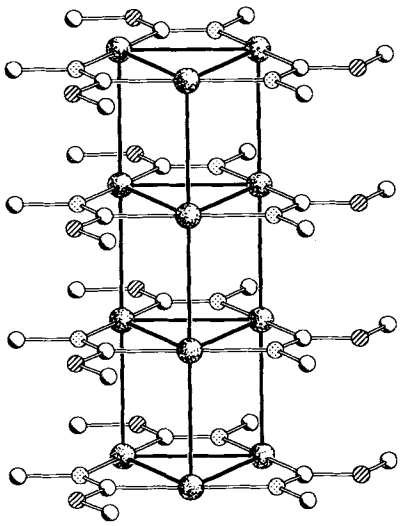

Figure 4. A drawing of the more ordered stack in crystalline **1**. The solid lines again emphasize the gold ··· gold contacts. The flip disorder is not included in this drawing.

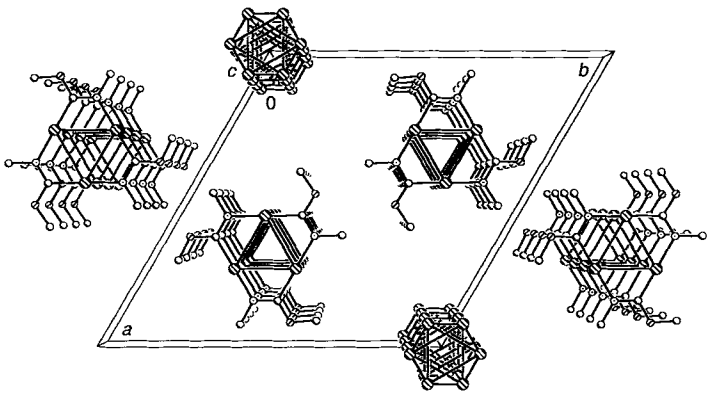

Figure 5. A view down the *c* axis of the unit cell in **1**. For clarity only the positions of the gold atoms and not the ligand atoms are shown in the more disordered stacks.

any liquid-triggered luminescence. Consequently we believe that the extended supramolecular aggregate present in the columns of molecules in **1** is important for the energy storage within the solid and may also be involved with the liquid contact triggered luminescence. Charge or electron separation may be responsible for the energy storage with emission resulting from recombination that occurs when the stacks of molecules in the solid are exposed to solvent. The remarkable luminescence shown in Figure 1 may result from sites near the surface that are either exposed by dissolution of the solid or modified through interaction with the liquid. Migration of charge through the stacks of molecules could facilitate energy transfer from the bulk to the surface. The presence of several types of disorder within this solid offers a multiplicity of sites that could function as traps and thus be responsible for the energy storage.

Further studies of the chemical, photophysical, and physical properties of **1** and related trinuclear complexes are in progress as are studies of the utility of **1** as a sensor for various liquids in remote environments and as an energy storage device.

Experimental Section

Compound **1** was prepared as described previously [1]. The emission spectrum in Figure 2C was obtained with an Olis rapid-scan spectrometer with the light beam path reversed in direction. Crystal data for colorless needles grown from chloroform/diethyl ether: crystal dimensions $0.045 \times 0.017 \times 0.016$ mm; hexagonal crystal system; space group $P6/m$; unit cell dimensions, $a = b = 19.410(4)$, $c = 3.3463(5)$ Å, $V = 1091.8(4)$ Å^3; $Z = 9$; $\rho_c = 3.683$ g cm^{-3}; $T = 130(2)$ K; $2\theta\max = 112.1°$; $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å); 2θ-ω scans; 1220 measured reflections, 582 independent reflections, 582 refined reflections; absorption correction with XABS2 [10], $\mu = 55.8$ mm^{-1}; max. and min. transmission factors, 0.48 and 0.34; structure solution by direct methods (SHELXTL version 5.03); refinement by full-matrix least-squares on F^2 (SHELXTL version 5.03); 33 parameters; 14 restraints; $wR2 = 0.1647$ for all data and a conventional $R_1 = 0.064$ for 498 reflections with $I > 2\sigma I$ after correction for absorption; largest difference electron density peak and hole, 2.872 and -2.117 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper along with a discussion of the disorder have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-179-173. Copies of the data can be obtained free of charge on application to The Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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Remarkable Template Effect of a Lewis Acidic Receptor in Intramolecular Radical Cyclizations**

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Over the last decade free-radical cyclization has developed as a powerful method for constructing ring systems by C-C bond-forming processes and it is now routinely utilized as one of the most reliable tools in organic synthesis.[1] Although the chemo-, regio-, and stereoselectivities of many classes of radical cyclizations are well understood, the full potential of this reaction including stereochemical control at the newly created centers is yet to be realized, and hence only limited structural types of cyclization products have been accessible by this reaction.[1, 2] In this context, we were interested in achieving stereoselective intramolecular radical additions to multiple bonds of halo ethers as model substrates by complexation with a rationally designed Lewis acid. Our recently developed, structurally defined aluminum tris(2,6-diphenylphenoxide) (ATPH, Figure 1)[3]

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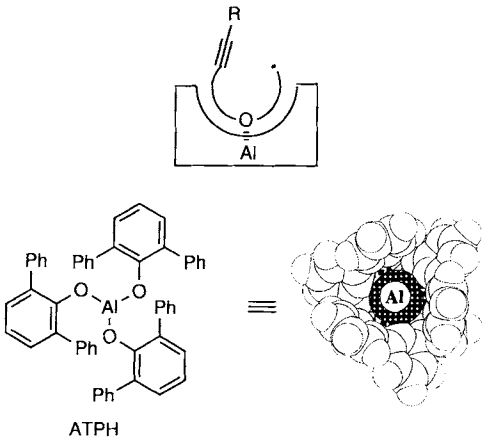
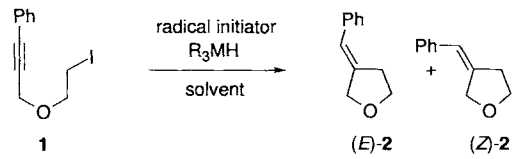


Figure 1. Template effect of a rationally designed Lewis acid such as ATPH in intramolecular radical cyclizations.

seemed quite suitable for this purpose, since it should allow an appropriate proximity of carbon radical to multiple bond in the transition state, thereby smoothly facilitating the otherwise difficult cyclization and yet reversing the stereoselectivity.

The intramolecular radical cyclization of the β-halo ether 2-iodoethyl 3-phenylpropynyl ether (**1**) was attempted in several ways (Scheme 1). Under standard radical reaction conditions



cat AIBN/Bu_3SnH/benzene, 80°C, 1h : 96% (*E*/*Z* = 50 / 50)
cat Et_3B/Bu_3SnH/toluene, −78°C, 1h : 94% (*E*/*Z* = 61 / 39)
ATPH/*cat* Et_3B/Bu_3SnH/toluene, −78°C, 1h : 99% (*E*/*Z* = 14 / 86)
ATPH/*cat* Et_3B/$(Me_3Si)_3SiH$/toluene, −78°C, 1h : 99% (*E*/*Z* = <1 / >99)

Scheme 1. Influence of the reaction conditions on the cyclization of **1** to **2**.

(catalytic amount of AIBN, Bu_3SnH, benzene, reflux) the reaction gave rise to an *E*/*Z* mixture of the cyclic ether 3-benzylidenetetrahydrofuran (**2**) in 96% yield (*E*/*Z* = 50:50).[4] The reaction of **1** with Bu_3SnH and a catalytic amount of Et_3B as radical initiator at −78 °C yielded **2** in 94% yield with higher stereoselectivity (*E*/*Z* 61/39).[5] In contrast, initial complexation of **1** with ATPH (2 equiv) in toluene and subsequent addition of Bu_3SnH (1.5 equiv) and catalytic Et_3B (0.2 equiv) afforded **2** quantitatively with a totally opposite preference of olefin geometry (*E*/*Z* = 14/86), indicating that the Lewis acidic receptor ATPH changes the conformation of the transition state in the hydrogen abstraction process (Figure 2).[6] The stereoselectivity was further improved by the use of $(Me_3Si)_3SiH$ instead of Bu_3SnH (Scheme 1).

We also examined intramolecular cyclization of the one-carbon elongated halo ether 3-iodopropyl 3-phenyl-2-propynyl

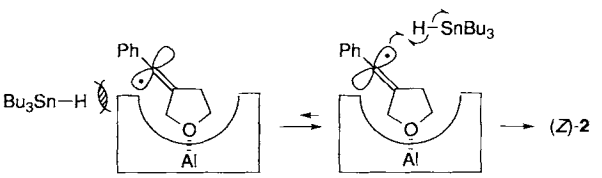
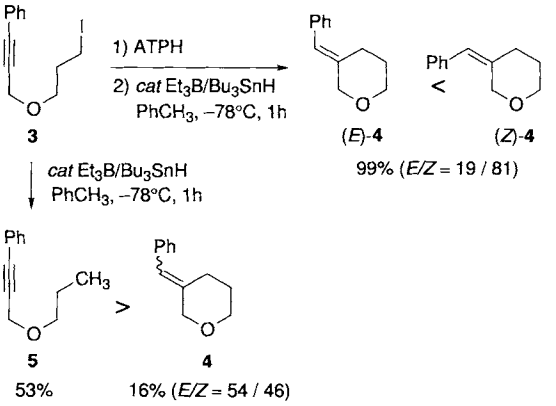


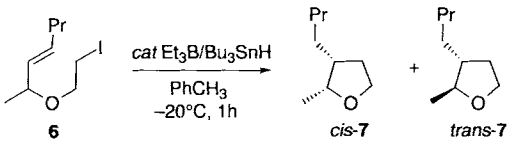
Figure 2. Hydrogen abstraction from Bu_3SnH by a π system in the presence of ATPH.

ether (**3**), which can be categorized as a heptynyl radical cyclization. Surprisingly, radical cyclization of **3** under the influence of ATPH gave the desired cyclic ether **4** as the sole isolable product in quantitative yield, whereas in the absence of ATPH the yield of **4** decreased dramatically (16%) and the reduction product **5**



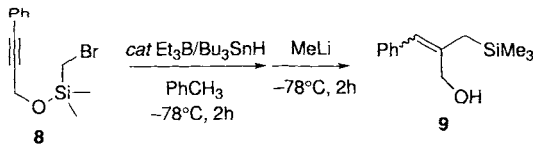
(53% yield) was formed predominantly.[4] Noteworthy is that the *E*/*Z* selectivity in the cyclization products **4** is again opposite in the presence or absence of ATPH, and that nearly perfect *Z* selectivity was also obtained with $(Me_3Si)_3SiH$, despite the significant rate retardation under similar reaction conditions (30% yield of **4**; *E*/*Z* = <1/>99 and 70% recovery of **3**). The origin of the remarkable template effect observed herein could be ascribable to the well-defined reaction environment created at the aluminum coordination center (see Figure 1); this enables appropriate proximity of the initially generated carbon radical to the triple bond in the transition state, so that the cyclization proceeds smoothly and the undesired intermolecular reduction pathway is suppressed.[7]

Encouraged by the results, we turned our attention to the diastereoselective radical cyclization of 2-iodoethyl *trans*-1-methyl-2-hexenyl ether (**6**), which proceeded in toluene at −20 °C with Bu_3SnH and a catalytic amount of Et_3B to furnish tetrahydrofurans **7** in 95% yield with excellent diastereoselectivity (*cis*/*trans* 3/97).[8] In marked contrast, initial treatment of **6**



with ATPH followed by the addition of Bu_3SnH and a catalytic amount of Et_3B at −20 °C resulted in formation of **7** almost quantitatively with totally opposite diastereoselectivity (*cis*/*trans* 92/8). This excellent *cis* selectivity is certainly unattainable under ordinary radical reaction conditions.

Our strategy has been successfully applied to the radical cyclization of [(bromomethyl)dimethylsilyl]propargyl ethers. This process is usually carried out in refluxing benzene with a catalytic amount of AIBN by slow addition of R_3SnH (R = Ph or Bu) with a syringe pump to avoid the undesired side reaction of the relatively stable α-silyl radical.[9] Indeed, an attempt to cyclize **8** in toluene by employing Bu_3SnH and a catalytic amount of Et_3B at −78 °C for 2 h without using a syringe pump and subsequent reaction of MeLi (3 equiv) at −78 °C for 2 h produced allylic alcohol **9** in only 5% yield. Interestingly, the reaction



5% (*E*/*Z* = 28 / 72)

ATPH: 70% (*E*/*Z* = 54 / 46)

with ATPH under otherwise identical reaction conditions gave rise to **9** in 70% yield, again demonstrating the ability of ATPH as an efficient template to facilitate the cyclization step.

Experimental Section

Radical cyclization of **1** in the presence of ATPH: A solution of 2,6-diphenylphenol (740 mg, 3 mmol) in toluene (5 mL) was degassed and a 2M hexane solution of Me_3Al (0.5 mL, 1 mmol) was added at room temperature under argon. The slightly yellow solution was stirred for 30 min. After the solution had been cooled to −78 °C, **1** (143 mg, 0.5 mmol) in toluene (1 mL) was added and then Bu_3SnH (200 μL, 0.75 mmol) and Et_3B (100 μL, 0.1 mmol) were introduced sequentially. The solution was stirred at −78 °C for 1 h and then poured into an aqueous saturated solution of $NaHCO_3$. After extraction with ether, the combined ethereal extracts were dried over Na_2SO_4. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (ether/dichloromethane/hexane 1/2/16 as eluant) gave the cyclic ether **2** (79.6 mg, 0.496 mmol) as a colorless oil (99% yield, *E*/*Z* = 14/86): ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 7.10–7.40 (5H, m, Ph), 6.45 and 6.37 (1H, m, CH=C for *Z* and *E* isomer, respectively), 4.58 and 4.46 (2H, m, C=CCH_2–O for *Z* and *E* isomer, respectively), 4.01 and 3.90 (2H, t, *J* = 6.9 Hz, CH_2–O for *E* and *Z* isomer, respectively), 2.73–2.86 (2H, m, CH_2).

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Conjugate Allylation to α,β-Unsaturated Aldehydes with the New Chemzyme *p*-F-ATPH**

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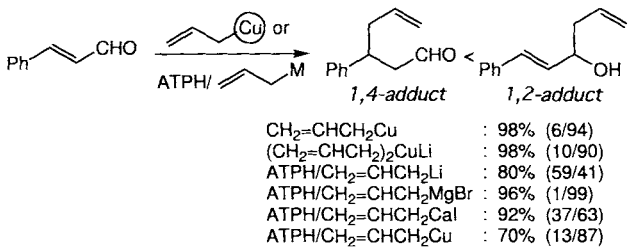
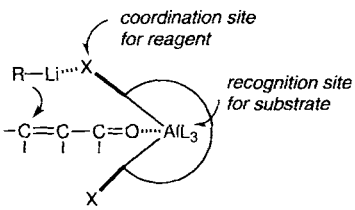
Conjugate allylation to α,β-unsaturated aldehydes is an extremely difficult, hitherto unattainable transformation in organic synthesis, and no effective procedure has yet been developed to a useful level due to the lack of a satisfactory reagent.[1, 2] Even organocopper reagents, which have been employed successfully in the conjugate alkylation to α,β-unsaturated carbonyl compounds,[3] gave very disappointing results for the conjugate allylation. For instance, the reaction of cinnamaldehyde with allylcopper or lithium diallylcuprate gave predominantly the 1,2-adduct *trans*-1-phenyl-1,5-hexadien-3-ol (Scheme 1). Our recently developed new conjugate alkylation procedure with the Lewis acidic receptor aluminum tris(2,6-diphenylphenoxide) (ATPH)[4] was also found to be less effective for the present conjugate allylation, and only the ATPH/allyllithium system gave modest 1,4-selectivity (Scheme 1). This



CH_2=$CHCH_2Cu$	: 98% (6/94)
$(CH_2$=$CHCH_2)_2CuLi$	: 98% (10/90)
ATPH/CH_2=$CHCH_2Li$	: 80% (59/41)
ATPH/CH_2=$CHCH_2MgBr$	: 96% (1/99)
ATPH/CH_2=$CHCH_2CaI$	: 92% (37/63)
ATPH/CH_2=$CHCH_2Cu$	: 70% (13/87)

Scheme 1. Preliminary attempts at the conjugate allylation to cinnamaldehyde.

tendency is contradictory, for example, to our previous observations on the ATPH/BuM system for the conjugate alkylation to cinnamaldehyde, in which the 1,4-selectivity is enhanced by changing nucleophiles (BuM) from BuLi (ratio of 1,4-/1,2-adduct 50/50) to BuMgCl (90/10) and BuCaI (98/2).[4a] After consideration of the wide availability and versatility of organolithium reagents,[5] this lack of selectivity prompted us to design a new Lewis acidic receptor possessing appropriate coordination sites for alkyllithium nucleophiles (Scheme 2).[6] Here we report the realization of such a new system by presenting the first successful conjugate addition of allyllithium reagents to α,β-un-



Scheme 2. Schematic representation of the structural requirements for a Lewis acidic receptor in order for it to be a suitable for the conjugate allylation to α,β-unsaturated aldehydes.

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