, for example in the molybdenum complexes of Scheme 4. If in complex **5** one of the two enantiotopic CO



Scheme 4. Transformation of the prochiral complex **5** into the two diastereomers **6a** and **6b** with the help of a chiral phosphane ligand.

groups is replaced, the diastereomeric complexes **6a** and **6b** are formed with the same *R* configuration at the asymmetric carbon atom of the ligand and with mirror-image configurations at molybdenum.[29, 31] The two diastereomers **6a** and **6b**, which can be separated by chromatography as well as by fractional crystallization, show distinctly different ^{1}H NMR spectra.

All the complexes in Schemes 1–4 are half-sandwich complexes with the structure of a three-legged piano stool. Indeed, they contain four different ligands. Therefore, they are pseudotetrahedral, an aspect which is emphasized by the dotted frame in the formulas. However, the η^5-C_5H_5 ligand occupies three facial coordination sites, which means that the geometry of these complexes is in fact octahedral. This is also clear from the angles between the monodentate ligands. These angles are frequently close to the octahedral angle of 90°.[32]

4. Square-Pyramidal, Octahedral, and Tetrahedral Complexes with an Asymmetric Metal Atom

Half-sandwich complexes with the structure of a four-legged piano stool can contain up to five different ligands. While permutation of the four ligands L^1–L^4 at the corners of a tetrahedron results in only two isomers (image and mirror image), permutation of five ligands at the corners of a square pyramid yields 30 isomers, which subdivide into 15 pairs of enantiomers.[33] The isomer situation of a square pyramid with five different ligands is identical to that of an octahedron with six different ligands, because the free coordination site (a phantom ligand) in the square pyramid is equivalent to the sixth ligand in the octahedron. The total of 30 isomers which is possible for the most general case of a square pyramid with five different ligands can be reduced to only two, image and mirror image, with three constraints which can easily be realized experimentally.[33]

The first constraint is to always leave ligand L^1 at the top of the pyramid; the second contraint is to make two ligands on the base identical ($L^4 = L^5$). These two constraints reduce the number of 30 isomers to only three, which are shown at the top of Figure 2: one pair of enantiomers with the ligands L^2

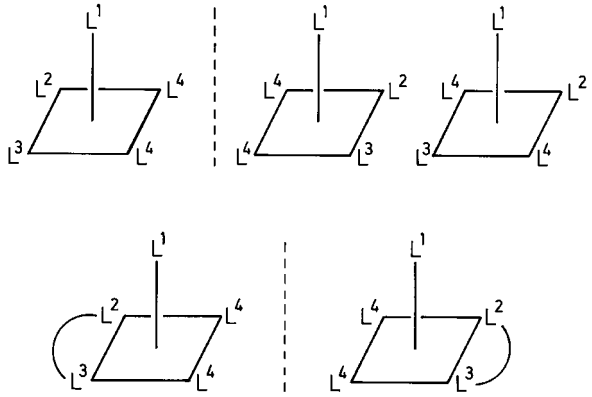
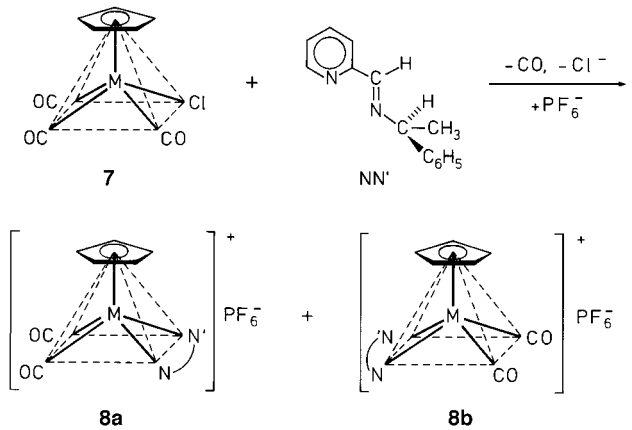


Figure 2. Reduction of the number of isomers for complexes with a square-pyramidal structure by restriction on the ligands used. See text for details.

and L^3 *cis* to each other and a third isomer with the ligands L^2 and L^3 *trans* to each other. The *trans* isomer contains a symmetry plane which passes through L^1, L^2, and L^3. To exclude this achiral *trans* isomer, a third constraint is introduced. Instead of two different monodentate ligands L^2 and L^3 an unsymmetrical bidentate ligand L^2-L^3 is used. Such a chelating ligand can only occupy *cis* positions at a square. Therefore, the *trans* isomer is excluded, and the two *cis* isomers at the bottom of Figure 2 are the only ones left.[33]

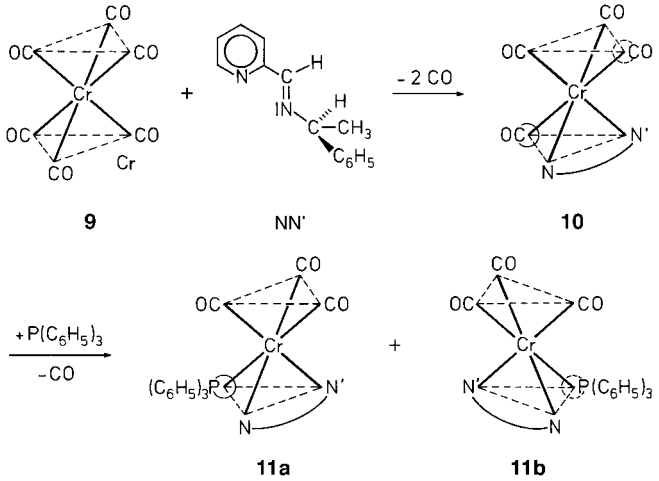
These three constraints can be realized in one synthetic step starting from the commercially available complexes [(η^5-C_5H_5)M(CO)$_3$Cl] (M = Mo, W; **7**), which have a square-pyramidal structure, that is, the four-legged piano-stool geometry (Scheme 5). In these complexes the cyclopentadienyl ring always occupies the top of the pyramid. As an unsymmetrical chelating ligand the pyridine-imine ligand NN′



Scheme 5. Synthesis of the diastereomeric complexes **8a** and **8b** with square-pyramidal structure. NN′ = unsymmetric chelating ligand, M = Mo, W.

is used, which can be synthesized by a Schiff base condensation of 2-pyridinaldehyde and the optically active primary amine (*S*)-1-phenylethylamine.[33, 34] In the reaction of the chelating ligand NN′ with **7**, a carbonyl ligand and the covalently bound chloro substituent are displaced from the complex; the latter becomes the counterion Cl^-, which is replaced by PF_6^- in a metathesis reaction. The two empty coordination sites on the base of the square pyramid are occupied by the chelating ligand NN′. There are only two possibilities for this. The diastereomers **8a** and **8b** are obtained, which differ only in the configuration at the metal atom.[33–35] They could be separated on the basis of solubility differences for M = Mo and W.[33, 34]

With the help of the unsymmetrical, optically active chelating ligand NN′ and use of the *trans* effect of the carbonyl ligands in the introduction of triphenylphosphane, it is possible to convert the highly symmetric hexacarbonylchromium (**9**) into the *cis*-trisubstituted diastereomers **11a** and **11b** in two steps (Scheme 6).[36] First, two *cis* carbonyl



Scheme 6. Conversion of hexacarbonylchromium (**9**) into the diastereomeric complexes **11a** and **11b**. NN′ = unsymmetric chelating ligand.

ligands are replaced by the NN′ ligand. In the reaction with the complex $[Cr(CO)_4(NN')]$ (**10**) thus formed, the ligand triphenylphosphane does not enter *trans* to N or N′, where the carbonyl ligands are bound tightly, but in the two positions marked in Scheme 6, where the two carbonyl groups are mutually labilized by their strong *trans* effect. Substitution in these two positions leads to the diastereomers **11a** and **11b**, which differ only in the configuration at the metal atom. The diastereomers could be separated by fractional crystallization, and analogous reactions were carried out for $[Mo(CO)_6]$ and $[W(CO)_6]$.[36] As the three remaining carbonyl groups occupy facial coordination positions, the octahedral complexes **11** correspond to the half-sandwich complexes in Schemes 1–4, in which a cyclopentadienyl ligand binds to three *cis* coordination sites.

Complexes with four different ligands of tetrahedral, and not only pseudotetrahedral, structure were also resolved with respect to the metal configuration. Examples are the iron complexes **12**[37] and the carbonyl(nitrosyl)cobalt complexes with unsymmetrical chelating ligands, for example 1-methyl-1,2-ethanediylbis(diphenylphosphane) (prophos; **13a**[38]), or two different ligands, for example triphenylphosphane and (*S*)-1-phenylethylisocyanide (**14**[39]); Figure 3 shows only one diastereomer of each.

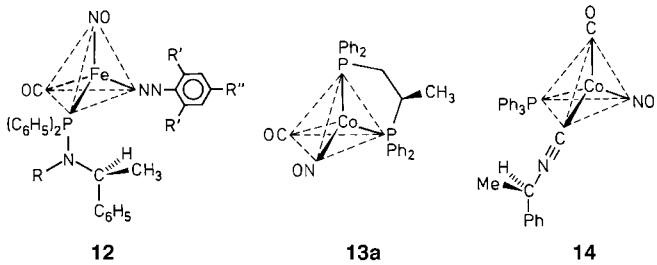


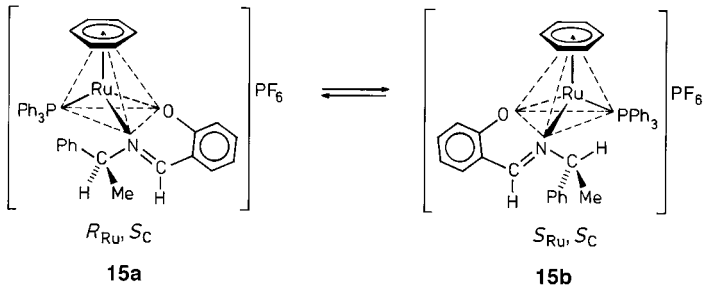
Figure 3. Examples of tetrahedral complexes with four different ligands whose isomers can be separated with respect to the metal configuration. **12**: R = benzyl, R′ = R″ = methyl.

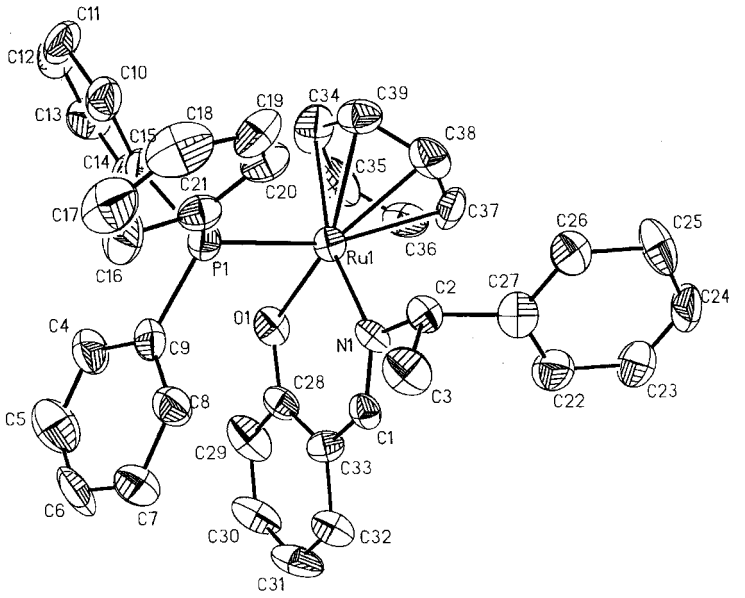
5. Absolute Configuration and Chiroptical Properties

Organometallic compounds of the transition metals crystallize excellently. Therefore, the absolute configurations at the metal atom in optically active complexes can be determined by X-ray crystallography either by means of anomalous X-ray scattering or by internal comparison with a known absolute configuration in the ligand. For assignment of the configuration symbols *R*/*S* the Cahn–Ingold–Prelog system[40–42] is extented to π-bonded ligands.[43, 44] Polyhapto-bound ligands are taken as pseudoatoms with an atomic number equivalent to the sum of the atomic numbers of the atoms bound to the metal atom. According to this definition η^6-C_6H_6 and η^5-C_5H_5 are pseudoatoms with atomic numbers 36 and 30.

For the $(-)_{579}$ diastereomer **4a** (see Scheme 3) the absolute configuration at the iron atom has been determined to be S_{Fe}, the priority of the ligands being η^5-$C_5H_5 > PPh_3 >$ COOmenthyl > CO.[45, 46] According to Ruch[47] tetrahedral complexes and half-sandwich complexes of the three-legged piano-stool type belong to chirality class *a*, for which an achiral border between *R* and *S* exists. In contrast, complexes with square-pyramidal and octahedral skeletons belong to chirality class *b*, for which there is no such achiral border.

The areneruthenium complexes **15a** and **15b** in Figure 4 contain as an unsymmetrical ON chelating ligand the anion of the salicylaldimine derived from (*S*)-1-phenylethylamine. Thus, in the ligand an *S*-configured carbon atom is fixed, whereas *R* and *S* configuration can result at the metal atom. As explained later on, the diastereomer equilibria of these complexes are shifted strongly to the side of the R_{Ru},S_C diastereomers. For **15** the equilibrium ratio R_{Ru},S_C:S_{Ru},S_C in $CDCl_3$ at room temperature is 95:5.[48, 49] Depending on the crystallization conditions the R_{Ru},S_C isomer **15a** is obtained in two modifications. Crystallization in chloroform at 5 °C preferentially gives tetrahedron-like crystals; crystallization in chloroform at room temperature yields small plates. X-ray structure analyses confirm the R_{Ru},S_C configuration in both cases, the priority of the ligands being η^6-$C_6H_6 > PPh_3 > O >$





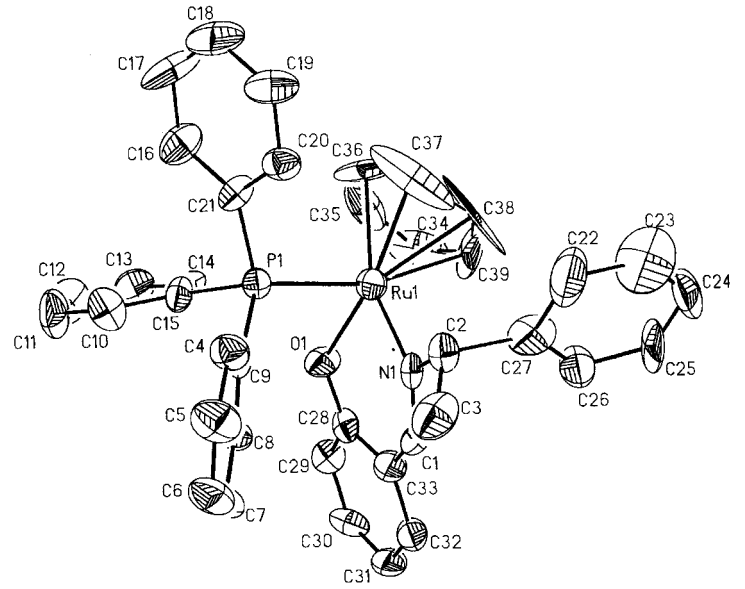


Figure 4. Top: Complexes **15a** and **15b** are in equilibrium with each other (**15a**:**15b** = 95:5 in $CDCl_3$ at room temperature). Bottom: ORTEP plots of the isomers of the cations of **15a**, which differ only in the propeller sense of the triphenylphosphane ligand.

N. They demonstrate that both isomers differ only in the propeller sense of the triphenylphosphane ligand.[48, 49] In the tetrahedron-like crystals the triphenylphosphane ligand has an *M* conformation (*M* = minus),[41] whereas in the small plates it has a *P* conformation (*P* = plus)[41] (Figure 4, bottom). Up to now, the ruthenium complexes (R_{Ru},S_C,M_{PPh_3})-**15a** and (R_{Ru},S_C,P_{PPh_3})-**15a** are the only example of a pair of diastereomers whose components have opposite chirality of the triphenylphosphane propeller.

In general, transition metal compounds are strongly colored. This leads to Cotton effects in the visible part of the spectrum. Therefore, the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra are characterized by many passages through zero. Owing to the change in sign of

the bands the ORD and CD spectra contain more information than the UV/Vis spectra. However, their potential for assignments has not been used up to now. The ORD and CD spectra are dominated by the metal chromophores. Therefore, diastereomers which contain asymmetric carbon atoms of the same configuration in the ligand but differ in the configuration of the metal often have almost mirror-image chiroptical properties. An example are the CD spectra of the diastereomeric manganese complexes **2a** and **2b** (Figure 5).

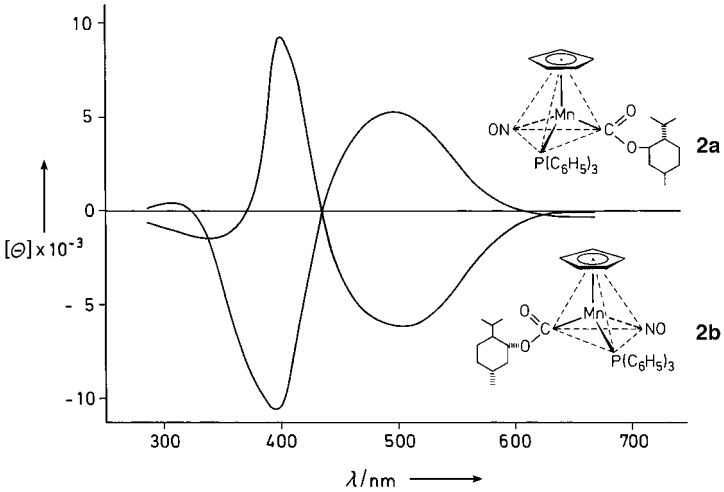


Figure 5. CD spectra of complexes **2a** and **2b** (concentrations about 10^{-3} mol L^{-1} in toluene).

As a rule, the rotational values of optically active organometallic compounds at the Na_D line and the mercury lines in the visible part of the spectrum are large.

6. Elucidation of Reaction Mechanisms

Schemes 1–6 have demonstrated that transition metal complexes with chiral metal atoms can be prepared with many different ligand combinations and geometries, and resolved with respect to the metal configuration.[24, 50–52] An attractive application of these complexes, which are stereochemically labeled at the metal atom, is the elucidation of the spatial course of reactions.[35, 51–53]

Stereochemical investigations have played and continue to play a prominent role in the establishment of reaction mechanisms in organic chemistry. In their classic studies in the 1930s Ingold and Hughes demonstrated that either racemization or inversion takes place in nucleophilic substitution reactions at the tetrahedral carbon atom, depending on whether the reactions proceed according to an S_N1 mechanism via a planar carbenium ion or according to an S_N2 mechanism by a Walden inversion.

In the nucleophilic substitution at the asymmetric silicon atom the S_N1 mechanism can be excluded. These reactions proceed either by an S_N2–Si inversion mechanism, which is comparable to the organic S_N2 reaction, or by an S_Ni–Si retention mechanism, whose analogue in organic chemistry is rare.[2] Thus, the homologues carbon and silicon behave in a distinctly different way. With the help of the new, optically active transition metal complexes the stereochemical course of organometallic reactions can be studied. The crucial point is the configurational stability at the metal atom. Some of the optically active complexes are configurationally stable; their metal configuration does not change even at higher temperatures. Other complexes are labile with respect to the metal configuration; the separated diastereomers interconvert more or less rapidly. In both cases different mechanistic studies are possible.

7. Complexes That Are Configurationally Stable at the Metal Atom: Mechanisms

The reaction of the menthyl ester **4a** (see Scheme 3) with methyllithium provides an example of an unusual inversion mechanism. It leads to the elimination of lithium mentholate, and at the iron atom an acetyl substituent is formed. Starting from the $(+)_{546}$ menthyl ester **4a** the acyl complex **16b** is obtained with $(-)_{546}$ rotation (Figure 6); the $(-)_{546}$ menthyl ester **4b** yields the $(+)_{546}$ acetyl complex **16a** (not shown).[54] The optical rotations of starting material and product have

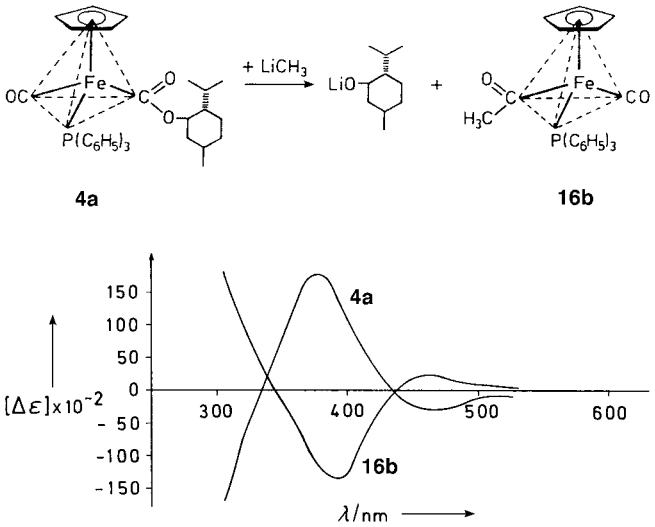


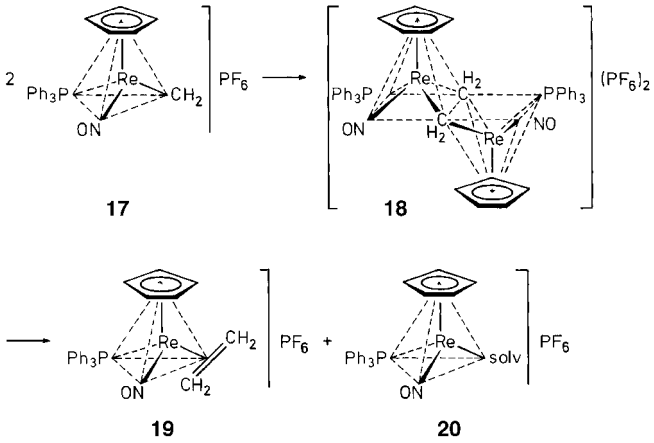
Figure 6. Top: Inversion of the configuration in the reaction of **4a** with $LiCH_3$ to give **16b**. Bottom: CD spectra of **4a** and **16b** (concentrations about 10^{-3} mol L^{-1} in benzene).

opposite signs, and the CD spectra of **4a** and **16b** are nearly mirror images (Figure 6, bottom).[54] These chiroptical data suggest an image–mirror image relationship between starting material and product and therefore an inversion mechanism. This has been confirmed by the X-ray determination of the absolute configuration at the iron atom in starting material and reaction product.[45, 46, 55]

The reaction mechanism can be explained as follows. The attack of methyllithium does not occur as expected at the ester group of the starting material, but at the carbonyl group, which is transformed into the new functional group, the acetyl substituent. The mentholate ion dissociates from the ester group, the former functional group, transforming it into the new carbonyl group of the product. Thus, in the reaction of Figure 6 two substituents of the iron complex **4a**, the carbonyl

group and the functional group, change their roles. This is equivalent to an inversion of the metal configuration upon going from **4** to **16**, although none of the bonds to the iron atom is broken. Only attack of methyllithium at the carbonyl group can explain the inversion at the iron atom, as attack at the ester group would lead to retention of configuration.[55]

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]$ proved to be a versatile chiral fragment; J. A. Gladysz et al. used it for a "stereochemical deep-hole drilling".[56–58] A special role was played by chiral Lewis acids, conformational analyses, and molecular recognition; an example of this is the coupling of two methylene ligands to an ethene ligand shown in Scheme 7. The methylidene complex **17**[60] couples to the ethene complex **19** at room

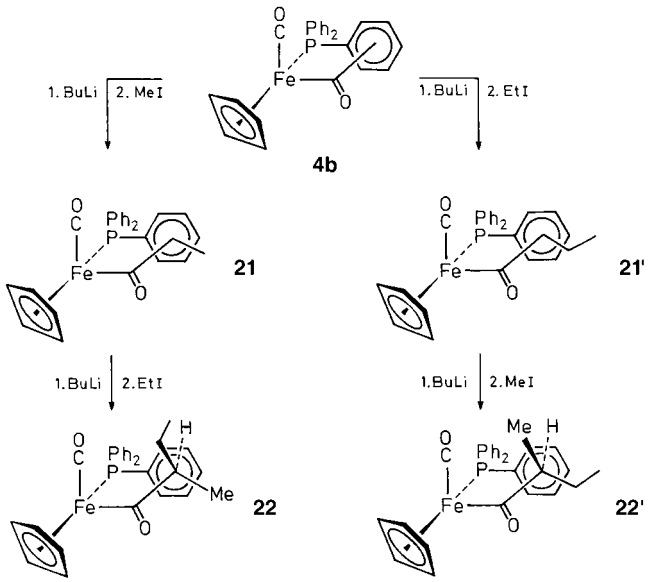


Scheme 7. Molecular recognition in the coupling of two methylidene ligands in **17** to an ethene ligand in **19**.

temperature in dichloromethane in about 50% yield, that is, quantitatively. The reaction is second-order. Surprisingly, the enantiomerically pure complexes react 2.3 times faster than their racemic mixture. Cross-coupling experiments confirm that in the coupling the homochiral *R*,*R* and *S*,*S* transition states, for example **18**, are preferred over the heterochiral *R*,*S* transition state (self-recognition of enantiomers).[59] This is surprising because nonlinearity and chiral amplification in enantioselective catalysis are based on the formation of binuclear complexes, for which *R*,*S* dimers are more stable than *R*,*R* and *S*,*S* dimers.[61–63] The *meso* dimers contain an inversion center. In these heterochiral dimers the substituents of the two halves of the molecule can best avoid steric interactions; in homochiral dimers such as **18** this is not possible. The coupling product **19** forms with greater than 98% retention at the rhenium atom, and the solvated intermediate **20a** can be trapped in the presence of nitriles with retention of configuration at the rhenium atom.[59]

8. Complexes That Are Configurationally Stable at the Metal Atom: Organic Synthesis

Optically active transition metal complexes can also be used in reactions which do not occur at the chiral metal atom but at the ligands, and thus find applications in enantioselective organic synthesis. The complexes (+)- and (−)-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe)]$ were developped as optically active auxiliaries; they are highly selective stoichiometric reagents that are commercially available and allow the synthesis of a variety of interesting compounds by the enolate chemistry of the acyl substituent.[64–68] This is demonstrated in the double alkylation sequence of Scheme 8.



Scheme 8. $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe)]$ as a chiral auxiliary: synthesis of both configurational series of carboxylic acids that are chiral at the α-C atom.

Complex **4b** can be deprotonated with butyllithium at the methyl group of the acetyl ligand to provide the enolate.[69] The reaction with methyl iodide to give **21** is almost quantitative. If **21** is subjected to another cycle of metalation and alkylation, a new chiral center is formed in the acyl substituent, provided an alkylation reagent is used which has a different alkyl group than the first alkyl halide. The use of ethyl iodide in the second alkylation gives the 2-methylbutyryl group (**22**). If this double alkylation is carried out with **4b**, which is *R*-configured at the iron atom, **22** is formed with *R* configuration in the acyl fragment with an optical purity of greater than 200:1.[70–72] If the sequence of alkylation is inverted, the complex **22′**, which is *S*-configured in the acyl substituent, is also formed with an optical purity of greater than 200:1.[70–72] With Br_2/H_2O the iron–acyl bond is cleaved, and the corresponding carboxylic acids can be isolated in almost optically pure form. Thus, double metalation/alkylation yields carboxylic acids, which are chiral at the α-C atom, of both configurational series.

The X-ray structure analysis of **4b** showed that one of the phenyl rings of the triphenylphosphane ligand completely shields one side of the acetyl group. Thus, attack is only possible from the other side (Scheme 8). This shielding is one of the prerequisites for the observed unusually high stereoselectivities. Furthermore, the alkyl group of the acyl fragment in the complex prefers a uniform conformation. The acetyl oxygen atom and carbonyl ligand occupy *anti* positions, and the β-C atom of the alkyl chain is located *syn* with respect to the small acyl oxygen atom (and *anti* with respect to the

large [CpFe(CO)(PPh_3)] fragment), as shown in Scheme 8 both for the *n*-propionyl intermediate **21** and for the *n*-butyryl intermediate **21′**. Similarly, the chirality at the Fe atom controls the formation of new asymmetric carbon atoms in the α-, β-, and γ-position of the acyl fragment in aldol condensations and Michael reactions with high enantioselectivity.[68–72]

9. Complexes That Are Configurationally Labile at the Metal Atom: Mechanisms of the Change of the Metal Configuration

Optically active organometallic compounds with chiral transition metal atoms are configurationally stable in the solid state. In many cases, however, a change of the metal configuration takes place in solution by different mechanisms.

The configurational changes at the metal atom can be monitored by polarimetric measurements. In these reactions enantiomeric complexes which contain only chiral metal atoms approach the 1:1 racemization equilibrium, and optical activity is lost. If in these studies diastereomers are used which contain configurationally stable asymmetric carbon atoms in addition to the configurationally labile metal atom, the epimerization at the metal atom results in diastereomer equilibria with optical rotations other than zero and equilibrium ratios differing from 1:1. Figure 7 shows an example for

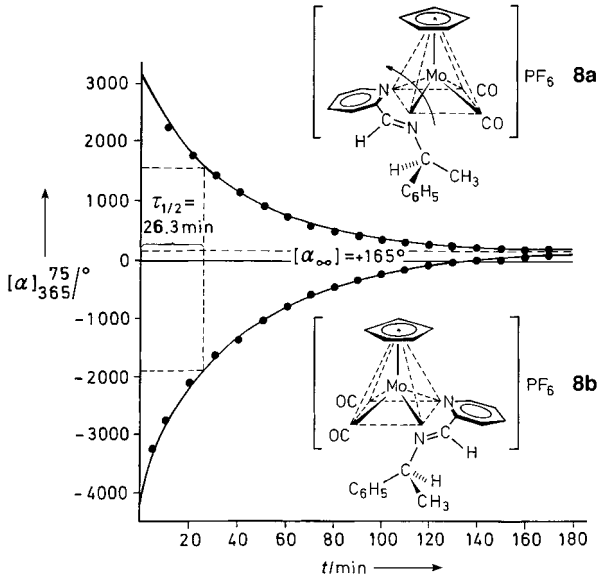


Figure 7. Decrease of the optical rotation in the epimerization of complexes **8a** and **8b** in dimethylformamide at 75 °C.

the drop of optical activity[73] and the approach to epimerization equilibrium for the square-pyramidal complexes **8a** and **8b** (M = Mo), which differ in the metal configuration (see Scheme 5 for their synthesis[33, 34]) and whose absolute configurations are known.[74, 75]

Because optically active organometallic complexes are mostly colored and absorb strongly in the visible section, the transparency in the polarimetric measurements is limited. Therefore, only dilute solutions can be studied, and their air sensitivity represents a possible source of error. As mentioned before, diastereomers frequently differ in their ^{1}H NMR spectra. Therefore, the kinetics of the configurational change at the metal atom can be followed by integration of suitable signals as a function of time. In this technique larger quantities can be used, the possibilities for exclusion of air are better, and therefore the results are more reliable than those obtained from polarimetry. Figure 8 shows the change in the

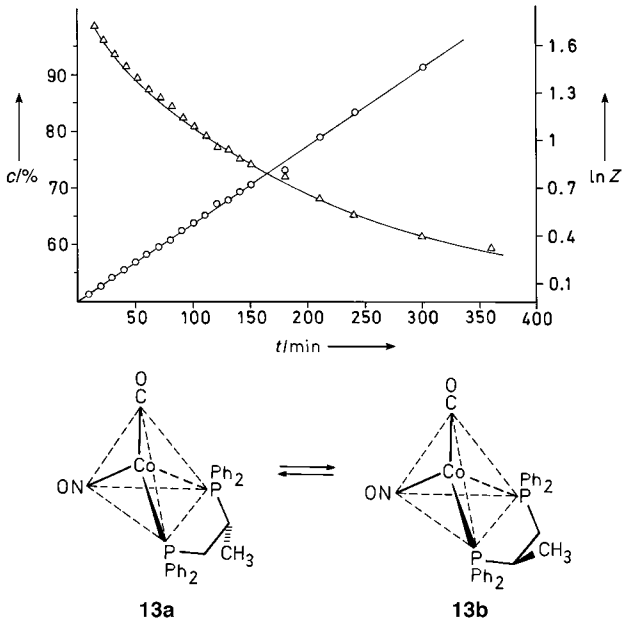


Figure 8. Epimerization of complex **13a** in [D_6]benzene at 35 °C (equilibrium ratio **13a**:**13b** = 50:50) and interpretation according to first order. The change in the concentration c of **13a** was measured by integration of the methyl signal in the ^{1}H NMR spectrum. $Z = ([\mathbf{13a}]_0 - [\mathbf{13a}]_\infty)/([\mathbf{13a}] - [\mathbf{13a}]_\infty)$.

concentration of the (S_{Co},R_C)-cobalt–prophos complex **13a** as a function of time measured by ^{1}H NMR spectroscopy during approach of the epimerization equilibrium and its interpretation according to first order.[38]

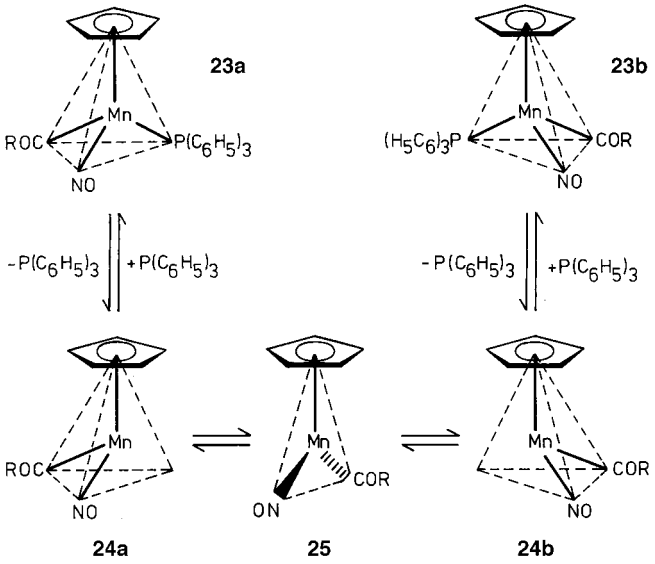
In most cases the configurational change at the metal atom is a first-order reaction. Therefore, the half-lives are a gauge for the configurational stability. The square-pyramidal complexes **8** (Figure 7) have a half-life of 26.3 min in DMF at 75 °C.[33] Thus, solutions of these complexes can be handled at room temperature for a short time without a change of configuration at the metal atom. The half-life for the approach to the epimerization equilibrium for the cobalt–prophos complexes **13a** and **13b** (Figure 8) is 141 min in [D_6]benzene at 30 °C. In this case a slow change of configuration at the cobalt atom has to be expected at room temperature in solution.[38]

All the previous results indicate that the change of configuration of the square-pyramidal complexes takes place intramolecularly by a pseudorotation mechanism, which ultimately leads to rotation of the unsymmetrical chelating ligand by 180°, as shown by the arrow in the upper formula of Figure 7.[35, 50, 73, 76, 77] Such intramolecular isomerizations at the metal atom can also be investigated by ^{1}H NMR spectroscopy with the help of diastereotopic probes, a resolution with respect to the metal atom being unnecessary. These coales-

cence measurements, however, cover relatively rapid reactions and thus a rate range competely different from that of the kinetic data accessible by integration of suitable diastereomer signals as a function of time.

10. Complexes That Are Configurationally Labile at the Metal Atom: Stereochemistry and Mechanisms

If intermediates are formed upon the change of the configuration at the metal atom, more information can be gained from racemization and epimerization experiments with the help of stereochemical labeling by optical activity than from dynamic NMR spectroscopy. Examples are the acylmanganese complexes **23** (Scheme 9), the racemization of



Scheme 9. Change in the configuration of complexes **23a** and **23b** via the chiral intermediates **24a** and **24b** and the achiral transition state **25**. R = methyl, phenyl, *para*-substituted benzene ring.

which involves the cleavage of the manganese–triphenylphosphane bond. The half-life of the benzoyl compound **23a** (R = Ph) is 49.4 min at 20 °C in toluene.[78]

Kinetic and stereochemical arguments indicate that in the dissociation of the triphenylphosphane ligand from **23a** a pyramidal intermediate **24a** is first formed[78–84] which still has the chirality of the starting material. This pyramidal intermediate can invert via the planar transition state **25** (as with an ammonia derivative). Addition of triphenylphosphane to the inverted intermediate **24b** leads to the opposite configuration at the metal atom in **23b** and subsequently to racemization. Stereochemical proof for the formation of chiral intermediates in the racemization of the manganese complexes **23a** and **23b** is provided by the formation of optically active substitution products when the intermediates are trapped with suitable phosphane ligands.[79, 80] The products have the same relative configuration as the starting material. The formation of pyramidal intermediates of the type **24** was supported by calculations,[85] which have been confirmed recently.[86]

Instead of the unsaturated intermediates **24a** and **24b**, which have a certain pyramidal stability, saturated intermediates of the type **26**, which contain η^2-bound acyl substituents, can be formulated to explain the retention upon phosphane substitution in the manganese complexes **23a** and **23b** (Figure 9). In **26** the manganese atom would remain chiral.

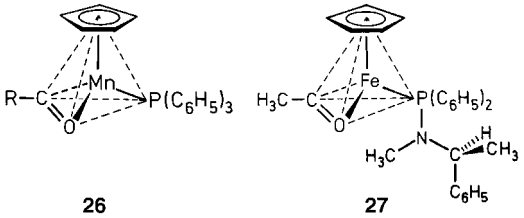
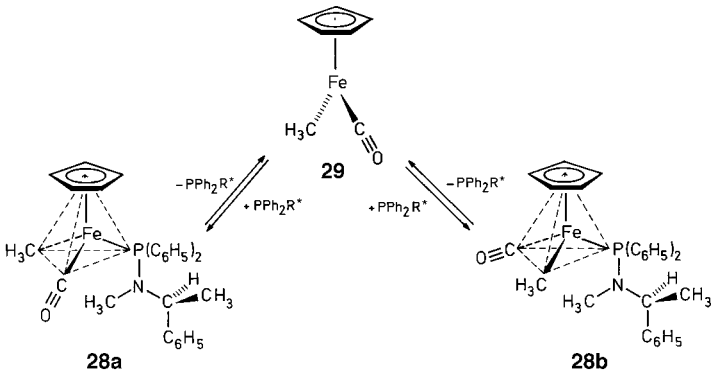


Figure 9. Possible η^2-acyl intermediates in the change of the configuration at the metal atom. R = methyl, phenyl, *para*-substituted benzene ring.

Backside attack of the acyl oxygen atom would lead to inversion, while frontside attack would give retention. In the reaction of the η^2-acyl intermediate with a phosphane ligand the processes would occur in the opposite direction (microscopic reversibility). Originally, this explanation had not been taken into consideration; the first stable η^2-acyl complex was published only after the described experiments had been carried out.[87] That this kind of stabilization cannot be neglected is obvious from the fact that retention in substitution reactions up to now could only be observed in complexes with acyl and ester ligands, but not in complexes whose substituents lack the ability to enter into η^2 bonding. Thus, the acyl(aminophosphane)iron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(COR)(PPh_2NR'R^*)]$,[88–90] which correspond to the manganese complexes **23**, also react in the phosphane substitution with partial retention of configuration; η^2-acyl intermediates of type **27** (Figure 9) have been discussed.[91] However, there has been no evidence for the formation of chiral intermediates in the phosphane substitution of the corresponding alkyl(aminophosphane)iron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(Me)(PPh_2NR'R^*)]$ (**28a**[92, 93] and **28b**,[94] Scheme 10). Phosphane



Scheme 10. Change in the configuration of complexes **28a** and **28b** via the planar intermediate **29** with loss of the stereochemical information at the metal atom.

substitution in **28a** and **28b** occurs with loss of the stereochemical information at the iron atom. It proceeds via the planar intermediate **29**, which can be attacked by the phosphane from the frontside or from the backside, leading

to the two diastereomers with opposite iron configuration in the diastereomer equilibrium.[94]

The epimerization of the alkyliron complexes **28a** and **28b** in [D_6]benzene at 70 °C takes place with a half-life of 70 min. However, electron transfer catalysis[95] in the case of an oxidative start with [Cp_2Fe]PF_6 at 20 °C leads to complete epimerization within 5 min. This means that by the catalytic formation of a 17-electron species the epimerization at the Fe atom can be drastically accelerated compared to the thermal reaction of the 18-electron species.[94]

11. Diastereomer Equilibria

If the synthesis temperatures of organometallic complexes are distinctly below the temperatures at which epimerization at the metal atom takes place, the optically active metal complexes are formed under kinetic control. Then, the diastereomer ratio is a measure for the optical induction of the stable chiral centers within the ligands for the formation of the metal configuration during the reaction. Various successive or decomposition reactions of the frequently air-sensitive diastereomers may modify the isomer ratios as well as fractionations which take place during workup of the reaction mixtures.[96]

It is much better to investigate diastereomer equilibria which result in the change of the configuration at the metal atom. If specific intramolecular interactions are lacking, the diastereomer equilibria are frequently about 50:50.[96] With the use of special effects, for example C–H···π interactions[97] such as the β-phenyl effect (see below), extreme diastereomer ratios can be reached.[77] The shift of the diastereomer equilibria of thioamidato and amidinato complexes of four-legged piano-stool structure from 50:50 to 99:1 by simple substituent variation has already been reported.[77, 96] Also the areneruthenium complexes,[48, 49, 98–107] which represent catalyst precursors[108–114] and have been intensely studied recently, show extreme diastereomer ratios. The equilibrium ratio of the pair of complexes **15a**/**15b** (Figure 4) in chloroform at room temperature is R_{Ru},S_C:S_{Ru},S_C = 95:5. In these complexes the β-phenyl effect[77, 115] is the reason for the stabilization of the R_{Ru},S_C diastereomer **15a** relative to the S_{Ru},S_C diastereomer **15b**. In **15a** the phenyl ring of the 1-phenylethyl substituent is oriented towards the π-bound benzene ligand to give a distorted T-shaped structure.[116] This geometry can be seen in the two ORTEP plots in Figure 4.[48, 49] The ^{1}H NMR spectra demonstrate that this structural element is maintained as the preferred conformation in solution. There is a high-field shift of the signal of the π-bound arene lying within the inner anisotropy cone of the phenyl ring of the 1-phenylethyl substituent. This additional stabilization through the C–H··· π interaction[97] results in the observed preference of the R_{Ru},S_C isomer **15a** in the diastereomer equilibrium.

A recent example for this C–H···π interaction and its consequences is the complex pair **30a**/**30b** (Figure 10), the components of which only differ in the ruthenium config-

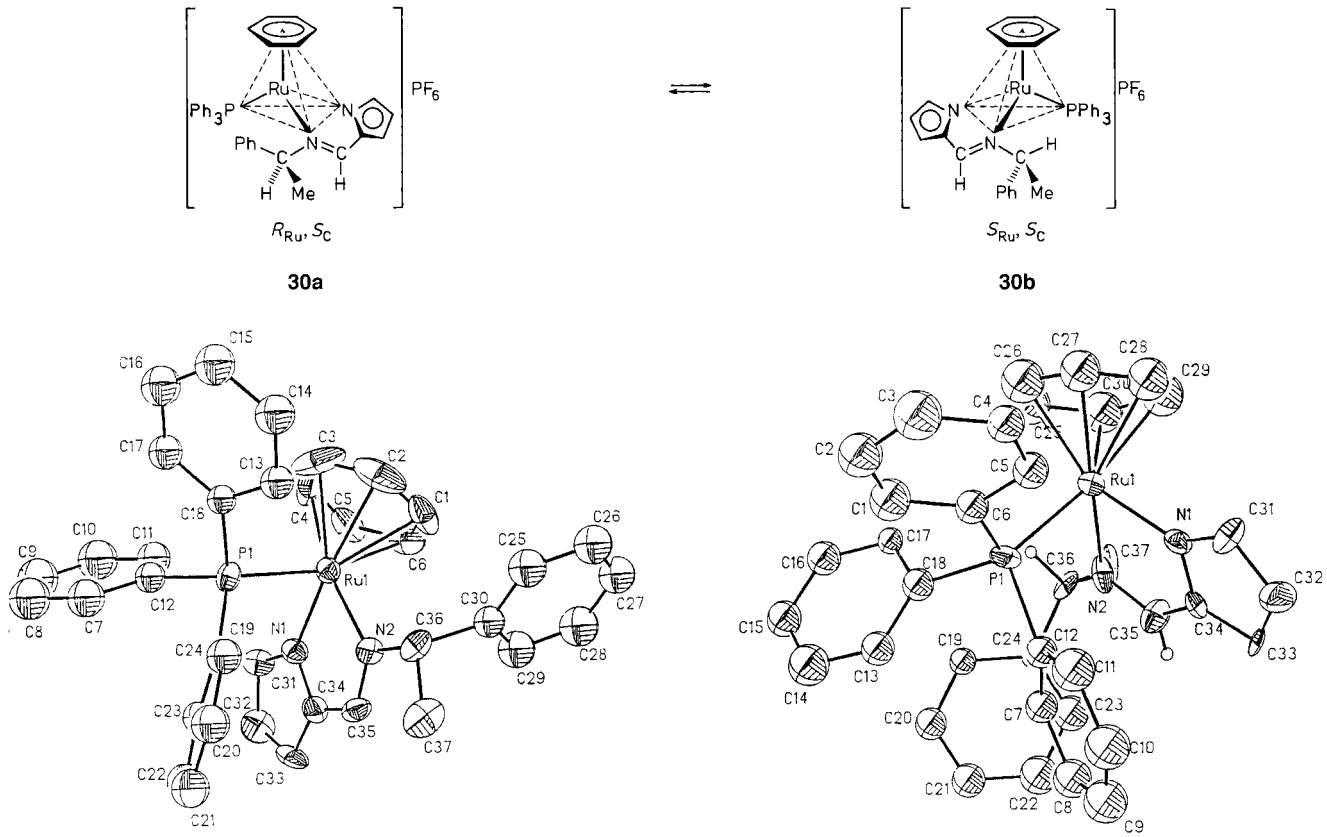


Figure 10. Complexes **30a** and **30b** (the equilibrium ratio in [D_3]nitromethane at 85 °C is 93.5:6.5) and ORTEP plots of the cations of **30a** and **30b**, which differ only in the configuration at the ruthenium atom.

uration.[101] The R_{Ru},S_C isomer **30a** dominates in the diastereomer equilibrium (93.5:6.5). The C–H···π interaction of the π-bound benzene ligand with the phenyl ring C25–C30 of the 1-phenylethyl substituent is clear from the ORTEP plot (Figure 10, bottom left). In the S_{Ru},S_C isomer **30b** this stabilizing interaction is lacking; the phenyl ring C19–C24 of the 1-phenylethyl substituent in the ORTEP plot "hangs downwards" and is far away from the π-bound benzene ring (Figure 10, bottom right). In solution, the C–H···π interaction shows itself in the signal intensities as well as the chemical shifts: Whereas the "normal" position for the signal of the π-bound arene in **30b** is at $\delta = 6.37$, the β-phenyl effect in the R_{Ru},S_C diastereomer **30a** leads to a high-field shift to $\delta = 5.68$. Compounds **30a** and **30b** are areneruthenium complexes with a relatively high configurational stability.[48, 49, 101, 104] The half-life for the epimerization in nitromethane at 85 °C is 58 min.

12. Complexes with Chiral Metal Atoms in Enantioselective Catalysis

In the formation of chiral products from prochiral precursors the distance between inductor and substrate plays an important role. The smaller this distance is, the better the chirality transfer and thus the optical induction should be. In general, for enantioselective catalysis with transition metal compounds optically active ligands are used whose chirality is mostly in the substituents or in the chelating skeleton (① in Figure 11). Therefore, the inducing chirality is rather far away from the metal atom at which catalysis takes place. Nevertheless, special mechanisms of chirality transfer ensure that many of these reactions proceed with extraordinarily high enantioselectivity. In the hydrogenation of dehydroamino acids a specific chiral conformation in the chelating skeleton of the ligand and, as a consequence, the arrangement of the phenyl substituents at the phosphorus atoms in plane/edge orientation are responsible.[117–119]

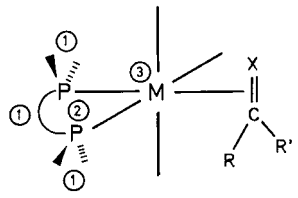
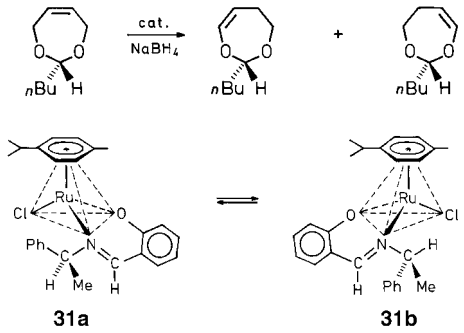


Figure 11. An octahedral phosphanemetal complex catalyst, in which a prochiral substrate RR′C=X is transformed into a chiral product. The inducing chirality can be located in the chelating ring or in the phosphorus substituents (①), at the coordinating phosphorus atoms (②), or at the metal atom (③).

In the Horner phosphanes[120] and in ligands such as dipamp[14] the inducing chirality is at the phosphorus atoms (② in Figure 11) and thus closer to the metal atom. The synthesis of compounds that are chiral at phosphorus is tedious, however, and unfavorable for a broad use. If the metal atom (③ in Figure 11) of the catalyst would be the inducing chirality, this would be the shortest possible distance. Strong effects on the transformation of prochiral substrates into chiral products within the coordination sphere of the metal atom would be the consequence. As organometallic complexes of the kind presented here are similar to the common enantioselective catalysts, there were repeated attempts to use transition metal complexes with chiral metal atoms as catalysts in enantioselective reactions. However, there is still no solution to this problem.[121] The complexes were either too stable or unsuitable as catalysts for the reactions planned.

At present, the efforts to utilize optically active complexes with chiral metal atoms for enantioselective catalytic transformations are concentrated on areneruthenium complexes.[108–114] Whereas in Noyori's catalyst precursor $[(\eta^6\text{-arene})Ru(binap)X]^+$ (binap = 1,1′-binaphthalene-2,2′-diylbis(diphenylphosphane), X = halogen) the arene is lost during hydrogenation,[122] in the olefin isomerization shown in Scheme 11 it remains in the complex.[114] This olefin isomerization starts from 2-*n*-butyl-4,7-dihydro-1,3-dioxepin, which



Scheme 11. Desymmetrization of the prochiral 2-*n*-butyl-4,7-dihydro-1,3-dioxepin. The reaction is catalyzed by complexes **31a** and **31b**.

can easily be obtained from *cis*-1,4-butenediol and valeraldehyde.[123] It contains a symmetry plane which disappears in the catalytic isomerization. In this desymmetrization the olefinic double bond migrates from the allyl to the vinyl position. The *n*-butyl-substituted carbon atom becomes a stereogenic center. In this reaction enantiomeric excesses of 12–13% were obtained[123] with rhodium and ruthenium catalysts of the ligand 4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane (diop),[124] which is derived from tartaric acid. Recently, the enantioselectivity (for the *tert*-butyldihydrodioxepin) with nickel–chiraphos catalysts[125] (chiraphos = 1,2-dimethyl-1,2-ethanediylbis(diphenylphosphane)) could be increased to 67%.[126]

Areneruthenium complexes **31a** and **31b**[48, 49] proved to be catalytically active in the olefin isomerization shown in Scheme 11. With this catalyst optical inductions of up to 61% *ee* were obtained.[114] Areneruthenium complexes with chiral metal atoms and optically active chelating ligands were also used successfully as enantioselective catalysts in Diels–Alder reactions.[112, 113, 127] Although the diastereomer equilibrium **31a** ⇌ **31b** is established for complex **31** under the conditions of the olefin isomerization (20 °C, 24 h), such equilibria are, as mentioned, strongly shifted to one side. How the configurationally favored and disfavored diastereomers contribute to the enantioselectivity of the catalytic olefin isomerization and how the two diastereomers differ in their reactivities are yet to be explained. In the hydrogenation of dehydroamino acids with rhodium catalysts according to Halpern and Brown, the diastereomer which is disfavored in the equilibrium determines the product configuration.[128]

13. Future Prospects

In the hydrogenation of dehydroamino acids with complexes similar in type to Wilkinson's catalyst, the rate-determining step is the oxidative addition of hydrogen to the square-planar complexes **32a** and **32b** (Figure 12). These

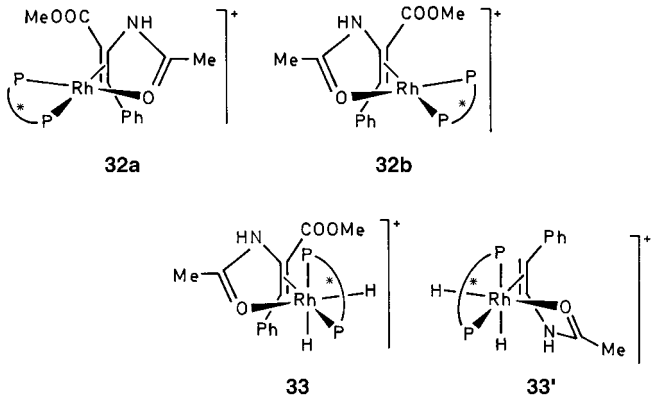


Figure 12. Intermediates in the enantioselective hydrogenation of methyl α-*N*-acetylaminocinnamate. Top: the diastereomers **32a** and **32b** with different coordination of the olefinic double bond. Bottom: the intermediates **33** and **33′** (formed in the oxidative addition of hydrogen to **32b**), which differ in the metal configuration. In **33′** the COOMe group has been omitted for the sake of clarity.

complexes are in equilibrium with each other and are diastereomeric to each other (same optically active chelating phosphane P*P and frontside or backside coordination of the prochiral olefin). In the oxidative addition of H_2 to **32a** and **32b** octahedral complexes are formed, to which structures such as **33** are ascribed.[128] In these complexes the metal atom is stereogenic. For **33** a diastereomer with mirror-image metal configuration (**33′**) is possible without a change in the *cis*/*trans* arrangement of the ligand skeleton.[77, 129–131] The two diastereomers **33** and **33′** belong to the product-determining branch, which starts from the disfavored but very reactive square-planar complex **32b**. The chiral metal complexes **33** arise anew in each catalytic cycle. However, the products are formed by reductive elimination, leading back to the square-planar rhodium complexes **32**, in which the rhodium atom is no longer stereogenic. Thus, in each catalytic cycle controlled by the P*P ligand chiral metal complexes are built up and disappear, albeit in a passive manner that cannot be influenced with respect to the metal configuration. Therefore, active use of chirality at the metal atom in enantioselective catalysts remains a challenge for the future.

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[1] W. Hieber as well as F. Basolo told the author later that they had attempted to verify this idea with their groups—apparently not with the right systems.

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