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Framework chirality and optical activity of organometallic cluster compounds

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Abstract

The contributions by the author's research group towards the preparation and the investigation of physical and chemical properties of optically active clusters are reviewed. Such clusters with EM_3 tetrahedrane frameworks can be prepared by stepwise synthesis or by metal exchange. Enantiomer separation is possible by means of optically active phosphine ligands via the intermediate formation of diastereomeric substitution derivatives or by means of chromatography on triacetyl cellulose. The optical properties of the diastereoisomers and the enantiomers (molar rotations, rotatory dispersion) are extreme. The optical activity of the clusters containing light transition elements is lost in the presence of donor ligands (CO, phosphines, catalysis substrates) due to the opening of metal–metal bonds. Reactions in the ligand sphere, however, can be performed with up to 100% diastereoselectivity.

Introduction

Just like the simplest optically active organic compounds can be derived from the asymmetric tetrahedron, the simplest chiral clusters are derivatives of the tetrahedrane molecule. Scheme 1 which shows this is also meant to demonstrate that it should be an order of magnitude more difficult to obtain chiral clusters in a designed fashion: while the introduction of four different methane substituents requires the change of one bond at a time, the formation of tetrahedrane-type molecules involves the making and breaking of several bonds for each step. It should not come as a surprise, therefore, that optically active clusters [1] appeared on the scene one hundred years later than the asymmetric tetrahedron [2], 70 years later than the first optically active metal complex [3], and 10 years later than the first optically active tetrahedral organometallic complex [4].

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Methane
ML_4 complex

Tetrahedrane
M_4 or EM_3 complex

Scheme 1. Asymmetric tetrahedra.

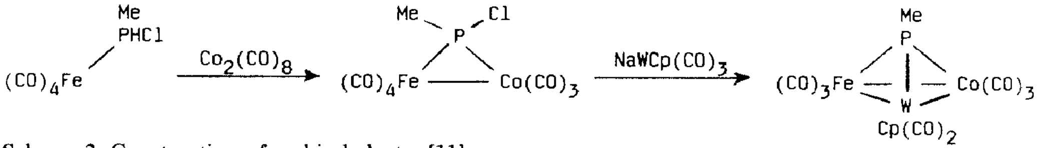
Our motivation to work in the field of chiral clusters resulted mainly from our interest in the reactivity of metal–metal bonds [5,6]. In addition to this, the challenge of cluster catalysis is an obvious factor. Since the chiral center of an optically active cluster is close to each reacting metal atom, such a cluster bears the possibility of efficient optical induction in catalytic reactions. Furthermore, as was first pointed out by Norton [7], due to the framework chirality optically active clusters can provide the proof that a cluster as a whole, and not one of its fragments, acts as a catalyst.

It became possible to gain access to chiral clusters when we found the metal exchange reaction [8,9]. This reaction, developed by H. Beurich, has laid the basis for all further work on cluster construction, enantiomer separation, and reactivity studies of chiral clusters.

Preparations

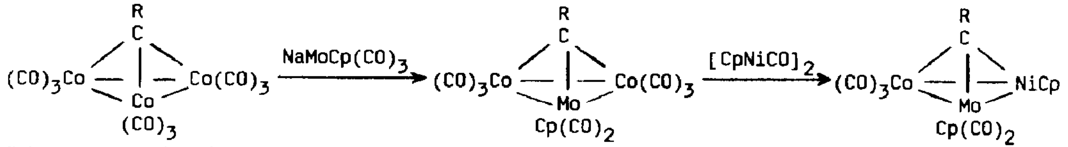
Many syntheses of clusters involve the uncontrolled combination of building blocks. But since it is unlikely that four different building blocks can be put together this way, the advent of chiral organometallic tetrahedrane molecules required the development of systematic synthetic procedures. Such procedures exist now, and various types of chiral clusters are accessible by them.

One of our approaches is the step-by-step construction of EM_3 tetrahedrane molecules [10–13]. In these syntheses *E* is a main group element whose presence serves two purposes: it provides the functional groups that are necessary to attach sequentially the three different metal atoms, and it serves to give the cluster a higher stability by means of its μ_3 bridging position. Scheme 2 gives an example of such a cluster construction using the molecule of RPHCl as the source of a phosphinidene cap.



Scheme 2. Construction of a chiral cluster [11].

While the step-by-step construction procedure represents a logical synthetic sequence, our alternative method, the metal exchange procedure, seems less rational. Nevertheless it is more efficient and more versatile, and most of our optically active EM_3 clusters have resulted from it [9,14–21]. In all cases a $Co(CO)_3$ cluster fragment is expelled and replaced by a different organometallic fragment. This must involve, in a tetrahedrane molecule, the breaking of three chemical bonds and their subsequent re-formation. The chemical reagents to achieve this and the mechanistic implications have been discussed in a review article [9]. An example for the alkylidyne bridged trimetal clusters is given in Scheme 3.



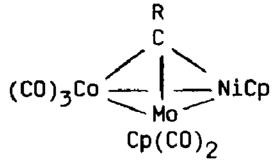
Scheme 3. Metal exchange at the CCo_3 cluster [15].

The EM_3 tetrahedrane framework ensures chirality for a cluster with three different metal atoms. Analogously, tetrametal clusters of this type can be envisaged, and higher nuclearity clusters with three or more different types of metals should be chiral for most compositions and framework geometries. Naturally, these clusters pose even more complex synthetic problems which have yet to be solved. But we have been able to prepare clusters with four different metal atoms [22–24], examples being $FeCoMoWS(AsMe_2)Cp_2(CO)_7$ with a tetrahedral and $FeRuCoAu(PMe)(CO)_9PPh_3$ with a butterfly-shaped metal atom arrangement. Since enantiomer separations of the chiral tetrametal clusters have not been performed yet, the studies related to optical activity have, until now, been done with the EM_3 cluster systems. Representative synthetic procedures for these systems are now available in "Inorganic Syntheses" [25].

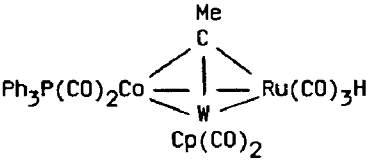
Enantiomer separations

The chirality of the new EM_3 clusters was first established by the classical NMR method, introducing diastereotopic groups in the form of PMe_2Ph ligands [26]. Series of crystal structure determinations have followed, putting each new case on a firm ground. But throughout the work NMR measurements, which recently have been applied in a more sophisticated way by McGlinchey [27], were essential to identify the clusters and to assess their chemical and optical purity.

In our attempts to obtain the pure enantiomers we found that a general separation procedure cannot be given for all types of chiral clusters. While it would be desirable to perform a direct separation (i.e. by chromatography over an optically active adsorbent) it turned out that this method was only applicable to special types of clusters, and even there it was time-consuming and inefficient. Thus the advantage of the method (no auxiliary reagents) was offset by its limited usefulness. Small amounts of the clusters **1** and **2** were obtained optically pure this way [13,28].



1, R = Ph, C(O)Ph, COOPh



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More successful were the enantiomer separations via the formation of diastereoisomers. For this method the auxiliary optically active groups could be attached as a

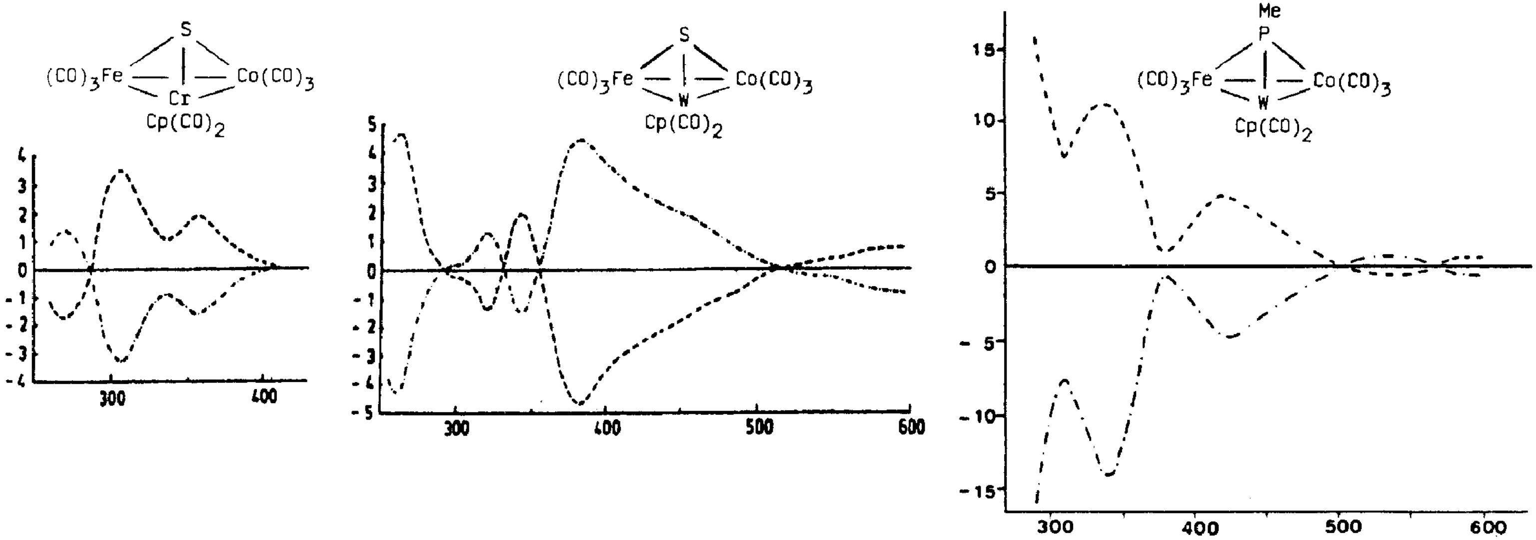
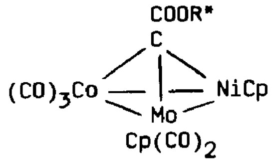
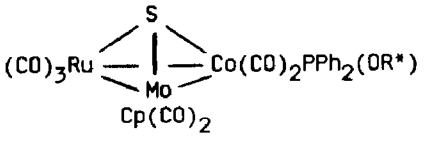


Fig. 1. ORD curves of both enantiomers of three optically active clusters. Abscissa: wavelength (nm), Ordinate: molar rotation Φ (deg$\times 10^{-4}$).

substituent at the μ_3 capping ligand or as a phosphine ligand at the cobalt atom. The separations of the diastereoisomers by fractional crystallisation or chromatography were successful in most cases after sufficiently intensive efforts for finding the right combination of cluster and auxiliary group. However, in some cases the auxiliary groups could not be removed after separation without destruction of the cluster or loss of the optical activity. Thus the clusters **3** and **4** were obtained optically pure only as diastereoisomers [18,28].

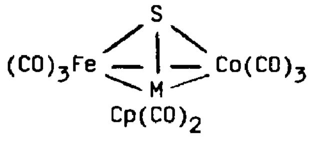


3, R* = (—)-Menthyl

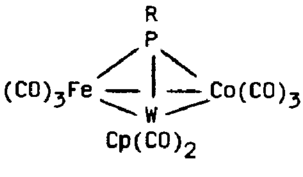


4, R* = (—)-Menthyl

High yield syntheses as well as efficient enantiomer separations were found for the cluster types **5** and **6** [29,30]. For **5** the auxiliary reagent was the phosphine (−)-PMePrPh, for **6** the phosphine (−)-Menthyl-OPPh$_2$. In both cases the auxiliary reagents could be removed after separation and replaced by CO under CO pressure. The final optical purity of the clusters **5** was close to 100%, while the removal of the phosphine ligand for **6** was accompanied by a reduction of optical purity to ca. 60–70%. This can be correlated with a cluster opening during the substitution process (see below).



5, M = Cr, Mo, W



6, R = Me, t-Bu, Ph

Optical activity and absolute configuration

The optical rotations of the chiral cluster compounds are extreme. In the visible range the molar rotations Φ go up to 10000–40000 degrees, in the ultraviolet range they are still higher. This can be correlated with the high optical absorption, most of the compounds being black in the solid state and deeply coloured in solution. This actually has caused problems in determining the rotation values since only highly diluted solutions and short pathlengths could be used, resulting in errors of the reported Φ values in the order of at least 20%.

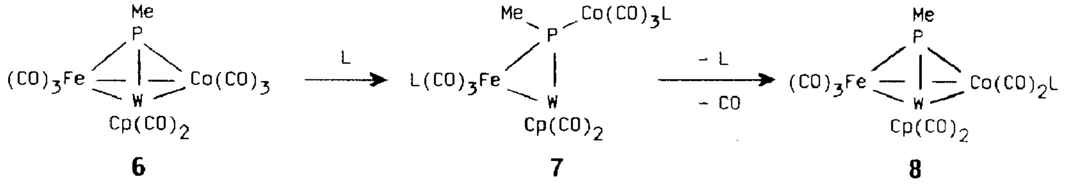
The rotatory dispersion is quite pronounced in all cases where it has been measured. It is actually much more structured than the optical absorption of the compounds which is mostly unresolved in the visible range and rises steadily towards the UV range. Figure 1 shows three representative examples of ORD curves [29,30]. Although the three clusters involved have a very similar composition, each containing a $Fe(CO)_3$, a $Co(CO)_3$, and a $MCp(CO)_2$ unit, the three curves are distinctively different. Thus a modification in the metal triangle (i.e. replacing W by Cr) causes as much a variation as a modification in the capping ligand (i.e. replacing μ_3-S by μ_3-PR). On the other hand the optical rotation is mainly determined by the EM_3 cluster core, as can be seen by a comparison of the ORD curves of the enantiomers with those of the corresponding diastereoisomers; the auxiliary optically active phosphine ligand modulates the ORD curves but does not change their general appearance [28,29].

The novelty of our chiral tetrahedrane derivatives required a new definition in terms of the *R*,*S* nomenclature which in turn required the determination of at least one absolute configuration. For the definition we decided to use the analogy to the tetrahedral case and relate the four corners of the tetrahedrane to an imaginary chiral center in the middle of the EM_3 core. The absolute configurations of the Mo and W clusters **5** were determined by standard crystallographic methods. From this it results that the Mo and W clusters **5** as drawn above have the (−)-R configuration with the minus sign indicating the optical rotation at 589 nm [29].

Racemisation

With respect to possible catalytic applications it was important to know the configurative stability of the optically active clusters. All of them were therefore subjected to severe reaction conditions. They showed quite variable behaviour, and each of them required a different set of conditions for racemisation [28–30]. The SFeCoM clusters are unaffected by CO pressure or by heating up to 100 °C in solution, but lose their optical activity upon UV irradiation without significant decomposition. The PFeCoM clusters seem to be chemically and configurationally stable towards irradiation, but are racemized under CO pressure (90 bar, 3 days) at room temperature. The CCoMoNi clusters are the most labile, being decomposed by UV irradiation and by heating to 80 °C in solution, although without racemisation, but being racemized under CO pressure. Irradiation, heat, or an excess of donor ligands are characteristic conditions for the opening of metal–metal bonds. This leads to the conclusion that metal–metal bond breaking which opens the tetrahedrane framework is the initial step in the racemisation process.

That this is the case could be proved for the cluster **6** by a mechanistic study [31]. At room temperature, two equivalents of PMe_2Ph are quickly added to **6** yielding the open cluster **7**. **7** initially maintains all the optical activity of **6** but loses it in a first order reaction with a half-life of about 1 h. Thermal treatment converts **7** to **8** with loss of CO and PMe_2Ph. Thus the racemisation as well as the ligand substitution of these clusters involve cluster opening and an addition elimination sequence (Scheme 4). And it can be easily envisaged that an open structure like **7** is more easily inverted than the closed tetrahedrane framework.



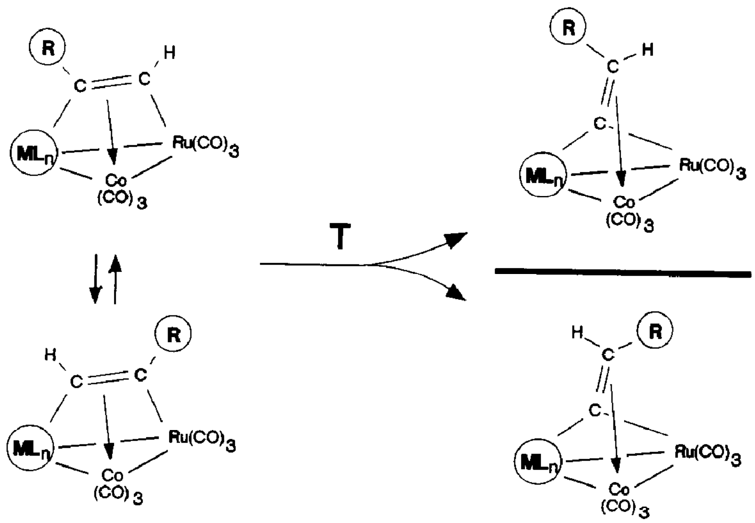
Scheme 4. Cluster racemisation and substitution [31].

Stereoselective reactions

The simplest indication of a discriminating ability of the chiral clusters towards substrates would be chiral recognition. This was actually observed in one case: During the formation of the diastereomeric compound **4** one enantiomer of the cluster reacts faster such that with insufficient amounts of the ligand $Ph_2P{-}OR^*$ a 4/3 enrichment of (−)-4 over (+)-4 occurs [18]. Thus in a one-step reaction an enantiomeric excess of one of the chiral clusters can be obtained.

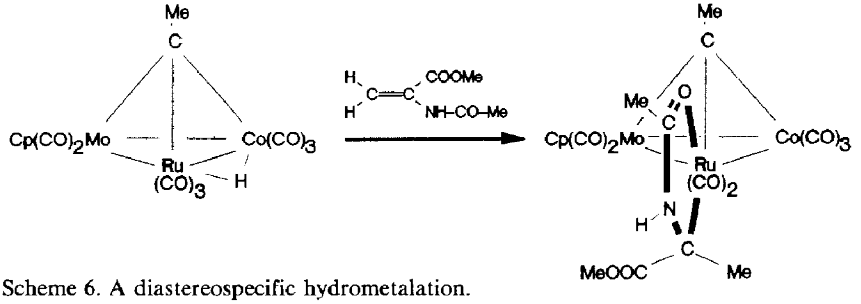
The use of the chiral clusters for optical induction in catalytic reactions, although promising, has not been brought to a successful application yet. We could demonstrate that the ruthenium-containing clusters are good hydrogenation catalysts [32], that hydroformylations are possible with the cobalt containing clusters [33], and that the Mo and W clusters **5** perform a photo-initiated hydrosilylation of acetophenone [34]. For each of the catalytic systems, however, the conditions for catalytic activity (heat or CO pressure or irradiation) are the same as the conditions for cluster racemisation. This supports the assumption that metal–metal bond opening is an initial step in the catalytic cycles just as it is in racemisation. But according to this it also means that successful optical induction requires the use of clusters with only heavy transition metals which are much more inert towards metal–metal bond breaking.

For organic reactions in the ligand sphere of chiral clusters we could find cases where the diastereoselectivity goes up to 100%. One of these cases is the alkyne-vinylidene rearrangement, as outlined in Scheme 5 [21]. The stereochemical yield of this reaction, i.e. the preference of the *R*,*S* diastereoisomer over the *R*,*R* diastereoisomer, depends on the nature of the ML_n unit and on the size of the R group. For ML_n = NiCp there is an exact 50/50 composition of both products. For ML_n = $MoCp(CO)_2$ or $WCp(CO)_2$ the composition ranges from about 75/25 for R = Me and R = Ph to 100/0 for R = t-Bu. The maximum of selectivity for the large $MCp(CO)_2$ metal component and the large t-butyl substituent points to a sterically controlled reaction.



Scheme 5. Diastereoselective alkyne-vinylidene rearrangement.

Electronic control seems to prevail in the reaction outlined in Scheme 6. This olefin insertion into a cluster–hydrogen bond [35] and a series of similar reactions with W or Os containing clusters and fumaric or maleic acid esters [36] is completely diastereospecific. The metallacyclic olefin insertion product combines three unusual or hitherto unisolable features: it is uncontaminated by the other diastereoisomer, it represents the long-sought intermediate of enantioselective hydrogenation possessing a metal–carbon σ bond, and it contains a tertiary α-carbon atom. The reactions outlined in Schemes 5 and 6 have so far not been done with the pure enantiomers since these could not be obtained yet. Their value therefore rests in the new reaction types that they represent.



Scheme 6. A diastereospecific hydrometalation.

The compounds and reactions presented in this review provide a basis for synthetic and catalytic applications of chiral clusters. As with many other areas of cluster research they show more the potential of this field of chemistry than immediate practical uses. The products obtained, their stereochemistry and their interconversions are of relevance for basic as well as for application-oriented cluster chemistry. They demonstrate the advantages and possibilities resulting from the electronic adaptability and steric control of mixed metal cluster compounds.

Acknowledgment

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