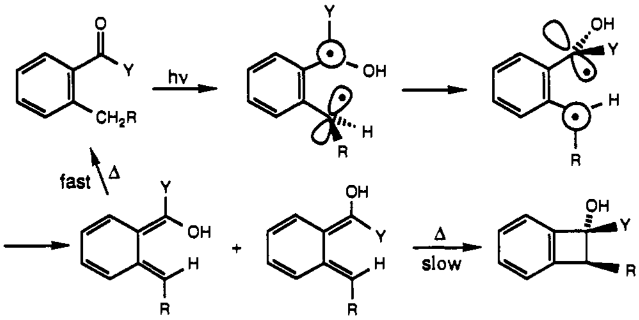
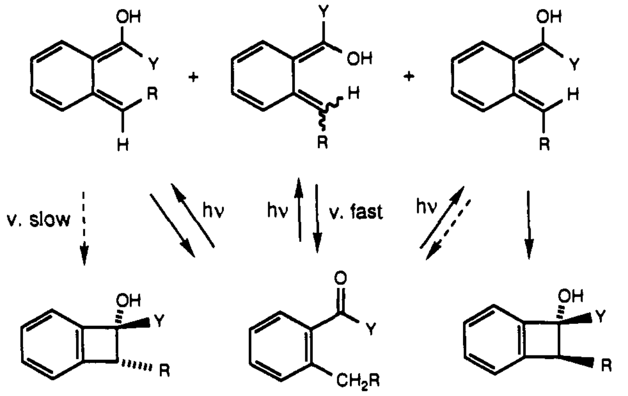
as a few seconds unless trapped with dienophiles or acid.[14,15,18] Since only the *E* enols are trapped by dienophiles,[1] we assume that they also are the ones that rearrange to cyclobutenol.

Matsuura studied the cyclization of 2,4,6-triethylacetophenone and -benzophenone.[13] The former gave only the *E* product, as we have observed for all ketones studied. The latter gave different amounts of *E* and *Z* products depending on solvent, in contrast to our findings. Matsuura suggested that cyclobutenols are formed by stereospecific conrotatory cyclization of the dienols, with product distribution reflecting the distribution of the possible enols. Our results appear to corroborate this mechanistic picture for both *o*-alkyl and 2,6-dialkyl ketones, except that only one of the two possible *E* enol products is formed. Since Matsuura analyzed the cyclobutenols *after* workup, we strongly suspect that some acid-catalyzed *E* → *Z* isomerization took place. We presume that the reaction quenching that we observed in unpurified methanol is caused by typical acid impurities[19] trapping dienols before they can rearrange.

Why is only one *E* enol apparently formed? The overall reaction is known to occur by triplet-state γ-hydrogen abstraction[20] that yields a triplet 1,4-biradical, which coincidentally happens to be the triplet of the enol product.[14,15] We invoke the common assumption that the biradical triplet enol resembles a triplet diene[21] in having one conjugated benzylic radical site and one twisted 90° out of conjugation. The biradicals are quite long-lived[14,15] and apparently can undergo facile coupled rotation about both ring-benzylic carbon bonds; otherwise *Z* and *E* enols could not both be formed.[14,15] The *E* enol that thermally produces the observed cyclobutenols clearly is the less congested *E* enol. We conclude that the biradical assumes a conformation with the α-methyl site conjugated and the hydroxy site twisted before intersystem crossing to ground-state enol occurs. In the benzophenone-derived systems, the second benzene ring can stabilize the hydroxy radical site, as has been observed in other biradicals.[22] In the acetophenone-derived systems, conjugation of the hydroxy radical with the oxygen lone pair may be sufficient to fix the twisting preference. Whatever the exact cause, the observed stereoselectivity of cyclization indicates that the methyl radical site has time to assume its more stable geometry before biradical decay.



An alternative possibility is that the other *E* enol also is formed but closes to cyclobutenol much more slowly, so that it is completely trapped by trace acid. It is well-known that there is a much larger barrier to the interconversion of cyclobutenes and dienes that have terminal alkyl or alkoxy groups pointed in.[23] Therefore the possibility that the observed diastereoselectivity of cyclobutenol formation represents vastly different rates of closure of isomeric *E* enols cannot be dismissed. We are conducting additional experiments to define the generality and mechanistic causes of the diastereoselectivity already observed.



This picture of dienol behavior is in accord with the general belief that steric congestion favors cyclobutenol formation.[1,13] The rate at which the first-formed dienol closes to cyclobutenol presumably is greatly increased by additional buttressing *o*-alkyl groups, since the two benzylic centers cannot both lie coplanar with the benzene ring. The fact that such cyclobutenols are much more stable thermally than those from monoalkyl ketones also demonstrates the effect of steric congestion of dienol energy. The difficulty in detecting transient intermediates in these congested systems[15] also may be due to unusually short-lived enols. The fact that 2,4,6-triethylbenzophenone cyclizes in the same methanol that totally quenches the cyclization of *o*-ethylbenzophenone is further evidence for sterically enhanced reactions of the intermediate dienols.

Acknowledgment. This work was supported by NSF Grant No. CHE-88-15052 and NIH Grant No. GM39821. The NMR machines were funded by NIH Grant No. RR04750 and NSF Grant No. CHE-88-00770.

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Novel Transition-Metal–Main-Group Hybrid Cages: Synthesis and Characterization of $[MoAs_2Se_{10}]^{2-}$ and $[W_2As_2Se_{13}]^{2-}$

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Group 16 elements have a very rich coordination chemistry with transition metals.[1] They form an enormous number of metal complexes of both theoretical and practical interest. Though sulfur has been the most heavily investigated member of the group,[2] we[3] and others[4] have recently extended this work to selenium and

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(1) (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. (c) Fenske, D.; Ohmer, J.; Hachgenie, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277.

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tellurium. A potential limitation to this chemistry, however, is the tendency of chalcogens to be divalent, which hinders their use as cage-building species. The incorporation of one or more trivalent atoms into a molecule greatly increases the possibility of three-dimensional cage and cluster formation.[5] In this communication, we report the extension of our work to include clusters containing group 15 atoms, giving a preliminary report of the synthesis and characterization of two new metal clusters containing novel arsenic selenide cages.

Our recent discovery of a simple and convenient route to the tetraselenometalates makes these suitable starting materials for synthetic investigations.[6] We use them to extend a reaction reported several years ago, exploiting the nucleophilicity of MoS_4^{2-} toward main-group cages.[7] Recently we have shown that WSe_4^{2-} reacts with P_4Se_4 to form the novel compound $[Se{=}W(PSe_4)(PSe_2)]^{2-}$.[8] This paper describes the reaction of WSe_4^{2-} and $MoSe_4^{2-}$ with As_4Se_4 to form two new molecules with unusual cage frameworks, namely, $[W_2As_2Se_{13}]^{2-}$ (I) and $[MoAs_2Se_{10}]^{2-}$ (II).

$$[(C_6H_5)_4P]_2[WSe_4] + \text{excess } As_4Se_4 \xrightarrow{\text{DMF}} [(C_6H_5)_4P]_2[W_2As_2Se_{13}]$$

$$[(n\text{-Bu})_4N]_2[MoSe_4] + \text{excess } As_4Se_4 \rightarrow [(n\text{-Bu})_4N]_2[MoAs_2Se_{10}]$$

The reactions take place readily at room temperature, and the products are isolated in low but usable yield.[9] The mechanism probably involves nucleophilic attack of the tetraselenometalate on the arsenic selenide cage, but beyond that is unknown. It is likely that several compounds are formed in each reaction, but only these two have been isolated so far.

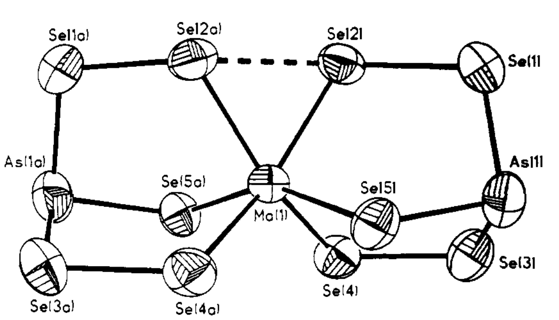


Figure 1. Thermal ellipsoid plot (50% probability) of dianion I, $[W_2As_2Se_{13}]^{2-}$. Some important distances in angstroms: W1–W2 2.903 (2), W1–Se1 2.461 (4), W1–Se2 2.540 (4), W1–Se3 2.534 (4), W1–Se4 2.514 (4), W1–Se5 2.462 (4), W1–Se7 2.465 (5), W2–Se1 2.520 (4), W2–Se2 2.483 (3), W2–Se3 2.497 (5), W2–Se9 2.503 (4), W2–Se10 2.495 (3), W2–Se12 2.468 (5), As1–Se4 2.386 (7), As1–Se6 2.358 (8), As1–Se8 2.340 (6), As2–Se9 2.382 (5), As2–Se11 2.374 (6), As2–Se13 2.416 (7), Se5–Se6 2.390 (6), Se7–Se8 2.409 (6), Se10–Se11 2.375 (6), Se12–Se13 2.389 (6).

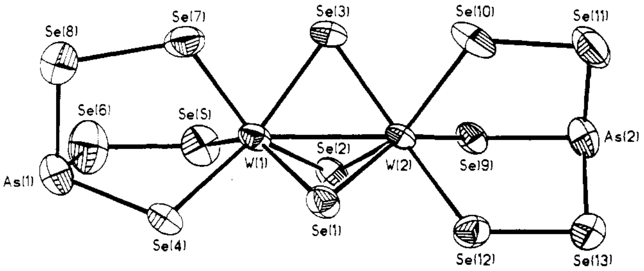
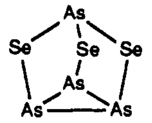
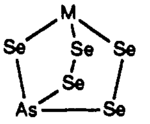


Figure 2. Thermal ellipsoid plot (50% probability) of dianion II, $[MoAs_2Se_{10}]^{2-}$. Some important distances in angstroms: Mo1–Se2 2.500 (3), Mo1–Se4 2.441 (3), Mo1–Se5 2.497 (3), As1–Se1 2.348 (4), As1–Se3 2.343 (5), As1–Se5 2.404 (4), Se1–Se2 2.419 (4), Se3–Se4 2.409 (3), Se2–Se2a 2.702 (4), Se4–Se5a 3.017 (4).

Dianion I, $[W_2As_2Se_{13}]^{2-}$, consists of two tungsten centers each of which is ligated by six selenium atoms in an irregular coordination environment (see Figure 1).[11] Three selenides bridge the metal centers, and each tungsten atom is also ligated by a tridentate $AsSe_5$ group. The overall shape of each fragment is that of a "bird cage" similar to the familiar P_4S_3 or As_4Se_3 shape, with the apical element now a tungsten atom, and two of the basal trivalent atoms replaced by selenium atoms as shown in the drawing. Several examples of mixed main-group cages ligated to transition metals have been reported,[12] but the fragment reported here is new.





Each tridentate fragment can be considered as trianionic $AsSe_5^{3-}$, making the tungsten atoms formally 5+. The W–W distance is 2.903 (2) Å, which is well within accepted bonding distance. Also Gouy measurements show the molecule to be diamagnetic and, thus, valence precise. Accordingly, all of the other distances in the molecule are within normal ranges. The two $AsSe_5^{3-}$ cage fragments are rotated 122.0 (9)° relative to each other.

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(9) All reactions were performed under argon with standard Schlenk techniques, with solvents that were purified in the conventional manner. The As_4Se_4 glass was prepared in a slight modification of the literature method,[10] by combining the elements in proper stoichiometry in a quartz tube and heating to 600 °C for 16 h. Slow cooling to room temperature produced a red glass of the composition As_4Se_4, which was powdered and stored under argon. Product I was prepared by adding 0.80 g (1.30 mmol) of powdered As_4Se_4 to 0.560 g (0.477 mmol) of $[(Ph)_4P]_2[WSe_4]$ in 10 mL of DMF. The red brown solution was stirred for 24 h, after which it was filtered and layered with 10 mL of THF and stored at 4 °C overnight. The resultant white powder was filtered and the solution again layered with 10 mL of THF and stored again in the refrigerator. Dark brown crystals slightly contaminated with an unidentified white powder but suitable for X-ray diffraction were formed in approximately 20% yield. Anal. Calcd for $C_{51}H_{47}NOP_2W_2As_2Se_{13}$: C, 26.68; H, 2.06; Se, 44.71; As, 6.52. Found: C, 25.80; H, 1.81; Se, 50.50; As, 4.53. IR (cm^{-1}; Nujol mull on polyethylene plates): 350 (m), 255 (m), 227 (m), 214 (m), 151 (m). UV–vis: 467.0 nm (molar absorptivity = 3363). Attempts to recrystallize the product from a variety of solvents led to impure powders. Molecule II was prepared by combining 0.50 g (0.812 mmol) of As_4Se_4 with 0.540 g (0.454 mmol) of $[(t\text{-Bu})_4N]_2[MoSe_4]$ in 10 mL of DMF and stirring for 24 h at 25 °C. The resulting purple solution was filtered and the DMF removed under vacuum. The tar was extracted with 10 mL of CH_2Cl_2 and the solution layered with 3 mL of diethyl ether. Storage at 4 °C resulted in formation of black crystals in 10% yield. Anal. Calcd for $C_{32}H_{72}N_2MoAs_2Se_{10}$: C, 25.26; H, 4.74; Se, 51.97; As, 9.87. Found: C, 25.44; H, 4.85; Se, 52.87; As, 10.00. IR (cm^{-1}; Nujol on polyethylene plates): 303 (m), 279 (m), 254 (m), 227 (s), 151 (m). UV–vis only showed a featureless tail into the far UV.

(10) Belin, C. H. E.; Charbonnel, M. M. *Inorg. Chem.* **1982**, *21*, 2504.

(11) Crystal structure data for $[(C_6H_5)_4P]_2[W_2As_2Se_{13}]\cdot(CH_3)_2NCOH$: small dark brown platelet sealed in epoxy, space group triclinic, $P\bar{1}$, a = 11.195 (3) Å, b = 13.282 (5) Å, c = 22.960 (8) Å, α = 94.73 (3)°, β = 91.66 (3)°, γ = 113.41 (2)°, V = 3115 (2) Å^3, Z = 2, D_{calcd} = 2.45 g cm^{-3}, μ(Mo Kα) = 124.31 cm^{-1}, ψ scans (transmission factors 0.63–1.00), T = 21 °C. Measured 6226 reflections (3.5° $\leq 2\theta \leq$ 45°), of which 5828 were unique (R_{int} = 0.031); data were corrected for absorption by using the ψ scan technique; refinement used 3525 reflections with $F_o^2 > 3\sigma(F_o^2)$ and resulted in residuals of R = 0.0603 and R_w = 0.0760 (385 parameters; hydrocarbon atoms isotropic, all other atoms anisotropic).

(12) (a) Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 790. (b) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1985**, *291*. (c) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* **1983**, 903.

Molecule II, $[MoAs_2Se_{10}]^{2-}$, obtained by the same procedure as I, but isolated as the *n*-butyl ammonium salt, contains one molybdenum atom chelated by two $AsSe_5$ groups (see Figure 2).[13] Again, the metal is apical and there are two selenium atoms in the base instead of arsenic atoms. The coordinated selenium atoms of the two cages are rotated 24° away from fully eclipsing each other. In addition, one of the corners of each cage is tipped toward the other. This tipping is quite pronounced and does not appear to be caused by any steric crowding or crystal-packing effects. All of the other distances and angles in the molecule appear to be reasonable and are nearly identical with those in I.[14] Gouy measurements show that this molecule is also diamagnetic.

The close Se(2)···Se(2a) contact is 2.702 (4) Å. This is somewhat long for a true Se–Se bond, which is usually on the order of 2.35 Å. However, the distance is considerably shorter than a van der Waals interaction and has been assigned as bonding in other selenium cage molecules.[15] Alternatively, it may also be caused by a somewhat crowded coordination environment created by the large selenium atoms around a high-valent molybdenum. The distances between the other corner selenium atoms (3.017 (4) Å) can be considered beyond bonding distance. The short Se–Se interaction in II leads to some difficulty in assigning formal oxidation states. If the Se–Se interaction is not considered, there is a formal charge of 4+ on the metal site. However, a bond between the two selenium atoms results in a formal oxidation state of 2+ on the molybdenum. The unusual environment around the bonded selenides does not lead to any substantial differences in the bond lengths to the metal center (2.500 (3) Å versus 2.47 (4) Å).

The reason for the unusual tipping is not clear at this point. To our knowledge there is no precedent for this type of behavior. There have been several examples of hybrid transition-metal–main-group cages reported in the literature, but most could be explained by using classical bonding arguments.[5]

Both I and II are isolated in low yields, but the procedure is simple enough that reasonable amounts of each product can be obtained conveniently. Use of other arsenic selenide sources leads to similar products but no improvement in yield. The molecules are thermally stable if protected from air and are soluble in polar aprotic solvents, but all attempts to recrystallize them do not lead to any cleaner products. Nevertheless, we have demonstrated a reasonable synthetic entry to a novel series of mixed main-group transition-metal cages.

Acknowledgment. We are indebted to the National Science Foundation for support of this work (CHE-8802217).

Registry No. $[(C_yH_5)_4P]_2[W_2As_2Se_{13}]$, 130984-14-4; $[(C_6H_5)_4P]_2[W_2As_2Se_{13}]\cdot(CH_3)_2NCOH$, 130984-15-5; $[(n\text{-}Bu)_4N]_2[MoAs_2Se_{10}]$, 130955-19-0; $[Ph_4P]_2[WSe_4]$, 112988-67-7; $[(n\text{-}Nu)_4N]_2[MoSe_4]$, 130955-20-3; As_4Se_4, 12006-05-2.

Supplementary Material Available: Complete structural data, listing of positional and thermal parameters for all atoms, complete distances and angles, and hydrogen atom coordinates for molecules I and II (12 pages); listing of observed and calculated structure factors for molecules I and II (33 pages). Ordering information is given on any current masthead page.

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(13) Crystal structure data for $[(C_4H_9)_4N]_2[MoAs_2Se_{10}]$: deep purple parallelepiped sealed in epoxy, space group monoclinic, $C2/c$, $a = 18.277$ (9) Å, $b = 15.445$ (8) Å, $c = 17.983$ (7) Å, $\beta = 104.04$ (4)°, $V = 4925$ (4) Å^3, $Z = 4$, $D_{calcd} = 2.05$ g cm^{-3}, μ(Mo Kα) = 89.31 cm^{-1}, ψ scans (transmission factors 0.74–1.00), $T = 21$ °C. Measured 3348 reflections ($3.5° \leq 2\theta \leq 45°$), of which 3227 were unique ($R_{int} = 0.072$); data were corrected for absorption by using the ψ scan technique; refinement used 1898 reflections with $F_o^2 > 2.58\sigma(F_o^2)$ and resulted in residuals of $R = 0.0667$ and $R_w = 0.0752$ (214 parameters; all non-hydrogen atoms anisotropic).

(14) It is difficult to distinguish between arsenic and selenium atoms on the basis of crystallography alone, and it could be postulated that these atoms might be trivalent arsenic. However, this would conflict with elemental analysis and would still provide an electron counting problem, since this distance is too long to be a legitimate As–As single bond.

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Self-Assembly of a Hydrogen-Bonded 2 + 3 Supramolecular Complex[1]

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Received August 13, 1990

We are designing and synthesizing three-dimensional supramolecular assemblies based on the pattern of hydrogen bonds present in the 1:1 complex between cyanuric acid and melamine (CA·M). We have previously shown that $hubM_3$ (Scheme I) organizes three melamine units into a geometry compatible with the CA·M lattice and forms a 1:3 complex with neohexyl cyanurate.[2] Here we report that $hubM_3$ reacts with the bis(cyanuric acid) $R(CA)_2$ (Scheme I) in $CHCl_3$ and forms a 2:3 complex, $(hubM_3)_2(R(CA)_2)_3$, that incorporates two layers of the CA·M lattice into a well-defined three-dimensional structure.[3,4]

We monitored the titration of $hubM_3$ in $CDCl_3$ with aliquots of $R(CA)_2$ by ^1H NMR spectroscopy (Figure 1). The spectrum of uncomplexed $hubM_3$ (bottom trace) has resonances that are broadened by self-association and restricted rotation around the amide and RNH–triazine bonds. At intermediate points in the titration, the spectrum shows resonances for $(hubM_3)_2(R(CA)_2)_3$ against a background of uncomplexed $hubM_3$. The complex appears to be predominantly a single conformation, and exchange between $(hubM_3)_2(R(CA)_2)_3$ and uncomplexed $hubM_3$ in solution is slow on the NMR time scale. Beyond the 2:3 stoichiometry, there is no further change in the spectrum. The $hubM_3$ units in $(hubM_3)_2(R(CA)_2)_3$ are chiral. From the ^1H NMR spectrum, we cannot tell whether the complex exists as a racemic mixture of *R,R* and *S,S* species or as a meso compound, *R,S*. The simplicity of the spectrum suggests, however, that only racemic or meso complexes are present, and not a mixture of the two.

Two features of Figure 1 support the assigned structure for $(hubM_3)_2(R(CA)_2)_3$: First, several equivalent protons of $hubM_3$ (g, g′; q, q′; and r, r′) and $R(CA)_2$ (w, w′ and x, x′) are diastereotopic in $(hubM_3)_2(R(CA)_2)_3$ and thus appear as separate resonances. Second, the two sets of imide NH protons (y, y′) of $R(CA)_2$ are in different hydrogen-bonding environments and thus appear as separate resonances in the complex, even though they are equivalent by symmetry in uncomplexed $R(CA)_2$. NOE studies also support our proposed structure. We observed several positive intermolecular NOEs between $hubM_3$ and $R(CA)_2$ that are consistent with a CPK model of the $(hubM_3)_2(R(CA)_2)_3$ complex (Scheme I). The NOEs between the imide NH protons (y, y′) of $R(CA)_2$ and the melamine NH protons (n, o, o′, p) of $hubM_3$ confirm the 3-fold nature of the hydrogen-bonded network.

Two other analytical methods support the 2:3 stoichiometry of $(hubM_3)_2(R(CA)_2)_3$. Vapor pressure osmometry (VPO) of the complex indicated MW ≈ 5300 (calcd for $(hubM_3)_2(R(CA)_2)_3$: 5519) over the concentration range 2–16 mM in $CHCl_3$ at 37 °C with a sucrose octaacetate standard.[5] Titration of $hubM_3$ (0.1 mM in CH_2Cl_2) with $R(CA)_2$ monitored by UV spectroscopy also indicated a 2:3 complex.[6]

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(1) The National Science Foundation supported this work (Grants CHE-88-12709 to G.M.W. and DMR-89-20490 to the Harvard University Materials Research Laboratory).

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(3) For other supramolecular assemblies, see: Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245–255 and references therein. Bryant, J.; Ericson, J.; Cram, D. *J. Am. Chem. Soc.* **1990**, *112*, 1255–1256. Etter, M. *Acc. Chem. Res.* **1990**, *23*, 120–126. Manka, J. S.; Lawrence, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 2440–2442. Ashton, P.; Goodnow, T.; Kaifer, A.; Reddington, M.; Slawin, A.; Spencer, N.; Stoddart, J.; Vincent, C.; Williams, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396–1399.

(4) All new compounds gave satisfactory ^1H NMR (500 MHz), ^{13}C NMR (125 MHz), and elemental analyses.

(5) The molecular weight of the complex estimated by using other standards was as follows ($MW_{complex}$, standard $MW_{standard}$): 5890, perbenzoyl β-cyclodextrin 3321; 5390, polystyrene 5050 (polydispersity = 1.05); 4430, *N,N′*-bis(*tert*-butyloxycarbonyl)gramicidin S 1342. We suggest that the gramicidin S derivative was associated in solution and, hence, unsuitable as a standard.

0002-7863/91/1513-712$02.50/0