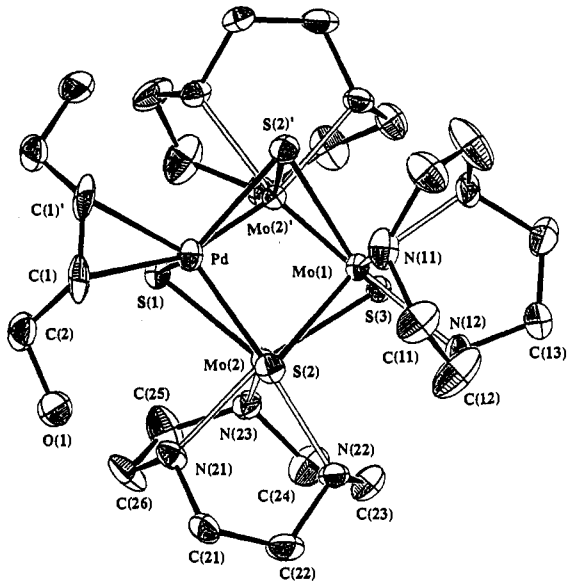

Figure 3. ORTEP drawing of the cation in **5**. Selected distances (Å): Pd-Mo(1), 2.815 (3); Pd-Mo(2), 2.830 (2); Mo(1)-Mo(2), 2.805 (2); Mo(2)-Mo(2)', 2.787 (2); Pd-C(1), 2.26 (2); C(1)-C(1)', 1.38 (3).

this product from 2 M HCl gave $[Mo_3PdS_4Cl(tacn)_3]Cl_3 \cdot 4H_2O$ (**3**) in 30-50% yield, the structure of which has been unambiguously determined by an X-ray analysis (Figure 1).[11] Complex **3** has a cubane-type Mo_3PdS_4 core with three tacn ligands coordinated to the Mo atoms and one Cl ligand on the Pd site, which totally comprises a pseudo-C_3 configuration around the Cl(1)-Pd-S(4) vector. An interesting feature observed in **3** is that the Pd atom has a tetrahedral structure not commonly observed in Pd(II) chemistry. The Pd-S distances (2.35-2.38 Å) are normal and not significantly different from those reported for the sulfido-bridged complex $[\{(\eta^3\text{-}C_3H_5)Pd\}_2WS_4]$ (2.33-2.35 Å).[12]

Anion metathesis, which was performed by eluting **2** adsorbed on a Dowex 50W-X2 column with 4 M *p*-toluenesulfonic acid (TsOH), resulted in the formation of a purple-blue solution. When left for several weeks, dark blue single crystals of $[Mo_6Pd_2S_8(H_2O)_{18}](OTs)_8 \cdot 24H_2O$ (**4**) precipitated from this solution. The X-ray crystallography has also been undertaken for **4**, which disclosed the double cubane-type structure shown in Figure 2.[13] The X-ray structure of this cation is not centrosymmetric, and the Pd_2S_2 plane is slightly folded, with a dihedral angle of 168° along the Pd-Pd vector. Analogous interconversion between the double and single cubane-type structures depending on the nature of the anion has already been suggested for the Mo_3CuS_4 cluster in TsOH or HCl media, although only the double cubane-type structure has been clarified in detail by the X-ray analysis.[6]

Treatment of **2-4** with various alkenes in H_2O or MeOH resulted in a rapid color change from blue to red. However, we could not isolate any stable clusters with coordinated alkenes in pure form from these reaction mixtures. Alternatively, when the anion exchange of **3** by ClO_4^- was carried out followed by treatment with *cis*-$HOCH_2CH{=}CHCH_2OH$ in H_2O, the resultant reaction mixture afforded the stable single cubane-type cluster $[Mo_3PdS_4(tacn)_3(HOCH_2CH{=}CHCH_2OH)](ClO_4)_4 \cdot 2H_2O$ (**5**). The X-ray analysis of **5** has been performed, which clearly demonstrates that this alkene coordinates to the Pd site in a side-on manner (Figure 3).[14] The C-C bond distance in the coordinated alkene [1.38 (3) Å] is comparable to those in the other Pd(II) alkene complexes such as $[(COD)PdCl_2]$ (1.37-1.39 Å; COD = 1,4- or 1,5-cyclooctadiene),[15] [(cyclooctatetraene)$PdCl_2$] [1.38 (1), 1.39 (1) Å],[16] and [(norbornadiene)$PdCl_2$] [1.37 (1) Å].[17] Further study on the reactivity of the alkene ligand coordinated to the unique Pd site in this and analogous Mo_3PdS_4 clusters is now in progress.

Acknowledgment. We thank Miwa Totani and Noriko Miyata for their experimental assistance and Drs. Kimiko Kobayashi (The Institute of Physical and Chemical Research) and Akiko Kobayashi (Department of Chemistry, The University of Tokyo) for X-ray data collection of **4** and **5**, respectively. Financial support by the Ministry of Education, Science, and Culture of Japan (to M.H. and to S.Y.) is greatly appreciated.

Supplementary Material Available: Tables listing detailed X-ray crystallographic data, positional and thermal parameters, and bond distances and angles for **3-5** and table presenting ^1H NMR data for **3** and **5** (26 pages); tables of structure factors for **3-5** (84 pages). Ordering information is given on any current masthead page.

(11) Crystal data of **3**: orthorhombic, space group $P2_12_12_1$, a = 17.549 (3) Å, b = 20.032 (4) Å, c = 10.256 (2) Å, V = 3605 Å^3, Z = 4, d_{calcd} = 2.05 g cm^{-3}, μ(Mo Kα) = 20.44 cm^{-1}. Block-diagonal least-squares refinements of 389 parameters obtained by using 4014 reflections [$F_o > 3\sigma(F_o)$] collected by a MAC MXC-18 diffractometer gave residuals of R = 0.051 and R_w = 0.062. Refinements obtained by inverting the coordinates of all atoms did not improve the R values. Anal. Calcd: C, 19.23; H, 4.76; N, 11.21; S, 11.41; Cl, 12.61. Found: C, 18.81; H, 4.57; N, 11.14; S, 10.70; Cl, 13.28.

(12) Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 3561.

(13) Crystal data of **4**: triclinic, space group $P\bar{1}$, a = 15.799 (4) Å, b = 18.079 (6) Å, c = 11.873 (1) Å, α = 108.75 (2)°, β = 108.73 (1)°, γ = 70.87 (3)°, V = 2944 Å^3, Z = 1, d_{calcd} = 1.79 g cm^{-3}, μ(Mo Kα) = 10.78 cm^{-1}. Block-diagonal least-squares refinements of 1316 parameters obtained by using 10089 reflections [$F_o > 5\sigma(F_o)$] collected on a Nonius CAD4 diffractometer gave residuals of R = 0.028 and R_w = 0.036. Structure solutions and refinements were carried out by selecting the space group of both $P1$ and $P\bar{1}$, but only the choice of $P1$ resulted in the successful solution and refinement of all non-hydrogen atoms in the cation, OTs anions, and solvated H_2O molecules. Anal. Calcd: C, 21.21; H, 4.46; S, 16.18. Found: C, 22.10; H, 4.09; S, 16.16. The atomic ratio of Mo to Pd determined by inductively coupled plasma (ICP) emission spectroscopy was 3.09:1.

(14) Crystal data of **5**: monoclinic, space group $P2_1/m$, a = 12.314 (1) Å, b = 12.732 (2) Å, c = 15.736 (2) Å, β = 94.01 (1)°, V = 2461 Å^3, Z = 2, d_{calcd} = 1.90 g cm^{-3}. Block-diagonal least-squares refinements of 362 parameters obtained by using 2743 reflections [$F_o > 5\sigma(F_o)$] collected on a Rigaku AFC5R diffractometer gave residuals of R = 0.068 and R_w = 0.081. Anal. Calcd: C, 18.66; H, 4.06; N, 8.90. Found: C, 19.02; H, 4.13; N, 8.97.

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(16) Baenziger, N. C.; Valley Goebel, C.; Berg, T.; Doyle, J. R. *Acta Crystallogr.* **1978**, *B34*, 1340.

(17) Baenziger, N. C.; Richards, G. F.; Doyle, J. R. *Acta Crystallogr.* **1965**, *18*, 924.

Resolution and Asymmetric Synthesis of Ortho-Substituted (Benzaldehyde)tricarbonylchromium Complexes

Alex Alexakis,* Pierre Mangeney, and Ilane Marek

Laboratoire de Chimie des Organoéléments
URA CNRS 473, Université P. et M. Curie
Tour 44-45 E2, 4 Place Jussieu
75252 Paris Cedex 05, France

Françoise Rose-Munch,* Eric Rose, and Assia Semra

Laboratoire de Chimie Organique, URA CNRS 408
Université P. et M. Curie, Tour 44-45 E1
4 Place Jussieu, 75252 Paris Cedex 05, France

Francis Robert

Laboratoire de Chimie des Métaux de Transition
URA CNRS 419, Université P. et M. Curie
Bâtiment F, 4 Place Jussieu
75252 Paris Cedex 05, France

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(π-Arene)tricarbonylchromium complexes play a very important role in stereoselective reactions, and some asymmetric syntheses

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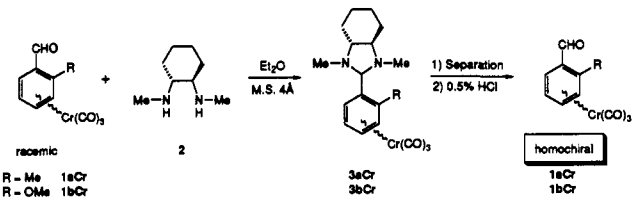
Scheme I



are based on the use of optically pure chiral complexes, such as substituted (benzaldehyde)tricarbonylchromium derivatives.[1-3] In this communication, we describe a new and easy method for the resolution of chiral benzaldehyde complexes protected by 1,2-bis(*N*-methylamino)cyclohexane and the simple formation of arene chromium complexes of these aminals using kinetic or thermodynamic methods with a high degree of stereocontrol.

The usual method for obtaining chiral arene chromium aldehydes is resolution through semioxamazone derivatives[2] or oxazolidines of valinol,[3] through enantioselective microbial reduction,[4] and through use of chiral solid supports.[5] In the course of our studies on chiral diamines having a C_2 axis of symmetry,[6] we have described a method for the resolution of chiral aldehydes through the formation of diastereomeric aminals.[7] In the case of ortho-substituted benzaldehyde chromium tricarbonyl complexes **1aCr** (R = Me) and **1bCr** (R = OMe), (*R*,*R*)-1,2-bis(*N*-methylamino)cyclohexane (**2**) was found to be the best diamine for this study. The reaction occurs smoothly by stirring, at room temperature in Et_2O, equimolecular amounts of the diamine **2** and the aldehyde **1aCr** or **1bCr** in the presence of 4-Å molecular sieves. On TLC plates (SiO_2, Et_2O/Et_3N = 99/1) two spots are clearly distinguished with a high degree of separation.[8] The same reaction is performed on a preparative scale (10 mmol of aldehyde **1aCr** or **1bCr**), and the two diastereomers are completely separated by flash column chromatography to afford (2*R*)-**3aCr** and (2*S*)-**3aCr** or (2*R*)-**3bCr** and (2*S*)-**3bCr** as light yellow crystals (Scheme I).

Chiral aminals **3aCr** and **3bCr** are sensitive to traces of acids, and their hydrolysis to the homochiral aldehydes **1aCr** and **1bCr** is easily and quantitatively performed with 0.5 N HCl in a few seconds. The rotations of the homochiral aldehydes **1aCr** and **1bCr** correspond to the maximum literature data.[2,9] Another way to check the enantiomeric purity of homochiral aldehydes **1aCr** and **1bCr** is to form again an aminal with the enantiomeric diamine *ent*-**2**; a single spot appeared on the TLC plate. To have an even greater accuracy, it is advisable to check the diastereomeric compositions by NMR. Indeed, we have shown that the formation of chiral aminals is an excellent analytical method to determine

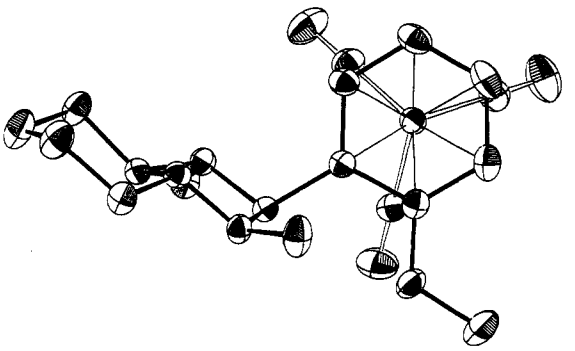
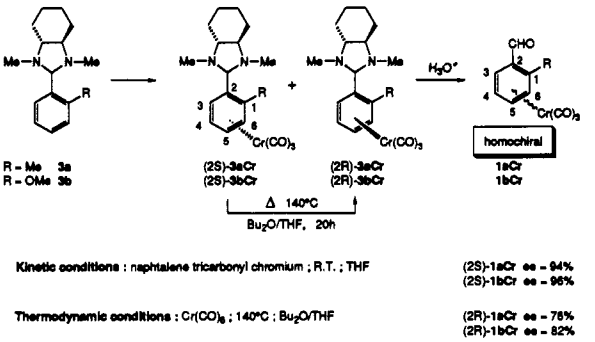


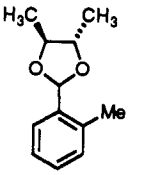
Figure 1. ORTEP view of compound (*R*)-**3bCr**.

Scheme II



the enantiomeric excess of chiral aldehydes (by ^1H, ^{13}C, and ^{19}F NMR or by HPLC).[10] In the present case, the ^1H NMR spectrum shows a singlet for the aminalic proton at 4.28 ppm for (2*R*)-**3aCr** and at 3.52 ppm for (2*S*)-**3aCr**, a difference of 0.76 ppm! Such differences are encountered with all of the aminals of this type that we have worked with (4.59 ppm for (2*R*)-**3bCr** and 3.90 ppm for (2*S*)-**3bCr**). Thus, the formation of aminals of ortho-substituted (benzaldehyde)tricarbonylchromium and diamine **2** is an exceedingly powerful tool for the measure of their optical purity.

We have also considered a more promising approach to homochiral (*o*-benzaldehyde)tricarbonylchromium complexes: the direct asymmetric introduction of the chromium tricarbonyl moiety. Very poor diastereoselective induction of (*o*-benzaldehyde)tricarbonylchromium complexes using acetal **4** had been reported.[2] With chiral aminals, which are much more sterically



4

demanding groups and also much more discriminative, we could expect higher diastereoselectivity. Indeed, as shown in Scheme II, when the reaction is performed on aminal **3a** using $Cr(CO)_6$ (1.5 mol equiv) at 140 °C,[11] we obtained the (arene)tricarbonylchromium complexes (2*R*)-**3aCr** and (2*S*)-**3aCr** in an 88/12 ratio, corresponding to 76% diastereomeric excess (60% yield). Simple chromatographic separation (as shown above) allows the obtention of the pure diastereomer. In the case of the aminal **3b**, (2*R*)-**3bCr** and (2*S*)-**3bCr** are isolated in a 91/9 ratio under the same conditions (55% yield).

(1) See for example: (a) Davies, S. G.; Goodfellow, C. L. *Synlett* **1989**, 59. (b) Solladié-Cavallo, A. *Adv. Metal Org. Synth.* **1989**, *1*, 99. (c) Solladié-Cavallo, A.; Quazzotti, S.; Colonna, S.; Manfredi, A.; Fischer, J.; Decian, A. *Tetrahedron Asymmetry* **1992**, *3*, 287. (d) Solladié-Cavallo, A.; Bencheroun, M. *J. Orgamomet. Chem.* **1991**, *403*, 159. (e) Baldoli, C.; Del Buttero, P. *J. Chem. Soc., Chem. Commun.* **1991**, 982. (f) Brocard, J.; Pelinski, L.; Lebibi, J. *J. Organomet. Chem.* **1987**, *337*, C47. (g) Brocard, J.; Mahmoudi, M.; Pelinski, L.; Maciejewski, L. *Tetrahedron* **1990**, *46*, 6995. (h) Meyer, A.; Dabard, R. *J. Organomet. Chem.* **1972**, *36*, C38.

(2) Solladié-Cavallo, A.; Solladié, G.; Tsamo, E. *J. Org. Chem.* **1979**, *44*, 4189.

(3) (a) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans.* **1989**, 192. (b) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans.* **1990**, 393. (c) Bromley, L. A.; Davies, S. G.; Goodfellow, C. L. *Tetrahedron Asymmetry* **1991**, *2*, 139.

(4) (a) Top, S.; Jaouen, G.; Gillois, J.; Baldoli, C.; Maiorana, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1284. (b) Yamazaki, Y.; Hosono, K. *Tetrahedron Lett.* **1990**, *31*, 3895.

(5) Bitterwolf, T. E.; Hubler, T. L.; Todime, R. *J. Macromol. Sci. Chem.* **1990**, *A27*, 1437.

(6) Alexakis, A.; Lensen, N.; Mangeney, P. *Tetrahedron Lett.* **1991**, *32*, 1171 and references cited therein.

(7) Mangeney, P.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1988**, *29*, 2677.

(8) R_f values: 0.55 and 0.45 for **3aCr** and 0.5 and 0.3 for **3bCr**.

(9) Satisfactory spectral and analytical data have been obtained for all new compounds.

(10) Cuvinot, D.; Mangeney, P.; Alexakis, A.; Normant, J. F. *J. Org. Chem.* **1989**, *54*, 2420.

(11) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

Monocrystals of (2*R*)-**3bCr** were submitted to an X-ray crystallographic study[12] in order to determine not only the exact conformation of this new complex in the solid state but also to confirm the assignment of the aminalic proton chemical shift of this diastereomer by ^{1}H NMR. The ORTEP plot of aminal (2*S*)-**3bCr** is shown in Figure 1 and indicates, as expected,[13-16] an eclipsed chromium carbonyl bond versus the methoxy group.

Chromium transfer from (naphthalene)tricarbonylchromium is known to allow the introduction of the tricarbonylchromium moiety with higher diastereoselectivity and under milder conditions,[17] and the major diastereomer is still the same as the one obtained under thermic conditions.[18] In our case, reaction of **3a** with (naphthalene)tricarbonylchromium (1 mol equiv), at room temperature for 4 days, gives an 80% yield of the diastereomeric aminals (2*R*)-**3aCr** and (2*S*)-**3aCr** in a 3/97 ratio. Thus, the opposite diastereomer (2*S*)-**3aCr** is, now, the major one, with very high de (94%)! This inversion of selectivity is unprecedented, to our knowledge, and might be due either to a chelation by one of the nitrogen atoms of the imidazolidine ring or to the steric requirements of the aminal group itself. Heating of the above mixture at 140 °C for 20 h allowed a "thermodynamic" equilibrium to be reached,[19] and we obtained as the major diastereomer the aminal (2*R*)-**3aCr** with the same 76% de as found previously, in 95% isolated yield. This surprising "isomerization" presumably involves dissociation and recomplexation of the arene to the opposite diastereoface.[19]

For aminal **3b**, these "kinetic" conditions ((naphthalene)tricarbonylchromium) worked as well, and we obtained the diastereomeric aminals (2*R*)-**3bCr** and (2*S*)-**3bCr** in a 2/98 ratio. The isolation of the homochiral aldehydes **1aCr** and **1bCr** is achieved quantitatively by hydrolysis of the corresponding chiral aminals. Thus, for the first time, an efficient method exists for the *enantioselective* introduction of the Cr moiety on aromatic aldehydes.

In conclusion, our preliminary results show that chiral diamines having a C_2 axis of symmetry can be considered as an original and efficient tool for the asymmetric formation and resolution of aminals of ortho-substituted (benzaldehyde)tricarbonylchromium complexes, which is achieved very easily on a preparative scale with high yields.

Supplementary Material Available: A listing of complete crystallographic data of compound (2*R*)-**3bCr**, ^{1}H NMR spectral data of (2*R*)-**3aCr**, (2*S*)-**3aCr**, (2*R*)-**3bCr**, and (2*S*)-**3bCr**, and full experimental procedures with analytical data (3 pages). Ordering information is given on any current masthead page.

(12) Crystal data for (2*R*)-**3bCr** (from ether/petroleum ether): $CrC_{19}H_{24}O_4N_2$, fw 396.41, triclinic, space group *P*1; a = 8.071 (2) Å, b = 10.722 (2) Å, c = 11.414 (2) Å, V = 934 (5) Å^3, Z = 2, ρ(calcd) = 1.41 g cm^{-3}, μ (Mo Kα) = 6.21 cm^{-1}, T = 296 K. The structure was solved by direct methods; 3286 measured reflections in which 2963 are considered as observed ($I > 3\sigma(I)$). All coordinates of H atoms were calculated. Final residuals: R = 0.0308, R_w = 0.0319.

(13) Semmelhack, M. F.; Clark, G. *J. Am. Chem. Soc.* **1977**, *99*, 1675.

(14) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092.

(15) Solladié-Cavallo, A.; Wipff, G. *Tetrahedron Lett.* **1980**, *21*, 3047.

(16) (a) Boutonnet, J. C.; Rose-Munch, F.; Rose, E.; Jeannin, Y.; Robert, F. *J. Organomet. Chem.* **1985**, *297*, 185. (b) Rose-Munch, F.; Aniss, K.; Rose, E.; Vaisserman, J. *J. Organomet. Chem.* **1991**, *415*, 223. (c) Rose-Munch, F.; Bellot, O.; Mignon, L.; Semra, A.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1991**, *402*, 1.

(17) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* **1985**, *286*, 183.

(18) (a) Uemura, M.; Kobayashi, T.; Minami, T.; Hayashi, Y. *Tetrahedron Lett.* **1986**, *27*, 2479. (b) Uemura, M.; Minami, T.; Hayashi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5277. (c) Uemura, M.; Minami, T.; Hirotsu, K.; Hayashi, Y. *J. Org. Chem.* **1989**, *54*, 469. (d) Ohlsson, B.; Ullenius, C.; Jagner, S.; Grivet, C.; Wenger, E.; Kündig, E. P. *J. Organomet. Chem.* **1989**, *365*, 243.

(19) A referee suggested that the pure "thermodynamic" diastereomer should also be submitted to these equilibration conditions. Thus, a pure sample of (2*R*)-**3aCr** was heated for 20 h at 140 °C in Bu_2O and was recovered unchanged. It might be speculated whether the 88/12 ratio reflects a true "thermodynamic" equilibrium or whether 20 h are not enough to attain the complete equilibration. However, heating for more prolonged periods gives rise to partial decomposition and extensive decomplexation. Further work is underway which is beyond the scope of this communication.

The Origin of Greater Than 200:1 Enantioselectivity in a Catalytic Diels-Alder Reaction As Revealed by Physical and Chemical Studies

E. J. Corey,* Teck-Peng Loh, Thomas D. Roper, Mihai D. Azimioara, and Mark C. Noe

Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

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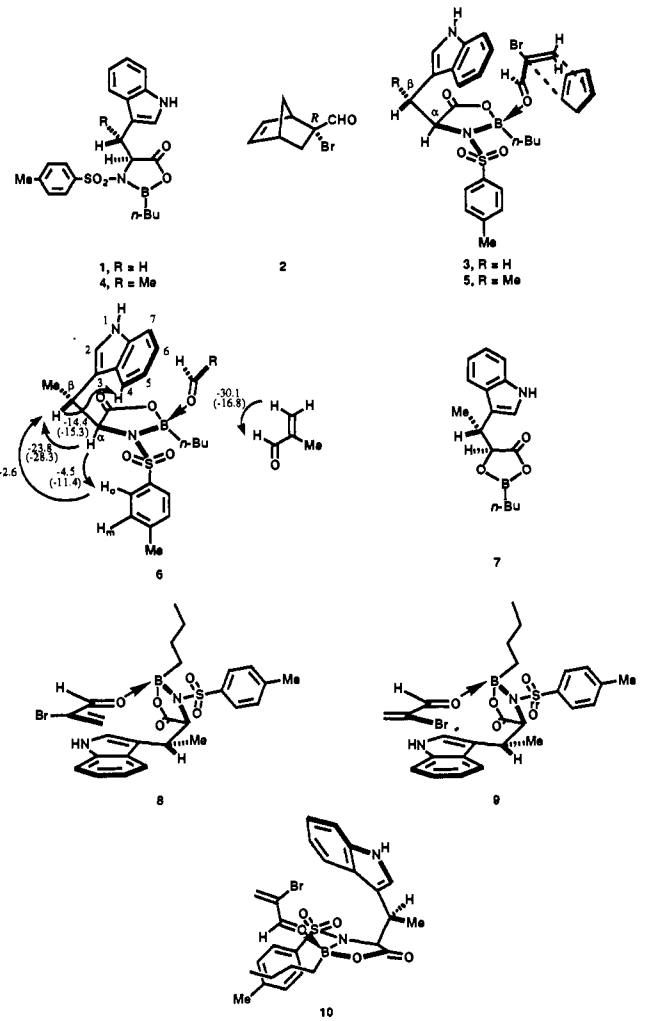
The (*S*)-tryptophan-derived oxazaborolidine **1** catalyzes the Diels-Alder reaction between 2-bromoacrolein and cyclopentadiene to form the chiral adduct **2** with unprecedented (>200:1) enantioselectivity (5 mol % **1**, CH_2Cl_2, -78 °C, 30 min),[1] a result consistent with the working hypothesis of a preferred transition state assembly **3**. The interlocking physical and chemical studies reported herein provide experimental support for **3**.

Chart I



A. Catalyst **4**, derived from ($\alpha S,\beta R$)-β-methyltryptophan[2] and *n*-butylboronic acid as described for **1**,[1] also catalyzes the reaction of cyclopentadiene and 2-bromoacrolein to form **2** with >200:1

(1) Corey, E. J.; Loh, T.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8966-8967.

(2) Racemic *N*-tosyl-β-methyltryptophan was synthesized (see: Behforouz, M.; Zarrinmayeh, H.; Ogle, M. E.; Riehle, T. J.; Bell, F. W. *J. Heterocycl. Chem.* **1988**, *25*, 1627-1632) and resolved to the ($\alpha S,\beta R$) enantiomer by recrystallization of the diastereomeric 1:1 salts with (-)-norephedrine from ethanol. This chiral *N*-tosyl derivative and that of (*S*)-tryptophan each had $[\alpha]^{23}_D$ -42° (c = 1 in EtOH). The structure of *N*-tosyl-($\alpha S,\beta R$)-β-methyltryptophan was also verified by a single-crystal X-ray diffraction study (paper in preparation). The study of catalyst **4** was advantageous for NMR measurements and especially for determination of the $HC_\alpha C_\beta H$ dihedral angle.

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