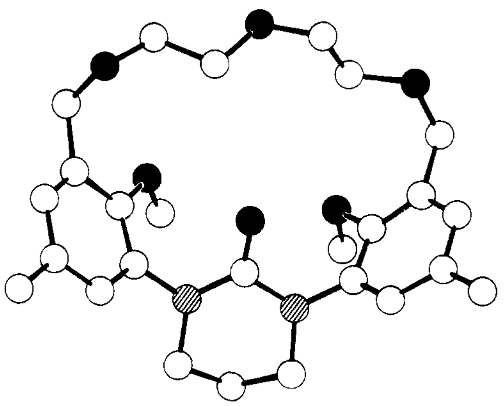
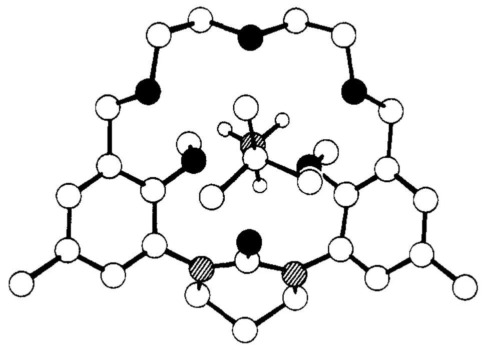


7, U(AD)$_2$D



8, U(AD)$_2$D·t-BuNH$_3^+$

(1), the CH$_3$ groups are found at δ 1.43. In models of this complex, the methyls are far removed from all aryl groups since the guest complexes from the face opposite to that of the hosts containing the urea unit.[3]

The free energies were determined for hemispherands **1–6** binding the alkali metal, ammonium, and alkylammonium picrates in CDCl$_3$ saturated with D$_2$O.[5] The $-\Delta G°$ values were determined by extracting 0.05 or 0.001 M salt solutions in D$_2$O with solutions of hosts in CDCl$_3$ at 25 °C.[2b]

The profiles in Chart I of the six hosts generally correlate their structures and complexing properties to provide the following conclusions. (1) As a class the hemispherands are better binders by several kcal mol^{-1} than 2,3-naphtho-18-crown-6, whose $-\Delta G°$ values (kcal mol^{-1}) for the picrate salts are as follows: Li$^+$, 5.9; Na$^+$, 8.3; K$^+$, 10.8; Rb$^+$, 9.6; Cs$^+$, 8.3; NH$_4^+$, 9.5; CH$_3$NH$_3^+$, 7.5; t-BuNH$_3^+$, 6.9.[4] The C$_6$H$_5$OCH$_3$ unit is intrinsically poorer as a ligand than the CH$_2$OCH$_2$ unit, but this property is more than compensated for by the self-organization for complexation of three adjacent anisyl groups. (2) The binding profiles of the three hemispherands containing three anisyl units resemble those of their corresponding analogues in which a cyclic urea unit is substituted for the central anisyl unit. This generalization applies to all guests except CH$_3$NH$_3^+$ and t-BuNH$_3^+$. As models suggested and crystal structure comparisons bore out, two attached anisyl groups organize the cyclic urea unit for binding in a way similar to the way they organize a central anisyl group. (3) Rigidification of the hosts and augmentation of the number of ligating sites by incorporation of the extra bridge in A′(A)(D)(DDD)A′ (**3**) and A′(U)(D)(DDD)A′ (**6**) generally improve binding, particularly toward K$^+$ and t-BuNH$_3^+$. These two hosts slightly favor complexation of K$^+$ over Na$^+$, but the four more flexible hosts favor Na$^+$ over K$^+$ by varying degrees. (4) Substitution of a pyridine for a CH$_2$OCH$_2$ unit[5] reduces complexation toward all ions except for the case of U(AD)$_2$P (**5**) binding CH$_3$NH$_3^+$ and t-BuNH$_3^+$. It also enhances the favored binding of Na$^+$ over that of K$^+$. (5) The hosts containing the urea units are particularly good complexers of CH$_3$NH$_3^+$ and t-BuNH$_3^+$, providing values that range from 8.5 to 9.5 kcal mol^{-1}.

This study demonstrates that the hemispherands are a family of hosts with binding properties in between those of the chorands and the spherands.[2] Employment of an organized urea ligating site greatly expands the number of structural options available to the designer of host–guest complexes.

Supplementary Material Available: Preparation of hemispherands **2–6** (3 pages). Ordering information is given on any current masthead page.

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[5] Slightly different and more accurate values are given here for **1** than were reported previously[1] and resulted from using the lower concentration of aqueous picrate salt concentrations when the $-\Delta G°$ values exceeded 10 kcal mol^{-1}.

Spherand Hosts Containing Cyclic Urea Units[1]

Donald J. Cram,* Ira B. Dicker, Carolyn B. Knobler, and Kenneth N. Trueblood

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024

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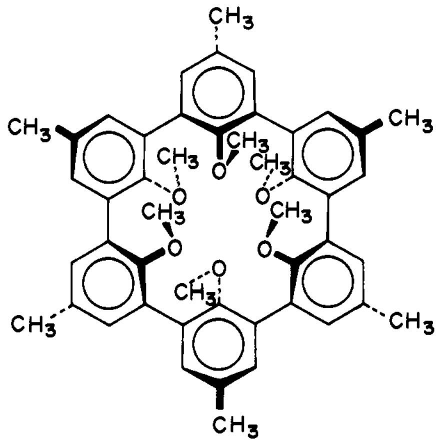
Earlier work demonstrated that the spherands, of which **1** is



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the prototype, are highly selective and powerful binders of Na$^+$ and Li$^+$.[2] Since anisyl units are intrinsically poor ligands for complexing ions, the enforced, ideal organization of the oxygens in **1** prior to complexation is responsible for the host systems' unique complexing properties.[3] The oxygens of urea units should be generally superior ligands to those of anisyl oxygens.[4] Examination of molecular models (CPK) of six-membered cyclic urea units indicated they might be substituted for some of the anisyl units of **1** to produce hosts whose oxygens are also organized during synthesis rather than during complexation. This paper reports the syntheses, binding properties, and structures of new spherand hosts **2–5** (Chart I), which combine cyclic urea and anisyl binding units with appropriate hydrocarbon spacer units (CH$_2$ or o-CH$_2$C$_6$H$_4$CH$_2$). Sequences of capital letters will specify the formulas, in which A stands for 2,6-disubstituted anisyl, A′ for

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[1] We thank the National Science Foundation for Grant NSF CHE 81-09532 and Grant NSF CHE 80-22525 and the Public Health Service for Grant GM 12640, which supported this research.

[2] Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Lein, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 6752–6754.

[3] (a) Trueblood, K. N.; Knobler, C. B.; Maverick, E.; Helgeson, R. C.; Brown, S. B.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 5594–5596. (b) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *Ibid.* **1981**, *103*, 6228–6232. (c) Lein, G. M.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 301–304.

[4] (a) Mitsky, J.; Jaris, L.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 3442–3445; (b) Atkins, H. W.; Gilkerson, W. R. *Ibid.* **1973**, *95*, 8551–8559.

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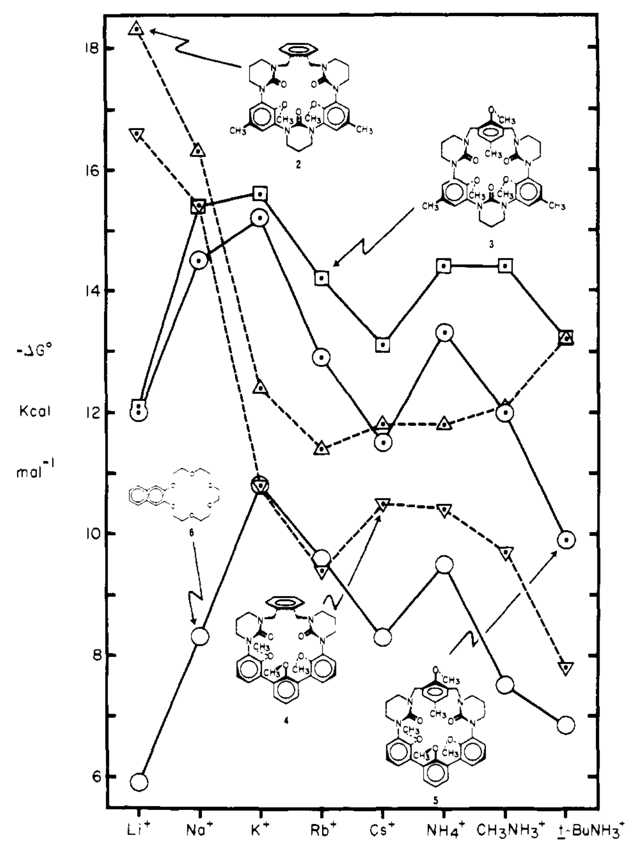
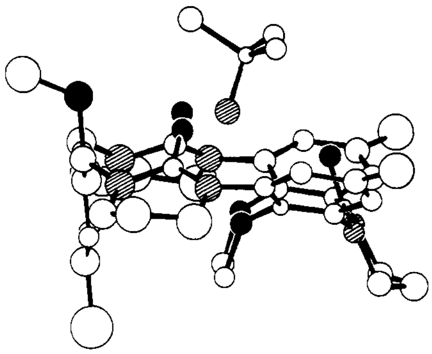
Chart I



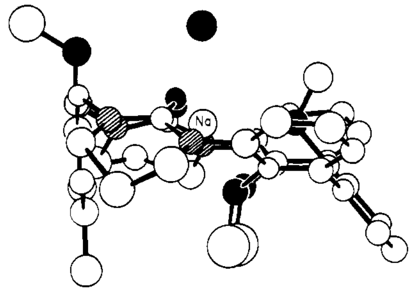
its p-methyl derivative, U for the N,N-disubstituted cyclic urea, and B for o-phenylene units. The new hosts' binding properties are compared with those of spherand **1**[3c] and of 2,3-naphtho-18-crown-6 (**6**).[5]

Synthons U(A′UH)$_2$ and A(AUH)$_2$ were prepared in 22% and 54% yields, respectively, from available starting materials (see supplementary material). Base-catalyzed cyclizations went in the following yields: U(A′UH)$_2$ and (BrCH$_2$)$_2$B gave U(A′UCH$_2$)$_2$B (**2**, 7%); U(A′UH)$_2$ and (BrCH$_2$)$_2$A′ gave U(A′UCH$_2$)$_2$A′ (**3**, 11%); A(AUH)$_2$ and (BrCH$_2$)$_2$B gave A(AUCH$_2$)$_2$B (**4**, 3.1%); A(AUH)$_2$ and (BrCH$_2$)$_2$A′ gave A(AUCH$_2$)$_2$A′ (**5**, 32%). Hosts **2**–**5** were isolated and purified through their (CH$_3$)$_3$CNH$_3$ClO$_4$ or NaBr complexes. Decomplexations were driven by crystallizations of the free hosts by evaporation of methanol from hot aqueous methanolic solutions. All new compounds gave C, H, and N analyses within 0.30% of theory and ^{1}H NMR and mass spectra compatible with their assigned structures.

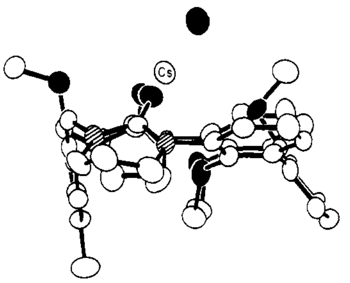
Preliminary crystal structures of complexes U-(A′UCH$_2$)$_2$A′·(CH$_3$)$_3$CNH$_3$ClO$_4$ (**7**), A(AUCH$_2$)$_2$A′·NaBr·H$_2$O (**8**), and A(AUCH$_2$)$_2$A′·CsClO$_4$·H$_2$O (**9**) showed that the conformations of the complexed hosts are nearly guest independent. All oxygens converge on the occupied cavity, and the attached methyl groups diverge from the cavity. Each oxygen of the UA′UA′U or UAAAU assembly is anti to its flanking oxygens. The oxygen of the additional CH$_2$A′CH$_2$ unit is syn to its flanking oxygens. The plane of the CH$_2$A′CH$_2$ unit is tilted away from the binding face at an angle greater than 90° to the best plane defined by the atoms connecting the six units. This arrangement brings the aryl methyl portion of the CH$_2$A′CH$_2$ unit into close contact with the methoxymethyl groups of the two nearest A and A′ groups to form a closed surface of carbon–hydrogen or carbon–carbon bonds on one face of the macroring. In **7d** the (CH$_3$)$_3$CNH$_3^+$ is hydrogen bonded in tripod fashion to three upturned urea oxygens to provide a perching complex. In **8** the Na$^+$ forms a nesting complex, with the electron pairs of the five oxygens of the UAAAU groups lining a nest capped by the water ligand. In **9** the Cs$^+$ is too large to *nest* in the cavity. Instead, it *perches* on the four syn oxygens but does not contact the more distant two anti (methoxyl) oxygens. It is also ligated by a water molecule and by a carbonyl of a neighboring complex. Thus two hosts appear to be held together by two Cs$^+$ guests and probably by the hydrogen bonds of two water molecules to form a crystallographic dimeric complex.



7, U(A′UCH$_2$)$_2$A′·(CH$_3$)$_3$CNH$_3^+$



8, A(AUCH$_2$)$_2$A′·Na$^+$·H$_2$O



9, A(AUCH$_2$)$_2$A′·Cs$^+$·H$_2$O

Chart I correlates the structures of hosts **2**–**6** with their binding free energies of the alkali metal, ammonium, and alkylammonium picrates in CDCl$_3$ saturated with D$_2$O. The $-\Delta G°$ values were determined by extracting 0.001 M salt solutions in D$_2$O with solutions of hosts in CDCl$_3$ at 25 °C.[3c] Hosts **2** and **4** resemble each other in ring size (19-membered), in shapes, and in binding patterns (except toward (CH$_3$)$_3$CNH$_3^+$). The host with three urea oxygens (**2**) always binds 1 or 2 kcal mol^{-1} better than does the host containing two urea oxygens (**4**). Hosts **2** and **4** bind the smaller ions (Li$^+$ and Na$^+$) 4–5 kcal mol^{-1} better than the larger ions. The maximum structural recognition in complexation of the eight guests by any of the four hosts is $\sim$9 kcal mol^{-1} and involves A(AUCH$_2$)$_2$B (**4**) binding Li$^+$ better than (CH$_3$)$_3$CNH$_3^+$. Molecular model (CPK) examination of **2** and **4** shows they contain enforced cavities lined with unshared electron pairs of five oxygens that nicely contact spheres the diameters of Li$^+$ and Na$^+$. When larger ions are inserted, strain is induced and the π bonds of the urea units line the enlarged nests. Likely, the smaller ions form nesting complexes and the larger ions perching complexes, the former being the more stable. The phenylene of the o-CH$_2$C$_6$H$_4$CH$_2$ group in models of **2** and **4** must occupy a plane nearly perpendicular to the best plane of the oxygens. This phenyl can orient either syn or anti to the CH$_3$O groups. In the ^{1}H NMR

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[5] Helgeson, R. C.; Weisman, G. R.; Toner, J. L.; Tarnowski, T. L.; Chao, Y.; Mayer, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 4928–4941.

spectra of **2** and **4**, the CH_2 hydrogens provide two very broad singlets and the CH_3O hydrogens on the sides of the mirror plane one broad singlet. Apparently at ambient temperature both conformations are present and are not equilibrating rapidly on the ^1H NMR time scale. When either host is complexed with Na^+ or $(CH_3)_3CNH_3^+$, the CH_2 hydrogens produce a normal AB quartet and the CH_3O hydrogens give sharp singlets. When complexed, single conformations appear to be produced, whose structures await elucidation.

Spherands U(A′UCH$_2$)$_2$A′ (**3**) and A(AUCH$_2$)$_2$A′ (**5**) also resemble one another in ring sizes (20-membered), in shapes, and in binding patterns. All of the $-\Delta G°$ values for **3** and **5** binding any of the eight guests lie between 11.8 and 15.8 kcal mol^{-1} except for **5** binding $(CH_3)_3CNH_3^+$ (9.9 kcal mol^{-1}). A molecular model of **3** is far more conformationally mobile than those of **2** and **4**. The CH_2 or CH_3O groups of **3** can rotate through the ring, and the cavity can be intramolecularly filled by an inward-turned CH_3 group. At ambient temperature in $CDCl_3$, the ^1H NMR spectrum of **3** exhibits four different AB quartets for the NCH_2Ar hydrogens and five different CH_3Ar hydrogen signals. Shaking a solution of **3** with aqueous solutions of salts of either Na^+ or $(CH_3)_3CNH_3^+$ instantaneously produces a spectrum of a single complex. A molecular model of **5** indicates the methyl groups of the AAA unit can occupy only positions that diverge from the cavity, which is lined with the unshared electron pairs of five oxygens and the π system of the A′ unit. Experimentally, **5** and its complexes exhibit ^1H NMR spectra consistent with their existing as single conformers of the host structure drawn. Thus the fourth methoxyl in **5** forces more organization on the system than does the third urea oxygen in **3**. These data suggest that some burden of conformational reorganization is placed on the guest during complexation of **3**, a smaller burden during complexation of **2** or **4**, and very little during complexation of **5**.

The binding patterns of spherands **3** and **5** resemble those of chorand **6**, except that the spherands are the better complexers (6 to 3 kcal mol^{-1}), a fact attributed to the spherands' semienforced organization for binding prior to complexation and to the superior binding properties of urea units. Uncomplexed chorands do not possess cavities.[6] The binding patterns of **2** and **4** resemble that of A′(A′A′)$_2$A′ (**1**), which binds Li^+ with >23 and Na^+ with 19 kcal mol^{-1} [3c] but does not complex the other ions detectably.[3c] A dramatic difference between **1** and **2–5** is that the former in $CHCl_3$ solution extracts guests from water very slowly[3c,6] and the latter very rapidly. This difference is explained by the ready accessibility of the urea oxygens to potential guest cations prior to their shedding their water ligands. To ligate the oxygens of **1**, guest cations must pass through a lipophilic sleeve in which there is no room for water ligands.

These studies introduce a new family of strongly binding and ion differentiating spherands designed by application of the *principle of preorganization* to molecular model examination.

Registry No. 2, 83604-21-1; **2**·$(CH_3)_3CNH_3$·picrate, 83604-22-2; **2**·NaBr, 83615-34-3; **3**, 83604-23-3; **4**, 83604-24-4; **5**, 83604-25-5; **5**·NaBr, 83604-26-6; **6**, 17454-52-3; **7**, 83615-35-4; **8**, 83615-36-5; **9**, 83615-38-7; O_2N-A′-NO_2, 29455-11-6; O_2N-A′-NH_2, 83604-27-7; O_N-A′-NHCONH-A′-NO_2, 83604-28-8; O_2NA′-U-A′NO_2, 83604-29-9; H_2NA′-U-A′NH_2, 83604-30-2; U(A′NHCONHCH$_2$CH$_2$Cl)$_2$, 83604-31-3; HU-A′-U-A′-UH, 83604-32-4; HU-A′-U-A′-UH·2Na, 83604-33-5; BrCH$_2$-A′-CH$_2$Br, 60232-82-8; HA-A-AH, 83604-34-6; HO$_2$CA-A-ACO$_2$H, 83604-35-7; N$_3$OCA-A-ACON$_3$, 83604-36-8; OCNA-A-ANCO, 83604-37-9; A(ANHCONHCH$_2$CH$_2$CH$_2$Br)$_2$, 83604-38-0; HU-A-A-A-UH, 83604-39-1; HU-A-A-A-UH·2Na, 83615-39-8; BrCH$_2$-B-CH$_2$Br, 91-13-4; $COCl_2$, 75-44-5; $Br(CH_2)_3Br$, 109-64-8; $Cl(CH_2)_3NCO$, 13010-19-0; $Br(CH_2)_3NH_3Br$, 5003-71-4.

Supplementary Material Available: Experimental procedures are outlined, physical properties are given for precursors of **2–5** and for **3** and **4**, and detailed procedures are given for preparing **2** and **5** (4 pages). Ordering information is given on any current masthead page.

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(6) Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43–106.

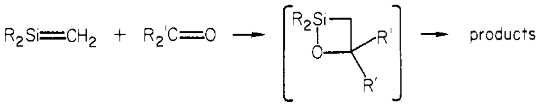
1,2-Silaoxetane. Isolation and Characterization in the Reaction of Silaethylene with Ketone

Wataru Ando,* Akira Sekiguchi, and Takashi Sato

Department of Chemistry, The University of Tsukuba
Niihari-gun, Ibaraki 305, Japan

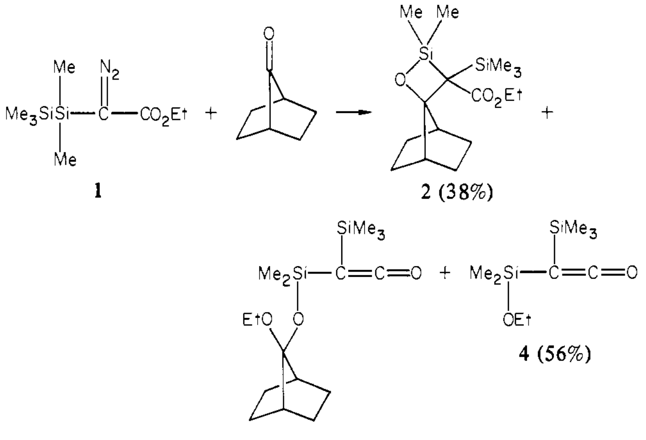
Received May 10, 1982

Much effort has been devoted to the isolation of 1,2-silaoxetanes because they have been thought to explain the products of silaethylenes and carbonyl compounds.[1] In spite of the recent activity in this area, such labile molecules have been postulated only as reaction intermediates.



We now report here the first isolation of a stable 1,2-silaoxetane and demonstrate its unique reaction feature.

When ethyl pentamethyldisilanyldiazoacetate (**1**; 242 mg, 0.99 mmol) was heated in 7-norbornone (660 mg, 6.0 mmol) at 185 °C for 25 min under an atmosphere of nitrogen, 1,2-silaoxetane **2** was obtained along with the ketene **3** and **4**.[2] Surprisingly, the silaoxetane **2** was directly collected from the reaction mixture by preparative gas chromatography, but it was contaminated with a small amount of ketene **3**. The structure of the silaoxetane **2** was determined by the following spectra data: **1H** NMR (CCl_4) δ 0.04 (s, 9 H, SiMe$_3$), 0.17 (s, 6 H, SiMe$_2$), 0.94–1.54 (m, 4 H, norbornyl CH), 1.27 (t, 3 H, OCCH$_3$), 1.54–2.23 (m, 6 H, norbornyl CH), 3.98 (q, 2 H, OCH$_2$); ^{13}C NMR ($CDCl_3$) δ 0.9



1 **2** (38%) **4** (56%) **3** (5%)

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(1) (a) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18. (b) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (c) Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615. (d) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (e) Coleman, B.; Jones, M., Jr. *Rev. Chem. Intermed.* **1981**, *4*, 297. (f) Ando, W.; Sekiguchi, A.; Migita, T. *J. Am. Chem. Soc.* **1975**, *97*, 7159. (g) Ando, W.; Sekiguchi, A. *J. Organomet. Chem.* **1977**, *133*, 219.

(2) All new compounds showed NMR and IR spectra as well as either high-resolution mass spectra or satisfactory elemental analyses consistent with the structures assigned. Some representative data are as follows. (a) **3**: NMR (CCl_4) δ 0.21 (s, 9 H, SiMe$_3$), 0.32 (s, 6 H, SiMe$_2$), 0.95–1.51 (m, 4 H, norbornyl CH), 1.16 (t, 3 H, OCCH$_3$), 1.51–2.00 (m, 6 H, norbornyl CH), 3.58 (q, 2 H, OCH$_2$); IR (NaCl) 2095 (C═C═O), 1070 cm^{-1} (Si–O–C); mass spectrum, M^+ 326.1737 (calcd 326.1732). (b) **4**: NMR (CCl_4) δ 0.22 (s, 9 H, SiMe$_3$), 0.26 (s, 6 H, SiMe$_2$), 1.17 (t, 3 H, OCCH$_3$), 3.68 (q, 2 H, OCH$_2$); IR (NaCl) 2080 (C═C═O), 1080 cm^{-1} (Si–O–C). Anal. Calcd for $C_9H_{20}O_2Si_2$: C, 49.94; H, 9.31. Found: C, 49.64; H, 9.25. (c) **8**: NMR (CCl_4) δ −0.10 (s, 6 H, SiMe$_2$), 0.06 (s, 9 H, SiMe$_3$), 0.92 (t, 3 H, OCCH$_3$), 3.90 (q, 2 H, OCH$_2$), 7.25 (br s, 5 H, Ar H), 7.31 (br s, 5 H, Ar H); IR (NaCl) 1705 (C═O), 1050 cm^{-1} (Si–O–Si); mass spectrum, M^+ 398.1766 (calcd 398.1732). (d) **10a**: NMR (CCl_4) δ 0.10 (s, 9 H, SiMe$_3$), 0.23 (s, 3 H, SiMe), 0.26 (s, 3 H, SiMe), 1.21 (t, 3 H, OCCH$_3$), 1.38–1.75 (m, 4 H, CH$_2$), 1.76 (s, 1 H, SiCHSi), 1.80–2.23 (m, 4 H, C═C—CH$_2$), 4.02 (q, 2 H, OCH$_2$), 4.63–4.90 (m, 1 H, C═CH); IR (NaCl) 1705 (C═O), 1670 cm^{-1} (C═C); mass spectrum, M^+ 314.1736 (calcd 314.1732).

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