168. Semicorrin Metal Complexes as Enantioselective Catalysts

Part 1

Synthesis of Chiral Semicorrin Ligands and General Concepts[1])

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An efficient synthesis of chiral semicorrin ligands is described (see **6–9**, *Schemes 2* and *3*). Both enantiomers are readily obtained in enantiomerically pure form starting either from D- or L-pyroglutamic acid (**1**). Semicorrins of this type possess several features that make them attractive ligands for enantioselective control of metal-catalyzed reactions. Their structure is characterized by C_2 symmetry, a conformationally rigid ligand system, and two stereogenic centers adjacent to the coordination sphere. In a metal complex, the two substituents at the stereogenic centers shield the metal atom from two opposite directions and, therefore, are expected to have a pronounced effect on the stereochemical course of a reaction occurring in the coordination sphere. The structure of these two substituents can be easily modified in a variety of ways. A series of (semicorrinato)copper(II) complexes (see **10–14**, *Scheme 4*) has been prepared, and in one case (**14**), the three-dimensional structure has been determined by X-ray analysis *(Fig. 1)*.

1. Introduction. – Chemists have always been intrigued by the ability of enzymes to distinguish between two enantiotopic sites in a molecule. For a long time, the stereoselectivity of enzymatic reactions was considered beyond reach for artificial catalysts. However, with the development of efficient enantioselective hydrogenation catalysts around 1970 [2] [3], it became evident that enzyme-like stereoselectivity can in fact be achieved with synthetic catalysts. Since then, an exponential increase of research in this area resulted in substantial progress, particularly in the field of metal-catalyzed processes [3a] [4]. Among the most prominent achievements are the highly enantioselective hydrogenations catalyzed by chiral phosphine complexes of Rh [3] and Ru [5] as well as the Ti-tartrate-mediated enantioselective epoxidation of allylic alcohols, discovered by *Katsuki* and *Sharpless* [6]. In both cases, the chiral ligand attached to the metal center efficiently controls the stereochemical course of the metal-catalyzed process. Although an impressive number of other enantioselective catalysts have been described [4], very few of them meet the standards of selectivity, reliability, and general applicability set by the Rh- and Ru-phosphine hydrogenation catalysts and the *Sharpless* epoxidation. Thus, the

[1]) Taken in part from the Ph. D. thesis of *H. F.*, ETH-Zürich (in preparation); for a preliminary communication, see [1].

[2]) Correspondence concerning X-ray structural data should be addressed to these authors.

search for new, efficient enantioselective catalysts will continue to be one of the major directions of research in asymmetric synthesis.

Beyond that, the development of a more rational basis for designing new types of enantioselective catalysts will become more and more important. Our present knowledge of the various factors determining the stereochemical course of metal-catalyzed reactions is still on a rather primitive level, limiting both the application of existing methods as well as further advances in the development of new catalyst systems. Even in cases like the Rh-phosphine-catalyzed hydrogenation of 2-acetamido-2-alkenoic-acid derivatives [3] or the *Sharpless* epoxidation [6c] which have been mechanistically investigated in great detail, the origin of enantioselection is still open to debate.

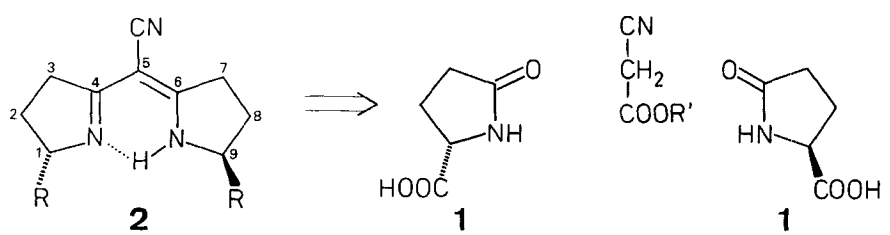
In the present work, we discuss the synthesis and properties of chiral, C_2-symmetric semicorrins (*cf.* structure **2**, *Scheme 1*)[3]), a class of bidentate N-chelate ligands specifically designed for enantioselective control of metal-catalyzed reactions. Due to their structural characteristics, ligands of this type should be well suited for a wide range of applications in enantioselective catalysis and, moreover, allow a rather straightforward, rational development of enantioselective metal catalysts[4]).

2. Synthesis of Chiral 1,9-Disubstituted Semicorrin Ligands. – Semicorrins have been previously prepared as intermediates in the synthesis of corrinoid and corphinoid compounds [7] [9]. Their structure is characterized by a vinylogous amidine system embedded in a conformationally rigid scaffold built from two hydropyrrol rings. Our synthesis of chiral 1,9-disubstituted semicorrins **2** is based on the retrosynthetic analysis shown in *Scheme 1*. The construction of bicyclic vinylogous amidines by this route originates in the work of *Eschenmoser* and coworkers and has been successfully applied in the synthesis of numerous corrinoids [9].

The two halves of the C_2-symmetric ligand **2** are both derived from pyroglutamic acid **1**, a moderately priced starting material which is commercially available as well in the D- as in the L-form in high enantiomeric purity. The actual synthesis is summarized in *Scheme 2*. By this route, the semicorrin **6** can be readily prepared in multigram quantities. The overall yield of crystalline enantiomerically pure diester **6**, based on pyroglutamic acid **1**, ranges between 30 and 40%.

Esterification of L-pyroglutamic acid ((−)-**1**) in MeOH, catalyzed by acidic ion-exchange resin, gave the corresponding methyl ester in essentially quantitative yield without notable racemisation. Methyl pyroglutamate

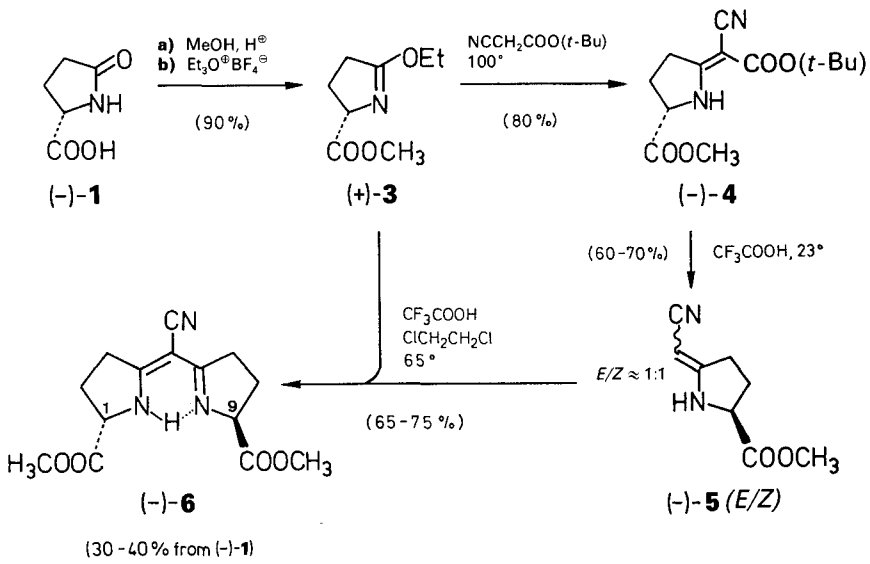
Scheme 1



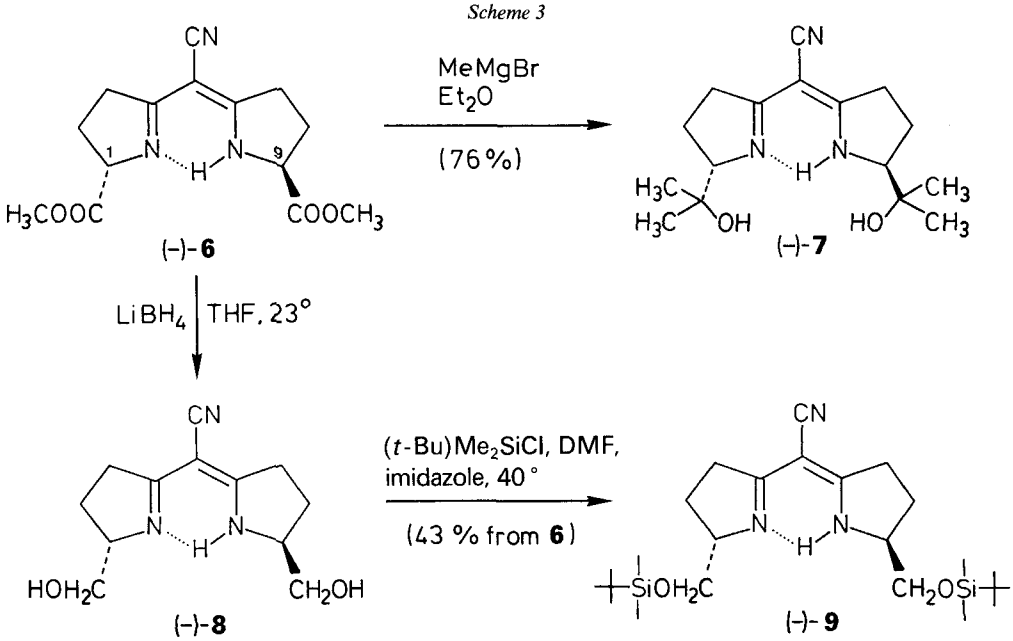
[3]) The name 'semicorrin' for vinylogous amidines of this type has been originally proposed by *Stevens et al.* [7]. Dipyrrin numbering is used in connection with this trivial name. Systematic name of the parent ligand system: 3,4-dihydro-5-[(pyrrolidin-2-ylidene)methyl]-2*H*-pyrrole.

[4]) For a review of chiral ligands for enantioselective catalysis, (see [8]).

Scheme 2



Scheme 3



was converted to the cyano-enamine (−)-**5**, following the procedures of *Bühler et al.* [10] who had previously prepared this compound as an intermediate in the synthesis of optically active corrins. *O*-Alkylation of the lactam function with triethyloxonium tetrafluoroborate and subsequent condensation of the resulting imino ester (+)-**3** with *tert*-butyl cyanoacetate led to the crystalline *tert*-butyl ester (−)-**4** in high yield. All these steps can be easily carried out on a molar scale. Cleavage of the *tert*-butyl ester followed by decarboxylation produced a mixture of the (*E*)- and (*Z*)-cyano-enamines (−)-**5** which was used in the next step without separating the two isomers. The yields of this transformation critically depend on the reaction time and temperature. Under optimized conditions on a 0.1- to 0.2-molar scale, they ranged between 50 and 70%. On a larger scale, the yields were less reproducible. Initial attempts to couple the two monocyclic building blocks (+)-**3** and (−)-**5** using the iminoester-enamine condensation method [9] were unsuccessful. Under neutral or weakly basic conditions which had been previously applied in similar cases [9], the desired condensation to the semicorrin (−)-**6** did not take place. Strongly basic conditions, on the other hand, had to be avoided in order to prevent racemization. Addition of acid finally brought about the desired effect. In the presence of CF_3COOH (1 mol-equiv. based on (+)-**3**) which presumedly activates the iminoester by N-protonation, the two components smoothly reacted to the semicorrin (−)-**6** upon warming to 65°. Other acids such as AcOH, TsOH, or $BF_3 \cdot Et_2O$ gave less satisfactory results. As a side reaction, the iminoester (+)-**3** was cleaved to the corresponding lactam and, therefore, was used in excess. After chromatography and recrystallization, analytically pure semicorrin (−)-**6** was isolated in *ca.* 70% yield based on (−)-**5**. As judged by ^{1}H-NMR spectroscopy in the presence of the chiral shift reagent tris(3-trifluoroacetyl-*d*-camphorato)-europium(III) ([Eu(tfc)$_3$]), the compound was enantiomerically pure.

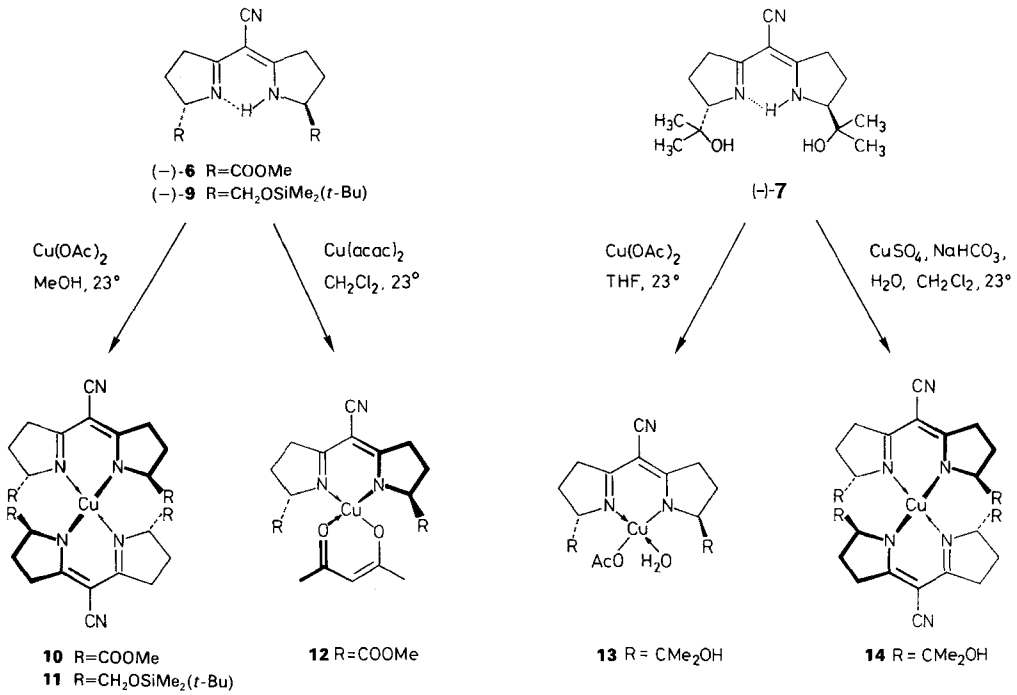
The two methoxycarbonyl groups of the semicorrin (−)-**6** can easily be modified in a variety of ways *(cf. Scheme 3)*. *Grignard* reaction with an excess of MeMgBr produces the diol (−)-**7** in good yield. The coordination sphere of this ligand is shielded by the two bulky substituents at the stereogenic centers. Reduction using either $LiAlH_4$ or $LiBH_4$ leads to the bis(hydroxymethyl)semicorrin (−)-**8** which offers a wide range of possibilities for further structural modifications. One of the compounds prepared from the diol (−)-**8** is the (*tert*-butyl)dimethylsilyl ether (−)-**9**. The two trialkylsilyl groups render this ligand and corresponding metal complexes highly soluble in most organic solvents, even in hydrocarbons like hexane.

Nucleophilic reagents such as $LiAlH_4$, organomagnesium compounds, and even the more reactive MeLi selectively attack the semicorrin **6** at the ester carbonyl functions, leaving the vinylogous amidine system and the nitrile group intact. This is not unexpected, as the electrophilicity of the nitrile group is markedly decreased by conjugation with the nucleophilic vinylogous amidine system. Moreover, removal of the NH-proton under the reaction conditions further reduces the reactivity of both, the nitrile group and the semicorrin π-system towards nucleophiles.

3. Formation and Structure of Semicorrin Metal Complexes. – As expected for chelate ligands of this type [11], the semicorrins **6**–**9** all have a strong tendency to form complexes with metal ions. The diester **6**, *e.g.*, readily forms a Zn complex during chromatography on silica-gel plates impregnated with a Zn-containing fluorescence indicator. TLC analyses of semicorrins, therefore, have to be carried out using metal-free silica-gel plates.

The reactivity of the semicorrin ligands (−)-**6** and (−)-**9** towards transition-metal ions was briefly examined in a series of preliminary experiments with $CoCl_2$, $NiCl_2$, $Ni(OAc)_2$, $Cu(OAc)_2$, and $Pd(OAc)_2$ in organic solvents such as MeOH, MeCN, or THF. In all cases, UV/VIS spectroscopy or TLC analysis as well as a characteristic color change upon addition of the metal salt indicated spontaneous and essentially quantitative complex formation, even in the absence of an external base. The preparation of various types of (semicorrinato)copper(II) complexes is summarized in *Scheme 4*. In the presence of 0.5 mol-equiv. of $Cu(OAc)_2$ in MeOH, the semicorrins (−)-**6** and (−)-**9** instantaneously and

Scheme 4



quantitatively react to the violet-blue bis(semicorrinato) complexes **10** and **11**, respectively. Using a large excess of $Cu(OAc)_2$, a mixture of mono- and bis(semicorrinato) complexes was obtained. The greenish mono(semicorrinato) complexes derived from (−)-**6** and (−)-**9** proved to be too labile to allow isolation. They readily disproportionated to the corresponding bis(semicorrinato) complexes and free $Cu(OAc)_2$. Starting from equimolar amounts of copper(II) acetylacetonate ($Cu(acac)_2$) and the semicorrin (−)-**6**, however, the crystalline (acetylacetonato)[mono(semicorrinato)]copper(II) **12** was obtained in essentially quantitative yield. In contrast to the semicorrins (−)-**6** and (−)-**9**, the sterically more demanding ligand (−)-**7** selectively formed a green mono(semicorrinato) complex **13** with $Cu(OAc)_2$ under neutral conditions. Upon addition of base, however, **13** was quantitatively converted to the corresponding violet bis(semicorrinato) complex **14**. In a two-phase system containing CH_2Cl_2 and aqueous $NaHCO_3$ solution, (−)-**7** and 0.5 mol-equiv. of $Cu(OAc)_2$ cleanly reacted to the stable bis(semicorrinato)copper(II) **14** (isolated in 94% yield after recrystallization). The three-dimensional structure of complex **14** which was determined by X-ray analysis is shown in *Fig. 1*.

The central Cu(II) atom is surrounded by two semicorrin ligands. In the complex, the four coordinating N-atoms form a distorted tetrahedral arrangement. The planes of the two ligands are tilted relative to each other with an angle of 62°. The observed coordination geometry of the Cu-ion is readily explained as a consequence of steric interactions between the two semicorrin ligands. The steric requirements of the hydropyrrole rings of the two ligands are incompatible with a planar arrangement of the four N-atoms, as it is

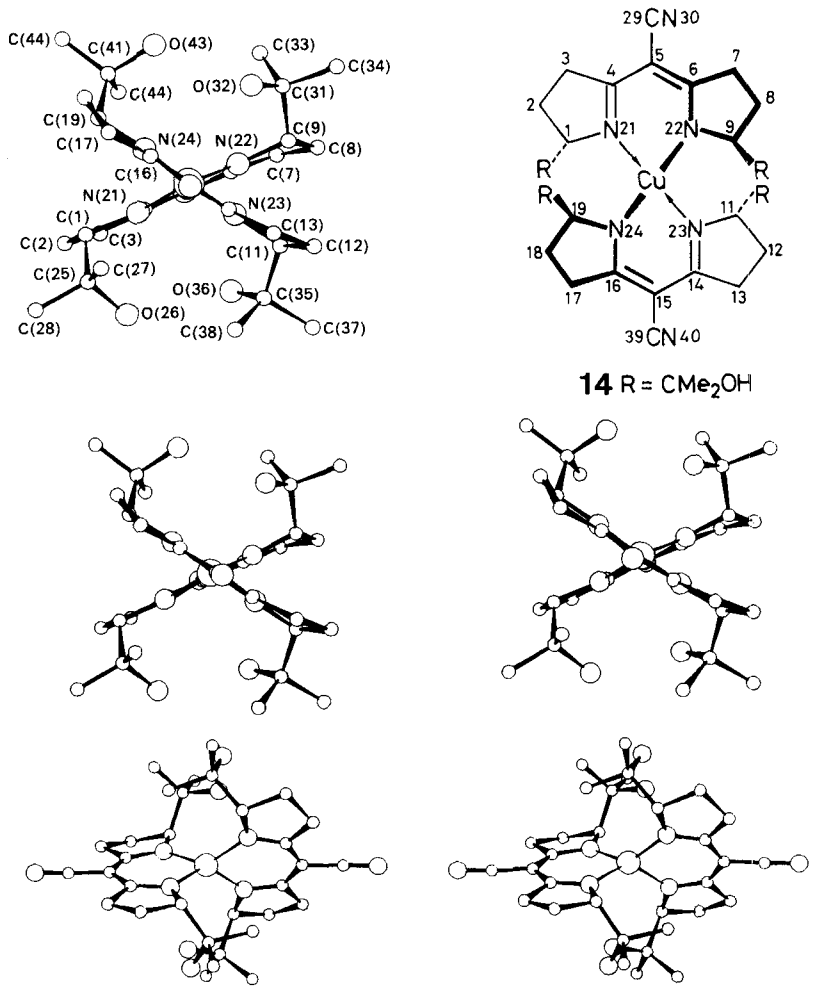


Fig. 1. *Crystal structure, atomic numbering, and stereoscopic views of* **14**

normally preferred by Cu(II) complexes in the absence of steric restrictions [12]. A tetrahedral coordination geometry, on the other hand, would bring about severe steric repulsion between the bulky hydroxyalkyl substituents.

The ligands are interconnected by two H-bridges between adjacent OH groups (2.72 and 2.78 Å). One of the two OH groups of each ligand seems to be weakly coordinated to the metal center forming a Cu–O bond (3.15 and 3.17 Å, resp.) *ca.* orthogonal to the plane of the adjacent ligand. The two hydropyrrol rings which carry the coordinating hydroxyalkyl substituents are puckered in such a way that these substituents occupy pseudoaxial positions, a conformation which allows a shorter Cu–O distance than the corresponding pseudoequatorial arrangement. Of the remaining two hydropyrrol rings, one is puckered with the hydroxyalkyl group in a pseudo-equatorial position; the other one is essentially planar.

Space filling models show that the Cu(II) atom is completely shielded by the two semicorrin ligands and, therefore, is not likely to have any tendency to coordinate additional ligands. On these grounds, in bis(semicorrinato) complexes of this type, the

metal center is not expected to exhibit any catalytic activity unless one of the two semicorrin ligands dissociates from the coordination sphere.

4. Enantioselective Control of Metal-Catalyzed Reactions by Semicorrin Ligands: General Aspects. – Semicorrins of the structural type **2** possess several features that make them attractive ligands for controlling the stereochemical course of metal-catalyzed processes. First of all, both enantiomers are readily prepared in enantiomerically pure form on a multigram scale, starting either from D- or L-pyroglutamic acid (see *Scheme 2*). The geometry of the vinylogous amidine system is ideal for coordinating metal ions. Accordingly, semicorrins have a strong tendency to form chelate complexes (see *Section 3* and [11]). The generally high stability of such complexes should ensure that the ligand remains attached to the metal center during the course of a metal-catalyzed reaction. An important point to be considered with regard to potential applications concerns the stability of the ligand under the conditions of a particular metal-catalyzed reaction (see, *e.g.* [13]). As discussed in *Section 2 (cf. Scheme 3)*, the semicorrin ligand is highly resistant to nucleophiles and bases. Due to the (primarily nucleophilic) reactivity of the vinylogous amidine system, the presence of strong acids or electrophiles is more critical. However, conjugation with the CN group which originally was introduced for synthetic considerations *(cf. Scheme 2)*, markedly reduces the reactivity of the π-system towards electrophiles. Thus, avoiding strongly electrophilic reagents, semicorrins should be sufficiently stable to tolerate a wide range of reaction conditions.

The planar π-system and the two five-membered rings bring about considerable conformational rigidity. The rigid conformation of the ligand framework and its C_2 symmetry[5]) considerably simplify the structure of corresponding metal complexes and reduce the number of possible arrangements of the chiral catalyst and a coordinated substrate. This should greatly facilitate an analysis of the interactions between the catalyst and the substrate which determine the stereoselectivity of a metal-catalyzed process.

In (semicorrinato)metal complexes, the two substituents at the stereogenic centers of the ligand are in close proximity to the coordination center. They shield the metal atom from two opposite directions and, therefore, are expected to have a distinct effect on the stereochemical course of a reaction occurring in the coordination sphere of the complex (*cf. Figs. 1* and *2*). As illustrated in *Scheme 3*, these two substituents can be easily modified in a variety of ways. This allows the structure of the ligand to be adjusted to the

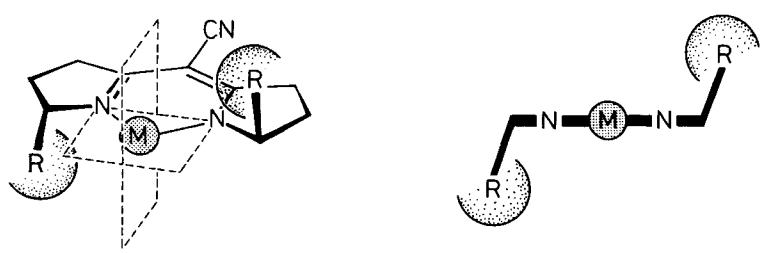


Figure 2

[5]) The advantages of ligands, catalysts, and reagents possessing C_2 symmetry have been documented in numerous cases. See, *e.g.* [3] [5] [6] [8] [13b] [14].

specific requirements of a particular application and provides a means to optimize the selectivity of a metal catalyst in a systematic manner. Moreover, by studying the effects that result from changing the ligand structure, informations may be obtained about the mechanism of a particular metal-catalyzed process and the individual factors that determine its stereoselectivity. The interpretation of structure-selectivity relations from experiments of this kind should be considerably facilitated by the conformational rigidity and the C_2 symmetry of the semicorrin ligand system.

In summary, the structural properties of chiral 1,9-disubstituted semicorrins should make it possible to approach the problem of designing an enantioselective catalyst in a rather straightforward, rational way. Considering the wealth of synthetically useful metal-catalyzed reactions that are known, many potential applications can be envisaged for this class of ligands. As a first test of our concepts, we have investigated the cyclopropane formation from olefins with diazo compounds, using the (semicorrinato)copper(II) complexes depicted in *Scheme 4* as catalysts. A detailed account on these studies is given in the following communication [15].

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Experimental Part

1. General. – CH_2Cl_2, Et_2O, AcOEt, hexane: technical grade, distilled before use. 1,2-Dichloroethane, $CHCl_3$: *Fluka puriss.*, filtered through basic alumina. DMF: *Fluka puriss.*, dist. over CaH_2 and stored over 3-Å molecular sieves. EtOH, MeOH, toluene: *Fluka puriss.* Anh. Et_2O and THF: *Fluka purum*, dist. over Na/benzophenone. Anh. CH_2Cl_2: dist. over CaH_2. CF_3COOH: *Fluka purum*, redist. *tert*-Butyl cyanoacetate: *Fluka purum*, redist. Imidazole, D- and L-pyroglutamic acid: *Fluka puriss. Dowex 50 W X 8: Fluka p.a.*, strongly acidic ion-exchange resin, 200–400 mesh, H^+ form. Basic alumina: *ICN Biomedicals*, activity super 1. $Cu(OAc)_2 \cdot H_2O$: *Riedel-DeHaen, p.a.* $Cu(acac)_2$: *Fluka pract.* $CuSO_4 \cdot 5\,H_2O$: *Fluka purum, p.a.* Unless otherwise stated, reactions were carried out under N_2 in an apparatus fitted with a N_2 balloon. Column chromatography (flash chromatography (FC) [16]): *Merck* silica gel *60*, 0.040–0.063 mm. TLC: *Merck* silica gel *60*, 0.25 mm, without fluorescence indicator; staining with basic $KMnO_4$ soln. (2 g $KMnO_4$ + 5 g K_2CO_3 in 100 ml H_2O). Specific rotation: *Perkin-Elmer-241* polarimeter, $d = 10$ cm, c in g/100 ml, 25°. UV/VIS (EtOH): λ in nm (ε). IR ($CHCl_3$): selected bands; in cm^{-1}. NMR ($CDCl_3$): δ in ppm *vs.* TMS, J in Hz; ^1H: 300 MHz; ^{13}C: 75 MHz; assignments based on DEPT or off-resonance spectra. MS: selected peaks; m/z (%).

2. Synthesis of Semicorrins (*cf. Schemes 2* and *3*). – *L-Methyl Pyroglutamate* (= *(2S)-Methyl 5-Oxopyrrolidine-2-carboxylate*). L-Pyroglutamic acid (500 g, 3.9 mol; **1**) was added to a suspension of 40 g of acidic ion-exchange resin *(Dowex 50 W X 8)* in 6.3 l of anh. MeOH. After heating to reflux for 4 h, the mixture was filtered and concentrated. The resulting oil was distilled through a 20-cm *Vigreux* column at 0.01 Torr to yield methyl pyroglutamate as a viscous colorless oil (536 g, 97%; b.p. 125–126°). $[\alpha]_D = -8.5$ ($c = 11.0$, $CHCl_3$). TLC (AcOEt): R_f 0.28. IR: 3440*m*, 3220*w* (br.), 3100*w* (br.), 1745*s*, 1710*s*, 1460*w*, 1440*m*, 1410*m*. ^1H-NMR: 2.21–2.52 (*m*, CH_2CH_2); 3.78 (*s*, CH_3O); 4.26 (*dd*, $J = 8.5, 5.1$, H–C(2)); 6.34 (br. *s*, NH). MS: 144 (5), 143 (4, M^+), 85 (5), 84 (100, $M^+ - COOCH_3$).

*(2S)-Methyl 5-Ethoxy-3,4-dihydro-2*H*-pyrrol-2-carboxylate* ((+)-**3**) [10]. L-Methyl pyroglutamate (50 g, 0.35 mol) in 100 ml of anh. CH_2Cl_2 was added to a soln. of $Et_3O^+BF_4^-$ [17] (84.6 g, 0.45 mol; washed with anh. Et_2O under N_2 and dried at 25°/0.01 Torr before use) in 200 ml of anh. CH_2Cl_2. The soln. was heated to reflux under N_2 for 5 h until the reaction was complete, as judged by TLC (AcOEt; R_f(educt) 0.28; R_f(product) 0.54). After cooling to 0° in an ice bath, 55 g (0.5 mol) of anh. Na_2CO_3 in 700 ml of H_2O were slowly added. After separating the two phases, the aq. layer was saturated with NaCl and extracted with CH_2Cl_2 (3 × 200 ml), the combined org. extract washed with sat. aq. NaCl soln., filtered through cotton, and evaporated, and the remaining oil distilled through a

10-cm *Vigreux* column at 0.06 Torr yielding 57.2 g (95%; b.p. 58–60°) of (+)-**3** as a colorless viscous oil. $[\alpha]_D = +53.1$ ($c = 9.0$, $CHCl_3$). IR: 1740*s*, 1640*s*, 1480*w*, 1460*m*, 1440*m*, 1405*m*, 1380*s*, 1340*s*. ^{1}H-NMR: 1.32 (*t*, $J = 7.1$, CH_3); 2.11–2.38 (*m*, CH_2(3)); 2.44–2.62 (*m*, CH_2(4)); 3.74 (*s*, CH_3O); 4.25, 4.30 (*XY* of A_3XY, $J_{XY} = 11.0$, $J_{AX} = J_{AY} = 7.1$, CH_2O); 4.54 (*ddt*, $J = 8.5$, 5.7, 1.1, H–C(2)). MS: 172 (3), 171 (5, M^+), 113 (5), 112 (76, $M^+ - COOCH_3$), 84 (100, $M^+ - COOCH_3 - CH_2CH_2$).

*(2S)-Methyl 5-{[(*tert*-Butyl)oxycarbonyl](cyano)methylidene}pyrrolidine-2-carboxylate* ((–)-**4**) [10]. A mixture of (+)-**3** (61 g, 0.36 mol) and *tert*-butyl cyanoacetate (210 g, 1.5 mol) was stirred under Ar at 100° for 23 h. During that period, 10 g of EtOH (60% of th.) were collected in a distillation head connected to the reaction flask. The yellow mixture was cooled to 25°. Upon standing for a few h, the product began to crystallize. After additional 16 h at +4°, the resulting white crystals were collected and thoroughly washed with hexane to give 63.3 g of (–)-**4** (m.p. 127–128°). The remaining *tert*-butyl cyanoacetate was recovered by distillation at 41–43°/0.1 Torr. From the residue (17 g), additional 12.8 g of (–)-**4** (m.p 127°) were obtained by recrystallization from CH_2Cl_2/hexane. The combined crystallized samples (76.4 g, 81%) were anal. pure and had the same spectroscopic data as described in [10]. TLC (AcOEt/hexane 1:1): R_f 0.45. $[\alpha]_D = -10.0$ ($c = 1.0$, $CHCl_3$). IR: 3340*w* (br.), 2207*s*, 1750*s*, 1670*s*, 1595*s*, 1480*w*, 1455*m*, 1440*m*, 1425*m*. ^{1}H-NMR: 1.51 (*s*, *t*-Bu); 2.19–2.30, 2.37–2.50 (2*m*, CH_2(3)); 2.88–3.08 (*m*, CH_2(4)); 3.80 (*s*, CH_3O); 4.54 (*dd*, $J \approx 8.7$, 5.6, H–C(2)); 9.15 (br. *s*, NH). MS: 266 (6, M^+), 210 (27), 193 (17), 152 (8), 151 (100). In some experiments, the product was contaminated by minor amounts of the corresponding (*tert*-butoxy)carbonyl ethyl ester, formed by transesterification with EtOH under the reaction conditions.

(2S)-Methyl 5-(Cyanomethylidene)pyrrolidine-2-carboxylate ((–)-**5**; (*E*/*Z*) mixture). CF_3COOH (110 ml) was added to (–)-**4** (24 g, 90 mmol) at 23° under N_2 with vigorous stirring. After 8 min, the mixture was diluted with ice-cold CH_2Cl_2 (300 ml) and cooled in an ice bath. Sat. aq. $NaHCO_3$ soln. (300 ml) was slowly added, followed by solid $NaHCO_3$ (*ca.* 120 g) in small portions until CO_2 evolution ceased. The aq. layer was saturated with NaCl, separated from the org. layer, and extracted with $CH_2Cl_2/CHCl_3$ 1:1 (3 × 150 ml). The combined org. extracts were filtered through cotton, evaporated, and passed through a short silica-gel column (5 × 7 cm) with Et_2O. Evaporation and drying at 0.01 Torr for 2 h gave a viscous, yellowish oil (13.9 g, *ca.* 80–90%) which was stored at –30° and used for the next step without further purification. NMR and TLC (Et_2O/hexane 5:1): 3:2 mixture of the (*E*/*Z*) isomers of (–)-**5** (R_f 0.40), contaminated by minor impurities (R_f 0.07, 0.22, 0.47). ^{1}H-NMR: 2.12–2.24, 2.30–2.46, 2.54–2.71, 2.80–2.87 (4 *m*, 2 CH_2); 3.76, 3.77 (2*s*, 1.2 and 1.8 H, CH_3O of the 2 isomers); 3.84, 4.14 (2 br. *s*, 0.6 and 0.4 H, CNC*H* = C); 4.28–4.36 (*m*, H–C(2)); 5.36, 5.62 (2 br. *s*, 0.4 and 0.6 H, NH); signals of impurities at 1.27–1.51 (*m*, 3 H), 3.74 (*s*, 0.3 H), 3.82 (*s*, 0.1 H), and 4.20–4.24 (*q*, 0.2 H). The spectroscopic data of a sample purified by FC (Et_2O/hexane 5:2) were identical with the data reported in [10]. The use of chromatographed (*E*/*Z*)-**5** obtained in 60–70% yield from **4**, did not improve the overall yield in the sequence **4**→**5**→**6**.

(1S,9S)-Dimethyl 5-Cyanosemicorrin-1,9-dicarboxylate (= *(2S)-Methyl 5-{Cyano[(5S)-5-(methoxycarbonyl)pyrrolidin-2-ylidene]methyl}-3,4-dihydro-2*H*-pyrrole-2-carboxylate;* (–)-**6**). CF_3COOH (6.4 ml, 84 mmol) was added to a soln. of crude (–)-**5** (13.9 g, *ca.* 70 mmol) and (+)-**3** (14.4 g, 84 mmol) in 45 ml of anh. CH_2ClCH_2Cl at 23°. The soln. was stirred at 65° under N_2. TLC[6]) after 1 h: intense spot of (–)-**6** (R_f 0.67), weaker spot of (–)-**5** (R_f 0.44), polar material ($R_f < 0.1$), practically no (+)-**3** (R_f 0.56). More (+)-**3** and CF_3COOH were added, 14.4 g and 6.4 ml, resp., after 1 h, and again after 3 h. After a total of 4.5 h at 65°, all (–)-**5** had been consumed (TLC). The mixture was diluted with 150 ml of CH_2Cl_2 and washed with sat. aq. $NaHCO_3$ soln. The aq. layer was extracted with CH_2Cl_2 and the combined org. phase washed with sat. NaCl soln. and evaporated. FC (8 × 20-cm column) of the crude product in two batches with CH_2Cl_2/hexane/Et_2O 10:5:2 gave a viscous oil (14.9 g) which was crystallized from Et_2O to give 14.1 g (54% based on (–)-**4**) of anal. pure, white (–)-**6**. M.p. 76–77°. $[\alpha]_D = -145.2$ ($c = 1.0$, $CHCl_3$). UV: 296 (16400); after addition of CF_3COOH: 304 (33800). IR: 3280–2840*w* (br.), 2200*m*, 1745*s*, 1615*s*, 1565*s*, 1445*w*, 1440*m*, 1430*m*, 1350*m*. ^{1}H-NMR: 2.07–2.19, 2.28–2.41 (2 *m*, CH_2(2,8)); 2.82–3.04 (*m*, CH_2(3,7)); 3.75 (*s*, 2 CH_3O); 4.65–4.70 (*m*, H–C(1,9)); 10.0–11.5 (br., NH). ^{13}C-NMR: 26.2 (C(2,8)); 34.4 (C(3,7)); 52.4 (2 CH_3O); 67.6 (C(1,9)); 71.3 (C(5)); 120.6 (CN); 172.1, 172.7 (C(4,6), COO). MS: 292 (1.5), 291 (12, M^+), 233 (14), 232 (100, $M^+ - COOCH_3$). Anal. calc. for $C_{14}H_{17}N_3O_4$: C 57.72, H 5.88, N 14.42; found: C 57.55, H 5.82, N 14.21.

In analogous experiments, starting from anal. pure (*E*/*Z*)-**5** (purified by column chromatography), the yields of recrystallized **6** were 62–75% (based on **5**).

The enantiomeric purity of (–)-**6** was checked by ^{1}H-NMR with [Eu(tfc)$_3$] (0.11M (–)-**6**, 0.017M [Eu(tfc)$_3$] in C_6D_6): only 1 signal for H–C(1,9) at 4.7 ppm (corresponding signal of (+)-**6**, prepared from D-pyroglutamic acid, at 4.2 ppm).

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[6]) CH_2Cl_2/Et_2O 5:1, the withdrawn samples were diluted with CH_2Cl_2 and neutralized by washing with aq. sat. $NaHCO_3$ soln.

(1S,9S)-1,9-Bis(1-hydroxy-1-methylethyl)semicorrin-5-carbonitrile (=[(2S)-3,4-Dihydro-2-(1-hydroxy-1-methylethyl)-2H-pyrrol-5-yl][(5S)-5-(1-hydroxy-1-methylethyl)pyrrolidin-2-ylidene]acetonitrile; (−)-7). MeMgBr (62 ml of a 1.35M soln. in Et_2O, 84 mmol) was slowly added within 15 min to 3.5 g (12 mmol) of (−)-**6** in 180 ml of anh. Et_2O with vigorous stirring at 0°. Formation of a yellowish gum-like precipitate was observed. After stirring for 0.5 h at 0° and additional 2 h at 23°, the reaction was quenched by addition of 40 ml of sat. aq. NH_4Cl soln. The mixture was extracted with CH_2Cl_2 (5 × 50 ml), the org. phase filtered through cotton and evaporated. Crystallization from AcOEt gave 2.41 g (69%) of (−)-**7** (m.p. 160–161°, $[\alpha]_D = -80.8$ ($c = 1.0$, $CHCl_3$)). FC (3 × 16-cm column) of the mother liquor: with AcOEt/CH_2Cl_2 2:1 (R_f (**7**) 0.23) and crystallization provided additional 245 mg of (−)-**7** (m.p. 161–162°). The combined crystallized samples (2.65 g, 76%) had the same spectroscopic properties as an anal. sample (m.p. 162°) from an analogous experiment which had been recrystallized twice from acetone/hexane. $[\alpha]_D = -82.0$ ($c = 1.0$, $CHCl_3$). UV: 297 (16900). IR: 3590*w* (br.), 3430*w* (br.), 2200*m*, 1610*s*, 1560*s*, 1470*w*, 1460*w*, 1430*w*. ^{1}H-NMR: 1.17 (*s*, 2 CH_3); 1.31 (*s*, 2 CH_3); 1.60 (br. *s*, 2 OH); 1.80–1.93, 1.98–2.10 (2 *m*, CH_2(2,8)), 2.76–3.00 (*m*, CH_2(3,7)); 3.94 (*t*, $J = 7.6$, H–C(1,9)); *ca.* 10–12 (very br., NH). ^{13}C-NMR: 22.9 (C(2,8)); 25.1 (2 CH_3); 27.5 (2 CH_3); 35.0 (C(3,7)); 70.0 (C(5)); 71.9 (2 C(OH)); 75.8 (C(1,9)); 121.3 (CN); 171.7 (C(4,6)). MS: 291 (3, M^+), 233 (28), 232 (100, $M^+ - CMe_2OH$). Anal. calc. for $C_{16}H_{25}N_3O_2$: C 65.95, H 8.65, N 14.42; found: 65.72, H 8.48, N 14.34.

(1S,9S)-1,9-Bis{[(tert-butyl)dimethylsilyloxy]methyl}semicorrin-5-carbonitrile(={(2S)-2-[(tert-Butyl)-dimethylsilyl-oxy)methyl]-3,4-dihydro-2H-pyrrol-5-yl}{(5S)-5-[(tert-butyl)dimethylsilyloxy)methyl]pyrrolidin-2-ylidene}acetonitrile; (−)-**9**). To a soln. of (−)-**6** (2.04 g, 7 mmol) in 40 ml of THF, 7 ml (14 mmol) of 2M $LiBH_4$ in THF were continuously added (1 h) [18]. Upon addition, a white precipitate was formed. The suspension was stirred at 23° for 20 h, then cooled in an ice bath. After addition of 10 ml of 1N HCl, the aq. layer was saturated with K_2CO_3, separated, and extracted with THF (2 × 50 ml), the combined org. phase dried (Na_2SO_4) and evaporated, and the residue dried at 50°/0.01 Torr for 10 h: 1.91 g of crude (−)-**8** which was converted to (−)-**9** without further purification. The silylation was carried out in 8 ml of anh. DMF with (*tert*-butyl)-(chloro)dimethylsilane (3.17 g, 21 mmol) and imidazole (2.86 g, 42 mmol) [19]. After stirring for 20 h at 40°, the orange-red mixture was diluted with 150 ml of H_2O and extracted with Et_2O (3 × 100 ml). The resulting oil was chromatographed (8 × 18-cm column) with hexane/AcOEt 6:1 to give 1.85 g of (−)-**9** R_f 0.30 (hexane/AcOEt 6:1). After crystallization from MeOH at −30°, 1.38 g (43% based on (−)-**6**) of anal. pure (−)-**9** was obtained. M.p. 75–76°. $[\alpha]_D = -64.7$ ($c = 1.0$, $CHCl_3$). UV: 296 (16200). IR: 3490 and 3140*w* (br.), 2195*s*, 1610*s*, 1560*s*, 1470*m*, 1460*m*, 1425*w*. ^{1}H-NMR: 0.02 (*s*, 2 CH_3Si); 0.04 (*s*, 2 CH_3Si); 0.88 (*s*, 2 *t*-Bu); 1.68–1.80, 1.99–2.11 (*m*, CH_2(2,8)); 2.73–2.94 (*m*, CH_2(3,7)); 3.58, 3.62 (*AB* of *ABX*, $J_{AB} = 10.1$, $J_{AX} = 5.7$, $J_{BX} = 5.4$, 2 CH_2OSi); 4.05–4.13 (*m*, *X* of *ABX*, H–C(1,9)); 10.0–12.0 (very br., NH). ^{13}C-NMR: −5.4 (CH_3Si); 18.2 ($(CH_3)_3C$); 24.3 (C(2,8)); 25.8 ($(CH_3)_3C$); 34.4 (C(3,7)); 66.5 (CH_2OSi); 68.4 (C(1,9)); 69.6 (C(5)); 121.9 (CN); 170.6 (C(4,6)). MS: 463 (1.9, M^+), 407 (9), 406 (30), 320 (6), 319 (25), 318 (100, $M^+ - (t\text{-Bu})Me_2SiOCH_2$). Anal. calc. for $C_{24}H_{45}N_3O_2Si_2$: C 62.15, H 9.78, N 9.06; found: C 62.13, H 9.83, N 8.96.

3. (Semicorrinato)copper Complexes *(cf. Scheme 4). – Bis[(1S,9S)-5-cyano-1,9-bis(methoxycarbonyl)-semicorrinato]copper(II)* (**10**). $Cu(OAc)_2 \cdot H_2O$ (300 mg, 1.5 mmol) was added to a soln. of (−)-**6** (874 mg, 3.0 mmol) in 40 ml of MeOH. The reddish-brown mixture was stirred at 23° for 30 min. The solvent was evaporated and the residue taken up in CH_2Cl_2. The soln. was washed with 0.1M aq. phospate buffer (pH 7), filtered through cotton, and evaporated. Crystallization from AcOEt/hexane gave 910 mg (94%) of dark purple **10** (m.p. 167–168°) with the same spectroscopic data as an anal. sample (m.p. 169–170°) which had been recrystallized a 2nd time from AcOEt. TLC (AcOEt/hexane 2:1): R_f 0.23. $[\alpha]_D = +3524$ ($c = 0.01$, EtOH). UV/VIS: 477 (1800), 329 (18100), 320 (17800), 247 (36400). IR: 2195*s*, 1740*s*, 1640*w*, 1575*s*, 1495*s*, 1455*s*, 1435*m*, 1360*s*. MS: 645 (1.2), 643 (2.4, $M^+(^{63}Cu)$), 355 (8), 354 (11), 353 (16, $M^+ - \mathbf{6}(^{63}Cu)$), 352 (10), 291 (11, **6**), 232 (100, **6** − $COOCH_3$). Anal. calc. for $C_{28}H_{32}CuN_6O_8$: C 52.21, H 5.01, N 13.05; found: C 52.16, H 5.10, N 13.08.

Bis[(1S,9S)-1,9-bis[(tert-butyl)dimethylsilyloxy)methyl]-5-cyanosemicorrinato]copper(II) (**11**). To a soln. of $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.20 mmol) in 4 ml of MeOH (−)-**9** (190 mg, 0.41 mmol) was added. After 30 min at 23°, the violet soln. was concentrated, diluted with CH_2Cl_2, and washed with sat. aq. $NaHCO_3$ soln. The resulting oil was chromatographed (2 × 15-cm column) with hexane/AcOEt 8:1 to give, after lyophilization from cyclohexane, a dark violet powder (191 mg, 97%). M.p. 150–151°. TLC (hexane/AcOEt 8:1): R_f 0.25. $[\alpha]_{436} = -5522$ ($c = 0.01$, EtOH). UV/VIS: 504 (2300), 334 (12500), 320 (14900), 247 (39400). IR: 2200*m*, 1575*s*, 1490*s*, 1470*m*, 1463*m*, 1450*m*, 1430*w*. FAB-MS: 990 (0.5 rel. int.), 989 (0.8), 988 (1.0), 987 (0.9, $M^+(^{63}Cu)$).

(Acetylacetonato)[(1S,9S)-5-cyano-1,9-bis(methoxycarbonyl)semicorrinato]copper(II) (**12**). To a soln. of $Cu(acac)_2$ (183 mg, 0.7 mmol) in 20 ml of CH_2Cl_2 (−)-**6** (204 mg, 0.7 mmol) was added. After stirring at 23° for 1 h, the soln. was evaporated, the green solid dried at 0.01 Torr and taken up in AcOEt, the soln. filtered and evaporated, and the residue crystallized from EtOAc/pentane: 302 mg (96%) of **12**. M.p. 164–165°. TLC (AcOEt/

hexane 1:1): R_f 0.47 (partial dec.). $[\alpha]_{546} = +125$ ($c = 0.01$, EtOH). UV/VIS: 580 (50), 383 (470, sh), 297 (22500), 241 (26600). IR: 2200*s*, 1740*s*, 1585*s*, 1520*s*, 1465*m*, 1440*m*, 1430*m*. MS: 454 (3.8), 452 (7.3, $M^+(^{63}Cu)$), 355 (50), 354 (20), 353 (100, $M^+ - acac(^{63}Cu)$). Anal. calc. for $C_{19}H_{23}CuN_3O_6$: C 50.38, H 5.12, N 9.28; found: C 50.17, H 5.23, N. 9.25.

Acetato(aqua)[(1S,9S)-5-cyano-1,9-bis(1-hydroxy-1-methylethyl)semicorrinato]copper(II) (**13**). To a soln. of $Cu(OAc)_2 \cdot H_2O$ (34.3 mg, 0.17 mmol) in 4 ml of THF (–)-**7** (25 mg, 0.085 mmol) was added. After 30 min at 23°, the solvent was evaporated, the residue taken up in CH_2Cl_2, and the green soln. washed with sat. aq. NaOAc soln. Drying ($MgSO_4$), evaporation, and crystallization from AcOEt/hexane gave 24.5 mg (67%) of **13** as green needles. M.p. > 300°; color change from light to dark green at 146°. UV: 317 (11200), 247 (22400). IR: 3670*m*, 3430*m* (br.), 2195*s*, 1595*s*, 1495*s*, 1460*s*, 1450*s*, 1400*s*, 1395*s*, 1340*s*. Anal. calc. for $C_{18}H_{27}CuN_3O_4 \cdot H_2O$: C 50.17, H 6.73, N 9.75; found: C 49.89, H 6.53, N 9.69.

Bis[(1S,9S)-5-cyano-1,9-bis(1-hydroxy-1-methylethyl)semicorrinato]copper(II) (**14**). $CuSO_4 \cdot H_2O$ (375 mg, 1.5 mmol) in 20 ml of H_2O was combined with a soln. of (–)-**7** (875 mg, 3.0 mmol) in 40 ml of CH_2Cl_2. The two-phase system was vigorously stirred at 23°. After 10 min, 10 ml of sat. aq. $NaHCO_3$ soln. was added (org. phase: green→violet; aq. layer:→colorless). After stirring for additional 15 min, the org. phase was diluted with 90 ml of CH_2Cl_2 and extracted with sat. aq. $NaHCO_3$ soln. (3 × 50 ml). The org. layer was filtered through cotton and evaporated. The dark-violet solid dissolved in CH_2Cl_2 (8 ml) and AcOEt (50 ml) was heated to the b.p. and diluted with 14 ml of hexane. Upon cooling to r.t., the product began to crystallize. From time to time, more hexane was added. Thus, 970 mg (94%, corrected for 0.5 mol-equiv. of AcOEt) of **14** was obtained. A second similar recrystallization did not raise the m.p. TLC: dec. M.p. 202°. $[\alpha]_{436} = -1574$ ($c = 0.01$, EtOH). UV/VIS ($CHCl_3$): 512 (380), 299 (20800), 247 (24200). IR: 3580 and 3430*w* (br.), 2195*s*, 1730*m* (AcOEt), 1610*s*, 1575*s*, 1495*s*, 1450*s*, 1430*m*. Anal. calc. for $C_{32}H_{48}CuN_6O_4 \cdot 0.5$ AcOEt: C 59.32, H 7.61, N 12.21; found: C 59.22, H 7.61, N 12.35.

X-Ray Analysis of **14** *(cf. Fig. 1).* Dark violet crystals from AcOEt/hexane (size: 0.2 × 0.15 × 0.12 mm). $F(000) = 2202$ (**14**·0.5 AcOEt). Space group $P3_221$ (the enantiomorphic space group $P3_121$ can be excluded based on the known absolute configuration of the ligand **7**); $a = 10.678(1)$, $b = 10.673(1)$, $c = 53.119(6)$ Å, $V = 5245(2)$ Å^3, $Z = 4$; determined by least squares refinement of the positions of 43 reflexions in the range $15 \leq 2\Theta \leq 40°$. Data collection: modified STOE four-circle diffractometer; CuK_α-radiation ($\lambda = 1.54178$ Å, Ni filter). Of the 2030 unique reflexions, 1697 had $F \geq 4\sigma(F)$ (ω-scan; scan width 1.0°; $2\Theta \leq 97°$, $\sin\Theta/\lambda \leq 0.486$). Non-bisecting settings had to be used in the range of $70 \leq 2\Theta \leq 97°$ (3.5% of the reflexions in this range were not accessible due to mechanical obstruction of the diffractometer). Intensities were corrected for *Lorenz* and polarization effects. The structure was solved by locating the heavy atom from a *Patterson* map [20]. Subsequent tangent expansion yielded the positions of all non-H-atoms. A disordered solvent molecule was observed near the C_2 axis. The anal. data (see above) and $d_m = 1.306$ g cm^{-3} (CCl_4/hexane) are in accordance with the presence of 0.5 mol-equiv. of AcOEt ($d_{calc} = 1.306$ g cm^{-3}). In the least-squares refinement [21], the highest peaks were included as C-atoms with a site-occupation factor of 0.5. Refinement of positional and isotropic thermal parameters (Cu anisotropic) by full-matrix least squares led to a residual $R = 0.0747$, $R_w = 0.0706$ ($1/\sigma^{-2}$ weights, 242 parameters, 1697 refl.).

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