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On some general regularities in the action of enantioselective hydrogenation catalysts *

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Abstract

Experiments on the asymmetric hydrogenation of prochiral keto compounds through intermediate catalyst-ligand-substrate triple complexes are summarized. Correlations of enantioselectivity of reaction on heterogeneous metallic catalysts modified with optically active amino acids are emphasized. Relationships of the stability constants of complexes corresponding to catalytic intermediates, to the optical yield in hydrogenation of ethyl acetoacetate and acetylacetone on Ni, Cu, and Co catalysts modified with (*S*)-phenylalanine, (*S*)-triptophane, and (*S*)-tyrosine are reviewed.

Correlations between enantioselectivity and chiral properties (magneto-optical rotatory dispersion and circular dichroism) of complexes are established. These provide a basis for the future selection of asymmetric metal catalysts for hydrogenation of prochiral keto compounds.

Studies of asymmetric catalysis over the last few decades have revealed great progress, so that now it is clear that almost 100% enantioselectivity in many catalytic process. We can define optical yields (p) in terms of enantioselectivity (E) thus **: $p = ([R] - [S])/([R] + [S]) \times 100\%$.

Table 1 lists examples of effective asymmetric reactions on metallic catalysts (x) and organometallic homogeneous catalysts (●) [1]. Particularly remarkable are the asymmetric hydrogenations of precursors of (*S*)-amino acids that have been achieved with Rh-phosphine complexes as chiral catalysts.

This field continues to develop rapidly. A large, and growing, number of new chiral ligands have been developed but the choice of new chiral catalytic systems has been on a pure empirical basis. There is a lack of theories to relate catalytic effectiveness to chiral ligand structure, which would enable us to predict the synthesis of new enantioselective catalysts.

* Dedicated to the memory of Professor Piero Pino.

** $E = R/S$; only small values of p (20–30%) can the relationship with E be assumed to be linear.

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In recent years there have been attempts to derive general stereochemical principles, from the structures of known intermediate complexes, which would permit prediction of the absolute configuration of products [2,3].

In this review we attempt to outline principles for predicting activity of metallic catalysts modified with optical active compounds, and of organometallic catalysts which incorporate chiral ligands. At the base of such principles are stereochemical correlations between the structure of the intermediate complex and that of the complex, along the same lines as the well-known principle of structural correspondence embodied in the Multiplet Theory of catalysis [4]. In asymmetric catalysts such a correspondence is not particularly close and it is best considered in terms of chirodiastatic interaction [5] of chiral ligands, or modifiers of catalyst with intermediate forms of the substrate. Here the main point is that the reaction proceeds via the formation of an intermediate triple complex:

$$C + L/M \longrightarrow [C-L/M] \longrightarrow \begin{matrix} [L/M \cdots S] \\ \vdots \\ C \end{matrix}$$

(C: catalyst; L: ligand; M: modifier; S: substrate)

This simple model was first proposed [6] for asymmetric hydrogenation on a Ni metal catalyst modified with optical active (*RR*)-tartaric acid (Tart) or (*S*)-amino acids. According to the model the intermediates are atoms, or cations of the metal bonded to the surface of the catalyst and coordinated with the chiral modifier (M), and with the prochiral substrate molecule (S), usually a ketone or diketone, also coordinated by the metal. This model has been discussed, and has been modified [7]. The bonds M–C, S–C and M–S can be considered separately here. M–S is the source of the chirodiastaltic interaction and is responsible for the stereochemical aspect of the reaction. M–C and S–C depend on the coordinating ability of the metal and, in case of an heterogeneous catalyst, on the catalyst surface.

Two kinds of steric hindrances arise, (i) from the structure of the reacting molecule and (ii) from the microrelief of the surface of the catalyst. The latter must, according to the Multiplet Theory, play the definite role in determining the stereochemistry of the process. For example in hydrogenation with Raney nickel of tripticene derivatives of successively complicated structure (from the annealing of benzene rings) the rate of hydrogenation decreases [8] as spacial hindrance increases. The shape and size of active centers on the catalyst can be determined from dimensions of the reacting molecules (Fig. 1).

On the surfaces of metallic catalysts [9,10] there are three principal kinds of sites, defined as ^{1}M (planes, faces or terraces), ^{2}M (edges or steps), and ^{3}M (corners or isolated atoms). Hydrogenation of (+)-apopinene (Scheme 1) has been used [11] as a molecular probe method to identify on the surface of Pd-catalysts the shapes of active centers, which are mainly ^{2}M and ^{3}M. Similarly the surface structures of Ni, Cu and Co catalysts modified with (*RR*)-tartaric acid has been deduced [12] from the asymmetric hydrogenation of the C=O group in ethyl acetoacetate or acetylacetone.

The size of metal crystallites on the surface of the catalyst play a major part in determining the efficiency of enantioselectivity in hydrogenation reaction. It was found (ref. 12, p. 127) that a Ru/SiO_2 catalyst modified with (*RR*)-tartaric acid has its greatest asymmetric ability in the hydrogenation of ethyl acetoacetate where crystallites are of dimension 45 Å. E values are smaller when the crystallites are

Table 1

Asymmetric reactions of metallic (○) and organometallic (×) chiral catalysts

Reaction		Metal											
		Ni	Cu	Co	Rh	Pd	Pt	Ir	Ru	Mo	Ti	Fe	V
Hydrogenation	C=O			×	×	×	×		×				
	C=O	○	○	×○	×			×	×				
	C=N	○	○	○	○×				×				
Hydroformylation				×	×	×							
Hydrocarboxylation				×	×								
Hydrosilylation	C=C				×	×							
	C=O				×	×	×						
	C=N				×								
Hydrovinylation		×											
Cross-coupling		×				×							
Cyclopropanation			×	×									
Polymerization		×									×	×	
Epoxydation										×	×		×
Isomerization				×					×				
Amination						×							

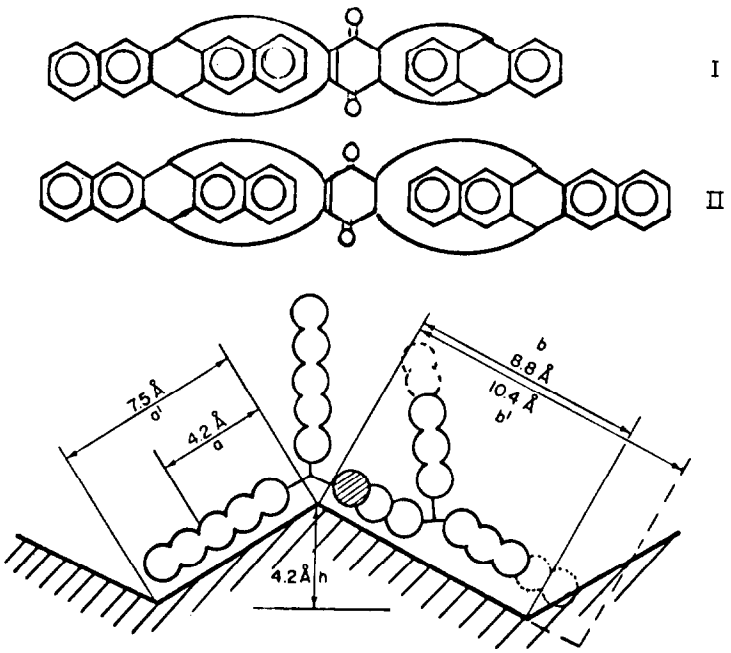
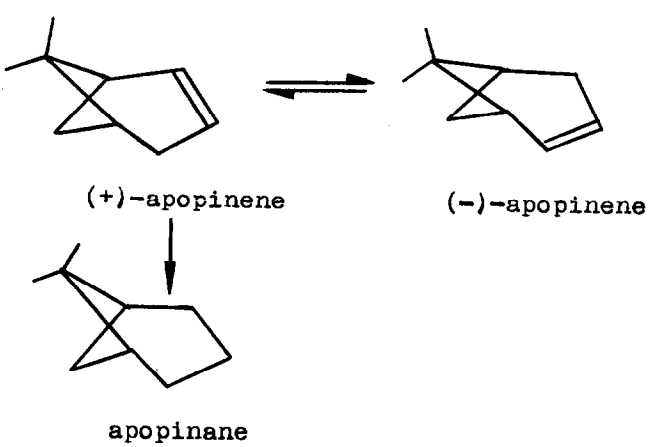


Fig. 1. The greatest dimensions of the active centre of hydrogenation. The model of hydrogenation tripticene derivatives (side view) I and II (dotted lines) on Ni, in solution of dimethylformamide, 45 °C, 1 atm.

smaller, implying that as in reference 13 the reaction is to be considered as spatially hindered. A similar dependence of p values in the hydrogenation of methyl acetoacetate, on Ni crystallite dimensions in Ni/SiO_2-Tart catalysts has been observed [14].

These studies clearly indicate the dependence of asymmetric hydrogenation on the nature of the surface of catalysts of cluster type. Further information on the cluster model of the catalyst surface has come from studies of asymmetric bimetallic catalysts modified with (*RR*)-tartaric acid. Asymmetric clusters are formed defined



Scheme 1.

by the nature of the surface and with minimal spacial and energetic constraint on contacts between the metal atoms and the molecules of modifier and substrate. Locations for such formations are centers like ^1M and ^2M on the crystallographic faces of the metal, which explains the high degree of sensitivity of asymmetric hydrogenation to the nature of the surface of the catalyst and particularly to the size of metal crystallites [12]. Further support for this view comes from the dependence of the p value in hydrogenation of ethyl acetoacetate using Ni–Cu catalyst on the temperature at which Ni and Cu mixed oxides had been reduced, and the H_2 concentration in the reducing atmosphere, in the process of formation of the catalyst. For instance, reducing the ratio H_2/He from 100 to 10% H_2 increases p values from 11 to 19% because the phase composition structure of the metal particles changes. Dalmon calculations using experimental data on the Cu–Ni composition dependence of p values revealed that clusters of enantioselective hydrogenation of ethyl acetoacetate include four times as many centres and extend over a greater area than the non-enantioselective clusters. This calculation was based on the presumption that only one pure enantiomer is formed on each enantioselective centre [15].

IR spectra of tartaric acid and acetylacetone adsorbed on number 20 o/o Cu–Ni/aerosil catalysts of different compositions indicated no coordinative interaction between the metallic phase and the chiral modifier [16]. Uneven adsorption of the two COOH groups is the result when tartaric acid interacts with the Cu–Ni phase. This follows from the dependence of the spectra on the composition of Cu–Ni catalysts, with the bonds between tartaric acid and the metals being less covalent in character when Cu–Ni (1 : 1) catalysts are considered. Comparing the $(\Delta_1 + \Delta_2)$ values ($\Delta = \nu_{as} - \nu_s$) with p values for the hydrogenation of acetylacetone on Cu–Ni catalysts demonstrates how the sum $(\Delta_1 + \Delta_2)$ changes as the composition of the metal phase of the catalyst changes. These data reveal the linear relationship of the p-value with $(\Delta_1 + \Delta_2)$ value. Thus, as catalyst composition changes, the strength of C–M bonds alters. This can be understood in terms of the reaction proceeding via an intermediate heteroligand complex (CMS) involving coordinative unsaturated atoms or cations on the surface of the metal catalyst. As the degree of covalence of the C–M bond increases formation of the C–S bond is hindered and the p value decreases.

Enantioselectivity as function of stability of intermediate complexes

Data on asymmetric hydrogenation on Ni-, Cu- and Co-modified catalysts (ref. 12, p. 183) were used to determine the relationships between the stability of heteroligand complexes formed on the surface of modified catalysts, and the enantioselective action of the same catalysts. In this consideration different approaches to this problem are possible. Identifying which factor determines the stability of the complex depends on understanding which of the bonds in the [MCS] complex define the enantioselective action of the catalyst. Published data, including our own studies on asymmetric hydrogenation of methyl acetoacetate, ethyl acetoacetate and acetylacetone on Raney nickel modified with chiral hydroxy and amino acids, have been analysed. There is a linear dependence of ln p (taken from data in ref. 17) on the stability constants, ln β for the reaction

$$C + nM \overset{\beta}{\rightleftharpoons} [CM_n].$$

The next step in the establishment of correlations between E and complex stability was taken when, as a means to quantify the strength of bonds of S with a surface complex [CM], e.g. [C–AA] where AA signifies amino acid, equilibrium constants for the reaction

$$2\,[\text{Cu–AA–EAA}] \overset{K_{CM-S}}{\rightleftharpoons} [\text{Cu(AA)}_2] + [\text{Cu(EAA)}_2]$$

were used. The range of variation of $\ln K_{CM-S}$ is rather wide and in our analysis [12] we found volcano-shaped curves like those of the Multiplet Theory of catalysis [4], relating the energetic barrier of the reaction and the adsorption potential of the catalyst. Such correlations were deduced for enantioselective hydrogenation of EAA, of acac on Cu, Co catalysts modified with a variety of chiral amino acids. For the cobalt catalyst in hydrogenation of EAA and for the copper catalyst in that of acac we found only straight curves that can be considered as branches of the volcano shaped curves.

A more general approach was developed [18] when, as a measure of stability the co-proportionality constant K_d (as defined in the equation below) was accepted

$$[\text{Cu(AA)}_2] + [\text{CuS}_2] \overset{K_d}{\rightleftharpoons} 2[\text{CuAA–S}].$$

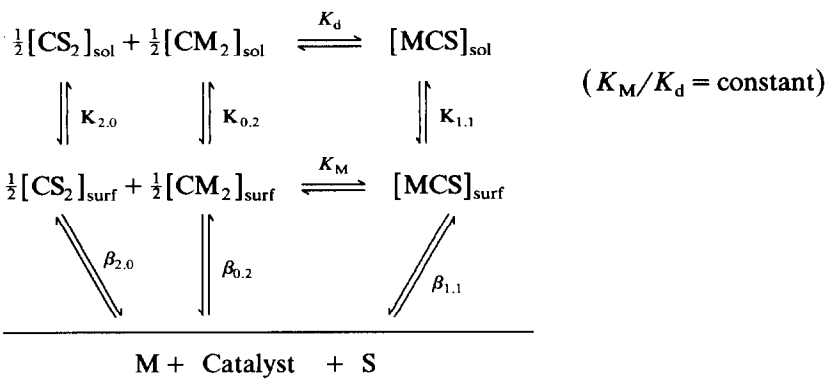
Here the overall stability of the complex is considered. K_d can be determined from:

$$\ln K_d = (\ln K_{KM-S} - \ln K_{KS-S}) + (\ln K_{KS-M} - \ln K_{KM-M}) \qquad (1)$$

The difference $(\ln K_{KM-S} - \ln K_{KS-S})$ is determined [19] by the difference of the enthalpies of formation of transition states on modified (CM) and non-modified catalysts according to the reaction:

$$CS + S \rightleftharpoons CS_2$$

It is also acknowledged [18] that equilibrium is possible among heteroligand complexes in solution, and among those on the surface of catalyst or carrier. The latter case has been studied [20] using Cu–AA complexes and Al_2O_3 carrier. The formation constants of heteroligand complexes of Cu with AA or acac in solution were found to be very similar to those for formation on the surface of the carrier. Further, it was found that [Cu–Tart] formed on the surface of the catalyst and went partly into solution in the process of chiral modification. Here, modifier–catalyst bonds seem to be very close in nature to the modifier–metal bonds found in complexes. Scheme 2 is, therefore, more in accordance with experimental results:



Scheme 2.

Scheme 2 is based on the complexes in solution and on the surface equilibrating quickly, and the K_d and K_M equilibrium constants for the formation of hetero-ligand complexes in solution and on the surface of catalyst being related thus: K_M/K_d = constant. This means that, considering a series of structurally similar ligands, K_M-values change in proportion to K_d, as has been found [19] in adsorption of [$CuAA_2$] and [$Cuacac_2$] complexes on Al_2O_3. Equation 2, relating the optical yield to the K_d values in a way susceptible to experiment [18] is based on Scheme 2.

$$\lg p = n \lg K_d + C \tag{2}$$

This equation has been checked with data from the enantioselective hydrogenation of MAA and EAA on Ni, Cu, and Co catalysts modified with chiral amino acids. The formation constants of the mixed complexes of Ni, Cu, and Co with AA, EAA, and acac were determined experimentally, and the good correspondence with equation 2 is illustrated in Fig. 2.

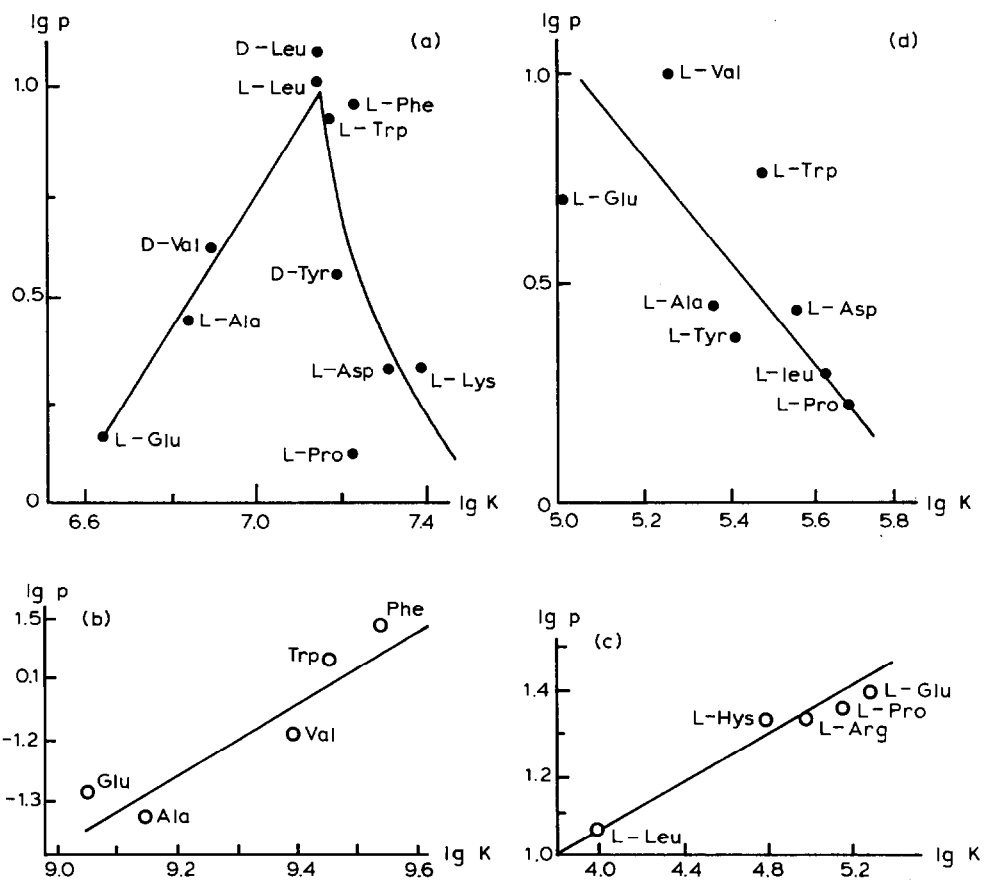


Fig. 2. Dependence of lg p on catalysts modified by amino acids in hydrogenation of (a) EAA on Cu, (b) acac on Cu, (c) EAA on Co, and (d) MAA on Ni from stability constants of complex-catalyst-amino acid.

Correlations of the extent of asymmetric action with the stability constants of intermediate complexes were investigated [21] using, as is more correct, E values instead of p values. The following linear equations [18,21] were found:

$$\ln E = a + \beta \ln K_{CM-S} \quad (3)$$

$$\ln E = b + 2\beta(\delta - 1) \ln K_d \quad (4)$$

Here the coefficient β signifies the extent of asymmetric action of the modifier, and the δ coefficient shows the extent to which the modifier influences the strength of the C–S bond in the heteroligand complex [MCS]. Coefficients b and δ have been evaluated [22] from experimental data (Table 2).

So far we have considered correlations between C–S and C–M bonds in the intermediate complex. In order to discover the chirodiastaltic interaction between modifier and substrate (M–S bonds) and to relate them to catalytic properties, we studied [12] the structure of the heteroligand complexes formed by Ni, Cu, and Co catalysts which are well known in enantioselective hydrogenation.

Firstly it has been stated [23] that in DMSO solution complexes like CL_1L_2 (where L_1 = AA's, EAA, MAA, acac, and L_2 = Trp, Tyr, Phe) are only dissociated to the extent of 10%. Also, the electronic interaction in the chelate knot, and the nature of Cu–N and Co–N bonds in complexes [CuAAacac] and [CoAAacac], have been studied by applying [24] the magneto-optical rotatory dispersion (MORD) technique (or Faraday effect). Here it was found that the increment in molecular MOR, $\Delta\,[\omega]^{\lambda}_{AA}$ was determined thus:

$$\Delta[\omega]^{550}_{AA} = [\omega]^{550}_{CAAacac} - \tfrac{1}{2}\left([\omega]^{550}_{C(acac)_2} - [\omega]^{550}_{CAA_2}\right)$$

in the range of d–d transitions (550 nm). This can be considered as a measure of the changes of polarity of bonds in the chelate knot of the heteroligand complex, in comparison with the corresponding bonds in the homoligand complex. For [Cu–acac] complexes with Tyr, Phe, and Trp we have obtained [23] $\Delta[\omega] \cdot 10^4$ values of 0.3, 0.2, and −0.05) respectively, which correspond to the electronic density in the chelate knot of each complex and which reflect changes in the stability constants K_d, the bond $Cu^{\delta+} \rightarrow N^{\delta-}$ in [Cu(acac)Tyr] being, for instance, more polar [24] than in [Cu(acac)Phe]. Also in a heteroligand complex of the type [Cu(acac)AA] chirodiastaltic interaction between modifier and substrate molecules has been

Table 2

Coefficients of equations 3, 4, 7

Complexes	Coefficients					
	a	β	b	δ	A	B
[Cu(AA)EAA]						
(AA = Glu, Ala, Val, Trp, Leu, Tyr, Phe)	0.065	0.14	0.090	3.10	0.093	0.086
[Cu(AA)acac]						
(AA = Glu, Val, Phe)	0.01	0.008	−0.60	1.32	–	–
[Ni(AA)MAA]						
(AA = Glu, Val, Ala, Ser, Leu, Pro, Asp, Tyr)	−0.035	−0.15	0.005	4.41	0.086	0.085
[Co(AA)EAA]						
(AA = Glu, Pro, Leu, Tyr, Arg, His)	−0.012	−0.03	−0.036	1.33	0.032	0.018

studied [25] using the circular dichroism technique. An induced Cotton effect was revealed in the adsorption band of the acac ligand in the complex. This means that acac in [Cu(acac)AA] became chiral as a result of molecule distortion under the influence of a chiral ligand, namely the optical active (*S*)-α-amino acid. The following differences in ellipticity values were found [26]: −2.10, −0.72, and −0.15 for Cu(acac) complexes with amino acids Trp, Tyr, and Phe, respectively. The differences $\Delta[\theta]^{590}$ were defined thus:

$$\Delta[\theta]^{590} = [\theta]^{590}_{Cu(acac)AA} - \tfrac{1}{2}[\theta]^{590}_{Cu(acac)_2}$$

Similarly, an induced circular dichroism was observed in absorption band of acetylamino cinnamic acid (AACA) (280 nm), when this compound acted as substrate with $RhCl(PPh_3)_3$ as catalyst (220 nm band) with a liquid crystal (cholesterol tridecanoate) as chiral template [27]. It is noteworthy that peak (16%) enantioselectivity was only revealed in the temperature range 58–66 °C, which is the temperature interval where the liquid crystal exhibits mesophase stability.

The positive Cotton effect that has been observed [26,28] corresponds to the λ-conformation of acac ligand in complexes of transition metals. Therefore the Cotton effects that have been observed for the Cu and Co complexes [C(acac)AA] and [C · EAA · AA] with (*S*)-AA indicate that in Cu complexes acac-ligand takes λ-conformation and in Co-complexes the δ-conformation. Inversion of the conformation of the acac ligand is observed if the (*R*)-AA is used instead of the (*S*)-AA in complexes. These observations have revealed the chirodiastaltic interaction between M and S in the asymmetric catalysis of triple heteroligand complexes.

Certain conformational characteristics (dichroic absorption, Δε, δ- or λ-conformations of acac, EAA, MAA ligands, and (*R*)- or (*S*)-configurations) of amino acids involved in complexes were compared with those seen in the enantioselective hydrogenation of acac, and EAA (or MAA) on Cu, Ni, and Co catalysts modified by the same amino acids (Trp, Tyr, and Phe). Table 3 shows the close correspondence of conformation (δ or λ) of the acac ligand and of pentanol-2-one-4, following the addition of H_2 to acac [16,29]. In this case, for Cu and Ni catalysts, the correlations λ → (*S*) and δ → (*R*) were observed.

It is well documented that in these cases Δε-values correlate with *p* and E following the equation

$$\ln E = A + B \ln(\Delta\epsilon) \tag{7}$$

This correlation can be explained by Δε very sensitively reflecting changes in bond strength, such as S-ligand (acac, EAA, MAA) with intermediate [C–AA] and of M-ligand (AA) with intermediate [C–S].

Data for lg K_{CM-S} and lg K_{CS-M}, obtained in previous work [18,21], with [29] Δε for systems [Cu(acac)AA] with Phe, Tyr, and Trp amino acids are shown below:

	Phe	Tyr	Trp
Δε	0.21	0.42	0.65
lg K_{CM-S}	0.02	−0.03	−0.40
lg K_{CS-M}	−0.01	−0.43	−0.09

These data shows how Δε increases as bonds CM–S and CS–M decrease in strength.

Table 2 also shows how the coefficients of equations 3, 4, and 7 reveal good correlations of *p* and E with Δε for heteroligand complexes, thereby characterizing

Table 3

Conformation characteristics of diketo compounds involved in metal surface catalysis of amino acid-modified heteroligand complexes, and configuration of hydrogenation product

Catalyst	Modifier	Temp. of modification (K)	Differential dichroic absorption $\Delta\epsilon$	Substrate		Product		
					conformation in complex		Absol. configuration	p (%)
Ni	(*S*)-Phe	373	–	acac	λ	ketol [a]	*S*	2.1
Ni	(*R*)-Tyr	373	0.150	acac	δ	ketol	*R*	2.3
Ni	(*R*)-Trp	373	0.900	acac	δ	ketol	*R*	3.2
Ni	(*S*)-Phe	273	–	MAA	λ	MHB [b]	*R*	– [17]
Ni	(*S*)-Phe	373	–	MAA	λ	MHB	*R*	– [17]
Co	(*S*)-Phe	373	4.150	acac	δ	ketol	*R*	1.0
Co	(*R*)-Tyr	373	0.163	acac	λ	ketol	*S*	0.4
Co	(*R*)-Trp	373	2.275	acac	λ	ketol	*S*	0.7
Cu	(*S*)-Phe	293	0.240	acac	λ	ketol	*S*	1.2
Cu	(*R*)-Tyr	293	0.200	acac	δ	ketol	*R*	0.2
Cu	(*S*)-Trp	293	0.350	acac	λ	ketol	*S*	1.4
Cu	(*S*)-Phe	293	0.210	EAA	λ	EHB [c]	*S*	9.3
Cu	(*R*)-Tyr	293	0.420	EAA	δ	EHB	*R*	3.4
Cu	(*S*)-Trp	293	0.650	EAA	λ	EHB	*S*	7.1

[a] Pentanol-2-one-4. [b] Methyl hydroxybutyrate. [c] Ethyl hydroxybutyrate.

chirodiastaltic interactions, namely changes in A and B being related to δ and inversely with β coefficients.

This is, therefore, the first experimental demonstration of quantitative evaluations in asymmetric catalyses of chirodiastaltic interactions in the intermediate triple complexes [M–C–S].

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