For supermolecules of the type discussed here, extended electron delocalization at the triplet level demands that the acetylene function is attached directly to the coordinated terpyridine ligand. The molecular axis can be lengthened while retaining rigidity by including aromatic groups in the polyacetylene wire. Such groups provide a facile means by which to modify the solubility, electronic charge, molecular shape, and photoproperties of the emergent multicomponent array. The acetylene unit ensures selective charge injection into the ditopic ligand under illumination, while the nature of the central aromatic core controls the extent of electron delocalization over the ditopic ligand. These two molecular fragments are highly complementary, and they act cooperatively to direct electronic charge along the molecular axis. In the case of the prototypic system **2**, where the terminal Ru^{II} cations are separated by about 23 Å, the photophysical properties can be fine-tuned by selective coordination of additional cations. Presumably, external complexation of this type could be used to modulate the rates of light-induced energy or electron transfer through the bridge in mixed-metal analogues of **2**. Provided high binding constants prevail, this strategy could be used to stimulate electron transfer between remote reactants by injection of a low concentration of a specific cation into the system. This situation is reminescent of biological regulatory mechanisms and is a future goal for our research.

Experimental Section

Synthesis and characterization of all new complexes will be reported elsewhere, but a typical experimental procedure is given for **2**: A Schlenk flask was charged with 5,5′-diethynyl-2,2′-bipyridine (0.010 g, 0.49 mmol), [Ru(terpy)(terpy-Br)](PF$_6$)$_2$ (0.091 g, 0.98 mmol), 10 mL degassed CH_3CN, [Pd(PPh$_3$)$_2$Cl$_2$] (0.004 g, 6% in mol) and CuI (0.002 g, 10% in mol). After purging with argon, (*i*Pr)$_2$NH (5 mL) was added. The solution was stirred at room temperature for 6 days before KPF_6 (0.018 g, 4 equiv.) in water (5 mL) was added and the solvent removed. The crude product was chromatographed on alumina with a mixture of CH_3CN and H_2O (gradient of water 0–25%). The analytically pure compound was obtained by recrystallization from CH_3CN/diethyl ether. Yield 70%. $R_f = 0.45$ (alumina, $CH_3CN/H_2O/KNO_3$, 80/20/0.5 as eluent). ^{1}H NMR (CD_3OD): $\delta = 9.24$ (s, 3H), 9.12 (s, 1H), 9.02 (d, 4H, $^3J = 8.3$ Hz), 8.86–8.67 (m, 6 lines, 11H), 8.52 (t, 3H, $^3J = 5.9$ Hz), 8.38 (dd, 2H, $^3J = 8.3$ Hz, $^4J = 1.9$ Hz), 8.08-7.97 (m, 8H), 7.59–7.51 (m, 8H), 7.35–7.26 (m, 8H). FAB-MS: $m/z = 1772.1$ [$M - PF_6$+H], 1626.0 [$M - 2PF_6$], 1481.0 [$M - 3PF_6$]. UV/Vis (CH_3CN): λ_{max} nm (ε M^{-1}cm^{-1}) 495 (41400), 258 (45000), 332 (56000), 308 (69400), 272 (58400). Analysis calcd for $C_{74}H_{48}Ru_2N_{14}P_4F_{24}$ ($M_r = 1915.30$): C 46.41, H 2.53, N 10.24; found: C 46.29, H 2.42, N 10.15.

Luminescence lifetimes were measured by a time-correlated, single-photon counting methodology following laser excitation at 440 nm (detection at the peak of the emission spectrum). Binding constants were determined by monitoring absorption and/or luminescence spectral profiles as a function of cation concentration and using global analytical iterative routines provided by the SPECFIT commercial software. Reduction potentials were measured by conventional cyclic voltammetry with Pt discs as working and counterelectrodes and an SCE reference, calibrated vs. ferrocene.

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Models for the Carbonyl–ene Cyclization Reaction: Open and Closed Transition States**

D. Christopher Braddock, King Kuok (Mimi) Hii, and John M. Brown*

During a study of stereospecific syntheses of menthol-related terpenoids we prepared racemic and enantiomerically pure 5-methyl-2-(1-methylethyl)hex-5-enal (**1**).[1] From preliminary experiments with simple Lewis acids, catalytic BCl_3, and catalytic or stoichiometric quantities of $SnCl_4$ gave cleanly the anticipated ene-cyclization products **2** and **3** (Scheme 1). In these two cases the ratio of **2** to **3** was 9:1, which is in accord with related results obtained by Snider and

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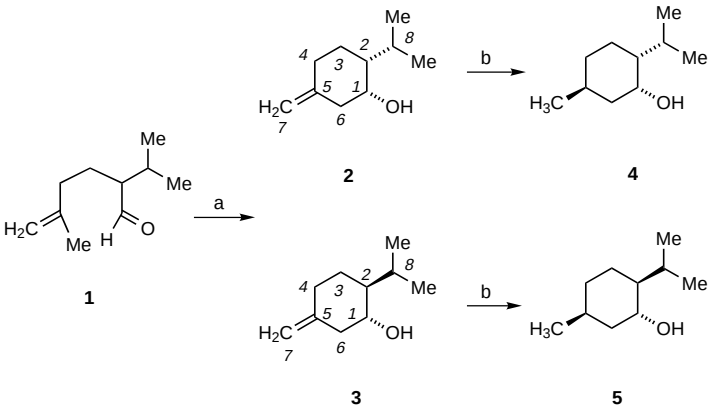
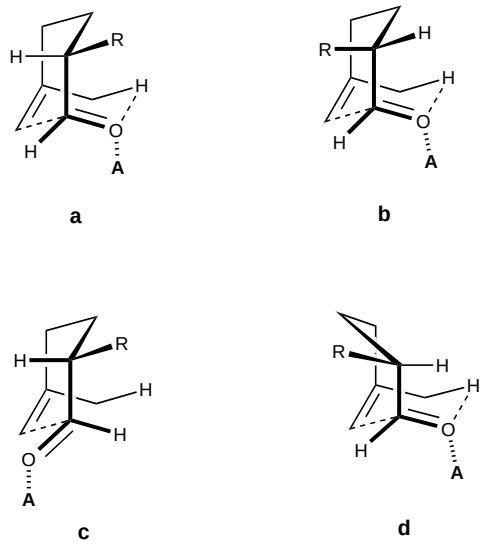


Scheme 1. Carbonyl–ene cyclization of 5-methyl-2-(1-methylethyl)hex-5-enal **1** and hydrogenation of the products: a) Lewis acid catalysts, see Experimental Section; b) $[Ir(COD)(PCy_3)(py)]PF_6$ (cod = 1,5-cyclooctadiene, Cy = cyclohexyl, py = pyridine) H_2, CH_2Cl_2.

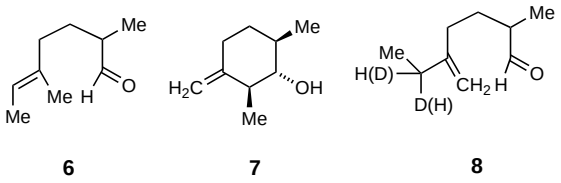
co-workers with Me_2AlCl.[2] The bulky monocyclic[3] methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) also gives a clean reaction but with the opposite stereochemical preference, as defined by Yamamoto and co-workers.[4] As in Yamamoto's work, the configuration of products **2** and **3** was confirmed by reduction; in our case OH-directed stereospecific addition of H_2 with Crabtree's catalyst[5] gave **4** and **5**, respectively (Scheme 1).

Early mechanistic understanding of the stereochemical course of ene cyclization reactions stems from the work of Snider and co-workers.[6] They proposed that the predominant *cis*-cycloadduct formed in the dimethylaluminum chloride mediated ene cyclization of 2-alkylhex-5-enal derivatives arises from a concerted path through a six-membered chairlike transition state (**a**, Scheme 2), in which the long alkyl chain also orients itself in a chairlike conformation; the alkyl substituent adopts an equatorial position. Strictly speaking, the model is based on a bicyclo[3.3.1]nonane framework



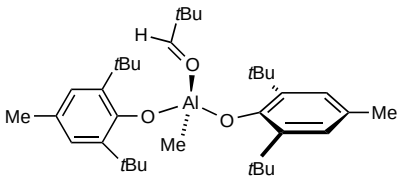
Scheme 2. Mechanistic models for ene–cyclization: a) Snider, leading to *cis*-product, b) Snider, leading to *trans*-product; c) Yamamoto's "open" model leading to *trans*-product, and d) boat precursor of *trans*-product proposed here.

(drawn in Scheme 2 so as to highlight this aspect). The *trans*-cycloadducts observed when bulky MABR reagents were used were explained by Yamamoto as arising through an open chairlike transition-state (**c**, Scheme 2). His results pertaining to *trans*-decalin products rule out the alternative closed transition state **b** (Scheme 2) where the alkyl substituent occupies an axial position.[4c] The possibility of a closed boatlike transition state for the MABR-promoted cyclization (**d**) was not considered. Yamamoto's explanation fits the stereochemical course of MABR-promoted cyclization from compound (*E*)-**6** to **7**, although cyclization of the *Z* stereoisomer of compound **6** is anomalous in that the *trans*-cyclization product is obtained with either MABR or Me_2AlCl. An open transition state, implying a lack of concert between the H transfer and C–C bond-forming steps, is not



easily reconciled with the stereospecific H or D transfers seen by Marshall and co-workers in the cyclization of the isotopomers of compound **8** with either Me_2AlCl or MABR, however.[7]

Models for the ene cyclization of enal **1** were made based on the transition state geometry calculated at the STO-3-21G level by Houk and co-workers for the ene-reaction between propene and formaldehyde.[8] The location of the aluminum Lewis acid was defined by analogy with the series of X-ray structures of Lewis acid complexes of bulky alanes, specifically the aldehyde complex **9** published by Barron's group.[9] An important feature of this and related compounds is that



the Al–O=C donor bond eclipses the aldehyde C–H bond and is thus in the nodal plane of the carbonyl group. In situations where the bulk of the aluminum substituents may be ignored, as in promotion of ene cyclization by Me_2AlCl, the Snider model shown in **a** (Scheme 2) accords very well with the theoretically derived geometry. Applying this model to the MABR-promoted cyclization reaction demonstrates exactly why reverse stereoselectivity is observed; only one face of the aldehyde is accessible for reaction, but only the boat conformation of **d** (Scheme 2) shown in Figure 1a makes the reagent and substrate sterically compatible. The chair transition state engenders a severe clash between the isopropyl group of enal **1** and an *ortho-tert*-butylphenoxy group on the aluminum center, indicated in Figure 1b. The required boat transition state in **d** (Scheme 2) also fits all of the other

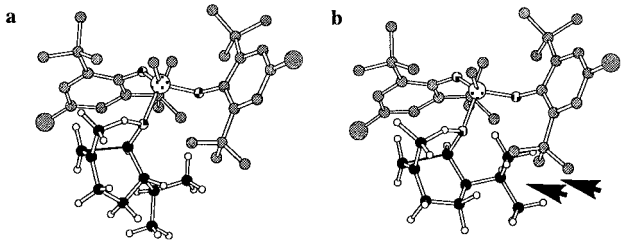
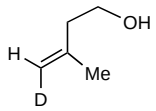


Figure 1. Models for the MABR cyclization based on the X-ray structure of the pivalaldehyde complex **9** and the ab initio transition state of the carbonyl–ene reaction. a) Boat conformation as in **d** (Scheme 2). b) Chair conformation as in **a** (Scheme 2). Hydrogen atoms are omitted from the ligand for clarity. The upper model is free of steric hindrance while the lower has a serious clash in the arrowed region. The diastereoisomeric form of b) is also sterically strained to a high degree. The MABR backbone is in grey, and that of **1** in black.

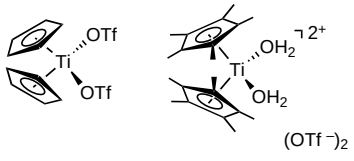
examples of intramolecular ene cyclizations promoted by MABR reported by Yamamoto and co-workers, with the exception of one observation involving a trisubstituted alkene.[4c] If this result can be reconciled, the need for mechanistic diversity would be removed.



(E)-**10**

The above conflicting possibilities were resolved by cyclization of stereospecifically labeled **1**. The key step involves Negishi's Zr-catalyzed carboalumination of butynol with $AlMe_3$. Workup with AcOD proceeds to give more than 98% (*E*)-**10**.[10] The remainder of the synthesis follows that of the racemic compound, and the configuration of (*E*)-[^{2}H]**1** was confirmed by NOE measurements. The NMR spectra of the products of ene cyclization of **2** and **3** were fully assigned by 1D and 2D NMR experiments, and demonstrated that the axial and equatorial protons at C6, derived from the vinylic methylene protons of aldehyde **1,** were distinguishable in both diastereoisomers of the cyclohexanol derivative.[11] For cyclization of (*E*)-[^{2}H]**1**, a single isotopomer of the major product was formed in each case. For the cyclization promoted by MABR, the product [^{2}H]**3** has an axial D-atom at C6, indicated by comparison between the ^{1}H NMR spectra of undeuterated (**A**) and deuterated products (**B**) in Figure 2. In contrast, the Me_2AlCl-promoted cyclization product [^{2}H]**2** has an equatorial D atom at C6, as evident from comparing the spectra of undeuterated (**C**) and deuterated (**D**) products. Given these results for a system perturbed only by an isotope, the preferred pathways for Me_2AlCl and MABR must involve the transition-state models shown in Scheme 2, **a** and **d**, respectively; the Yamamoto model of Scheme 2 **c**, would have predicted equatorial deuteration.

What then is the status of open transition-states in carbonyl ene–cyclizations? The two titanocene-derived Lewis acids **11a** and **11b** at 4 mol% gave different product distributions in Lewis acid catalyzed ene cyclization of aldehyde **1**.[12] The products of the reaction were now the isomeric cyclohexenols **12** and



11a **11b**

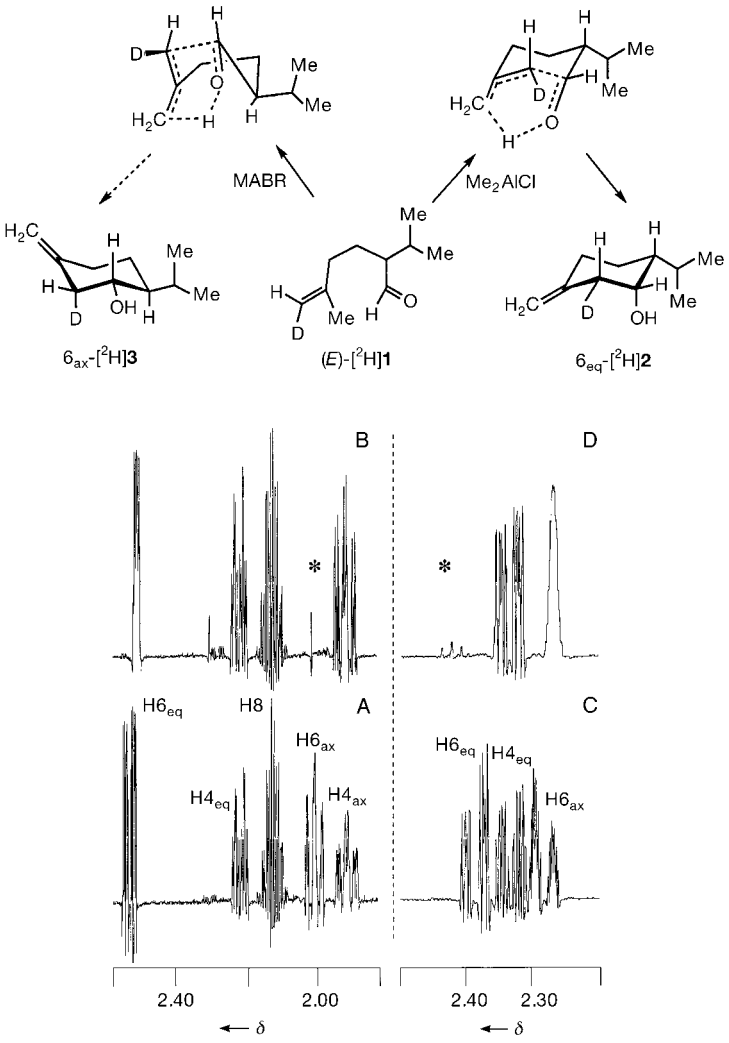


Figure 2. ^{1}H NMR spectra of cyclization products. A) Compound **3** from MABR reaction, in the 2.6–1.8 ppm range; B) as A), starting from *(E)*-[^{2}H]**1**; C) compound **2** from Me_2AlCl reaction in the 2.5–2.2 ppm range; D) as C), starting from *(E)*-[^{2}H]**1.**

13, formed in an approximate 3:1 ratio (Scheme 3). Their configuration was again demonstrated through directed hydrogenation with Crabtree's catalyst to the corresponding neomenthol isomers. The "expected" exocyclic alkenes **2** and **3** were shown not to isomerize under the standard reaction conditions, hence the Ti-catalyzed reaction cannot proceed by ene cyclization followed by isomerization.

Furthermore 20 mol% of $Sc(OTf)_3$ was an efficient catalyst, leading to the exclusive formation of **12** and **13** in a 7:3 ratio. This is explained by an open transition-state model analogous to that shown in **c** (Scheme 2). A methylcyclohexyl cation is generated from 1-methylcyclohexan-1-ol in superacid solution and exists as a rapidly equilibrating mixture of twist-boat and flattened-chair conformations whereby maximum hyperconjugation with the 2- and 6-axial C–H is maintained. The twist-boat conformation was estimated to be 2 kJ mol^{-1} more stable than the corresponding chair conformer.[13] A twist-boat intermediate is disposed to permit regiospecific intramolecular proton transfer to the Lewis acid

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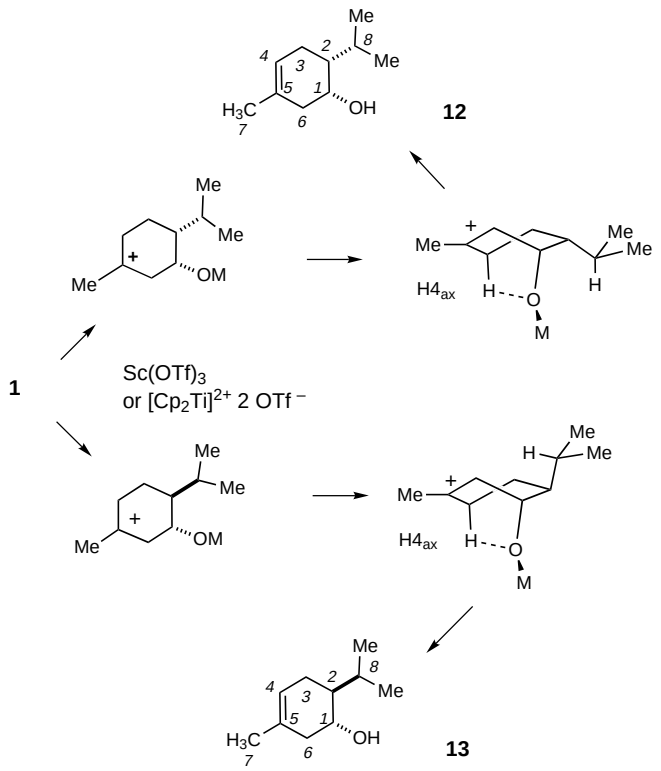

Scheme 3. Cyclization pathway proceeding via an open transition state with a cyclohexyl cationlike intermediate.

coordinated oxygen functionality from the pseudoaxial 4-proton, giving the experimentally observed *cis*- and *trans*-endocyclic cycloadducts.[14] The stereoisomeric twist-boat carbocation intermediates leading to the *cis*- and *trans*-cyclohexenols **12** and **13** are shown in Scheme 3.

Finally an acid-catalyzed cyclization was effected with Amberlyst 15, or 5 mol% *p*-TsOH. This intramolecular Prins reaction[15] was quite unselective and led to the above-mentioned endo- and exocyclic alcohols **2**, **3**, **12** and **13**, accompanied by the stereoisomers of (±)-piperitol (the Δ^5-isomers of **12** and **13**) as well as related endocyclic dienes α-phellandrene and α-terpinene. Hence the hydride transfer step of Scheme 3 is distinct from the purely stepwise intermolecular pathway observed in proton catalysis.

Experimental Section

(*E*)-**10**[10]: A solution of Me_3Al (2 M in hexanes, 100 cm^3) was added slowly to a stirred solution of $[Cp_2Zr]Cl_2$ (14.6 g, 20 mmol) in $ClCH_2CH_2Cl$ (200 cm^3) at room temperature, followed by a solution of 3-butyn-1-ol (4.6 g, 66 mmol) in $ClCH_2CH_2Cl$ (20 cm^3) at 0 °C. The reaction mixture was stirred at ambient temperature for 19 h before being quenched carefully with a 1 M solution of CH_3COOD/D_2O (25 cm^3) at 0 °C. Volatile compounds (< 80 °C) were removed by careful distillation with a 20 cm Vigreux column and the residue was extracted with diethyl ether (2 × 200 cm^3). The combined ether extracts were washed with saturated $NaHCO_3$ (100 cm^3) and water (100 cm^3), dried ($MgSO_4$), and carefully evaporated (< 60 °C). The product was purified by fractional distillation to yield the required deuterated alcohol as a colorless liquid. Yield 2.6 g, 45%; > 98% deuteration by integration of residual proton signal in the NMR spectrum.

2 and **3**: Following the procedures of Yamamoto et al.[4c] enal (±)**1** was mixed with Me_2AlCl in toluene at − 78 °C; (30:1 **2**:**3**, 83% yield of purified **2**) or with MABR in toluene at − 78 °C to − 40 °C; (1:20 **2**:**3**, 78% yield of purified **3**).

12 and **13**: (±)-**1** (208 mg, 2 mmol) was added to a solution of titanocene ditriflate **11a** (0.013 M, 6 mL, 4 mol%) prepared in situ in nitromethane.[12] After 10 min the orange solution was passed through a pad of silica and washed through with diethyl ether. The combined organic extracts were evaporated and the yellow residue was purified by flash chromatography on silica gel (10% ethyl acetate in pentane) to give first (1*R**,2*R**)-5-methyl-2-(1-methylethyl)-4-cyclohexen-1-ol (**12**; 0.112 g, 56%)[14a] and second (1*S**,2*R**)-5-methyl-2-(1-methylethyl)-4-cyclohexen-1-ol (**13**; 0.049 g, 25%).[14b]

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