**Figure 1.** KANVAS[6] drawing of 10-Sb-3 ADSbO.

Table I. Selected Bond Lengths and Angles in 10-Sb-3 ADSbO

bond lengths, pm		bond angles, deg	
Sb–O	214.4 (3), 216.5 (3)	O–Sb–O	149.6 (1)
Sb–N	206.4 (3)	N–Sb–O	74.7 (1), 74.9 (1)
C–O	132.5 (6), 131.5 (6)	C–O–Sb	115.0 (3), 114.4 (3)
C–C$_{ring}$	137.0 (7), 137.6 (7)	C–N–Sb	117.3 (3), 117.6 (3)
C–N	133.8 (6), 136.2 (6)	C–C–N	116.4 (4), 115.2 (4)
		C–C–O	116.4 (4), 117.9 (4)

Hexafluorobiacetyl reacts with 10-Sb-3 ADSbO to give a 1:1 adduct **1**.[7] The solid-state geometry of **1** was determined by
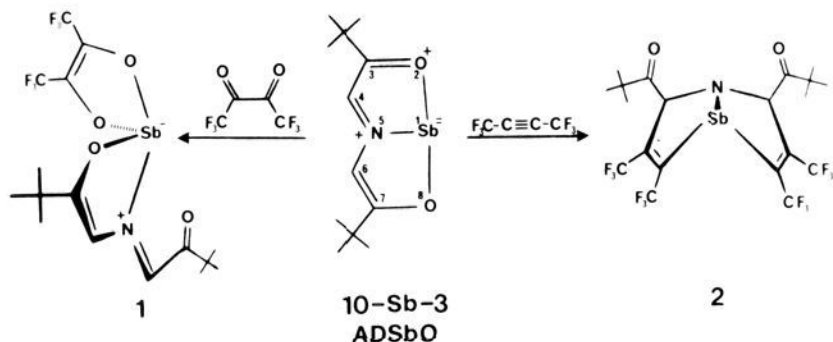
single-crystal X-ray diffraction. The structure can best be described as a four-coordinate stiboranide (10-Sb-4) with one loosely coordinated carbonyl of the diketo amine ligand (Sb–O 302 pm). However, in solution at room temperature the ^{1}H NMR spectrum of **1** reveals only two resonances; δ 1.25 (s, 18 H) and 7.72 (s, 2 H). In addition, the ^{19}F NMR spectrum shows only a singlet, δ −63.9, at ambient temperature. These observations indicate a rapidly equilibrating system.

The reaction of ADSbO with hexafluoro-2-butyne affords **2** in good yields.[8] The structure **2** was determined by multinuclear NMR (^{1}H, ^{13}C, and ^{19}F) and confirmed by an X-ray structure determination. Particularly noteworthy is the large upfield shift in the resonance for carbon 4(6) (δ 79.7) indicating an sp^3 hybridization. At present it is not known whether the addition of the acetylene across the antimony and C-4 centers occurs in a concerted or stepwise fashion. This reaction represents an un-

precedented mode of addition of an acetylene to a hypervalent species.

## Efficient Triple Coupling Reaction To Produce a Self-Adjusting Molecular Cage

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There has recently been great interest in synthetic hydrophobic cage molecules that could be used as binding groups in artificial enzymes and other biomimetic systems.[1] For instance, we have shown[2] that a two-dimensional Koga cyclophane[3] can be covalently linked to pyridoxamine, affording an artificial transaminase with good substrate selectivity. Three-dimensional cages are of potentially greater interest. The geometry of the binding site should be better defined, and substrates that efficiently fill the entire three-dimensional space should be particularly well bound. However, to permit entry into and exit from the cage, it is probably desirable that there be an open conformation that closes up around the substrate after it enters. We wish to describe the synthesis of a cage system that seems to have many of these desirable properties. Furthermore, the synthesis is remarkably efficient: the two half-cages are joined by three links in a one-pot triple-coupling reaction.

For the components of our cage, we selected two 1,1,1-triphenylethane units, to be joined by three diacetylene linkages. The 1,1,1-triphenylethane **1**, prepared from tri-*p*-anisylcarbinol and

1 R = CH$_3$
2 R = CH$_2$C≡CH
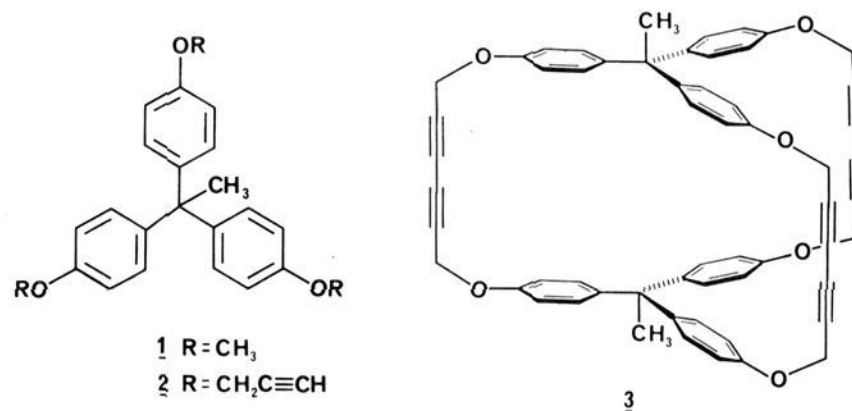
trimethylaluminum,[4] was converted to the tripropargyl ether **2** by O-demethylation with NaSEt in DMF[5] and then alkylation with propargyl bromide in K$_2$CO$_3$/DMF. The sequence gave **2**

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(7) Compound **1** can be crystallized from CH$_2$Cl$_2$ (−35 °C) in good yield (>80%) as a yellow-orange solid, mp 132–134 °C. ^{1}H NMR δ 1.27 (s, 18 H), 7.73 (s, 2 H); ^{13}C{^{1}H} NMR δ 26.6 (CH$_3$), 40.5 (C(CH$_3$)$_3$), 122.7 (CF$_3$) (q, $^1J_{CF}$ = 270 Hz), 123.0 (CH), 133.6 (CCF$_3$) (q, $^2J_{CF}$ = 44.5 Hz), 196.2 (CO); ^{19}F{^{1}H} NMR δ −63.9 (reference CFCl$_3$). All NMR spectra were run in CD$_2$Cl$_2$. Satisfactory analysis were obtained (CHN).

(8) Compound **2** can be crystallized from pentane as a colorless solid (moderate yield), mp 110–112 °C. ^{1}H NMR δ 1.22 (s, 18 H), 6.17 (s, 2 H); ^{13}C{^{1}H} NMR δ 27.1 (CH$_3$), 44.5 (C(CH$_3$)$_3$), 79.7 (CH), 121.8 (CF$_3$, q, $^1J_{CF}$ = 277 Hz), 124.9 (CF$_3$, q, $^1J_{CF}$ = 272 Hz), 145.2 (CCF$_3$, q, $^2J_{CF}$ = 27 Hz), 161.2 (CCF$_3$, q, $^2J_{CF}$ = 39 Hz), 211.6 (CO); ^{19}F{^{1}H} NMR δ −52.2 (q, J_{FF} = 10 Hz), −59.6 (q, J_{FF} = 10 Hz); ^{15}N NMR δ −318.7. All spectra were run in CD$_2$Cl$_2$; ^{19}F and ^{15}N NMR resonances were referenced to CFCl$_3$ and NH$_4^{15}NO_3$, respectively. Satisfactory analysis were obtained (CHN).

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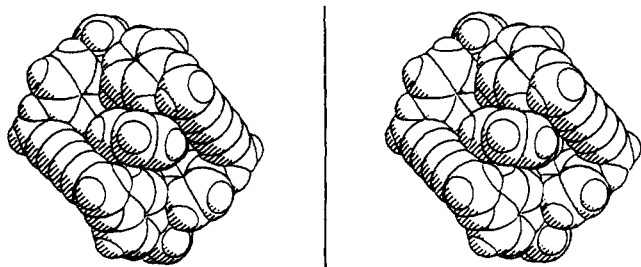(5) Feutrill, G. I.; Mirrington, R. N. *Aust. J. Chem.* **1972**, *25*, 1719.

Figure 1. Stereoscopic view of a computer-generated space-filling drawing, based on the X-ray coordinates of molecule **3**, with an included benzene molecule. van der Waals radii of 1.2 Å for H, 1.85 Å for C, and 1.4 Å for O were used. The benzene is clamped at the edge of **3**. Four other benzenes in lattice positions are not shown; two intrude into the cavity of **3**, while the other two are outside the cage. The X-ray data were collected at −100 °C to avoid crystal decomposition, probably benzene loss. The crystal of **3** obtained was triclinic, $P\bar{1}$, $Z = 2$, $a = 15.1221$ (29) Å, $b = 15.5931$ (30) Å, $c = 15.7000$ (41) Å, $V = 3463$ (1) Å³. A total of 5598 reflections were refined to a final R_w 0.141. Each unit cell contains one left-handed twist molecular complex as shown and one more right-handed mirror image of it.

in 66% yield from tri-*p*-anisylcarbinol.

The dimeric coupling reaction of **2** failed completely under standard and high-dilution coupling conditions (Cu(OAc)₂ in pyridine[1c] and Cu(I)–TMEDA–O₂[6]). However, we have devised a new copper coupling procedure that is extremely mild and efficient and that we have used for related couplings. Treatment of **2** (515 mg, 1.23 mmol) in O₂-free pyridine (1230 mL) with anhydrous CuCl (12.1 g, 123 mmol) and anhydrous CuCl₂ (2.0 g, 15 mmol) for 48 h at 0 °C gave the cage dimer **3**, mp 180 °C dec, in 35% yield after isolation by preparative plate chromatography (2 mm silica, R_f 0.85, CH₂Cl₂ eluent) and crystallization from benzene. The ¹H NMR in CD₂Cl₂ showed an AA′BB′ pattern for the aromatic hydrogens (7.10, 6.88 ppm, $J = 8.5$ Hz), while the propargyl methylenes and the bridgehead methyls were singlets at 4.78 and 2.05 ppm, respectively.

The crystals of **3** from benzene were suitable for an X-ray structure determination. The picture derived from the crystal structure (Figure 1) shows that one benzene molecule is tightly clamped in the cavity and shows no disorder and two others are more loosely held in the cavity, while two others occupy lattice positions around molecule **3**. Furthermore, as Figure 1 shows, the molecule **3** is twisted by rotation of one triphenylethane unit relative to the other. We show the molecule with a left-handed helical twist, but the unit cell actually contains one left- and one right-handed molecule, with interlocking acetylene chains. The "dihedral" twist angles between phenyl rings across the C₃ rotation axis[1d] are 28°, 35°, and 41°. The lack of a crystallographic C₃ axis reflects the presence of the three unsymmetrically included benzenes. *This twisting brings the two triphenylethane units together, clamping the tightly held benzene molecule in place.* In molecular models the untwisted structure, with the triphenylethane units further apart, is more open and more easily admits the benzene molecule.

The further elaboration of this type of cage molecule must involve the attachment of catalytic and water solubilizing groups. It will also be of interest to see whether with bulkier guest molecules inside the cavity the twist angle is smaller, as expected. The highly efficient one-pot synthesis should make it possible to explore all these questions.

Supplementary Material Available: Crystallographic data, ORTEP, atomic coordinates, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and temperature factors, and reflections, of the cage molecule (47 pp). Ordering information is given on any current masthead page.

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A-(Modified B₆)-B-[ω-amino(ethylamino)]-β-cyclodextrin as an Artificial B₆ Enzyme for Chiral Aminotransfer Reaction

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In Kyoto we have studied the regiospecific introduction of functional groups into cyclodextrin for the construction of enzyme mimics;[1] at Columbia pyridoxamine has been attached to cyclodextrin to promote substrate binding, and flexible chains carrying amino groups have been attached to pyridoxamine to promote proton transfers, including stereospecific amino acid synthesis.[2] We now wish to report the coalescence of these research lines: the synthesis of B₆-dependent aminotransferase model **3** (see Chart I): (1) converting certain keto acids into amino acids under mild conditions in water, (2) consisting of two cooperating units, a modified B₆ coenzyme grouping and an ω-amino apoenzyme grouping, (3) exhibiting almost exclusive L-chiral induction from keto-prochiral groupings (see eq 1).
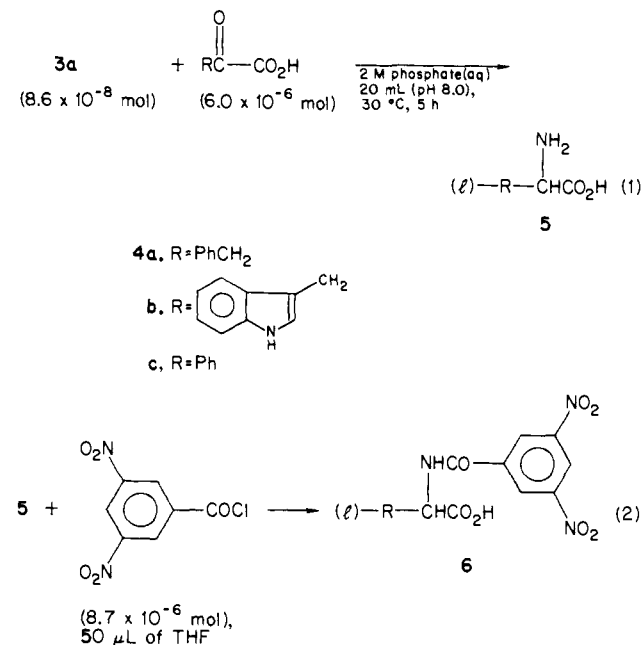
Thus, A,B-capped cyclodextrin **1** was converted to the B₆ model **3** via diiodide **2**[3] by using pyridoxamine thiol[2a,b] under the con-

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