Optical Induction in Organo-Transition-Metal Compounds and Asymmetric Catalysis

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Received December 27, 1978

If a new chiral center is formed under achiral conditions, both mirror image configurations arise with equal probability; consequently, a 1:1 ratio of both enantiomers results. The isomer ratio is different from 1:1 if the formation of a new chiral center occurs under the influence of an optically active substance. Under such chiral conditions the whole range from small to high stereoselectivity, even to stereospecificity, may be realized. The controlling optical activity can be present in the attacking reagent or in the molecule in which a prochiral group is to be transformed into the new chiral center. It can also be present in an added compound, in the solvent, etc.

An especially elegant way of inducing asymmetry is by use of an optically active catalyst. In this case the chiral information contained in a small amount of an optically active catalyst will show up in the optical activity of a large amount of product. The formation of chiral centers in living beings by enzymes is the best example of this concept of asymmetric catalysis. Another important field in asymmetric catalysis, intensively studied in the last decade, is the homogeneous catalysis by transition-metal complexes containing optically active ligands, mainly asymmetric hydrogenation.[1-11] An example is the asymmetric hydrogenation of α-(acetamino)acrylic acid (Scheme I) in which, depending on the enantioselectivity of the optically active catalyst used, different amounts of enantiomers of acetylalanine are formed. In this Account, the optical induction in organometallic compounds of the transition elements and its relevance to homogeneous asymmetric catalysis will be discussed.
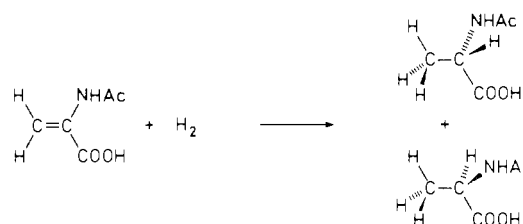
Optically Active Organo-Transition-Metal Compounds

Optically active organometallic compounds in which the transition element is the center of chirality have been available since 1969. Some examples of cyclopentadienyl and carbonyl complexes are shown in Scheme II, in which the transition metal M and the ligands L, L_1, L_2, L_3 can be varied within wide limits. The synthesis and resolution of these compounds have been reviewed.[12-15]
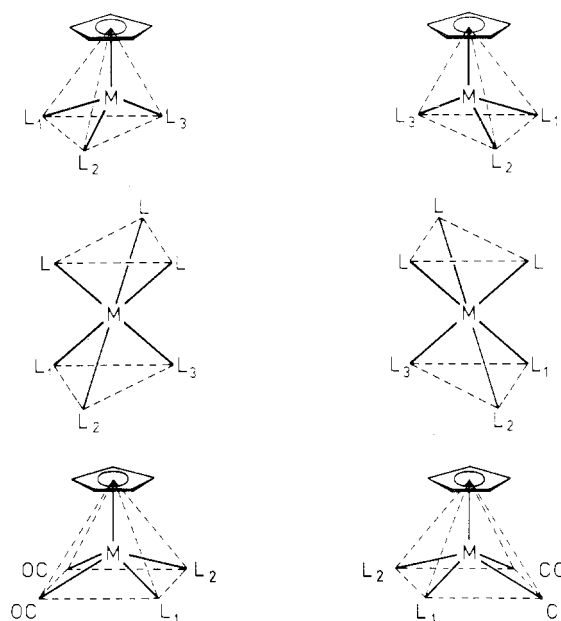
All the optically active compounds described hitherto are optically stable at the metal center in the solid state. As far as the behaviour in solution is concerned, the compounds can be divided into two groups: (a) those which are configurationally stable at the metal center until they start to decompose, (b) those which are configurationally labile at the metal center, racemizing

Scheme I

Scheme II

or epimerizing with respect to the metal atom prior to decomposition. With compounds of type a, the ste-

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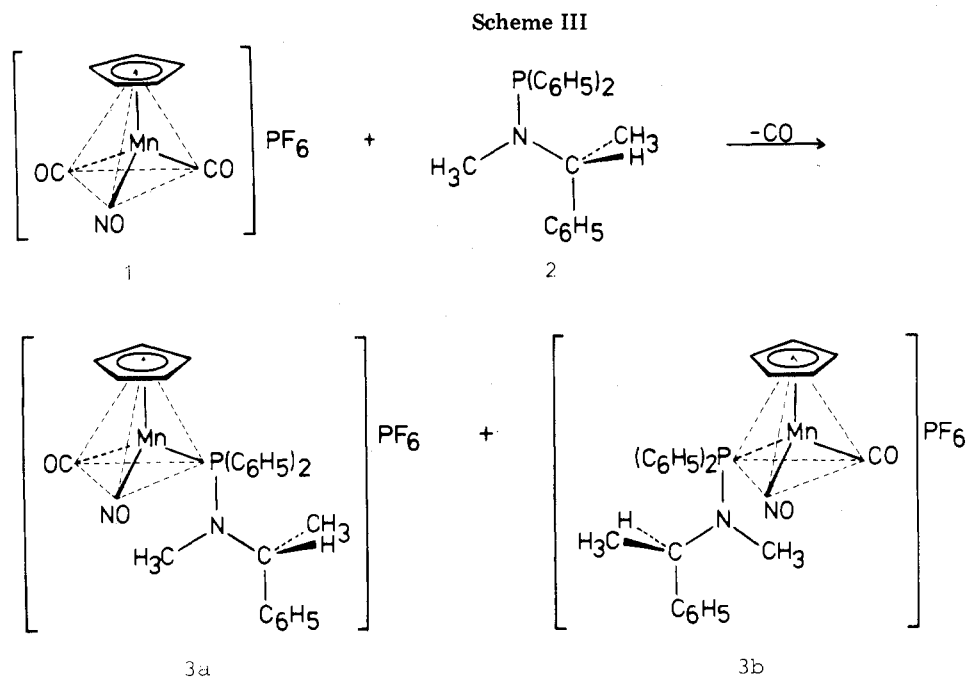
Scheme III

reochemistry of substitution reactions can be studied, whereas with compounds of type b, the mechanism of racemization and epimerization at the chiral metal atom can be investigated. The usefulness of these compounds in elucidating the stereochemical course of organo-metallic reactions has been summarized.[14-16] In the present Account, only questions associated with asymmetric induction in organometallic compounds will be considered.

Optical Induction in Organo-Transition-Metal Compounds. Kinetic Control

In the synthesis of optically active organometallic complexes, different approaches have been used.[13,14] Mostly, the chiral center at the metal atom is built up starting from a prochiral precursor, as exemplified in Scheme III. The cation of $[C_5H_5Mn(CO)_2(NO)]PF_6$ (1) contains a symmetry plane bisecting the cyclopentadienyl ring, the manganese atom, the nitrosyl group, and the angle between the two carbonyl groups on either side of it. If one of the two enantiotopic carbonyl groups is replaced by a monodendate ligand L, the metal atom becomes a chiral center. Under achiral conditions, substitution at both CO sites has the same probability, and both enantiomers arise to the same extent.[17-20] However, toward an optically active ligand L*, e.g., the aminophosphine 2 in Scheme III, the two Mn–CO sites are no longer equivalent, and the two diastereoisomers 3a and 3b, differing in the configuration at the metal atom, are formed in a ratio of 66:34.[21,22] As the diastereoisomeric products 3a and 3b are stable toward interconversion,[23-26] their ratio is
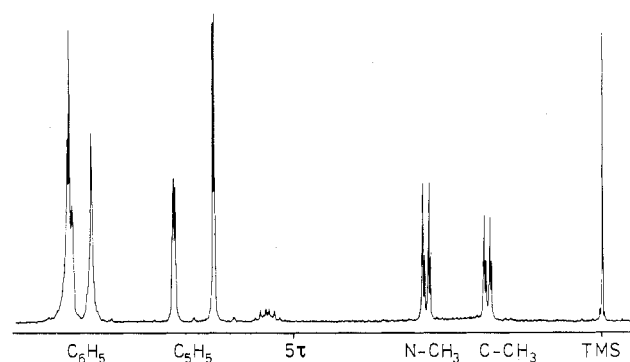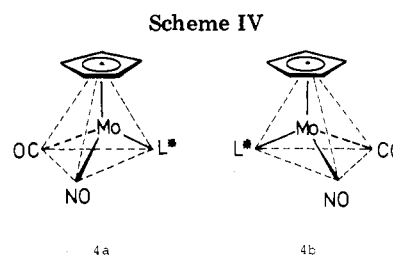

Figure 1. ^1H NMR spectrum of a mixture of 3a and 3b, enriched in 3a, in CD_3COCD_3 (internal $(CH_3)_4Si$), without solvent signals.

Scheme IV

a measure for the optical induction of (S)-$(C_6H_5)_2PN(CH_3)CH(CH_3)(C_6H_5)$ (2) in the substitution of Scheme III. It reflects the different activation energies for the formation of the two different diastereoisomers from the same prochiral precursor in this kinetically controlled reaction.

^1H NMR spectroscopy has proven valuable as an analytical method to determine the diastereoisomer ratio. In many cases, the two diastereoisomers with opposite configurations at the metal atom differ in their ^1H NMR chemical shifts.[13-16,27] This holds especially when phenyl rings are present in the molecules. The

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"beam effect" of the aryl anisotropy is the main reason for the chemical shift differences of diastereoisomers. The ^{1}H NMR spectra of organometallic compounds usually contain well-separated high-intensity ligand singlets or doublets. This is demonstrated in Figure 1 for the diastereoisomers **3a/3b**, which differ in the chemical shifts of their C_5H_5, N-CH_3, and C-CH_3 signals.[22] Thus, as for **3a/3b** by integration of the C_5H_5 doublets, the diastereoisomer ratios generally can be determined by integration of appropriate ^{1}H NMR signals.

The prochiral compound $[C_5H_5Mo(CO)_2(NO)]$ was converted into the two diastereoisomers **4a** and **4b** of Scheme IV by reaction with optically active ligands L* in the same way as shown in Scheme III for $[C_5H_5-Mn(CO)_2(NO)]PF_6$ (**1**). As optically active ligands L*, ten phosphorus derivatives were used in a study to investigate how a variation of L* affects the amount of optical induction and properties like diastereoisomer separability by preparative liquid chromatography or fractional crystallization.[28,29]

The optical inductions observed in the formation of **4a/4b** were low, the highest being 70:30 for L* = diphenylmenthylphosphine. All the other values ranged between 60:40 and 50:50. Interesting was the fact that the aminophosphine L* = **2**, which gave an optical induction of 32% at the Mn atom in the CO substitution of $[C_5H_5Mn(CO)_2(NO)]^+$ (Scheme III), did not lead to any optical induction at the Mo atom in the analogous CO substitution of $[C_5H_5Mo(CO)_2(NO)]$ for which the diastereomer ratio turned out to be **4a**:**4b** = 50:50. The main reason for this difference is that different reaction conditions are needed to bring about CO substitution in $[C_5H_5Mn(CO)_2(NO)]^+$ and $[C_5H_5-Mo(CO)_2(NO)]$. Compared to the Mo–CO bond in the neutral Mo compound, the Mn–CO bond in the cationic Mn complex is much weaker due to the strongly decreased π-acceptor interaction in the positively charged species.[17-20,30,31] As a consequence, CO substitution in $[C_5H_5Mn(CO)_2(NO)]^+$ occurs readily in acetone at room temperature, whereas for CO substitution in $[C_5H_5-Mo(CO)_2(NO)]$ the complex has to be heated with the ligand to 100–110 °C, these drastic conditions leading to reduced selectivity.

The formation of the complexes **3a/3b** and **4a/4b** may be considered a special case because two of the ligands at the asymmetric metal atom are very similar. Both the CO and the NO group are linear diatomic ligands with comparable bond lengths, so that the optical inductions might not be expected to be as large as in complexes in which the metal atom is surrounded by completely different ligands. However, CO and NO turn out to be stereochemically completely different ligands giving rise to high optical rotations and to good diastereoisomer separability. This is corroborated by the fact that in most of the cases described, the optical inductions in the conversion of prochiral precursors to chiral compounds are of the same order of magnitude as in the representative Schemes III and IV.[32] Only in very specific cases have high optical inductions been

observed. Thus, in the reaction of $C_5H_5Mo(CO)_3H$ with optically active aziridines, the tendency of the bulky substituents at the chiral carbon atoms to stay equatorial in the puckered five-membered ring, resulting from ring opening, CO incorporation, and metal coordination, controls the configuration both at the Mo and the N atom; only one isomer out of a total of eight possible isomers is formed.[32,33]

Although many asymmetric syntheses of the type shown in Scheme III have been carried out, the optical induction could be determined only for a few systems. One reason for this fact is that in many cases reaction conditions are so vigorous that diastereoisomers interconvert—a phenomenon which will be discussed in detail in the following section. Moreover, normally it is not possible to integrate the ^{1}H NMR spectra of crude reaction mixtures right after finishing the reaction because of signal broadening due to paramagnetic impurities or because of signal overlap of diastereoisomers and byproducts. Since the original diastereoisomer ratio may change during work-up, only the optical induction of some clean and high-yield reactions could be measured; in these the optically active ligands always were used in large excess to achieve good conversion of the organometallic component into the diastereoisomers. Experiments on kinetic resolutions in this field have only been reported for the titanocene series CpCp′TiXY.[34] Thus, only a limited amount of data on kinetically controlled optical inductions in organo-transition-metal chemistry is available.

Optical Induction in Organo-Transition-Metal Compounds. Thermodynamic Control

In the examples discussed so far, the diastereoisomer ratio reflects the different activation energies for the conversion of a prochiral precursor to the two different diastereoisomers. If under the reaction conditions the diastereoisomers are configurationally labile at the metal center, equilibration takes place, and the diastereoisomer ratio then reflects the energy difference between the two diastereoisomers.

Many of these isomer interconversions have been studied because usually these equilibration reactions are clean and there are no byproducts and paramagnetic impurities. Thus, the determination of the diastereoisomer ratio is straightforward by ^{1}H NMR integration. This ratio is needed to calculate the kinetic data and the equilibrium parameters, as shown for complexes with monodendate and bidendate optically active ligands.

Complexes with Monodendate Optically Active Ligands. Contrary to the configurationally stable compounds $[C_5H_5Mn(CO)(NO)PAr_3]PF_6$ (**3**, Scheme III), the complexes $[C_5H_5Mn(COR)(NO)PAr_3]$, derived from **3** by reaction with LiR,[22,35-38] are configurationally labile at the Mn center.[22,36-40] Depending on the

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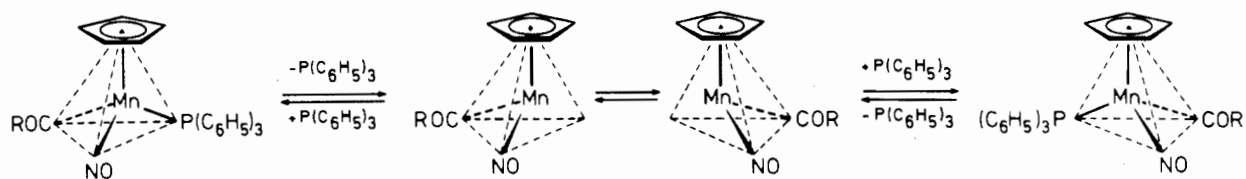
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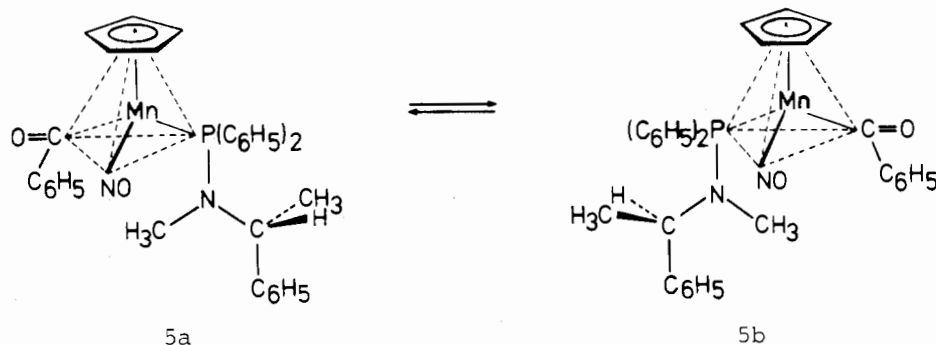
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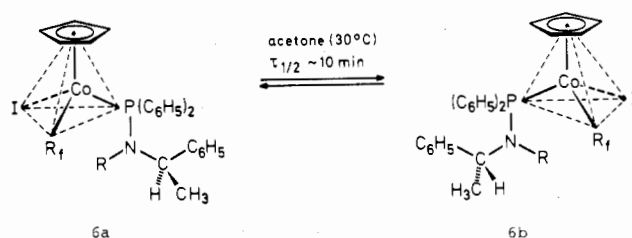
Scheme V

Scheme VI

5a   5b

substituents R = alkyl, aryl, or alkoxy and the triarylphosphine PAr_3, the optically active compounds $[C_5H_5Mn(COR)(NO)PAr_3]$ racemize in solution with half-lives of hours to minutes at room temperature. The mechanism for the triphenylphosphine derivative has been shown to be that shown in Scheme V.[41] In the rate-determining step triphenylphosphine dissociates, giving rise to a chiral intermediate.[36,37] Like ammonia, this chiral intermediate can invert to its mirror image, leading to the observed racemization. Instead of inverting, the chiral intermediate can also pick up triphenylphosphine at the vacant site to give the starting material without loss of optical activity.[36,37] Substitution reactions could be carried out by quenching the chiral intermediate with phosphines giving configurationally more stable complexes, with retention of configuration at the metal atom confirming the existence of the chiral intermediate.[22,36,40] The planar form between the two chiral intermediates could be shown by calculation to be a transition state.[42]

As phosphine, PX_3, in the complexes $[C_5H_5Mn(COC_6H_5)(NO)PX_3]$, the optically active aminophosphine **2** (Scheme III) was used, also. The two diastereoisomers **5a** and **5b** (Scheme VI), differing in the Mn configuration, interconvert in toluene solution.[22] Equilibrium is approached at 20 °C with a half-life of 19.2 min, which is very similar to that of 21 min for the corresponding $P(C_6H_5)_3$ complexes.[22,37,40]

Although racemization of an optically active complex $[C_5H_5Mn(COR)(NO)PX_3]$, in which PX_3 is triphenylphosphine or another achiral phosphine, inevitably leads to a 1:1 ratio of both enantiomers, epimerization of an optically active complex $[C_5H_5Mn(COR)(NO)PX_3]$, in which PX_3 is a chiral phosphine like **2**, gives two diastereoisomers in a ratio not equal to 1:1. These diastereoisomers both contain exactly the

Scheme VII

6a   6b

R = CH₃	(+) : (−)
$R_f = CF_3$	30 : 70
$R_f = C_2F_5$	30 : 70
$R_f = n\text{-}C_3F_7$	30 : 70

$R_f = n\text{-}C_3F_7$	(+) : (−)
R = H	52 : 48
R = CH₃	30 : 70
R = C₂H₅	14 : 86

same ligands; they only differ in the configuration at the manganese atom. In the equilibration reaction the labile configuration at the metal center is changing under the influence of the stable chirality in the optically active ligand. Thus, the optically active ligand controls the equilibrium concentration of the two mirror image metal configurations. A measure for these optical inductions from the ligand to the metal atom is the diastereoisomer ratio at equilibrium, identical with the equilibrium constant, which reflects the different energy content of both diastereoisomers, irrespective of the mechanism of the change in configuration at the metal atom.[43] For the diastereoisomers **5a** and **5b**, an equilibrium ratio of 34:66 was obtained. This ratio is exactly the same as that for **3a/3b** (Scheme III), but interestingly the manganese configuration favored in the asymmetric synthesis (Scheme III) is the disfavored configuration in equilibrium 6. As the absolute configurations for complexes **3** and **5** are not known, this only refers to the relative configurations.

Another pair of diastereoisomers for which epimerization at the metal atom is rapid is shown in Scheme VII. In the Co complexes **6a** and **6b**, the optical in-

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Scheme VIII

7a   7b
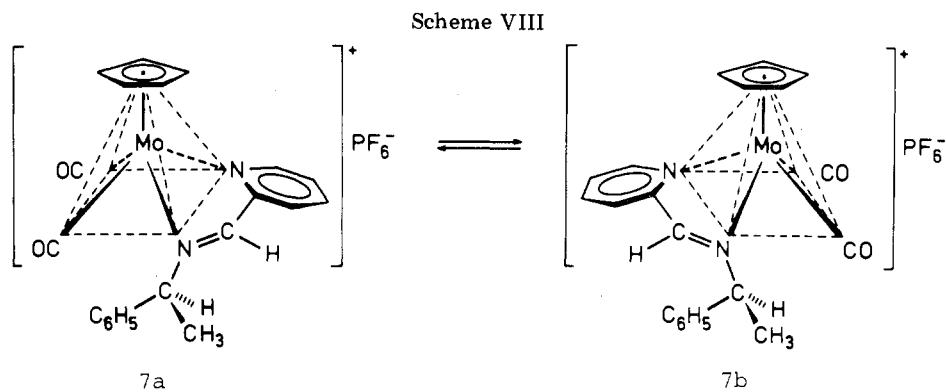
duction at equilibrium was studied as a function of the perfluoroalkyl group R_f and the substituent R at the nitrogen atom in the optically active phosphine.[44] According to the data in Scheme VII the equilibrium ratio for the two diastereoisomers **6a**/**6b** is 30:70 for R = CH$_3$, irrespective of whether the perfluoroalkyl group R_f is CF$_3$, C$_2$F$_5$, or n-C$_3$F$_7$. On the other hand, a variation of the N substituent in the optically active phosphine has a marked influence on the equilibrium ratio **6a**/**6b**. For R = H the ratio is 52:48; it rises to 30:70 for R = CH$_3$ and to 14:86 for R = C$_2$H$_5$, which means that in the last case the dominating isomer at equilibrium is present with an optical purity of 72%. It is not too surprising that a lengthening of the fluoroalkyl chain is not important for the equilibrium induction. The substituent at the nitrogen atom, however, located between the inducing chirality at the carbon atom and the changing chirality at the metal atom, seems to act as a "transmitter" of the chiral information.

Complexes with Bidentate Optically Active Ligands. The complexes C$_5$H$_5$ML^{1}L^{2}L^3 must be called octahedral if the C$_5$H$_5$ ligand is assumed to occupy three cis positions at the octahedron. As the C$_5$H$_5$ ring is only one rigid ligand, all stereochemical considerations of the compounds C$_5$H$_5$ML^{1}L^{2}L^3 reduce to the image/mirror image relationship of the tetrahedron with four different substituents. In the same way, the complexes C$_5$H$_5$ML^{1}L^{2}L^{3}L^4 with four-legged pianostool geometry can best be described as square-pyramidal.[14] By the following constraints, the general case of a square-pyramid for which 30 different isomers are possible is reduced to the problem of image and mirror image isomers only.[45] First, the C$_5$H$_5$ ligand in the compounds C$_5$H$_5$ML^{1}L^{2}L^{3}L^4 is at the top of the pyramid, in accord with the large body of structural evidence available.[14] Second, two carbonyl groups cis to each other, and third, an unsymmetrical chelate ligand, LL′, occupy the basis of the pyramid. Thus, the use of an achiral chelate ligand LL′ in [C$_5$H$_5$M(CO)$_2$LL′] leads to a pair of enantiomers, whereas an optically active bidentate ligand LL* gives rise to a pair of diastereoisomers differing only in the configuration at the metal atom.[13,14,16,45]

This concept was first realized with the C$_5$H$_5$Mo(CO)$_2$ complexes of the optically active 2-pyridinecarbimine, derived from 2-pyridinecarbaldehyde and (S)-1-phenylethylamine (Scheme VIII).[45-48] The two isomers

Scheme IX

8a   8b
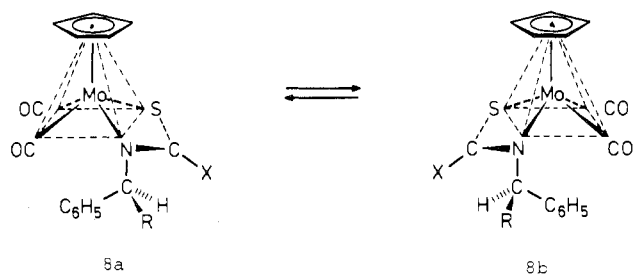
	R = CH$_3$	R = CH$_2$–CH$_3$	R = CH(CH$_3$)$_2$
X = H	50 : 50		
X = CH$_3$	69 : 31	89 : 11	98 : 2
X = C$_6$H$_5$	77 : 23	95 : 5	99 : 1
X = C$_{10}$H$_7$	87 : 13		

7a and **7b** could be separated by fractional crystallization.[45,47] Their optical purity can be checked because they differ in their ^{1}H NMR spectra.

In the solid state as well as in solution at room temperature both diastereoisomers **7a** and **7b** are configurationally stable. However, on heating solutions of **7a** or **7b** in DMF to temperatures of 60–90 °C a first-order approach to the epimerization equilibrium **7a** ⇌ **7b** takes place, the half-life for 75 °C being 26 min.[48] The mechanism of the change in configuration at the Mo atom occurs by what is supposed to be an intramolecular metal-centered rearrangement, most easily visualized as a 180° rotation of the unsymmetrical chelate ligand LL* with respect to the C$_5$H$_5$Mo(CO)$_2$ fragment.[14,16,45-53] The rate of this epimerization, which can be studied by polarimetry or by ^{1}H NMR spectroscopy, is strongly dependent on the nature of the chelate ligand LL*.[14,16,48,52,54-61] The equilibrium ratio

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7a/**7b** is 59:41 in acetone-d_6 (80 °C, sealed tube),[62] a value which is not very solvent dependent.[63]

For the $C_5H_5Mo(CO)_2$ complexes with the thioamidato ligands $SC(X)NCH(R)(C_6H_5)$ (Scheme IX) the equilibrium ratios of the two diastereoisomers **8a**/**8b** were studied as a function of the substituents X and R in thioamidato system. In the variation of substituent X with the amino component constantly being (S)-$NCH(CH_3)(C_6H_5)$, the following results were obtained (Scheme IX, first column): for the formic acid derivative X = H, the ^1H NMR integration at equilibrium gives a 50:50 ratio of both diastereoisomers. Thus, there is no optical induction in the equilibration of the labile metal configurations under the influence of the stable asymmetric center (S)-$CH(CH_3)(C_6H_5)$ in the thioformamidato ligand. For the acetic acid derivative with X = CH_3, the corresponding equilibrium ratio of **8a**/**8b** is 69:31. The benzoic acid thioamide as a ligand leads to an even larger ratio of 77:23 and the α-naphthoic acid derivative of 87:13. Thus, in the series X = H, CH_3, C_6H_5, $C_{10}H_7$ there is an increase in the optical induction at equilibrium from 0 to 74%.[14,57-59,63] All values were determined in toluene-d_8 at 40 °C at which temperature the equilibration of $C_5H_5Mo(CO)_2$ thioamidato complexes **8a** and **8b** has been shown to be rapid.[14,57-59]

In the variation of the alkyl substituent R at the asymmetric center, in which the X substituents were CH_3 and C_6H_5, respectively, even larger changes in the equilibrium ratios **8a**/**8b** were observed than in the variation of group X. As alkyl substituents, methyl, ethyl, and isopropyl were used (Scheme IX, rows 2 and 3).[64] In the acetic acid series, the corresponding diastereoisomer equilibria **8a**/**8b** were 69:31, 89:11, 98:2. For the benzoic acid series all ratios **8a**/**8b** were a little larger: 77:23, 95:5, and 99:1. That means that the stable asymmetric center with the substituents H, C_6H_5, and i-C_3H_7 in the acetic acid series (X = CH_3) gives an asymmetric induction of 96% and in the benzoic acid series (X = C_6H_5) of 98% at equilibrium.[64] Results similar to those with the thioamidato complexes **8a**/**8b** were obtained with the pyridinecarbimine complexes **7a**/**7b** on changing the substituents at the asymmetric center in the imine part of the ligand, but all the values are a litter smaller.[62]

A variation of the phenyl substituent at the asymmetric center was carried out for compounds **8a**/**8b**. It turned out that a p-methyl group as well as a m-methyl group in the phenyl ring had no effect on the equilibrium ratio. This was to be expected because para and also meta substituents, in contrast to ortho substituents, do not interfere with other parts of the molecule. Indeed, an o-methyl group makes the ratio rise to 88:12 in the acetic acid series, and to 92:8 in the benzoic acid series.[65] Again, the value for the acetic acid series is

Scheme X
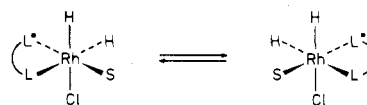
a little lower than that of the corresponding member of the benzoic acid series.

The variations of group X have been carried out with optically active ligands, giving two diastereoisomers with different metal configurations, whereas for the variations of group R and of the aryl group at the asymmetric center the ligands were used as racemic mixtures, leading to two enantiomeric pairs of diastereoisomers on complex formation. ^1H NMR analysis, however, does not differentiate between these two cases, as could be demonstrated experimentally.[64] The only difference is that in the latter cases the term optical induction has to be replaced by asymmetric induction.

The measured diastereoisomer ratios can only be rationalized on the basis of the stereochemical model of Ruch-Ugi[66,67] if—contrary to the λ parameters in organic chemistry[68-73]—for alkyl substituents big positive λ values and for phenyl a strongly negative λ value is applied.[64] The negative λ value for phenyl, which means that phenyl is "smaller" than hydrogen, has been interpreted in terms of a weak positive interaction between the MC_5H_5 group and the phenyl ring in position β to it. For a MC_5H_5/phenyl interaction there is also evidence from several X-ray structure analyses.[74,75]

The important result of the studies described is the possibility for varying the equilibrium induction at a chiral metal atom within wide limits by changing the substituents for a given ligand system. In the series of the $C_5H_5Mo(CO)_2$ thioamidato complexes it could be shown that, for the thioamidato ligand derived from formic acid and (S)-1-phenylethylamine, no optical induction was observed, whereas for the thioamidato ligand derived from benzoic acid and 1-phenyl-2-methylbutylamine a 98% equilibrium induction was found. Similarly, it should generally be possible to shift a diastereoisomer equilibrium from a situation where both isomers are present in equal amounts to situations where a favored isomer is dominating to a situation where only one isomer out of a pair of two is formed, just by varying the substituents of a given ligand system. Thus, the metal configuration in labile complexes can be controlled by asymmetric induction from optically active ligands.

Asymmetric Hydrogenation and Metal Configuration

In the last 10 years much work has been done to optimize Wilkinson-type catalysts for asymmetric

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hydrogenation.[1-11] At the outset instead of the $P(C_6H_5)_3$ ligand in $RhCl[P(C_6H_5)_3]_3$ optically active monodendate phosphines chiral in the side chain like $P(C_6H_5)_2R^*$ or chiral at the phosphorus atom like $P(CH_3)(C_6H_5)(C_3H_7)$ were used.[76-78] Six years ago Kagan developed his bidendate phosphine, Diop, derived from tartaric acid, which proved to be easily accessible and extremely versatile in asymmetric catalysis. In hydrogenation reaction I, an optical yield of 73% was reported.[79] With the optically active ligand Dipamp, the optical yield of the Rh-catalyzed asymmetric hydrogenation of eq I could be increased to 96%.[80] In that way the amino acid Dopa, a drug for Parkinson's disease, is prepared on a commercial basis. Two other optically active chelate phosphines, Chiraphos[81] and Prophos,[82] giving high optical yields in asymmetric hydrogenation reactions, were described by Bosnich.

The catalytic species originally was formulated by Osborn and Wilkinson as shown in Scheme X.[83] The Rh complex was supposed to contain the ligands LL* = $2P(C_6H_5)_3$, two Rh–H bonds from the oxidative addition of H_2, the Cl ligand already present in the precursor $RhCl[P(C_6H_5)_3]_3$, and S, a solvent molecule or the olefin to be hydrogenated. In this structure the Rh atom is a chiral center; for LL* = $2P(C_6H_5)_3$, **9a** and **9b** are enantiomers. Even species like $Rh(LL^*)HS_3$, with only one hydrogen ligand cis to LL*, are chiral at the Rh atom, the charge depending on whether S is a neutral solvent molecule or an anionic ligand like Cl^-.[84,85] The chirality at the Rh atom only disappears for a complex $Rh(LL^*)HS_3$, in which LL* and H are in one plane with the metal atom, this plane being a symmetry plane of the complex. For a ligand combination LL*/prochiral olefin, e.g., N-acetaminoacrylic acid, in an octahedral Rh complex, the situation is more complicated. Even for a planar arrangement of LL* and prochiral olefin, the Rh atom becomes an asymmetric center, because the plane defined by LL*, Rh, and the prochiral olefin is not a symmetry plane for the different substituents at the prochiral olefin. In the latter case, the Rh configuration is coupled to the configuration of the asymmetric carbon atoms formed by coordination of the prochiral olefin. For compounds of type 9 or cis-$Rh(LL^*)HS_3$, however, such a coupling does not exist, and the configurations of the Rh atom and the asymmetric carbon atoms of the coordinated prochiral olefin are independent of each other.

All the catalysts used so far contain the chiral information either in the side chains of the phosphines or at the phosphorus atom itself. As a first approximation, the optical induction should increase with decreasing distance between the inducing chirality and the newly forming asymmetric center. It therefore seemed promising to move the inducing chirality to the metal atom where the catalysis is occurring. In a complex optically active at the metal atom, the distance between the inducing chirality and the prochiral center would be a minimum, and, therefore, a catalyst of that type is expected to give especially high optical yields in asymmetric catalysis. Two ways to move the chirality in a catalyst to the metal atom can be envisaged, as shown for Rh complexes with unsymmetrical bidendate ligands LL* of type **9a/9b**:

First, in the introduction it was mentioned that organo-transition-metal compounds chiral at the metal atom have been available since 1969 and that many stereospecific reactions of these compounds are known.[13-16] Therefore, a possible approach to a catalyst optically active at the metal atom would be to synthesize an optically active Rh complex which can be converted stereospecifically into the catalytically active species. On the other hand, as also mentioned in the introduction, it has been shown that optically active organo-transition-metal compounds may be configurationally labile at the metal center.[14-16] Ligand dissociations may occur accompanied by rearrangement of the fragments before the ligand which dissociated or another ligand comes back to the vacant site. Pseudorotation-like intramolecular rearrangements with loss of optical activity may take place, especially in derivatives with reduced coordination number. Since, in catalytic reactions such as olefin hydrogenation, ligand dissociations and reductive eliminations are key steps, it is to be expected that the optical activity at the metal atom inevitably will be lost after one or at the most after a few catalytic cycles. Therefore, the use of an optically pure catalyst in an asymmetric catalysis will not necessarily result in a high optical yield.

A second approach seems to be more promising: if LL* is an optically active chelate ligand, it should be possible to control the metal configuration in a catalyst by optical induction from LL* even in the case of rapid equilibration in the same way as has been demonstrated for the $C_5H_5Mo(CO)_2$ thioamidato system.[14,58,59,63,64] At this point two problems arise, one with respect to the number of possible Rh configurations in a real catalyst and one with respect to the different reactivities of the resulting diastereoisomers.

It has already been mentioned that for an octahedron with 6 different ligands 30 isomers are possible; these subdivide into 15 pairs of enantiomers. In the active species of an asymmetric hydrogenation catalyst, the chelate ligand LL* with two different ligating centers, Rh–H bonds, the prochiral olefin, solvent molecules, and anions may be present, giving rise to a large number of possible isomers. For square-pyramidal complexes with 5 different ligands, the number of isomers is also 30 as for the octahedron because the empty coordination position in a square pyramid must be treated as a phantom ligand. Nevertheless, by introducing three constraints as described in the preceding paragraph, the number of isomers for the square-pyramidal complexes $[C_5H_5Mo(CO)_2LL^*]$ could be reduced to two, image and mirror image.[13,14,46] In the same way it should also be possible to reduce the large number of isomers of a catalyst by constraints of the following type: chelates can only occupy cis positions at an octahedron, different

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ligands show varying cis–trans preferences, and so on.

Let us assume the number of isomers of an octahedral Rh catalyst can be reduced to two species, differing only in their configuration at the Rh atom. Then, by the concept of optical induction from a chiral ligand LL* to the metal atom, it should be possible to shift the epimerization equilibrium far to one side, as in the case of the 98:2 and 99:1 equilibria of the $C_5H_5Mo(CO)_2$ complexes with appropriately substituted thioamidato ligands.[64] In spite of having brought the optical activity to the Rh atom and keeping it there, with the help of the concept of optical induction from the ligand, a high optical yield with such a catalyst is to be expected only if both diastereoisomers have about the same reactivity or if the favored isomer reacts faster to products than the disfavored isomer. A higher reactivity of the dis-favored isomer would have the effect of neutralizing what was gained by favoring one metal configuration in the equilibrium.

In spite of the limitations and open questions discussed, it is a tempting idea to use the concept of metal configuration and its control by optical induction from the ligand in the field of asymmetric catalysis. Specifically, it will be interesting to investigate whether a set of ligands LL*, containing different substituents, will give the same trends on the one hand in the optical induction at the metal center in mobile diastereoisomer equilibria like that of Scheme IX and, on the other hand, in the optical yield of asymmetric catalyses like that of Scheme I. A parallelism in these experimental criteria would be a good argument for the important role of the metal configuration in asymmetric catalysis.

Structure of Cyclic Pentacoordinated Molecules of Main Group Elements

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Ten years ago, only one structure of a cyclic phosphorane was known, the 1:1 adduct of phenanthrenequinone and triisopropyl phosphite, characterized as trigonal bipyramidal.[1] At that time, the trigonal bipyramid was the prevailing structural form for main group elements.[2]

Since then, more than 50 structural studies on cyclic phosphoranes have appeared.[3,4] It is particularly interesting that these compounds form a continuous range of conformations extending from the ideal trigonal bipyramid to the square or rectangular pyramid.[3,4] In this respect, pentacoordinated phosphorus is unique.

It is now apparent that the square pyramid, once regarded as a transition state in interpreting fluxional behavior of pentacoordinate phosphoranes,[5] may also be regarded as a ground-state conformation for certain cyclic species.[6] This raises the possibility that the trigonal bipyramid may, on occasion, assume the role of an activated state. Presumably, this reversal in the roles of ground state–transition state represents a possibility for pentacoordinated molecules of other less investigated main group elements containing cyclic components. Since an understanding of reaction mechanisms of many cyclic phosphorus derivatives depends on an intimate knowledge of postulated pentacoordinated states in rate-controlling steps,[7] it is essential to know when one or the other structure is favored for isolatable cyclic phosphoranes.

This Account is constructed to explore factors responsible for the observed structural preferences of individual pentacoordinated members and to point to the applicability of the resulting principles to mechanistic schemes involving cyclic derivatives. We shall first examine the range of cyclic structures observed for main group elements and then consider their relative fluxional character before outlining the proposed role of pentacoordination in reaction mechanisms.

Pentacoordination is widespread, but if we confine our attention to main group elements in monomeric species which have been structurally characterized by diffraction techniques or microwave spectroscopy, a more limited number of elements comes under consideration.[8] Further, characterization of five-coordi-

2B	3A	4A	5A	6A
	Al	Si	P	S
Zn			As	
	In	Sn	Sb	

nated species containing cyclic substituents is lacking for Al, In, Sn, and Sb. However, if we allow pseudopentacoordination, i.e., pentacoordination in which one

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