In summary these new bis(calix[4]diquinone) receptors represent a new design of redox-active ionophore which depend upon the length of the bridging methylene chain between the two calix[4]diquinone moieties. Their unique topological cavities can exhibit impressive selectivity preferences and novel electrochemical recognition properties towards the larger alkali metal cations Cs^+ and Rb^+.

Experimental Section

Experimental details are given in the Supporting Information. Crystal data for $[CsL^2]ClO_4$: $C_{82}H_{93}ClCsO_{19.5}$, $M_r = 1558.92$, monoclinic, space group $P2_1/n$, $a = 11.869(15)$, $b = 18.337(25)$, $c = 40.992(44)$ Å, $\beta = 91.00(1)^\circ$, $V = 8920$ Å^3, $Z = 4$, $\rho_{calcd} = 1.161$ Mg m^{-3}, $\mu = 0.506$ mm^{-1}. Intensity data was collected with $Mo_{K\alpha}$ radiation using the *MAR*research Image Plate System. The crystal was positioned 90 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 10 mins to give 8091 independent reflections. Data analysis was carried out with the XDS program.[16] The structure was solved by using direct methods with the SHELX86 program.[17] In the cesium complex of L^2 there are two independent perchlorate anions with occupancies refined to 0.56, 0.44 and two pairs of overlapping methanol molecules each with common oxygen atoms and occupancies refined to 0.49, 0.51 and 0.49, 0.51, respectively, and two water molecules with occupancies of 1.0 and 0.5. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using SHELXL.[18] The final R values for the cesium complex of L^2 were $R_1 = 0.0891$, $wR_2 = 0.2398$ for data with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-157775 and CCDC-157776. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[14] For redox-active receptors where through-space electrostatic interactions dominate the potential shift, ΔE (mV) can be calculated using the equation $\Delta E = (Q_{redox}e/4p\varepsilon\varepsilon_0 l)(z/r)$, where $Q_{redox} = ne$, the charge variation in the redox center upon electron transfer; e = charge on an electron; n = number of electrons transferred to or from the redox center; ε_0 = permittivity of a vacuum; ε = relative permittivity of the solvent; l = distance between the redox center and the complexed cation; z = valence of the complexed cation; and r = radius of complexed cation. (See: Z. Chen, A. J. Pilgrim, P. D. Beer, *J. Electroanal. Chem.* **1998**, *444*, 209.) For 4:1 CH_2Cl_2:CH_3CN $\varepsilon = 14.6$, $r(Cs^+) = 1.74$ Å, average Cs^+–O distance from crystal structure = 3.258 Å, $\Delta E = 173$ mV. (If the distance is taken between the centers of the complexed cation and quinone redox center, the value of ΔE would be smaller in magnitude.) This value is much smaller than the experimentally observed value of 260 mV (Table 2), which suggests the Cs^+ ion is bound closer to one of the two calix[4]diquinone redox centers.

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Cyclic Hexamer with a Cubic Cavity: Crystal Structure of [{Rh(6-Purinethione Ribosido)(Cp*)}$_6$](CF$_3$SO$_3$)$_6$

Kazuaki Yamanari,* Shiori Yamamoto, Rie Ito, Yoshihiko Kushi, Akira Fuyuhiro, Naoko Kubota, Tsuyoshi Fukuo, and Ryuichi Arakawa

The metal–ion binding capability of N^9-substituted nucleobases such as 9-alkyladenine (R-Hade) and adenosine (Hado) have been studied intensively in the past two decades.[1] Some cyclic polynuclear metal complexes that include such nucleobases have been synthesized recently based on self-assembling reactions.[2] Crystal structures have been reported for [{Rh(Me-ade)(Cp*)}$_3$](CF$_3$SO$_3$)$_3$ (Cp* = η^5-C$_5$Me$_5$),[3]

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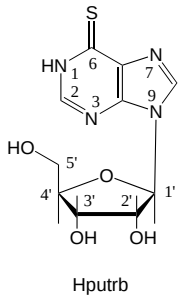
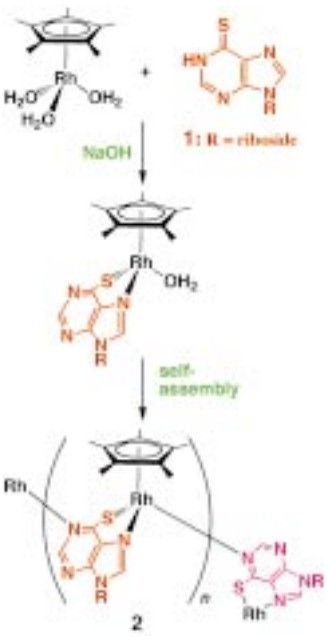
$[\{Ru(Et\text{-}ade)(cymene)\}_3](CF_3SO_3)_3$ (cymene = η^6-*p*-Me-C_6H_4*i*Pr),[4] $[\{Ru(5'\text{-}amp)(cymene)\}_3](CF_3SO_3)_3$ (5′-amp = adenosine 5′-monophosphate),[5] and $[\{Ir(Et\text{-}ade)(Cp^*)\}_3](CF_3SO_3)_3$.[6] Interestingly, they are all trinuclear species with C_3 symmetry.



Hputrb

Herein we report a similar kind of self-assembling reaction between $[M(Cp^*)(H_2O)_3]^{2+}$ (M = Rh and Ir) and 6-purinethione riboside (**1**, Hputrb), which has a similar ligand skeleton as adenosine, except that the NH_2 group in the 6-position is substituted by a thione group.[7] The crystal structure in the present system reveals that the isolated complex has a novel cyclic hexanuclear structure. The self-assembling reaction between $[Rh(Cp^*)(H_2O)_3]^{2+}$ and **1** gave $[\{Rh(putrb)(Cp^*)\}_6](CF_3SO_3)_6$ **2** in high yield (Scheme 1). The ^{1}H NMR spectrum of **2** showed a single methyl signal for Cp* and one set of signals for **1** (Figure 1), which indicates that complex **2** is composed of a single species. The electrospray ionization (ESI) mass spectrum[8] showed four dominant peaks at *m*/*z* 521, 655, 856, and 1191, which correspond to the ions of $[6M-6X]^{6+}$, $[6M-5X]^{5+}$, $[6M-4X]^{4+}$, and $[6M-3X]^{3+}$, respectively. This result means that **2** has a cyclic hexanuclear structure.

Figure 2 shows the stereoview of the cation in **2**.[9] This complex has a novel hexanuclear structure. Six Rh^{III} ions are crystallographically independent and the mean Rh ··· Rh distance is 5.963 Å. The putrb ligand adopts a μ-1κN^1:2$\kappa^2 S^6$,N^7 bridging mode: it coordinates to one Rh^{III} ion in a bidentate manner through the S^6 and N(7) donors, which form a five-membered chelate ring, and bridges to another Rh^{III} ion through the N(1) donor. The six purine rings are arranged on the six planes of a cube, thus forming a cubic cavity. The distances between the opposite purine planes are 8.5–8.8 Å, and hence the inner cubic void has average dimensions of 5.3 Å. Three ribose groups collect together toward each side of the longest cubic diagonal. These sites correspond to the outlets of the cubic cavity. Figure 3a represents the space-filling structure of **2** and Figure 3b clearly shows the inner cubic structure of the cavity after three putrb ligands have been removed from the foreground. To our knowledge, the present hexanuclear structure with a cubic cavity is unprecedented.



Scheme 1. Expected self-assembling process to form cyclic oligomers.

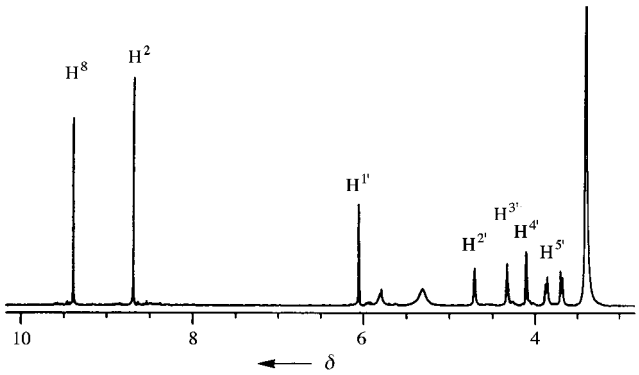


Figure 1. ^{1}H NMR spectrum of **2** in [D$_6$]DMSO.

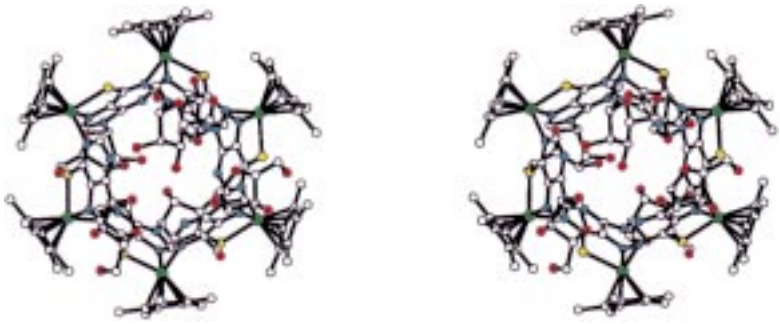


Figure 2. Stereoview of the cation in $[\{Rh(putrb)(Cp^*)\}_6](CF_3SO_3)_6\cdot 12H_2O$ (**2**): Selected distances [Å] and angles [°]: Rh-S 2.431, Rh-N(1) 2.155, Rh-N(7) 2.132, C(6)-S 1.73; S-Rh-N(7) 83.6, S-Rh-N(1)′ 91.2, N(7)-Rh-N(1)′ 90.2, S-C(6)-C(5) 116, Rh-N(7)-C(5) 112, Rh-S-C(6) 99.3, Rh-N(1)-C(6) 125, Rh′-N(1)-C(2) 117, S-Rh- N(1)′-C(6)′ ±144 (all values are averages).

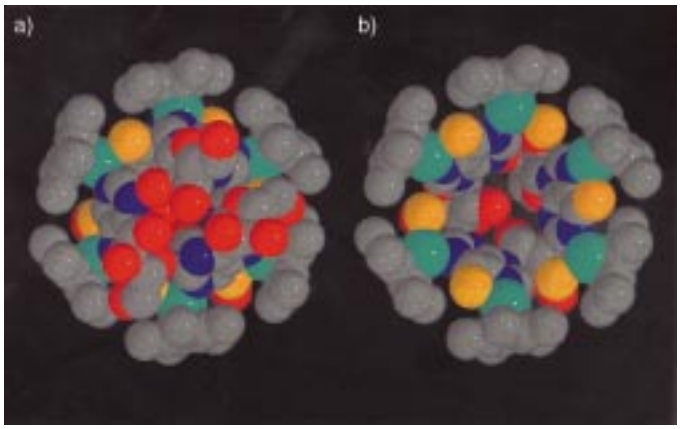


Figure 3. a) Space-filling structure of **2**, and b) the inner cavity structure after removing three putrb ligands from the foreground of **2**: green (rhodium), yellow (sulfur), red (oxygen), blue (nitrogen), gray (carbon).

The central Rh^{III} ions are chiral because of the unsymmetrical bridging mode of **1**. The unit Rh^{III} complex can be expressed as an arrow and the arrows must be arrayed in the same direction to form cyclic polynuclear complexes. Each unit complex has C (clockwise) or A (anticlockwise) chirality.[10] In the cyclic hexanuclear complex, eight geometrical isomers are possible: Figure 4 shows these isomers with their symmetries and the number of sets of NMR signals that are expected. The above structure of **2** corresponds to a S_6 isomer.

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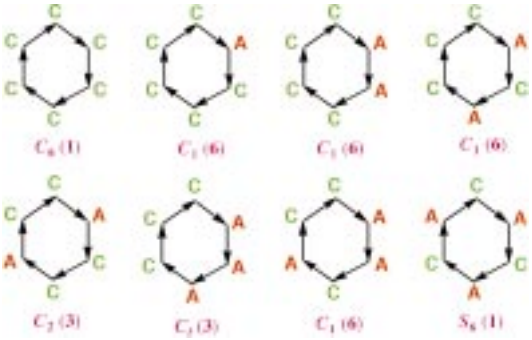

Figure 4. Possible geometrical isomers for a cyclic hexanuclear complex with an achiral bridging ligand. The characters C (clockwise) and A (anticlockwise) denote the chirality of the unit Rh^{III} complex. Each isomer is denoted by its complex symmetry, and the numbers in parentheses show number of sets of NMR signals that are expected.

The S_6 structure has the alternate cyclic array of chiralities CACACA. Hence there is no configurational contribution around metal ions but **2** becomes optically active because of the chiral ribose group of **1**. The circular dichroism (CD) spectrum of **2** shows a strong CD intensity as a vicinal contribution (Figure 5). Some CD spectra of complexes that contain nucleosides have been reported so far. Their CD intensities are, however, relatively weak because these complexes are mixtures of two diastereomers.[3b] It should be noted that the present Rh^{III} system contains only the pseudo-S_6 isomer, which was formed stereoselectively.

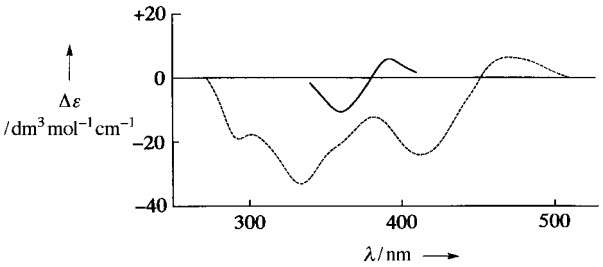

Figure 5. CD spectra of $[\{Rh(putrb)(Cp^*)\}_6]^{6+}$ (**2**; dotted line) and $[\{Ir(putrb)(Cp^*)\}_6]^{6+}$ (**3**; solid line).

Two cyclic purine hexamers have been reported so far.[11] $[\{Pt(thp)(CH_3)_3\}_6]\cdot 12\,CHCl_3$ (Hthp = theophylline)[11a] has the same S_6 symmetry as **2**: The thp ligand adopts a μ-$1\kappa N^9{:}2\kappa^2 O^6,N^7$ bridging mode. This complex also has the alternate cyclic array of CACACA, but the structure is completely different from that of **2**. We concluded that these two structures are types of conformational isomers, though the bridging modes, N(1) for **2** and N(9) for the Pt^{IV} complex, are different from each other. In the model study, the other pseudo-S_6 structure similar to $[\{Pt(thp)(CH_3)_3\}_6]$ can be easily constructed in the present system. The dihedral angle S-Rh-N(1)′-C(6)′ is on average $\pm 144^\circ$ ($+147$ to -146°) in **2** and expected to be near $\pm 35^\circ$ in the other pseudo-S_6 isomer. The two conformational isomers are produced only by the difference of this dihedral angle. The mutual exchange between the two conformational isomers is impossible in solution without breaking bonds.

The corresponding Ir^{III} complex $[\{Ir(putrb)(Cp^*)\}_6][CF_3SO_3]_6$ (**3**) was prepared in the same manner. Complex **3** gave rise to a very similar ^1H NMR spectrum to that of **2**, and its positive ESI mass spectrum showed dominant peaks at m/z 611, 763, and 991, which correspond to the ions of $[6M-6X]^{6+}$, $[6M-5X]^{5+}$, and $[6M-4X]^{4+}$, respectively. Therefore we concluded that **3** has the same cyclic hexanuclear pseudo-S_6 structure as **2**. The CD pattern at the lower energy side for **3** is similar to that of **2** (Figure 5).

Experimental Section

2 and **3**: Silver trifluoromethanesulfonate (0.33 g, 1.3 mmol) was added to a suspension of $[\{Rh(Cp^*)Cl_2\}_2]$[12] (0.2 g, 0.32 mmol) in water (30 mL), and the mixture was stirred at 40 °C for 1 h. The resulting precipitate of silver chloride was removed by filtration, and an aqueous solution (50 mL, adjusted to about pH 8 by adding aqueous NaOH) of Hputrb (0.18 g, 0.64 mmol) was added to the filtrate. The mixed solution was heated at 80 °C for 3 h, then cooled to room temperature and concentrated by using a rotary evaporator to give orange crystals, which were recrystallized from water and ethanol (70–85 % yield). ^1H NMR (270 MHz, $[D_6]$DMSO, 25 °C, TMS): $\delta = 9.38$ (H^8; s, 1 H), 8.69 (H^2; s, 1 H), 6.05 ($H^{1'}$; d, 1 H), 5.78 (s, 1 H), 5.31 (s, 1 H), 4.70 ($H^{2'}$; s, 1 H), 4.32 ($H^{3'}$; s, 1 H), 4.11 ($H^{4'}$; s, 1 H), 3.86 ($H^{5'}$; d, 1 H), 3.68 ($H^{5''}$; d, 1 H), 1.81 (Cp*; s, 15 H); ^{13}C NMR: $\delta = 172.43$ (C6), 155.40 (C2), 145.51 (C4), 144.42 (C8), 136.18 (C5), 102.18 (Cp*), 90.01 (C1′), 85.24 (C4′), 73.64 (C2′), 69.09 (C3′), 60.11 (C5′), 9.17 (Cp*); ESI MS (in acetone): m/z: 521 $[6M-6X]^{6+}$, 655 $[6M-5X]^{5+}$, 856 $[6M-4X]^{4+}$, 1191 $[6M-3X]^{3+}$; calcd for $[\{Rh(putrb)(Cp^*)\}_6](CF_3SO_3)_6\cdot 12H_2O$ (**2**; $C_{126}H_{180}F_{18}N_{24}O_{54}Rh_6S_{12}$) (%): C 35.70, H 4.28, N 7.93; found: C 35.22, H 4.21, N 7.92.

The corresponding Ir^{III} complex was prepared in the same manner (70–80 %). ^1H NMR (270 MHz, $[D_6]$DMSO, 25 °C, TMS): $\delta = 9.34$ (H^8; s, 1 H), 8.63 (H^2; s, 1 H), 6.01 ($H^{1'}$; d, 1 H), 5.74 (s, 1 H), 5.27 (s, 1 H), 4.64 ($H^{2'}$; s, 1 H), 4.28 ($H^{3'}$; s, 1 H), 4.07 ($H^{4'}$; s, 1 H), 3.82 ($H^{5'}$; d, 1 H), 3.64 ($H^{5''}$; d, 1 H), 1.81 (Cp*; s, 15 H); ESI MS (in acetone): m/z: 611 $[6M-6X]^{6+}$, 763 $[6M-5X]^{5+}$, 991 $[6M-4X]^{4+}$; calcd for $[\{Ir(putrb)(Cp^*)\}_6](CF_3SO_3)_6\cdot 9H_2O$ (**3**; $C_{126}H_{174}F_{18}Ir_6N_{24}O_{51}S_{12}$) (%): C 32.06, H 3.71, N 7.12; found: C 32.00, H 3.73, N 7.32.

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[9] Crystal data for $[\{Rh(putrb)(Cp^*)\}_6](CF_3SO_3)_6\cdot 12H_2O$ **2** were collected on a Rigaku AFC7R diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation($\lambda = 0.71069$ Å); $C_{126}H_{180}F_{18}N_{24}O_{54}Rh_6S_{12}$, $M_r = 4239.06$, $0.35\times0.30\times0.20$ mm; $T = 23$ °C; monoclinic, $P2_1$ (no. 4), $Z = 2$, $a = 16.88(1)$, $b = 29.29(1)$, $c = 18.697(10)$ Å, $\beta = 96.09(5)^\circ$, $V = 9194(9)$ Å^3, $\mu = 7.61$ cm^{-1}, $F(000) = 4320$, $\rho_{calcd} = 1.531$ g cm^{-3}, $\omega-2\theta$ scan, $2\theta_{max} = 60.1^\circ$. Of the 28227 reflections collected, 27370 were unique ($R_{int} = 0.069$). Final $R1 = 0.118$ for 9702 reflections with $I > 2\sigma(I)$ (776 parameters) and $wR = 0.437$ for all reflections. Significant disorder was observed and hence the locations of most $CF_3SO_3^-$ anions and H_2O molecules could not be determined. All calculations

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were performed by using the TEXSAN[13] crystallographic software package. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153832. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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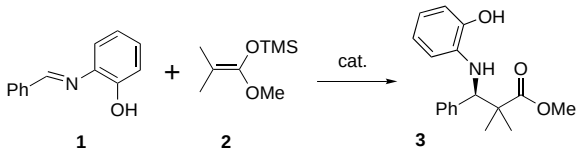
Table 1. Reactions of imine **1** with acetal **2** with various catalysts.[a]



1 **2** **3**

Entry	Ligand	mol% cat.	T [°C]	t [h]	Solvent	Yield **3** [%]	% *ee*
1	*S*-VAPOL	20	−45	10	CH_2Cl_2	50	80
2	*S*-VAPOL	20	−45	20	toluene	92	91
3	*S*-VAPOL	20	25	15	toluene[b]	94	89[c]
4	*S*-VAPOL	2	40	6	toluene[b]	100	86[d]
5	*S*-VAPOL	0.5	41	19	toluene	60	85
6	*R*-BINOL[e]	20	−45	19	CH_2Cl_2	80	36
7	*R*-BINOL[e]	20	25	4	CH_2Cl_2	100	28
8	*R*-Br_2BINOL[f]	10	−45	19	CH_2Cl_2	87	86
9	*R*-Br_2BINOL[f]	20	25	4	CH_2Cl_2	87	48
10	*R*-Br_2BINOL[f]	10	25	18	toluene	95	62

[a] Catalyst generated from $Zr(OiPr)_4$/*i*PrOH, (*S*)-VAPOL (2.2 equiv) and 1.2 equiv *N*-methyl imidazole (NMI) in either CH_2Cl_2 or toluene at 25 °C for 1 h. Unless otherwise specified, all reactions were performed with 1.2 equiv of **2** and 0.125 M in imine. [b] 15:1 toluene:CH_2Cl_2. [c] 0.5 M in imine. [d] 1.0 M in imine. [e] Catalyst generated from $Zr(OiPr)_4$/*i*PrOH, *R*-BINOL (2.2 equiv) and 1.2 equiv NMI in CH_2Cl_2 at 25 °C for 1 h. [f] Catalyst generated from $Zr(OtBu)_4$, (*R*)-6,6′-dibromoBINOL (2.2 equiv) and 1.2 equiv NMI in CH_2Cl_2 at 25 °C for 1 h.

Active Site Design in a Chemzyme: Development of a Highly Asymmetric and Remarkably Temperature-Independent Catalyst for the Imino Aldol Reaction**

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The asymmetric aldol reaction of an enolate or enolate equivalent with an imine is a reaction of established synthetic importance for the synthesis of chiral amines in general and β-amino esters in particular.[1] The development of chiral catalysts for this reaction has proven to be a difficult task and had eluded all attempts until recently when Kobayashi and co-workers examined imines derived from *o*-aminophenol.[2–4] Their method involves the catalysis of the reactions of these imines and ketene acetals with a catalyst generated from zirconium(IV) *tert*-butoxide and two equivalents of (*R*)-6,6′-dibromoBINOL (BINOL = 1,1′-binaphth-2-ol). Our interest in the synthesis of chiral amines led us to investigate the use of VAPOL-derived catalysts[5] (see Figure 1) for this reaction. Here we report the development of a remarkably temperature-independent and highly asymmetric method for this process that was guided by an analysis of models of intermediates that are suspected to be involved in the reaction.

A comparison of catalysts prepared from BINOL, 6,6′-dibromoBINOL and VAPOL ligands on the asymmetric induction in the reaction of the phenyl-substituted imine **1** and acetal **2** is summarized in Table 1. Following the Kobayashi protocol, the catalyst was prepared by reaction of the ligand with 0.5 equivalents of zirconium tetraalkoxide in the presence of 0.6 equivalents of *N*-methyl imidazole at room temperature for 1 h.[2] The VAPOL catalyst could be prepared in either methylene chloride or toluene, but for solubility reasons, the BINOL catalysts were prepared in methylene chloride. The VAPOL and Br_2BINOL catalysts were superior to the BINOL catalyst at −45 °C. The asymmetric induction dropped for the Br_2BINOL catalyst when the temperature was raised from −45 °C to room temperature, but curiously, the asymmetric induction for the VAPOL catalyst was essentially unchanged over this same temperature range. Only a small drop-off is noted (85% *ee*) when the temperature is raised to 41 °C and the substrate-to-catalyst ratio is raised to 200:1 (entry 5). Both the *R* enantiomers of BINOL and Br_2BINOL ligands give the *R* enantiomer of the product **3**, whereas with the VAPOL ligand, it is the *S* enantiomer that gives the *R* product. This reversal is not unexpected given the structures of the ligands where the zirconium is in the minor groove of the BINOL ligands and in the major groove of the VAPOL ligand.[6, 7]

The mechanism that has been proposed for the catalytic cycle for the Br_2BINOL–zirconium-mediated reaction involves a catalyst bearing two Br_2BINOL ligands on one zirconium and the coordination of the *o*-hydroxyphenylimine to the zirconium as a bidentate ligand.[2g] It is clear from the examination of space-filling CPK models that it is possible to bind two VAPOL ligands to one zirconium atom but only with a facial arrangement of the four oxygen atoms as is illustratred by structure **6** in Scheme 1. This is supported by ^{1}H NMR experiments on a catalyst generated from zirconium tetraisopropoxide and VAPOL in the presence of two equivalents of *N*-methyl imidiazole. A clean spectrum is only observed with two equivalents of VAPOL relative to zirconium and the spectrum is consistent with a single C_2-symmetrical species

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