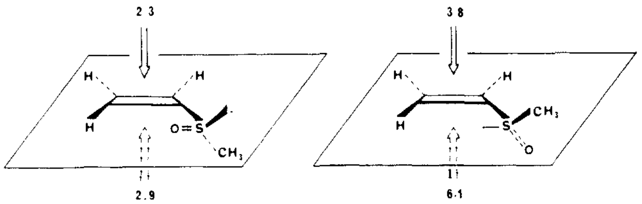
the SO and CC bonds are approximately syn are the more stable.[7,8]

Relative reactivities and stereochemical preferences of the two stable conformers of methyl vinyl sulfoxide have been obtained by direct comparison of the affinities of the diastereotopic faces of the incorporated olefin toward a test nucleophile, in our case hydride anion.[9] Information relating to the relative nucleophilic reactivities of the diastereotopic olefin faces may then be "extracted" either visually, by direct inspection of the reactivity information as superimposed onto the substrate electron-density surface, or by constructing average potentials.[13a-c]

Average hydride potentials for the diastereotopic faces of the two stable conformers of methyl vinyl sulfoxide are provided below.



These show that the favored direction of approach in both conformers is from the side of the methyl group, i.e., away from the sulfur lone pair in the ground-state structure, and anti to the SO bond in the higher energy form. While it is entirely reasonable that an approaching nucleophile would prefer to avoid areas of high electron density, this is contrary to steric considerations. The small difference in reactivities between the more reactive faces of the two conformers is not likely to be significant in view of the large conformational bias in favor of form **1**. Thus, we have interpreted the experimental data explicitly in terms of conformers analogous to **1**.[3,8]

The observed stereochemistry of the first two reactions illustrated in Table I are in accord with the results of the theory; that is, nucleophilic attack occurs preferentially anti to the sulfur lone pair. On the other hand, the experimental stereochemistry for the remaining three examples appears to disagree with the models. Note, however, that these are situations in which the reagent contains an electrophilic site, i.e., the metal of an organometallic reagent (entries 3 and 4 in Table I) or an acidic proton (entry 5 in Table I), which would allow for the possibility of ion pairing between the sulfur lone pair (or sulfoxide oxygen), and therefore lead to an overiding of the fundamental preference for the nucleophile to avoid centers of electron density.[14]

Acknowledgment. We thank Professor G. H. Posner (John Hopkins University) for helpful discussions during the course of preparation of this manuscript.

Registry No. 1, 10258-86-3; hydride anion, 12184-88-2.

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[7] Conformational preferences in vinyl sulfoxides have previously been rationalized on the basis of dipole minimization: Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

[8] Preliminary results indicate that substitution may destabilize forms such as **2**. Details will be presented in a full paper.

[9] Application follows in three stages from an appropriate quantum mechanical wave function.[10] First, a surface of constant electron density, corresponding to $\psi^2 = 0.002$ electrons/bohr^3, is defined.[11] Next, the test reagent, as defined by the radius of its electron-density surface,[12] is rolled upon the substrate density surface, to generate a series of points elevated above this surface (at the reagent/substrate "contact" distance). Finally, the energy of interaction between reagent and substrate is evaluated at each of these locations. In the simplest model, this energy accounts only for Coulombic interactions between the fixed charge distrubtions on the substrate and reagent. Reorganization of the electron distribution of the substrate, charge transfer between reagent and substrate, and geometrical relaxation have not been allowed for. Full details of the numerical procedures involved, as well as further examples of applications, have been presented elsewhere.[13]

[10] 3-21G$^{(*)}$ wave functions[5] have been used throughout.

[11] See: Francl, M. M.; Hout, R. F., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 563.

[12] 1.547 Å at the 3-21G level. See ref 11.

[13] (a) Pau, C. F.; Hehre, W. J. *J. Comput. Chem.*, submitted for publication. (b) Hehre, W. J.; Pau, C. F.; Hout, R. F., Jr.; Francl, M. M. "Molecular Modeling. Computer-Aided Descriptions of Molecular Structure and Reactivity"; Wiley: New York, 1987. (c) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.*, in press. (d) Kahn, S. D.; Pau, C. F.; Hehre, W. J. *Ibid.*, in press.

[14] The stereochemical role of the metal in organometallic additions to chiral vinyl sulfoxides, among other substrates, is currently under study in our laboratory.

A New Group of Ruthenium Complexes: Structure and Catalysis

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The isolation and structural characterization of intermediate transition-metal complexes that participate in catalytic processes are of prime importance in elucidating and understanding mechanistic features of homogeneous catalysis. Herein we report on the structure and catalytic aspects of a new class of ruthenium complexes.

Recently we have reported that complexes **1** and **2** are both active in the following catalytic reactions: (a) bimolecular dehydrogenation of primary alcohols to esters in the presence or absence of H acceptors;[1] (b) dehydrogenation of secondary alcohols to ketones;[1] (c) hydrogenation of ketones, olefins, and acetylenes under moderate hydrogen pressure and temperature.[2]

$(\eta^4\text{-}Ph_4C_4C{=}O)(CO)_3Ru$ **1**

$[(\eta^4\text{-}C_4H_4C{=}O)(CO)_2Fe]_2$ **2a**

$[(\eta^4\text{-}Ph_4C_4C{=}O)(CO)_2Ru]_2$ **2**

X-ray crystallography has revealed a η^4-bonding of the cyclopentadienone (CPD) ligand to ruthenium in complex **1**.[3] Refluxing **1** in propanol results in an orange crystalline solid (85%) for which we have previously proposed the dimeric formula **2**,[1,2] in analogy with the isoelectronic iron complex **2a**[4,5] and on the basis of analytical, spectral, and chemical data. Hubel et al.[4] proposed a centrosymmetric structure with two $>C{=}O{\rightarrow}Fe$ coordination bonds for the dimer **2a**. Since complex **2** plays a central role in our catalytic schemes, it is extremely important to ascertain its molecular structure. We could not crystallographically characterize **2**, as crystals were unsuitable for diffraction analysis.

Now we have reinvestigated the NMR spectrum of **2** which was found to exhibit a signal at δ −17.75, integrating as one hydrogen (hydride) relative to 40 aromatic hydrogens atoms, i.e., two Ru atoms. Obviously, structure **2** is incompatible with this finding. Therefore, we prepared several isoelectronic–isostructural derivatives complexes (Table I). Only **3** gave crystals which were suitable for X-ray crystallography (Figure 1).[6]

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[1] Blum, Y.; Shvo, Y. *Isr. J. Chem.* **1984**, *24*, 144.

[2] Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459.

[3] Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta* **1985**, *97*, L25.

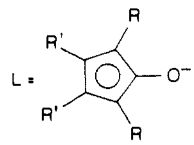
[4] Weiss, E.; Merenyl, R. G.; Hubel, W. *Chem. Ind.* (*London*) **1960**, 407.

[5] Reppe, W.; Vetter, H. *Justus Liebigs Ann. Chem.* **1953**, *582*, 133.

[6] Crystal data for $Ru_2Cl_4O_6C_{62}H_{38}$ $M = 1222.94$: monoclinic, space group $C2/c$, with $a = 26.961$ (7) Å, $b = 9.613$ (3) Å, $c = 20.367$ (5) Å, $\beta = 101.44$ (2)°, $V = 5174.0$ Å^3, $D_{calcd} = 1.570$ g·cm^{-3} for $Z = 4$; Mo Kα $\lambda = 0.71073$ Å. A total of 6433 reflections were collected using Enraf-Nonius automated diffractometer. The structure was solved by direct methods (Program MULTAN80) Fourier techniques and refined by using full-matrix least-squares methods (SDP program library with local modifications). Least-square refinement of 36 atoms (anisotropic), 18 hydrogen atoms (fixed isotropic), 390 variables, and 4572 observations converged to yield final $R = 3.09\%$ and $R_w = 4.06\%$ with $I \geq 3\sigma(I)$ and $2° \leq 2\theta \leq 55°$. A full description of the data collection and structure solution and refinement is provided in the supplementary material.

0002-7863/86/1508-7400$01.50/0

Table I.[a] Spectral Data for $[L(CO)_2RuH]_2$



	R	R′	ν(CO), cm^{-1}	δ(H), ppm
2	Ph	Ph	2035, 2010, 1980, 1970	−17.75
3	Ph	p-ClC_6H_4	2040, 2015, 1980, 1970	−17.91
4	Me	Ph	2035, 2005, 1965, 1955 sh	−18.40
5	CO_2Me	Ph	2045, 2020, 1985 br d	−14.80

[a] Infrared spectra were measured in KBr and NMR in benzene-d_6. All compounds gave satisfactory elemental analyses.

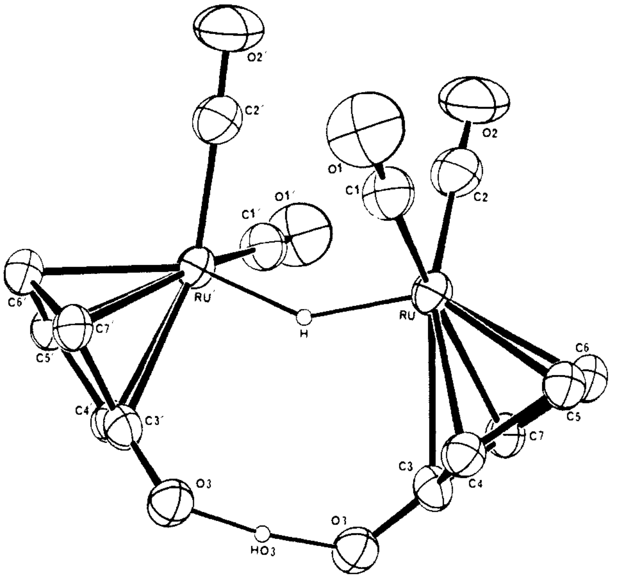
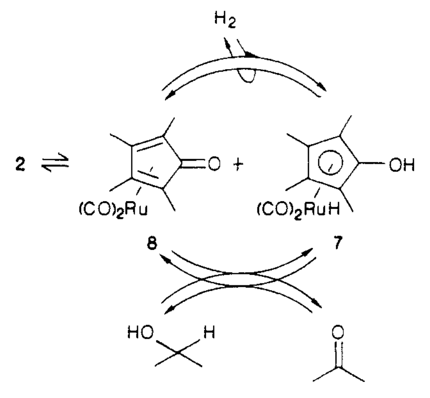


Figure 1. ORTEP plot of **3**. Selected bond lengths (Å) and angles (deg) are as follows: Ru–H = 1.681 (13), C(3)–O(3) = 1.286 (3), O(3)–H-O(3) = 1.270 (3), Ru–H–Ru′ = 147.0 (3), O(3)–HO(3)–O(3′) = 172.0 (4). Nonbonded distances: Ru–Ru = 3.223, H–HO(3) = 2.74 Å.

Dimerization by *both* bridging hydride and hydrogen-bonded oxygen atoms is unusual. Both H atoms, which were observed in difference maps, lie on the crystallographically imposed C_2 molecular axis. The crystallographic data clearly point out a planar η^5-bonding of the electronically delocalized five-membered rings. The Ru–Ru′ distance of 3.223 Å and the H–H(O3) distance of 2.74 Å preclude bonding between the respective atom pairs. The C(3)–O(3) bond length (1.286 Å) is in between a single and double bond. On the whole the dimer is electronically deficient (34e⁻). Although formally each Ru atom is assigned 17 valence electrons, the dimers (Table I) are not paramagnetic. The NMR signal of the oxygen-bridged H atom at ca. 8 ppm shows a strong concentration dependence. In contrast with the Ru–H–Ru signal, it disappears upon addition of D_2O to a NMR sample. Thus these dimers carry distinct acidic and hydridic H atoms differentiable by their spectral and chemical properties. It is noteworthy that **2a** does not exhibit a signal upfield from the Me_4Si resonance line.

Several bis(glyoximato) transition-metal complexes possessing an O–H–O but not a M–H–M bridging element are known.[7] They exhibit ill-defined infrared bands (2300–2700 cm^{-1}) that were assigned to the O–H–O stretching mode. We were unable to identify this band in the infrared spectra of complexes **2–4**, although a weak band at 1718 cm^{-1} (O–H–O bending)[7d] was detected in the FTIR spectrum of **2** (cyclohexane).

Scheme I[a]



[a] Phenyls are omitted.

Aside from **5**, all the compelxes in Table I are catalytically active in the dehydrogenation and hydrogenation reactions. The rate of hydrogenation of cyclohexanone in toluene shows a 0.5 order dependence on the concentration of complex **2**. This implies that **2** dissociates during hydrogenation, which was confirmed by a crossing over experiment (eq 1), carried out in toluene at 55 °C.

$$\mathbf{2} + \mathbf{4} \rightarrow \underset{\mathbf{6}}{[(Ph_4C_5O)(CO)_2Ru][(Ph_2Me_2C_5O)(CO)_2Ru]H_2} \qquad (1)$$

A new complex (**6**) was isolated after 45 min. Its NMR spectrum exhibits Ph, Me, and hydride signals in the ratio of 30:6:1. Having established that reaction 1 does not proceed by dissociation of the CPD ligands,[8] it must occur via fragmentation of the two H-bridges. Probable fragments are the even-electron species **7** and **8** (Scheme I), neither of which could be detected by infrared monitoring of reaction 1. Previously[2,3] we have shown that a mononuclear hydride complex, stable only in solution under H_2, is formed upon hydrogenation of **2**. It was assigned the η^4 structure (η^4-CPD)$(CO)_2RuH_2$. However, we favor the tautomeric η^5 formulation **7** on the following grounds: (a) That the carbonyl group of the CPD ligand of **7** has lost most of its π character was inferred from its low-frequency infrared stretching band at 1550 cm^{-1}, a location identical with that of **2**. The corresponding band of complex **1** is at 1655 cm^{-1}. (b) It was found that the ^{13}C NMR resonance line of the CPD "carbonyl" is structure-sensitive. In the η^4 complex **1** it is at 174.8 ppm, shifting upfield to 155.4 ppm in **2** and to 146.7 ppm in (η^5-Ph_4C_5OH)$(CO)_2RuCl$.[9] The hapticity of the CPD ligands in the above three complexes is known from X-ray diffraction studies.[3,9] Complex **7** in THF solution[10] exhibits a strong ^{13}C NMR signal at 137.3 ppm, indicative of the enhanced aromaticity of its CPD ligand, thus supporting the η^5-hydroxycyclopentadienyl structure **7**.

A plausible catalytic cycle, using the characterized complexes **2** and **7** as well as the putative **6**, can now be considered (Scheme I). It describes both hydrogenation and dehydrogenation processes, both initiated by the dissociation of **2**. It has been experimentally demonstrated that **7** can deliver its H atoms to a carbonyl substrate.[2] The reversibility of the hydrogenation–dehydrogenation cycles has now been demonstrated under a single set of reaction conditions whereby *trans*-4-*tert*-butylcyclohexanol was subjected to 500 psi of H_2 at 145 °C in the presence of a catalytic amount of **2** in toluene. There was obtained a constant-composition mixture of the cis (25.2 mol %) and trans (69.7 mol %) alcohols as well as cyclohexanone (5.0 mol %).[11]

Registry No. 2, 104439-77-2; **3**, 104439-78-3; **4**, 104439-79-4; **5**, 104463-66-3.

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(7) (a) Rundle, R. E.; Parasol, M. *J. Chem. Phys.* **1952**, *20*, 1487. (b) Blinc, R.; Hadzi, D. *J. Chem. Soc.* **1958**, 4536. (c) Burger, K.; Ruff, I.; Ruff, F. *J. Inorg. Nucl. Chem.* **1965**, *27*, 179. (d) Caton, J. E.; Banks, C. V. *Inorg. Chem.* **1967**, *6*, 1670.

(8) Complexes **2** and **4** are unreactive toward their irrespective CPD ligands under the conditions of reaction 1.

(9) Unpublished results.

(10) A THF solution of **7** was obtained by hydrogenating **2** (500 psi) at 105 °C for 20 min (ν(CO) 2014, 1955 cm^{-1}). The ^{13}C NMR spectrum of this solution was determined under hydrogen. Complex **2** does not generate detectable new complexes with THF under the above conditions.

(11) Similar composition was obtained starting from *cis*-4-*tert*-butylcyclohexanol.

Supplementary Material Available: Tables of atomic positions and thermal parameters and intramolecular bond lengths and angles and a full description of the data collection and structure solution and refinement (9 pages). Ordering information is given on any current masthead page.

Organoboron Compounds in Organic Synthesis. 2. Asymmetric Reduction of Dialkyl Ketones with (*R*,*R*)- or (*S*,*S*)-2,5-Dimethylborolane

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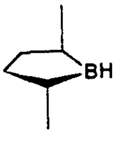
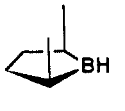
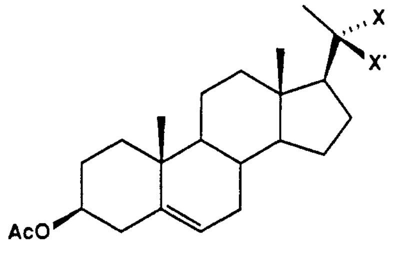
We wish to record herein the asymmetric reduction of two types of ketones $RCOR^1$ where R = Me, R^1 = alkyl (primary, secondary, and tertiary) for type I ketones and R = alkyl (primary), R^1 = alkyl (primary, secondary, and tertiary) for type II. The steric demands of R and R^1 being similar in both types of ketones, attainment of high enantiomeric excess in the reduction has been extremely challenging.[1] Successful examples are scarce and scattered (e.g., A–G in Table I) and there is no record of a reagent or reagents which meet the requirements set for the double-asymmetric strategy.[2] This difficult objective has been achieved in large measure through the use of (*R*,*R*)- or (*S*,*S*)-2,5-dimethylborolane (**1**).[3] The enantiomeric excess of hydroxyl compounds derived from type I ketones is 99–100% in most cases.



(R,R)-1

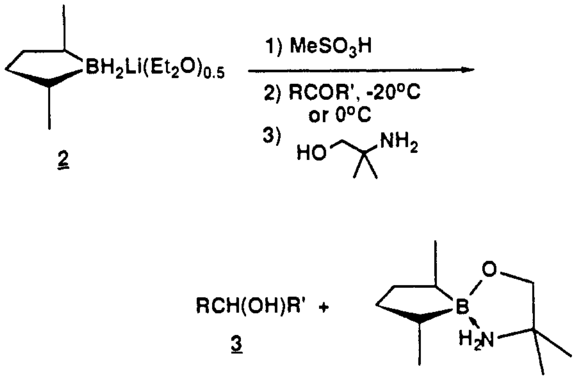


1a



4 X,X'=O
a X=H; X'=OH
b X=OH; X'=H

Thus, treatment of the dihydridoborate **2** (1.2 equiv) in pentane[4] with 1.4 equiv of methanesulfonic acid (eq 1) provides reagent I which is comprised of 1.0 equiv of **1** and 0.2 equiv of 2,5-dimethylborolanyl mesylate.[5] Reagent I was used to reduce a set of dialkyl ketones (1 equiv).



(1)

Table I summarizes the results obtained with reagent I and compares them with those obtained earlier with the known chiral reagents A–G. While methyl, unbranched primary alkyl ketones (entries 1 and 2) are reduced with approximately 80% ee, branching at the β-position of the primary chain (in R^1) brings about near perfect asymmetric induction (entries 3–6). Therefore, it is not surprising that methyl, secondary and tertiary alkyl ketones are converted into the essentially enantiomerically pure hydroxyl compounds (entries 7–10). More remarkably, reduction of two type II ketones exhibits asymmetric inductions as high as 96% ee (entries 11, 12). Note the absolute configurations of the product alcohols that result from the reduction with (*R*,*R*)-**1** are all *R*.

Encouraged by the above results we have carried out several typical double-asymmetric reductions of chiral ketones under conditions identical with or similar to those used above.[6] Reduction of pregnenolone (**4**) is representative. With the aid of (achiral) reagent II, prepared from the dihydridoborate corresponding to achiral 2,5-*cis*-dimethylborolane (**1a**), the diastereofacial selectivity (**4a**/**4b**) of **4** is estimated to be 7.5. Preselection of a chiral reagent for matched and mismatched pairs can be readily made and reductions of **4** with (*R*,*R*)-**1** and (*S*,*S*)-**I** provide a mixture of the corresponding alcohols **4a** and **4b** in a ratio of 990:1 (matched) and 1:73 (mismatched), respectively. The demonstrated "reagent-controlled" diastereoselections are indeed remarkable and are predicted by the now-established rule of double-asymmetric synthesis.

While Reagent **I** constitutes a powerful synthetic tool, the mechanism of its asymmetric induction is not straightforward. 2,5-Dimethylborolanyl mesylate present in reagent 1 plays a catalytic role, and this intriguing feature is detailed in the following paper.[5]

Procedure for the Reduction of a Ketone. Compound (*R*,*R*)-**2** (20.38 mmol) in pentane (70 mL) was stirred with methanesulfonic acid (23.77 mmol) at room temperature for 2 h and the resulting mixture was cooled to −20 °C. 4-Methyl-2-pentanone (1.73 g, 16.98 mmol) was added and after the mixture was stirred 48 h at −20 °C precipitated $MeSO_3Li$ was removed by the filtration through a Celite bed and washed with pentane (2 × 5 mL). The combined mixture of the filtrate, washings, and a solution of 2-amino-2-methyl-1-propanol (20.37 mmol) in ether (10 mL) was vigorously stirred at room temperature for 1 h to precipitate the borolane–amino alcohol complex as a white solid. The mixture was filtered and the precipitate washed with a 1:4 ether/pentane mixture (3 × 10 mL). The filtrate and washings were combined and processed in the usual manner. Final distillation provided 1.41 g (81%) of 4-methyl-2-pentanol, bp 46–47 °C (17 torr).

The crude amino alcohol complex (3.6 g, 97%) was recrystallized from either isopropyl alcohol or 1,2-dimethoxyethane to provide crystals which consisted of 99.28% of *R*,*R*, 0.45% of *S*,*R*, and 0.27% of *S*,*S* isomer (99.01% ee).

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(1) For recent reviews on asymmetric ketone reduction, see: (a) Morrison, J. D. *Asymmetric Synthesis*: Academic Press: New York, 1983; Vol. 2, Chapters 2–5. b) Brown, H. C. *Modern Synthetic Methods IV*; in press. (c) Hawkins, J. M. Ph.D. Dissertation, Massachusetts Institute of Technology, 1986.

(2) Masamune, S. Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

(3) Masamune, S. Kim, B. M.; Petersen, J. S.; Sato, T.; Veenstra, S. J.; Imai, T. *J. Am. Chem. Soc.* **1985**, *107*, 4549.

(4) Stored as a standard stock solution (see ref 3). The borohydride itself reduces dialkyl ketones with low percent ee (Sato, T.; Masamune, S., unpublished results).

(5) Masamune, S.; Kennedy, R. M.; Petersen, J. S.; Houk, K. N.; Wu, Y.-d., following paper in this issue.

(6) These results are summarized in the supplementary material.

0002-7863/86/1508-7402$01.50/0