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Mono(η-cyclopentadienyl)zirconium complexes: from coordination chemistry to enantioselective catalysis

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Abstract

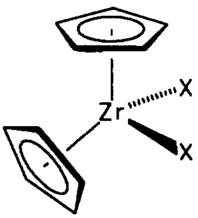
Several Cp(allyl)- and Cp(allyl)(conjugated diene)zirconium complexes were prepared from $CpZrCl_3$ and shown to undergo interesting types of rearrangements. The 12-electron organometallic Lewis acids $CpZrCl_3$ itself forms adduct complexes $[CpZrCl_3L_2]$ or $[CpZrCl_3L]_2$ with various two-electron donor ligands, e.g. with many organic carbonyl compounds. These were found to undergo rapid intermolecular exchange with the free L species in solution. This opened up ways of employing organometallic $CpZrCl_3L$ Lewis acids as catalysts in organic synthesis. The chiral (diborna-Cp)$ZrCl_3$ system is an efficient catalyst for an enantioselective aldol addition type carbon–carbon coupling reaction.

Introduction

Group 4 bent metallocene complexes, such as Cp_2ZrL_n and Cp-substituted analogues, exhibit a rich, experimentally nicely developed and theoretically well understood organometallic chemistry [1]. Zirconocene complexes are increasingly used as stoichiometric reagents in organic synthesis. Important catalytic processes are based on $(RCp)_2Zr$-containing systems [2].

Far less was known about simple mono(η-cyclopentadienyl)zirconium complexes, containing a single unsubstituted η-C_5H_5 ligand, when my group entered this field about a decade ago. At the time a good synthetic route was still needed for making sufficient quantities of a suitable starting material, such as $CpZrCl_3$, for use in preparing new organometallic (η-cyclopentadienyl)zirconium complexes. Although some rather stable Cp-substituted analogues had been made by simple substitution routes starting from zirconium tetrahalides and the corresponding cyclo-$(R_nH_{5-n}C_5)$ anion equivalents [3], the parent compounds $CpZrX_3$ were not obtained sufficiently selectively by this approach. An alternative approach, involving disproportionation between Cp_2ZrX_2 and ZrX_4 was also unsatisfactory on a preparative scale [4].

This was an unfortunate situation because development of the organometallic chemistry of the parent (η-C_5H_5)ZrL_n systems seemed a very attractive prospect to me and my coworkers. In contrast to the 16-electron pseudotetrahedral Cp_2ZrX_2 compounds, the 12-electron $CpZrX_3$ complexes were thought to adopt distorted octahedral molecular geometries, thereby allowing for the addition, and hence activation, of a pair of two-electron donor ligands L without leading to complete electronic saturation. Indeed, ligand exchange processes at $CpZrX_3L_2$ complexes, having a formal 16-electron configuration at the zirconium(IV) center, were later shown to be fast for a large variety of examples, opening new ways of using such complexes as catalysts for conversions of organic compounds.



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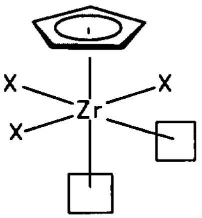

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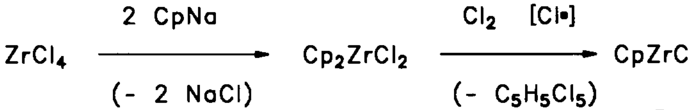
Our actual involvement with mono(η-cyclopentadienyl)zirconium chemistry began when we found a new convenient large scale preparation of pure $CpZrCl_3$ (**2**) [5]. A simple detour was used to overcome the selectivity problem encountered with the direct nucleophilic synthesis of **2** from $ZrCl_4$ and common Cp-anion equivalents. We converted zirconium tetrachloride into Cp_2ZrCl_2 and then selectively replaced one cyclopentadienyl ligand by chloride. The $Cp_2ZrCl_2 \rightarrow CpZrCl_3$ conversion was selectively achieved by means of a radical chain chlorination. Very pure $CpZrCl_3$ was obtained by carrying out the reaction strictly within the temperature range of 18–25 °C.



$$ZrCl_4 \xrightarrow[(-\ 2\ NaCl)]{2\ CpNa} \underset{\mathbf{1}}{Cp_2ZrCl_2} \xrightarrow[(-\ C_5H_5Cl_5)]{Cl_2\quad [Cl\bullet]} \underset{\mathbf{2}}{CpZrCl_3}$$

A.H. White et al. characterized by X-ray diffraction the (η-cyclopentadienyl)zirconium trichloride prepared by this method [6]. In the crystal $CpZrCl_3$ is oligomeric, exhibiting four μ-Cl bridges and one non-bridging chloride at each zirconium in a distorted octahedral coordination geometry. We used this material to prepare a variety of organometallic complexes containing the CpZr unit. Some characteristic features of these will be discussed in this account. In addition, we have coordinated a number of organic donor molecules, especially carbonyl compounds, to the organometallic Lewis acid (cyclopentadienyl)zirconium trichloride. These adducts show some interesting chemical and structural features; their importance for developing organic reactions catalyzed by organometallic Lewis acids will be discussed.

Organometallic mono(cyclopentadienyl)zirconium derivatives

The chlorides in $CpZrCl_3$ can be replaced by a variety of carbanionic ligands. Thus, thermally rather labile $Cp(allyl)_3Zr$ (**3a**), which rapidly decomposes in solution at temperatures > −25 °C, was obtained in good yield by treating $CpZrCl_3$

with an excess of allyl magnesium chloride. Subsequent comproportionation of **3a** with additional $CpZrCl_3$ in a 2 : 1 or 1 : 2 molar ratio at low temperature yielded the halogen-containing complexes $Cp(allyl)_2ZrCl$ (**4a**) or $Cp(allyl)ZrCl_2$ (**5a**), respectively.

Professor Carl Krüger and his coworkers at the Max-Planck-Institut für Kohlenforschung in Mülheim a.d. Ruhr, F.R.G., who carried out the X-ray structural studies in connection with our mono(cyclopentadienyl)zirconium work, collected the X-ray diffraction data for tris(allyl)cyclopentadienyl zirconium (**3a**) at −173 °C [7]. $Cp(allyl)_3Zr$ was found to have a remarkable molecular structure, containing three differently bonded allyl ligands. The coordination geometry around zirconium is distorted (pseudo)tetrahedral. One of the allyl ligands is π-bonded to zirconium [C(4)–C(6)]. Another is present in the σ-allyl mode [C(7)–C(9)], and the bonding of the third allyl group can best be described as a σ,π-type coordination [C(1)–C(3)], making this C_3H_5 unit somewhat different from the other two allyl moieties (Fig. 1).

In solution complex **3a** exhibits simple NMR spectra, showing only one set of allyl ligand resonances in addition to the Cp-singlet [$^1H/^{13}C$ NMR in $[D]_8$-toluene at $-78\,°C/-30\,°C$: δ 5.10 (5H)/106.4 (Cp), δ 5.27 (m, 3H)/135.3 (allyl-CH), δ 2.95 (d, 12H)/71.9 (dynamic allyl-CH_2)]. However, the structure of **3a** in solution is probably not very different from that in the solid state, but is apparently "symmetrized" by a very rapid dyamic $\sigma \rightleftharpoons \pi$-allyl ligand equilibration. Below −90 °C in toluene (< −130 °C in diethyl ether) a considerable broadening of the ^1H (400 MHz) and ^{13}C (100 MHz) methylene resonances was observed, whereas the Cp-signal remained sharp throughout. It is well conceivable that this rapid Zr(allyl) rearrangement process may proceed in a concerted fashion, i.e. involving all three differently coordinated allyl ligands at zirconium at the same time. Evidence for a similarly coupled rearrangement process involving the intramolecular reorganization of an allyl and a conjugated diene ligand at the CpZr-template will be discussed below.

Tris(allyl)(cyclopentadienyl)zirconium (**3a**) was comproportionated with a stoichiometric quantity of $CpZrCl_3$, to give a high yield of $Cp(allyl)ZrCl_2$ (**5a**), which was alkylated with methyl magnesium bromide at low temperature. Klaus Berg, who did most of the work described in this section [8a], characterized the resulting, rather thermolabile, $Cp(allyl)Zr(CH_3)_2$ (**6**) by a detailed NMR and IR spectroscopic investigation. Complex **6** and the analogous $Cp(allyl)ZrPh_2$ (**7**) both

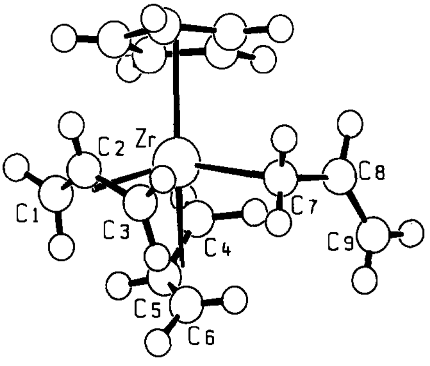
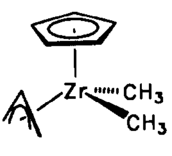


Fig. 1. A projection of the molecular structure of $Cp(allyl)_3Zr$ (**3a**).

exhibit π-dynamic allyl ligands [9] [**6**: $\Delta G^{\neq}(0\,^\circ C) = 13.2 \pm 0.3$ kcal/mol; **7**: $\Delta G^{\neq}(-15\,^\circ C) = 12.4 \pm 0.3$ kcal/mol].



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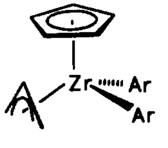


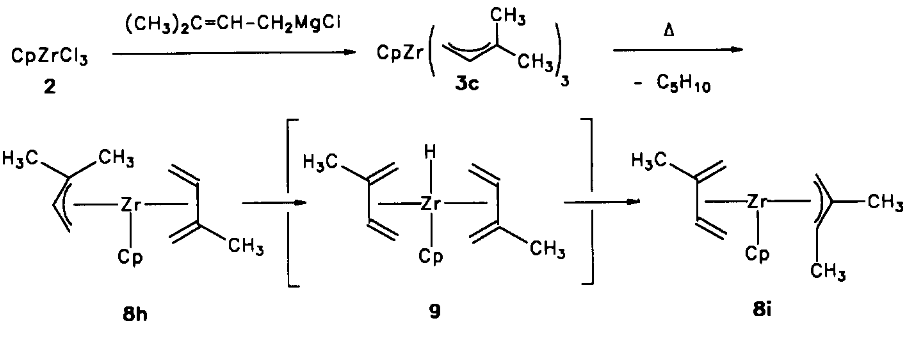
7 (Ar = p-tolyl)

Cp(allyl)$ZrCl_2$ (**5a**) reacted cleanly with the oligomeric butadiene-dianion equivalent "butadiene–magnesium" to give a single (η^3-allyl)(η^4-butadiene)(η^5-cyclopentadienyl)zirconium isomer (**8a**). Cp(allyl)$HfCl_2$ reacted in the same way to give Cp(allyl)(butadiene)Hf (**8b**) in good yield. This synthetic method was also used for attaching substituted conjugated diene ligands to the Cp(allyl)zirconium moiety. Treatment of Cp(allyl)$ZrCl_2$ with the appropriate $(R_nC_4H_{6-n})Mg$ reagents produced Cp(allyl)(isoprene)Zr, Cp(allyl)(2,3-dimethylbutadiene)Zr, and Cp(allyl)(2-phenylbutadiene)Zr (**8c–e**) [8b,10].

Complexes having substituted allyl ligands were prepared analogously [11]. Thus, $CpZrCl_3$ was treated with an excess of crotyl magnesium halide to give $Cp(crotyl)_3Zr$ (**3b**). Subsequent comproportionation with additional $CpZrCl_3$ gave Cp(crotyl)$ZrCl_2$ (**5b**), which upon treatment with one equivalent of "isoprene–magnesium" gave Cp(crotyl)(isoprene)zirconium (**8f**). Cp(crotyl)(butadiene)Zr (**8g**) was prepared similarly from Cp(crotyl)$ZrCl_2$ and "butadiene–magnesium".

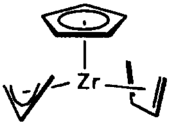
We found an attractive additional route to Cp(crotyl)(butadiene)zirconium. There were many reports demonstrating that (η^4-butadiene)transition metal complexes could be synthesized from (η^3-1-methylallyl)ML_n precursors by means of allylic H-abstraction [12]. Thus, the controlled thermolysis of $Cp(crotyl)_3Zr$ (**3b**) ($-20\,^\circ$C, 96 h) directly gave Cp(η^3-1-methylallyl)(η^4-butadiene)Zr (**8g**) plus butene [13].

Use of this approach led readily to the preparation of Cp(allyl)(conjugated diene)Zr complexes exhibiting more complex substitution patterns at the open π-ligands. In a typical example (cyclopentadienyl)tris(1,1-dimethylallyl)zirconium (**3c**) was prepared from $CpZrCl_3$ and $(CH_3)_2C{=}CH{-}CH_2MgCl$ in ether. Methylbutene was then eliminated at $-15\,^\circ$C to give Cp(η^3-1,1-dimethylallyl(isoprene)zirconium (**8h**). Complex **8h** itself turned out to be thermolabile. At



20 °C it isomerized slowly ($\tau_{1/2} \approx 40$ h) to give Cp(η^3-1,2-dimethylallyl)(isoprene)zirconium (**8i**). We suggested that this reaction proceeded by means of an intramolecular hydrogen transfer from the substituted allyl to the conjugated diene ligand, presumably via a zirconium hydride intermediate (**9**).

The family of Cp(allyl)(conjugated diene)Zr complexes, whose syntheses are described above, show some interesting structural and stereochemical features. (η^3-Allyl)(η^4-butadiene)(η^5-cyclopentadienyl)zirconium (**8a**) as obtained from the reaction between Cp(allyl)ZrCl$_2$ and "butadiene-magnesium" exhibits C_s molecular symmetry in solution according to its NMR spectra [^{13}C NMR in [D]$_8$-toluene: δ 108.8 (Cp); 125.5 (^1J(CH) = 153 Hz), 56.8 (dd, ^1J(CH) = 160, 146 Hz, allyl); 112.5 (^1J(CH) = 160 Hz), 45.8 (dd, ^1J(CH) = 154, 143 Hz, butadiene]. There are four conceivable C_s-symmetric Cp(allyl)(butadiene)Zr isomers (**8**, **10**–**12**), differing in the arrangement of the two open π-ligands relative to each other and to the η-Cp ligand. An X-ray crystal structure analysis and a detailed ^{1}H NMR NOE investigation revealed that the only Cp(allyl)(butadiene)Zr complex present under equilibrium conditions at ambient temperature is the isomer **8a**, which is characterized by opening of both the η^3-allyl and the η^4-butadiene ligands towards the Cp-group [14] (Fig. 2).



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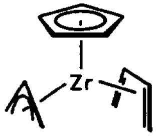

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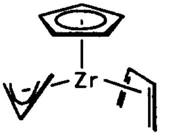

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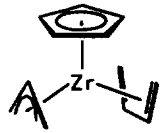

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According to their NMR spectra the thermodynamically favoured isomers of the Cp(allyl)(substituted diene)Zr complexes **8c**–**e**, as well as Cp(crotyl)(butadiene)Zr (**8g**) and Cp(allyl)(butadiene)hafnium (**8b**), are all of the same structural type as **8a**. The chiral system Cp(crotyl)(isoprene)Zr and the Cp(dimethylallyl)(isoprene)Zr isomers could each form two diastereoisomers. Under equilibrium conditions we observed only one of these in each case, namely **8f**, **8h**, and **8i**, in which steric crowding of the methyl substituents at the narrow side of the Cp(η^3-allyl)(η^4-conjugated diene)M "wedge" is avoided (see Scheme 1) [15].

A second geometric isomer of the Cp(allyl)(butadiene)Zr system can be prepared photochemically. Pyrex-filtered UV-irradiation at low temperature (< -40 °C, toluene solvent) almost completely converted **8a** into the isomeric Cp(allyl)(butadiene)Zr complex **10a**, in which the open sides of both the η^3-allyl and the η^4-butadiene ligand are oriented away from the η^5-cyclopentadienyl ligand [14].

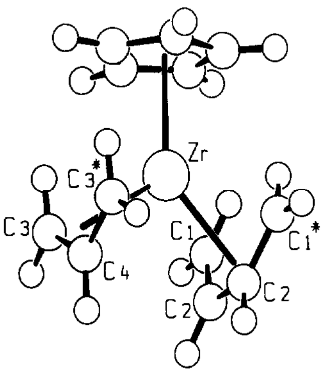
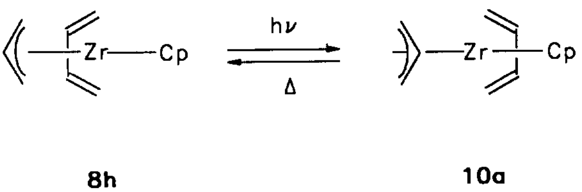
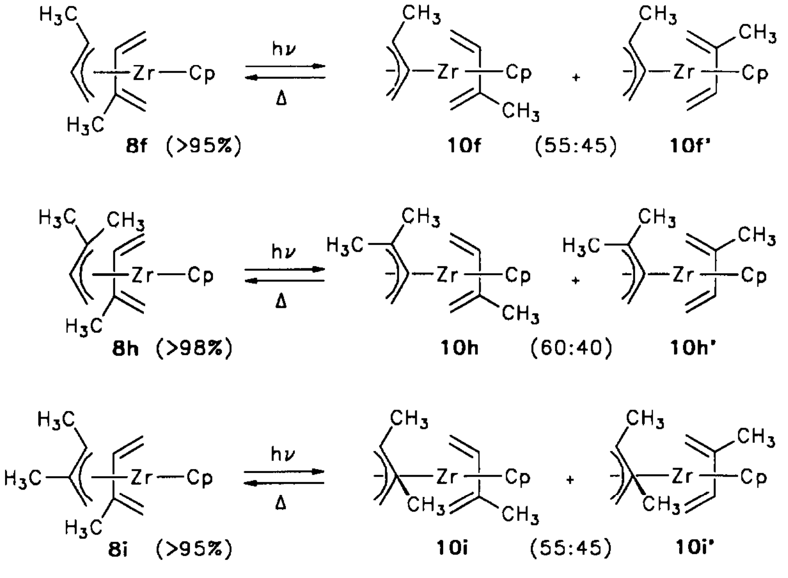


Fig. 2. Molecular structure of the Cp(allyl)(butadiene)zirconium complex **8a** in the crystal.



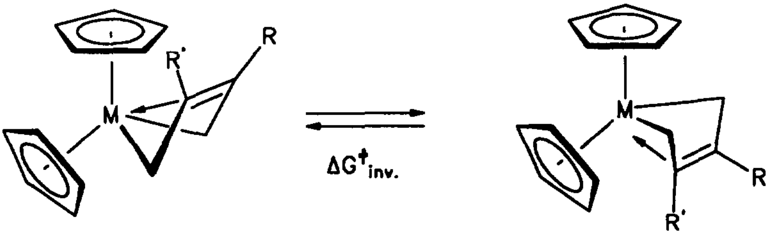
Irradiation of the substituted analogues of **8** also led to photostationary equilibria involving > 90% of the respective isomers **10**. The remarkably high diastereoselectivity, which is characteristic of the thermally equilibrated Cp(η^3-crotyl)(isoprene)Zr system, was lost upon establishing the respective photostationary equilibrium. Photolysis of **8f** (single isomer) rapidly produced a 55 : 45 mixture of the di-



Scheme 1. Isomerization of substituted Cp(allyl)(conjugated diene)zirconium complexes.

astereomeric "photoisomers" **10f** and **10f**′. The Cp(η^3-1,1-dimethylallyl)- and Cp(η^3-1,2-dimethylallyl)(isoprene)zirconium isomers (**8h**, **8i**) behaved analogously.

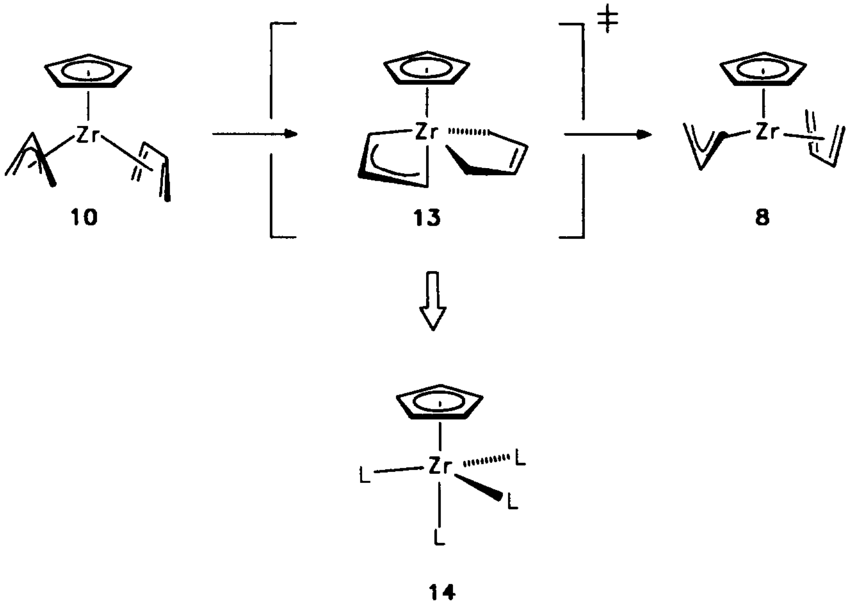
The uncatalyzed thermally induced **10a** → **8a** isomerization follows first-order kinetics with $k = 5.5 \times 10^{-5}$ s^{-1} at 10 °C in toluene solution, which corresponds to a Gibbs activation energy of $\Delta G^{\neq}(10\,°\mathrm{C}) = 22.1 \pm 0.3$ kcal/mol. The $\Delta G^{\neq}$ values of the intramolecular reorganization reaction were determined for several of the substituted analogues. Characteristically, the isomerization activation energies were all found to lie in very narrow range. Regardless of the specific substitution pattern at the η^3-allyl and η^4-conjugated diene ligands, Gibbs activation energies of about 20 kcal/mol were observed for this process [e.g. $\Delta G^{\neq}(10\,°\mathrm{C}) = 21.5 \pm 0.4$ kcal/mol for Cp(crotyl)(butadiene)Zr; $\Delta G^{\neq}(-10\,°\mathrm{C}) = 19.6 \pm 0.3$ kcal/mol for Cp(allyl)-(isoprene)Zr, $\Delta G^{\neq}(-10\,°\mathrm{C}) = 19.4 \pm 0.3$ kcal/mol for Cp(allyl)(2,3-dimethylbutadiene)Zr; $\Delta G^{\neq}(-10\,°\mathrm{C}) = 20.5 \pm 0.3$ kcal/mol for Cp(allyl)(2-phenylbutadiene)Zr]. This kinetic similarity even extended to the rearrangement of the respective Cp(allyl)(butadiene)hafnium isomers [**10b** → **8b**: $\Delta G^{\neq}(-5\,°\mathrm{C}) = 20.2 \pm 0.3$ kcal/mol]. This is in contrast to the activation energy profile of the formally related (η^4-conjugated diene)metallocene automerization process, where strongly metal and diene-substitutent dependent activation barriers of the diene inversion process were observed.



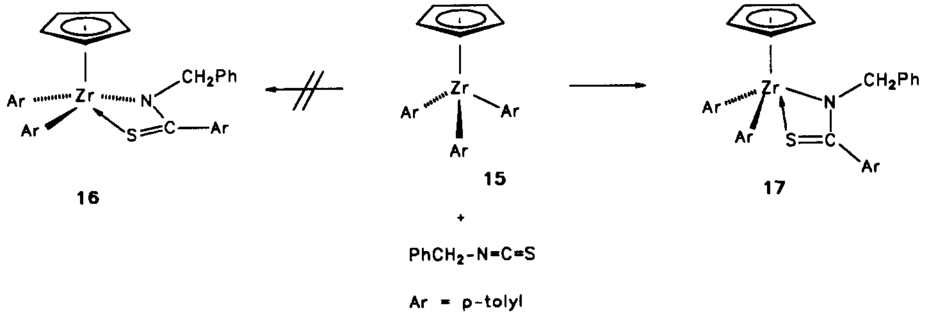
M= Zr, Hf ; R, R′= H, Alkyl, Cycloalkyl, Aryl.

Professor Heinz Berke, with whom we closely collaborated on this project, and his coworkers at Zürich University examined in great detail the mechanistic course of the rearrangement **10** → **8** by means of quantum mechanical calculations involving use of a modified extended-Hückel theory (MEHT) [10]. They came to the conclusion that the preferred pathway followed in the thermal isomerization process involved simultaneous allyl rotation and conjugated diene ligand inversion. According to these calculations the transition state (**13**) of this unique "synchronous" rearrangement process is derived from a distorted trigonal bipyramidal type complex geometry such as **14**. It may well be that coupled ligand reorganization processes, such as the isomerization **10** → **8**, and probably also the fast Cp(allyl)$_3$Zr automerization, are more common than is usually thought.

In one case we were able to find direct evidence for the formation of a stable isolable CpZrL$_n$ compound of the trigonal-bipyramidal structural type. CpZrCl$_3$ was treated with three molar equivalents of p-tolyllithium in ether at −10 °C to give (η-cyclopentadienyl)tris-p-tolylzirconium (**15**) in good yield (> 80%) [16]. Complex **15** reacted with an equimolar amount of benzylisothiocyanate at −30 °C selectively



by insertion into a single zirconium–carbon σ-bond to give the (cyclopentadienyl)bis-*p*-tolyl(thiobenzamidato) zirconium complex **17**. Even at low temperature (–80 °C, $[D]_8$-toluene), complex **17** exhibited signals due to two equivalent σ-aryl ligands at zirconium. The methylene hydrogens of the nitrogen-bound benzyl group appeared as a sharp singlet (δ 4.24) at all temperatures, indicating that the achiral (distorted trigonal bipyramidal) structural type is preferred in this case over the chiral (square pyramidal) geometry (**1b**), which was often observed for $CpML_4$ type complexes of later transition metals [17].

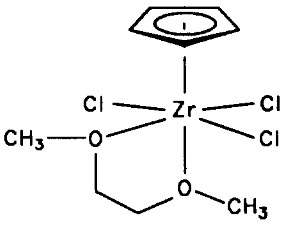


(η-Cyclopentadienyl)zirconium trichloride, a 12-electron organometallic Lewis acid

Many typical inorganic Lewis acids, such as BF_3, $AlCl_3$, and $TiCl_4$, serve as catalysts or stoichiometric kinetic auxiliaries in organic synthesis [18]. It would be highly desirable to have available similarly effective organometallic Lewis acids, which would permit a much wider structural variation, including the use of strongly bonded chiral ligand systems, to influence and control the selectivities of Lewis acid promoted transformations of organic substrates [19].

The (η-cyclopentadienyl)zirconium trichloride and Cp-substituted derivatives there of could be potentially interesting Lewis acid catalyst systems in this respect, if it were possible to make the monomeric 12-electron $CpZrCl_3$ system available from the easily accessible $(CpZrCl_3)_x$ oligomer or, more indirectly, by rapid donor ligand exchange from suitable molecular complexes $CpZrCl_3L_n$.

Mononuclear $CpZrCl_3L_2$-type complexes, exhibiting two easily exchangable donor ligands L at zirconium in a pseudooctahedral coordination geometry, are readily obtained by treating the oligomeric $(CpZrCl_3)_x$ with ether or amine ligands. Before my group became actively involved with the chemistry of bis-donor adducts of the $CpZrCl_3$ moiety, Professor Kenneth Caulton and his coworkers had prepared the chelate complex $CpZrCl_3$(dimethoxyethane) (**18**) and characterized it by X-ray diffraction. Later, Professor Carl Krüger's group determined the structures of $CpZrCl_3(thf)_2$ (**19**) and $(MeCp)ZrCl_3(thf)_2$ (**20**) [21].



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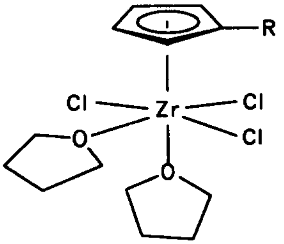
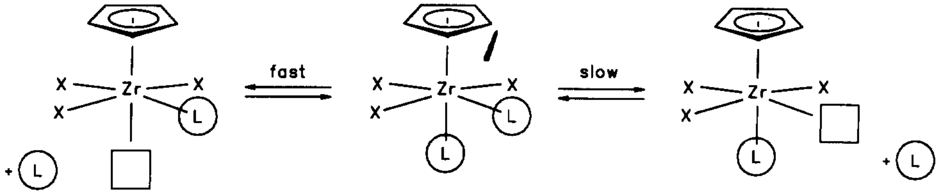


19 (R=H), **20** (R=CH_3)

All these pseudooctahedral complexes possessed etheral ligands *cis* and *trans* to the Cp group. In each case the *trans* donor ligand was more loosely bound than the *cis* OR_2 donor [e.g. **19**: $Zr{-}O_{cis} = 2.314(3)$ Å; $Zr{-}O_{trans} = 2.393(3)$ Å]. Christian Sarter, who studied the $CpZrCl_3L_n$ and related chemistry in my group, found that all these complexes exhibited dynamic properties in solution [8b]. The rapid exchange processes of coordinated thf or dme with the free etheral ligands in solution were monitored by variable-temperature dynamic NMR spectroscopy.

With regard to the exchange dynamics of the mononuclear $CpZrCl_3L_2$ species, complex $CpZrCl_3(dimethylformamide)_2$ (**21**) proved to be a particularly interesting example. In $[D]_2$-methylene chloride solution at 223 K two sets of ^1H NMR (400 MHz) dmf ligand signals at δ 8.32 (CHO), 3.04, 2.87 (NMe_2) and δ 8.00, 3.08, 2.99 were observed in addition to the resonances of uncoordinated dimethylformamide in solution (δ 7.91, 2.87, 2.77). Professor Reinhard Benn and his coworkers at the M.P.I. Mülheim, with whom we closely collaborated in our effort to gain some insight into the dynamic features of such donor adducts of an organometallic Lewis acid, were able to make a reliable stereochemical assignment of the dmf ligands at CpZr from ^1H NMR NOE experiments carried out with **21** in CD_2Cl_2 solution at 213 K. Subsequent monitoring of the dynamic NMR spectra at temperatures between 243 and 289 K revealed the rapid exchange of the dmf ligand *trans* to Cp with free dimethylformamide in solution (0.35 molar equivalents present in this particular experiment) on the NMR time scale. The considerably slower exchange reaction of the *cis* dmf ligand was only observed at higher temperatures or with a much higher concentration of free dmf in the solution [21]. Probably, the same order of relative ligand exchange rates also applies for other $CpZrCl_3L_2$ systems as well, favouring the rapid equilibration of free ligand with L oriented *trans* to Cp over that of L *cis* to the cyclopentadienyl group.



□ = free coordination site

This description of the dynamic situation corresponds to some details of the static structure of $CpZrCl_3(dmf)_2$ as revealed by X-ray diffraction [21] (Fig. 3). In the crystal the *cis*-dmf ligand of **21** seems to be bonded more strongly to zirconium [Zr–O(2) = 2.198(2) Å] in the distorted octahedral coordination environment than the *trans* dimethylformamide ligand [Zr–O(1) = 2.253(2) Å]. The ligands oriented *cis* to the Cp-ligand appear to exert considerable steric pressure on the *trans* dmf group: the zirconium atom lies 0.51 Å above the plane going through the three Cl-ligands and O(2).

The organometallic Lewis acid $CpZrCl_3$ coordinates to the amide C=O functionalities at the oxygen lone pair and becomes oriented towards the side of the smaller substituent bonded to the carbonyl carbon atoms [angles Zr–O(1)–C(1) and Zr–O(2)–C(4) are 130.6° and 128.4°, respectively]. Coordination of dimethylformamide to the $CpZrCl_3$ Lewis acid results in slightly increased C=O bond lengths in

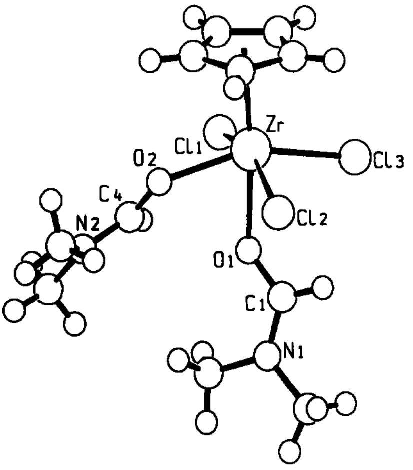


Fig. 3. A view of the molecular geometry of **21** as revealed by X-ray structure analysis.

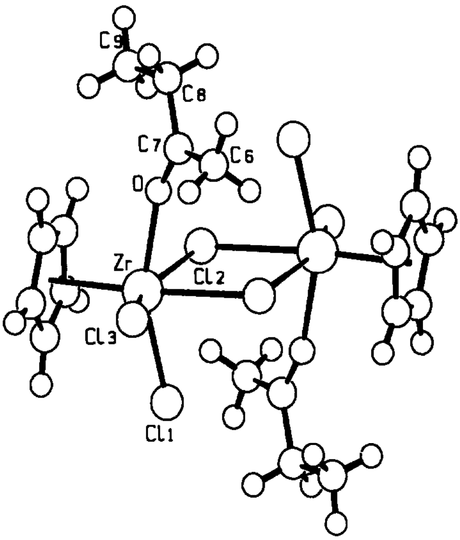


Fig. 4. Molecular structure of [$CpZrCl_3$(2-butanone)$]_2$ (**22**) in the crystal.

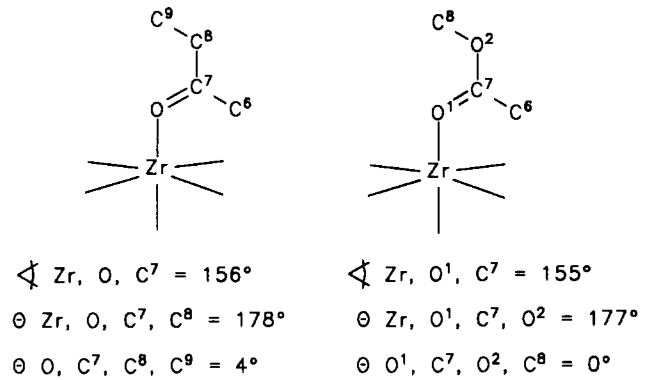
21 [O(1)–C(1) = 1.261(4) Å, O(2)–C(4) = 1.257(4) Å; cf. 1.24(1) Å in uncoordinated dmf]. A similar C=O bond elongation was observed in typical Hg(II) halide dmf complexes [e.g. $C_6H_4(HgCl)_2 \cdot$ dmf: O=C = 1.26(2) Å] [22]. A comparison of the IR ν(C=O) frequencies also indicated a similar Lewis acid character of mercury(II) halide systems and $CpZrCl_3$ [**21**: ν(C=O) = 1655, 1640 cm^{-1}; $C_6H_4(HgCl)_2 \cdot$ dmf: ν(C=O) = 1655 cm^{-1}; free dimethylformamide (neat liquid): ν(C=O) = 1670 cm^{-1}].

Aldehydes also gave mononuclear $CpZrCl_3L_2$ addition products, whereas the sterically more demanding ketones or esters, at least in the solid state, seemed to prefer binuclear $(CpZrCl_3L)_2$ adduct formation [23]. The complexes [$CpZrCl_3$(2-butanone)$]_2$ (**22**) and [$CpZrCl_3$(ethylacetate)$]_2$ (**23**) are typical examples. In the crystal both show C_i symmetric binuclear molecular structures, each having two chloride bridges *trans* to Cp and the carbonyl groups attached to the *cis*-coordination site at zirconium (Fig. 4). Some details of the bonding situation of the complexed ketone and ester groups are given in Scheme 2.

In this context two additional structures deserve to be mentioned. They both contain donor ligands bearing hydroxyl groups. We consider it remarkable that the organometallic $CpZrCl_3$ Lewis acid is able to coordinate OH functionalities reversibly without forming thermodynamically favourable persistent zirconium oxides or alkoxides possessing the extremely strong Zr–O or Zr–O–Zr σ-bonds [1a].

One of these structurally characterized complexes is the 1 : 1 $CpZrCl_3$/(−)-ethyl lactate adduct **24** [24]. The zirconium metal shows the typical distorted octahedral coordination geometry, with a chelating lactic ester bonded through the C=O group adopting a *cis*-position to the Cp ring [Zr–O(1) = 2.240(4) Å, C=O = 1.230(8) Å] and the hydroxyl oxygen *trans* to Cp [Zr–O(3) = 2.332(5) Å] [25], (Fig. 5).

It is even more remarkable that there is a solid state structure known of a stable [$CpZrCl_3(OH_2)_2$] addition product (**25**) [26]. This compound was formed by treating the oligomeric $(CpZrCl_3)_x$ with the crown ether 15-crown-5 containing a stoichiometric amount of water. In the solid state complex **25** contains one molar



∢ Zr, O, C^7 = 156° ∢ Zr, O^1, C^7 = 155°

Θ Zr, O, C^7, C^8 = 178° Θ Zr, O^1, C^7, O^2 = 177°

Θ O, C^7, C^8, C^9 = 4° Θ O^1, C^7, O^2, C^8 = 0°

Scheme 2. A comparison of characteristic bond and dihedral angles as found in the Lewis acid adducts $[CpZrCl_3(2\text{-butanone})]_2$ (**22**) and $[CpZrCl_3(\text{ethylacetate})]_2$ (**23**) in the solid state.

equivalent of this crown ether, some oxygen centers of which are hydrogen bonded to the $CpZrCl_3$ coordinated water molecules.

Again, the $CpZrCl_3L_2$ unit in **25** exhibits the usual distorted octahedral coordination geometry, with one water molecular oriented *trans* [Zr–O(1) = 2.295(6) Å] and the other *cis* to the η-cyclopentadienyl ligand [Zr–O(2) = 2.264(5) Å].

(η-Cyclopentadienyl)zirconium trichloride catalyzed reactions

The fact that $CpZrCl_3$ forms rapidly equilibrating adducts $CpZrCl_3L_2$ or $(CpZrCl_3L)_2$ fulfilled the necessary requirement for using this organometallic Lewis acid as a catalyst for the conversion of organic carbonyl compounds. Thus we used the $CpZrCl_3$ system to selectively catalyze the Diels–Alder-reaction between 2,3-dimethylbutadiene and metacrolein. It was known that the uncatalyzed thermally induced [4 + 2] cycloaddition must be carried out at 150 ° C to yield 1,3,4-trimethyl-3-cyclohexenyl-1-carbaldehyde (**26**). The C–C coupling reaction can effectively be catalyzed by common Lewis acids such as $TiCl_4$ or $SnCl_4$ but then does not stop at

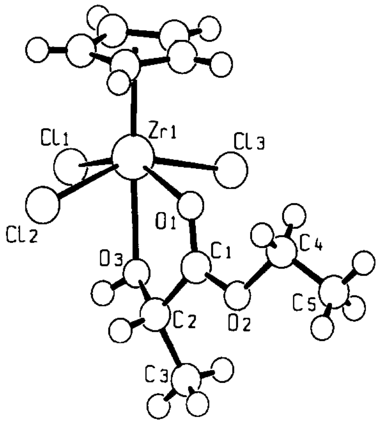
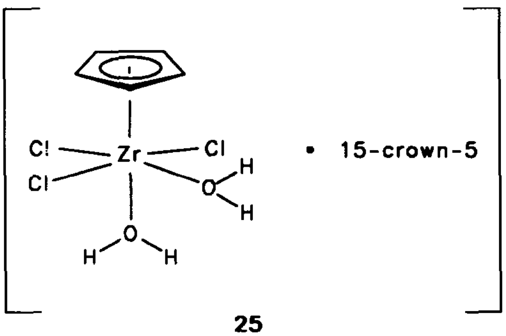
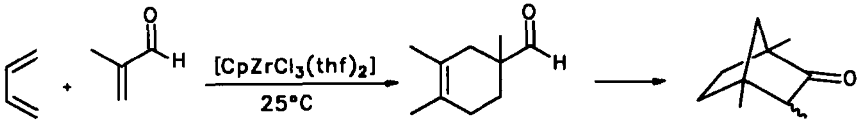


Fig. 5. Crystal structure of the $CpZrCl_3$/lactate 1 : 1 adduct **24**.



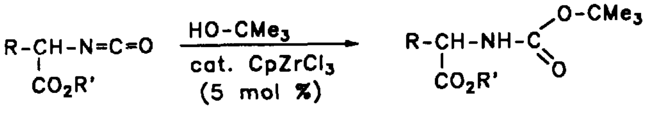
25

the desired product **26** because of the rapid subsequent acid-catalyzed rearrangement to give 1,3,4-trimethylbicyclo[2.2.1]heptan-2-one (**27**) [27]. Use of the $CpZrCl_3$ Lewis acid catalyst, introduced, e.g., as the bis-tetrahydrofuran adduct, led very selectively to the formation of the cyclohexene derivative **26** at ambient temperature. The $CpZrCl_3$-catalyzed **26** → **27** rearrangement only became effective at temperatures $\geqslant 100\,^{\circ}C$.



26 **27**

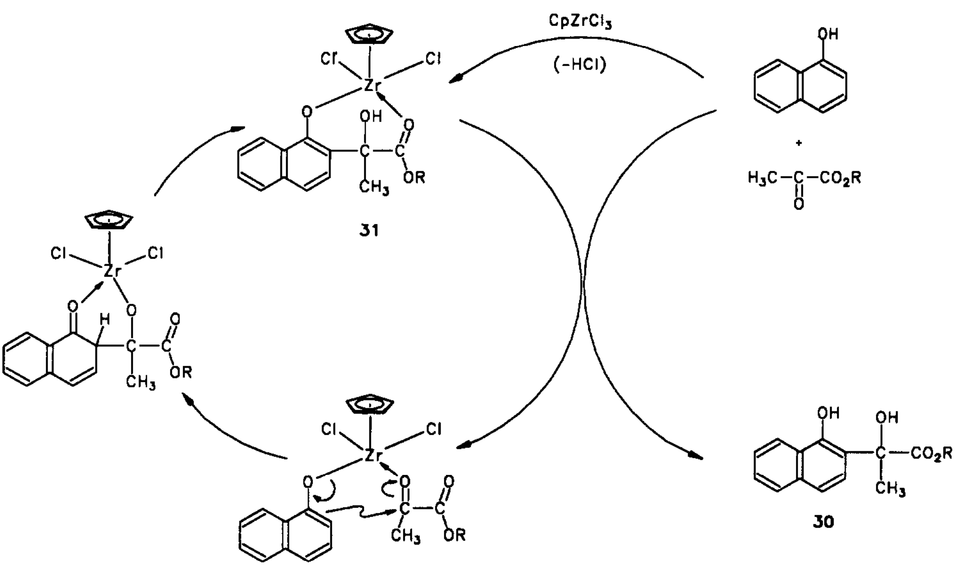
Knowing from Jutta Schamberger's and Christian Sarter's work in my group that hydroxyl-containing substrates could cleanly be added to $CpZrCl_3$ I was attracted by the possibility of using this organometallic Lewis acid catalyst to promote alcohol-addition reactions. We discovered an interesting novel route to *N*-boc protected amino acid derivatives. Sterically hindered tertiary alcohols were added to reactive heterocumulenes with the aid of a suitable Lewis acid catalys [28]. The $CpZrCl_3$-catalyzed addition reaction of tert-butanol to ester isocyanates (**28**) proceeded cleanly at ambient temperature to give the corresponding *N*-boc protected aminoesters (**29**). In some cases even 1-adamantol could be added to isocyanates under (η-cyclopentadienyl)zirconium trichloride Lewis acid catalysis [29].



$$\underset{\displaystyle CO_2R'}{R\text{-}\underset{|}{C}H\text{-}N{=}C{=}O} \xrightarrow[\text{cat. }CpZrCl_3\ (5\text{ mol }\%)]{HO\text{-}CMe_3} \underset{\displaystyle CO_2R'}{R\text{-}\underset{|}{C}H\text{-}NH\text{-}C}\begin{matrix}\nearrow O\text{-}CMe_3\\ \searrow O\end{matrix}$$

28 **29**

It would be very interesting to use organometallic Lewis acids which can be structurally varied in contrast to the commonly employed simple inorganic metal halide catalysts, for promoting aldol addition type reactions. A related C–C coupling reaction, the hydroxyalkylation of 1-naphthol with pyruvate esters to give the pharmacologically interesting 2-(1-hydroxy-2-naphthyl)lactates **30** [30], can effectively be catalyzed by $CpZrCl_3$ under mild conditions.



Scheme 3. Proposed catalytic cycle for the $CpZrCl_2X$-catalyzed hydroxyalkylation reaction of 1-naphthol with ethyl pyruvate.

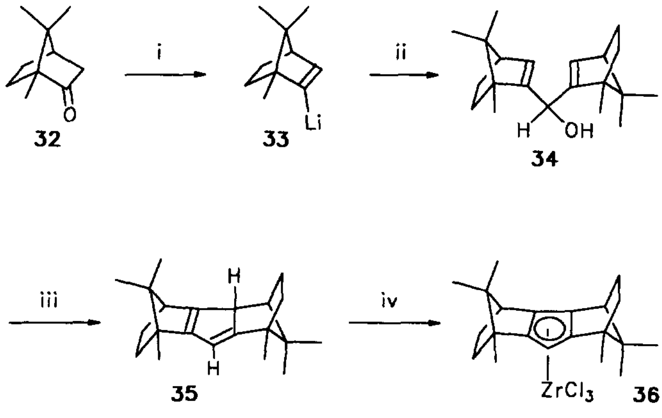
We first treated a stoichiometric amount of $CpZrCl_3$ with a 1 : 1 mixture of 1-naphthol and ethyl pyruvate, and obtained in good yield the $CpZrCl_3$ adduct **31** of the C–C coupling product of the two organic starting materials (Scheme 3). We assumed that a zirconium naphtholate was formed first (with liberation of one equivalent of HCl), and then underwent addition of the reactive H_3CCOCO_2R carbonyl component. Probably the carbon–carbon coupling process took place rapidly at the CpZr template, followed by hydrogen transfer to give the observed organometallic compound **31** [31].

The isolated chelate complex **31** itself served as an active catalyst for this type of C–C coupling. With a small amount of **31** a large excess of a 1 : 1 mixture of 1-naphthol and ethyl pyruvate was effectively converted into 2-(1-hydroxy-2-naphthyl)ethyllactate under mild conditions [31].

Enantioselective catalysis with (diborna-Cp)ZrCl$_3$

The 1-naphthol/pyruvate coupling reaction was, of course, a challenge for enantioselective catalysis using an optically active (η-cyclopentadienyl)zirconium trichloride derived chiral Lewis acid catalyst. After we had tried some (R^*-Cp)$ZrCl_3$ systems without much success, Dolf van der Zeijden prepared a very nice C_2-symmetric chiral Cp-ligand system and used it for the synthesis of a useful chiral organometallic zirconium based Lewis acid catalyst [31].

Dr. van der Zeijden used (+)-camphor (**32**) as a starting material for the chiral pool synthesis of the dibornacyclopentadiene ligand system in (+)-**36**. The bicyclic ketone was converted into 2-bornenyllithium **33** by means of the Shapiro reaction. The isolated alkenyllithium reagent was then added to ethyl formate (2 : 1 molar ratio) to give the dialkenylcarbinol **34**, which was then dehydrated under acid catalysis to afford the ring-closed product **35** (two diastereoisomers) [32]. Deproto-

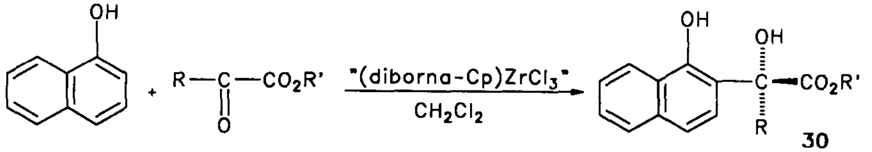


"(diborna-Cp)ZrCl$_3$", $[\alpha]_D$ = +51°

i: 1. 2,4,6-$(iPr)_3C_6H_2SO_2NHNH_2$, 2. sec-BuLi; ii: HCO_2Et; iii: $KHSO_4$, 100-150°C; iv: 1. n-BuLi, Et_2O, 2. $ZrCl_4$.

Scheme 4. Synthesis of the chiral Lewis acid (diborna-Cp)ZrCl$_3$.

nation with n-butyllithium and reaction with one molar equivalent of zirconium tetrachloride produced the organometallic Lewis acid (diborna-Cp)zirconium trichloride **36** ($[\alpha]_D = +51°$). The analogous reaction sequence starting from (−)-camphor yielded the enantiomeric Cp-substituted zirconium complex ent-**36** [33] (Scheme 4).



R = methyl, i-propyl; R' = methyl, ethyl, i-propyl, cyclohexyl

optimized for R = methyl, R' = ethyl:

temperature :	20°C,	0°C,	-5°C,	-10°C,	-20°C
(100:100:1:0, 24 h) ee :	21%,	32%,	46%,	54%,	53% ee
% transformation :	40,	65,	75,	85	
(100:100:1:0, -10°C)ee :	78%,	70%,	54%,	49% ee	
% transformation :		50,	70,	90	
(500:100:1:0, -10°C)ee :		53%,	42%,	32% ee	
% transformation :			70,	85,	≈100
(100:500:5:0, -10°C)ee :			80%,	80%,	72% ee
% transformation :		55,	70,	90*	
(100:500:5:27, -10°C)ee:		89%,	89%,	84% ee.	

Naphthol : pyruvat : catalyst : water

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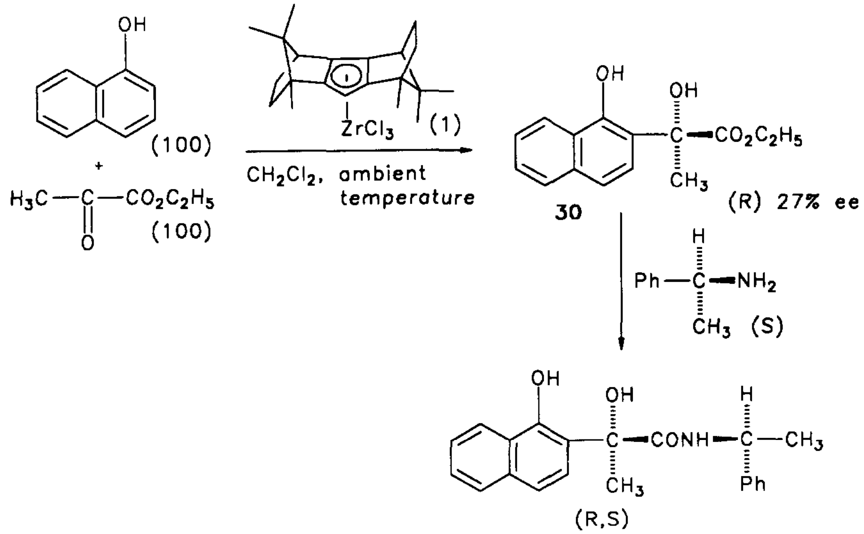
* prep. scale: 56% product isolated, Mp = 47°C, 84% ee, $[\alpha]_D$ = +118°.

Scheme 5. Optimization of the asymmetric hydroxyalkylation of 1-naphthol with pyruvate ester catalyzed by the organometallic Lewis acid (dibornaCp)ZrCl$_3$.

(Diborna-Cp)$ZrCl_3$ effectively catalyzed the C–C coupling reaction of 1-naphthol with pyruvate esters. The reaction of 1-naphthol and ethyl pyruvate with (+)-(diborna-Cp)zirconium trichloride in a 100 : 100 : 1 ratio at ambient temperature in methylene chloride afforded 2-(1-hydroxy-2-naphthyl)ethyllactate (70% isolated) with 27% e.e. The excess enantiomer was *R* configurated. This was shown by a reductive degradation to the stereochemically known 2-(1-hydroxy-2-naphthyl)propan-1,2-diol and the formation of a mixture of the diastereomeric amides **37** by treatment with enantiomerically pure 1-phenylethylamine [31]. Catalysis with (−)-(diborna-Cp)$ZrCl_3$ likewise produced the *S*-enantiomerically enriched product **30** [33].



This asymmetric catalytic carbon–carbon coupling process was subsequently somewhat improved. By lowering the reaction temperature we achieved about 50% e.e. Making the reaction faster by increasing the pyruvate (not the naphthol) concentration allowed us to approach the 75–80% e.e. region. Adding a small quantity of water to the reaction mixture then reproducibly increased the enantiomeric excess by an additional 10%. On a preparative scale, *R*(+)-2-(1-hydroxy-2-naphthyl)ethyllactate (**30**) was eventually obtained in a 56% isolated yield with 84% e.e. by reaction of 1-naphthol with ethyl pyruvate in the presence of (+)-(diborna-Cp)$ZrCl_3$ and water (in a 100 : 500 : 5 : 27 molar ratio) in methylene chloride at −10 °C (Scheme 5).

Future prospects

The results of the selected experiments carried out with the $CpZrCl_3$ system show that this 12-electron organometallic Lewis acid is potentially useful as a catalyst for organic synthesis. In some catalytic cycles it is probably involved as a derivative, i.e. having undergone halide/alkoxide exchange. In addition, the active species may in some cases actually have a higher electron count, as in $CpZrCl_2(OR)L$-type complexes. Similar species may also be present in solution when the dimeric $[CpZrCl_3(ketone)]_2$ and $[CpZrCl_3(ester)]_2$ adducts are dissolved. We observed that a mixture of dynamic complexes was formed which exhibited a number of well-resolved Cp singlets in the low temperature limiting ^1H NMR spectra.

Thus a variety of suitable $CpZrX_3L_n$ precursors is available to form the active organometallic Lewis acid catalyst under different reaction conditions. To me it would be most fascinating to develop a $CpZrX_n(OR)_{3-n}L$ Lewis acid catalyst that retains its catalytic activity in a hydroxylic reaction medium or even in water. I think that the prospects of doing so are not too bad. We have found a stable $CpZrCl_3(H_2O)_2$ species and characterized it by X-ray diffraction in the solid state. We even dissolved $CpZrCl_3(dmf)_2$ (**21**) in D_2O and observed very simple ^1H spectra (one Cp singlet and one set of dmf signals). Complex **21** was recovered unchanged from the aqueous solution upon removal of the H_2O solvent in vacuum. An EXAFS experiment, currently being carried out by Professor H. Bertagnolli, our colleague at the Universität Würzburg, and his coworkers, will probably reveal the actual nature of the organometallic species present in H_2O.

Our surprising experience that the addition of some water to the chiral (diborna-Cp)$ZrCl_3$ organometallic Lewis acid catalyst resulted in an enhanced enantioselectivity without causing much catalyst deactivation has indicated that the presence of H_2O is not at all prohibitive for using the Lewis acidity of the $CpZrX_3$ catalyst systems. This makes me hopeful that it may be possible to develop novel types of organometallic Lewis acid catalysts on the basis of, for example, (cyclopentadienyl)zirconium-type systems that will effectively catalyze selective transformations of organic substrates even in aqueous solution.

Acknowledgement

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