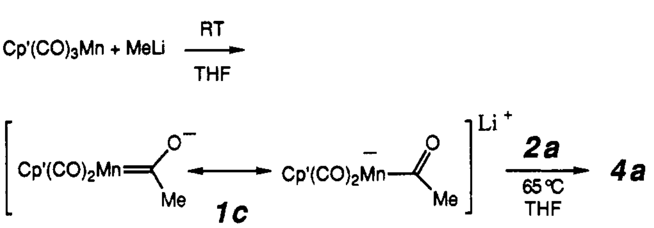
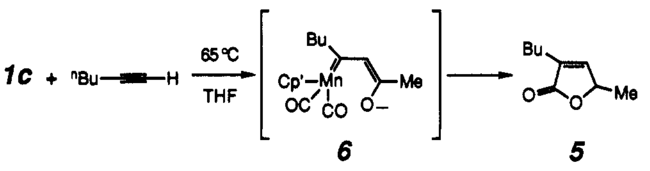
noteworthy that there was no evidence for competing formation of cyclobutanone, furan, or metathesis products, which were observed in reactions of the corresponding chromium complex $(CO)_5Cr{=}C(OMe)Me$ with **2a–d**.[3a] In this regard the manganese complex reacted similarly to (1-pyrrolidinoethylidene)pentacarbonylchromium, which also gave no products from carbonyl insertion and ketene formation with these enynes.[3b] The phenyl-substituted complex **1b**[1] also smoothly reacted[4a] with the enyne **2a** to give the bicyclic vinylcyclopropane **3e**, which underwent hydrolysis to the corresponding ketone **4e**.

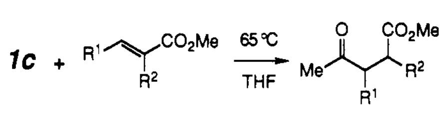
(b) The addition of simple carbanions to chromium hexacarbonyl results in an acyl metalate that may be considered a carbene complex with a particularly rich donor atom. We have recently shown that these anionic species themselves will enter into useful and efficient reactions with the enynes **2** and terminal alkynes.[3c] Reaction of $Cp'(CO)_3Mn$ with methyllithium to generate the manganate species **1c** and subsequent in situ reactions[4b] with the enyne diester **2a** also resulted in the formation of the cyclopropyl ketone **4a** in even higher yield (83%) than with the neutral analogue **1a**.



(c) The in situ reaction[4b] of the manganate anion **1c** with 1-hexyne resulted in the formation of butenolide **5** in 67% yield. This transformation is entirely analogous to that observed for the acylpentacarbonylchromate species, and we have previously proposed mechanistic pathways analogous to that by which the presumed vinylogous acylmetalate **6** might lead to **5**.[3c]



(d) The reaction[4b] of the manganate **1c** with the α,β-unsaturated esters **7a–c** resulted in the formation of the γ-keto esters **8a–c**, which are formally products of the addition of an acetyl anion in a Michael fashion to the enoates. This event is reminiscent of reactions of the



	R^1	R^2	yield, %	
7a	H	H	79	**8a**
7b	Me	H	68	**8b**
7c	H	Me	61	**8c**

nickel acylate species generated by addition of alkyllithium species to nickel tetracarbonyl.[5] We have observed this and related reaction types with the corresponding acylchromate species as well.[6]

The use of the neutral manganese carbene complexes **1a** and **1b** allows for a more economical[7] and environmentally acceptable access to some of the typical reaction pathways that have been previously demonstrated for the analogous chromium carbene complexes. In addition the chemistry of the anionic manganate **1c** further demonstrates the utility of these in situ generated "carbenes". The operational ease and convenience associated with this one-flask procedure, which avoids the necessity of isolating or handling the metal carbene complex, makes the use of these anions quite attractive and leads us to strongly recommend the use of this in situ methodology.

Acknowledgment. This investigation was supported by Grant GM-38854 awarded by the DHHS and by an award from the Alfred P. Sloan Foundation.

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(7) $Cp'Mn(CO)_3$ is currently nearly 1 order of magnitude less expensive (Johnson Matthey/Alfa) than $Cr(CO)_6$ on the basis of the molar equivalents of utilized CO ligands.

Synthesis, Structure, and Reactivity of an Organogermanium Lewis Acid

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Summary: The 8-Ge-4 spirogermanacycle **3** was prepared from hexafluorocumyl alcohol and its structure determined by X-ray crystallography. The distortion of the internal O–Ge–C angles leads to an enhanced Lewis acidity, which was illustrated by the promotion of pericyclic reactions involving activation of aldehyde carbonyl groups. Four 10-Ge-5 anionic complexes were prepared, and X-ray crystallographic analysis of the *n*-butyl adduct **4b** showed a trigonal-bipyramidal geometry.

The development and application of chiral Lewis acids as catalysts and promoters of organic reactions have dramatically increased in recent years. The majority of these highly specialized reagents is based on a limited set of central elements from the main-group (B,[1] Al,[2] Sn[3]), transition (Ti,[4] Zn,[5] Ru,[6] W,[7] Re[8]), and even lanthanide

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† To whom correspondence concerning the structure determinations should be directed.

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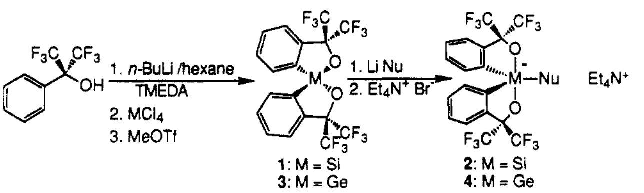
Table I. Selected Bond Lengths (Å) and Angles (deg) for 3 and 4b

3		4b			
Ge-O(1)	1.791 (4)	Ge-O(8)	1.984 (5)	Ge-C(9)	1.972 (8)
Ge-O(11)	1.781 (4)	Ge-O(16)	1.994 (5)	Ge-C(21)	1.947 (9)
Ge-C(8)	1.900 (6)	Ge-C(1)	1.930 (6)		
Ge-C(18)	1.896 (6)				
O(1)-Ge-O(11)	110.4 (2)	O(8)-Ge-O(16)	173.8 (2)	C(1)-Ge-C(9)	119.2 (3)
O(1)-Ge-C(8)	91.6 (2)	O(8)-Ge-C(1)	83.3 (2)	C(1)-Ge-C(21)	121.6 (3)
O(11)-Ge-C(18)	91.4 (2)	O(16)-Ge-C(9)	83.6 (3)	C(9)-Ge-C(21)	119.3 (3)
O(1)-Ge-C(18)	112.7 (2)	O(8)-Ge-C(9)	95.8 (3)	O(8)-Ge-C(21)	90.6 (3)
O(11)-Ge-C(8)	112.8 (2)	O(16)-Ge-C(1)	91.6 (2)	O(16)-Ge-C(21)	95.0 (3)
C(8)-Ge-C(18)	137.7 (3)				

Scheme I



Nu = CH_3 (**4a**), n-C_4H_9 (**4b**), $CH_2CH{=}CH_2$ (**4c**), C_6H_5 (**4d**)

(Eu[9]) series. Given the central role of the carbonyl group in synthetic organic chemistry, it is not surprising to find most of these studies concentrating on asymmetric reactions (direct or indirect) of that function.[10] The basic requirements for a chiral Lewis acid in this context are to (1) bind (and thus activate) the carbonyl substrate, (2) lower the symmetry of the environment such that the (normally) homotopic faces of the carbonyl become diastereotopic, and (3) release the product. The successful development of a chiral Lewis acid requires (inter alia) the creation and maintenance of a structurally well-defined environment (indeed, even a well-defined reagent) that exerts a significant diastereoface differentiation without sacrificing Lewis acidity. We were intrigued by the possibility of harnessing the novel concept of "strain release Lewis acidity" to design chiral Lewis acids based on readily available, stable, well-defined compounds of the group 14 elements.

In their elegant studies of hypervalent main-group structures, Martin and co-workers[11] reported that the spirosilane **1** (Scheme I) derived from hexafluorocumyl alcohol (R_FOH) displayed a surprising electrophilicity, forming stable anionic complexes **2** with both heteroatomic and carbon nucleophiles. This was understood in terms of the distortion of **1** away from an ideal tetrahedral geometry (C–Si–O internal angles 94.1°) and in the special ability of the ligand to stabilize the trigonal-bipyramidal (TBP) silicate complexes for geometrical and electronic reasons. To improve the still-modest Lewis acidity of **1**, we reasoned that further distortion of the tetrahedral geometry should impart a strain energy which may be released upon coordination of a Lewis base. This is most readily achieved by narrowing the internal angles closer to the TBP-optimal 90°. Using the same ligand system, we proposed to accomplish the angle narrowing by lengthening the bonds at the nexus of the spirocycle by replacing silicon with germanium. This communication reports the synthesis, structure, and reactivity of the 8-Ge-4 spirogermane **3** and its derived 10-Ge-5 anionic complexes **4**.

The preparation of **3** followed the method described by Martin, generating the dianion of R_FOH with n-BuLi/TMEDA and adding this dianion to a hexane solution of $GeCl_4$ at −78 °C.[11a] Schlenk filtration of LiCl and evaporation of the filtrate afforded the TMEDA adduct of **3**, already indicating an increased Lewis acidity compared to **1**. Decomplexation of **3**·TMEDA was accomplished by precipitation of the amine from benzene solution as its triflate salt by protonation (TfOH) or, preferably, methylation (MeOTf). The residue from concentration of the filtrate afforded **3** in 60% yield after recrystallization from hexane.[12] The spectroscopic properties of **3** are very similar to those for **1**, displaying the characteristic low-field resonance for H–C(ortho) (7.94 ppm) in the ^1H NMR spectrum. The CF_3 groups are anisochronous in **3** on both the ^{19}F (89.4 MHz, A_3B_3) and ^{13}C (75.5 MHz, two quartets) NMR time scales at room temperature.[13]

Although many spirocyclic compounds of germanium are known,[14] the X-ray crystallographic analysis of **3** (Figure

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(10) For an excellent review of carbonyl-Lewis acid structures see: (a) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem.* **1990**, *102*, 272. For recent theoretical studies of carbonyl-Lewis acid complexes see: (b) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14. (c) Birney, D. M.; Houk, K. N. *Ibid.* **1990**, *112*, 4127. (d) LePage, T. J.; Wiberg, K. B. *Ibid.* **1988**, *110*, 6642.

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(12) A suspension of dilithiohexafluorocumyl alcohol (8.19 mmol) and TMEDA (17.3 mmol) in hexane (5 mL) was added dropwise to a −78 °C solution of germanium tetrachloride (5.41 mmol) in hexane (20 mL). The reaction mixture was stirred at −78 °C for 1 h and then was warmed to room temperature. The residue from filtration and evaporation was dissolved in dry benzene (10 mL) and the solution filtered and evaporated to leave 1.68 g (61%) of **3**·TMEDA as an off-white solid. A cold (10 °C) solution of **3**·TMEDA (2.49 mmol) in benzene (10 mL) was treated with TfOH (5.48 mmol), resulting in the formation of a white precipitate. The resulting suspension was filtered and evaporated to leave **3** as a white solid. Recrystallization (hexane) gave 560 mg (40%) of white prisms: mp 153–155 °C; ^1H NMR ($CDCl_3$) 7.94 (br d, J = 7.5 Hz, 2 H, H–C(3)), 7.79–7.67 (m, 3 H, H–C(4), H–C(5), H–C(6)); ^{13}C NMR ($CDCl_3$) 140.24 (C(2)), 133.17 (C(6)), 132.44 (C(4)), 131.72 (C(5)), 126.58 (C(3)), 122.54, 122.35 (2 q, $^1J_{C\text{-}F}$ = 285.0 Hz, CF_3–C(2′)), 82.4 (septet, $^2J_{C\text{-}F}$ = 31.2 Hz, C(2′)); ^{19}F NMR ($CDCl_3$) −72.8, −73.5 (A_3B_3, $^4J_{F\text{-}F}$ = 8.9 Hz). Anal. ($C_{18}F_{12}H_8O_2Ge$) C, H, F.

(13) For a discussion of the mechanism of this process, see ref 11c.

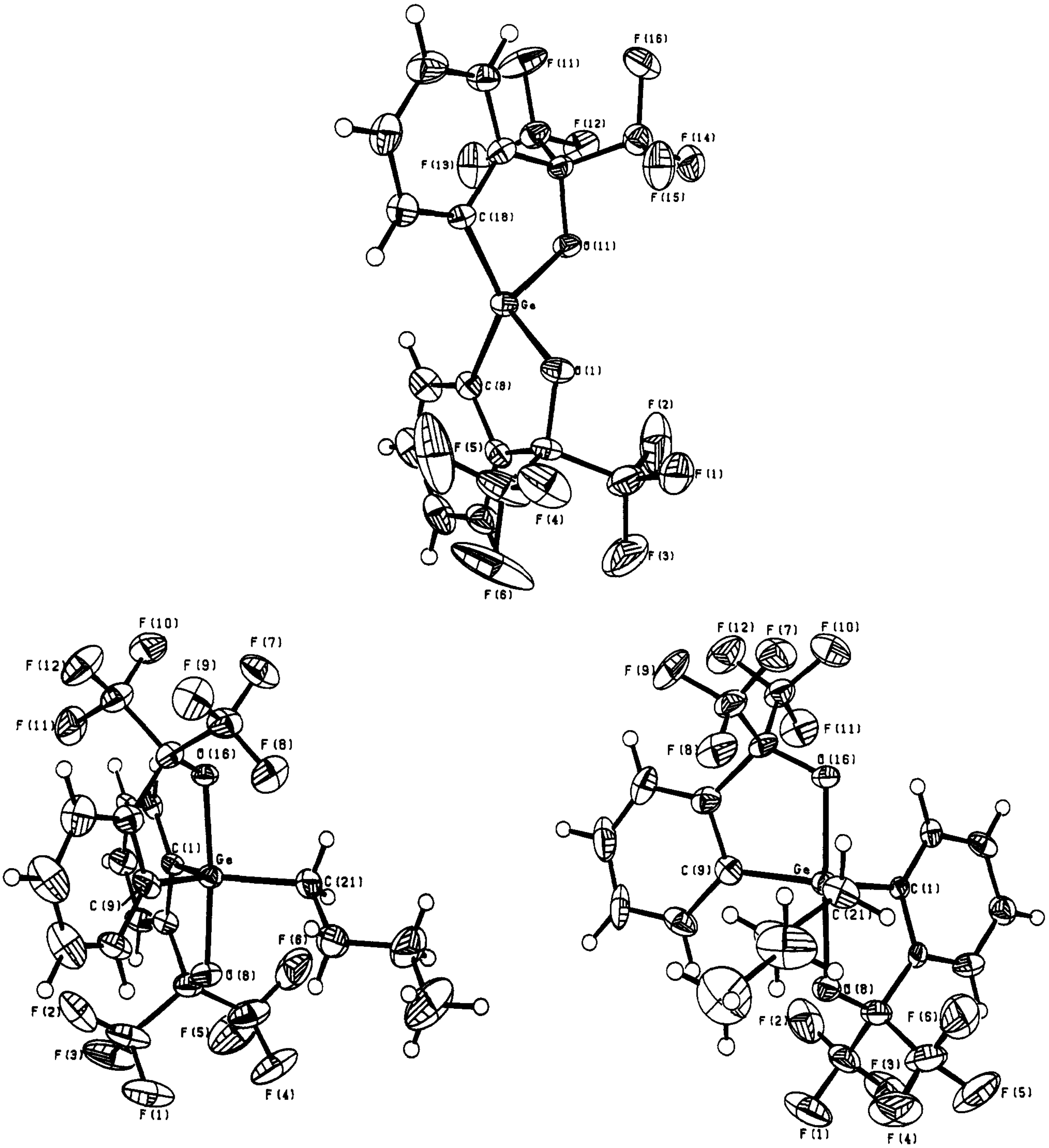

Figure 1. ORTEP plots of compound 3 (top) and the anion of 4b (bottom) (25% thermal ellipsoids).

1) constitutes only the second such determination in this class.[15,16] Selected bond lengths and angles are found in Table I. The geometrical features of 3 are similar to those reported for 1 with the expected deviations due to the longer bonds to germanium. Interestingly, the increase is greater for the Ge–O bonds (average Δ*d* 0.133 Å) than for the Ge–C bonds (average Δ*d* 0.063 Å). The Ge–O and Ge–C bond lengths fall in the expected ranges,[17] and the resulting distortion from ideal tetrahedral geometry is apparent. The constriction of the internal O–Ge–C angles (average 91.5 (2)°) is greater than in 1, as anticipated.

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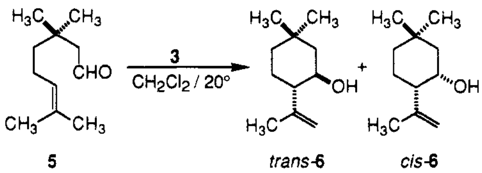
[16] X-ray crystal structure of 3: monoclinic space group $P2_1/n$; a = 8.660 (2) Å, b = 21.493 (4) Å, c = 11.131 (2) Å, β = 103.96 (1)°, V = 2010.6 (6) Å^3; Z = 4; d_{calcd} = 1.839 g/cm^3. A colorless, transparent crystal (0.3 × 0.3 × 0.8 mm) was mounted with grease in a thin-walled glass capillary. Out of a possible 2764 unique reflections, 1879 were considered to be observed at the $2.58\sigma(I)$ significance level. The structure was solved by heavy-atom methods; the correct position for germanium was deduced from a Patterson map. Non-hydrogen atoms were refined with anisotropic thermal coefficients, and a group isotropic thermal parameter was refined for idealized hydrogen atoms. Final residuals: R = 0.045, R_w = 0.057.

[17] Bond lengths: Ge–C, 1.92–1.98 Å; Ge–O, 1.74–1.80 Å. Bond strengths: Ge–O (Me_3GeOEt), 107 kcal/mol; Si–O (Me_3SiOMe), 126 kcal/mol. (a) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1979; Vol. 2, Chapter 10. (b) Bahr, G.; Kalinowski, H.-O. In *Houben-Weyl: Methoden der Organischen Chemie*; Kropf, H., Ed.; Georg Thieme Verlag: Stuttgart, 1978; Vol. XIII/6, pp 1–180.

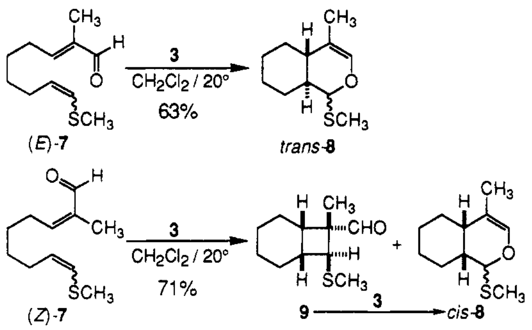
Scheme II



However, the external O-Ge-O and C-Ge-C angles are narrower (-2°) and wider (+10°), respectively, compared to those in 1. Thus, while the deviation of the endocyclic angles is in the desired direction toward a TBP, the exocyclic angles are distorted in such a way as to oppose that geometry. Finally, it is noteworthy that the dihedral angle between the two planes containing O(1)-Ge-C(8) and O(11)-Ge-C(18) is 97.5° compared to 90° for a perfect tetrahedron (96.1° for 1).

Treatment of 3 with methyl-, *n*-butyl-, allyl-, or phenyllithium produced the 10-Ge-5 anionic complexes, which were isolated as their tetraethylammonium salts **4a-d** (Scheme I).[18] The characteristic low-field shift for the hydrogens ortho to the central atom was observed (8.14-8.42 ppm). Moreover, the significant downfield shift of the *carbons* ortho to the germanium atom (average $\Delta\delta$ 4.20 and 7.53 ppm) suggested that the germanium is more positively polarized in the anionic complex and thus the negative charge is located on the oxygens. The X-ray crystal structure analysis of the *n*-butyl adduct **4b** verified our expectations (Figure 1).[19] This structure is analogous to that of the 10-Si-5 phenylsilicate reported by Martin,[11b] but unexpected deviations are noteworthy. As in the silicon series, the anionic complex **4b** is primarily TBP in nature as the O-Ge-O angle widens to 173.8 (2)° and the internal O-Ge-C angles narrow to an average of 83.5° (Table I). While the Ge-O and Ge-C bond lengths increased relative to those of 3, the increases were much different from those encountered in the silicon series. Once again the difference between Ge-X and Si-X bonds is apparent. In the rehybridization from 3 to **4b**, the Ge-O bonds lengthen much more than the Ge-C bonds (average increases 0.203 and 0.053 Å, respectively). While this is also true in the silicon series, the magnitude of the increases is quite different (average $\Delta d(1)$ 0.162 Å (Si-O), 0.085 Å (Si-C)). These differences cannot be reconciled by the change in hybridization or the greater electronegativity of germanium but are best ascribed to the weaker Ge-O bond[17] and the increased polarization of charge to the apical oxygen atoms.

Scheme III



The pentacoordinate state is uncommon in germanium chemistry. Most such species derive from internal coordination of a pendant heteroatom.[20,21] Recently the anionic complex $[(CF_3)_3GeF_2]^-$ has been shown to possess near-perfect TBP geometry by X-ray crystallography.[22]

The second orientation of **4b** shown in Figure 1 serves to illustrate the unique symmetry properties of the anionic complex and the dissymmetric environment experienced by the Lewis basic ligand in the equatorial plane. In a view down the C(21)-Ge bond, it is clear that the ligand is presented with a 2-fold symmetric motif of open and closed quadrants. The butyl chain in **4b** nicely senses this surface and is coincident (with near-perfect staggering) with the bisector of the C(9)-Ge-O(8) angle (torsional angle C(9)-Ge-C(21)-C(22), 42.95°). To maintain the configuration of this local environment, it will be necessary to prepare analogues of 3 from chiral fluoro alcohols such that the rapid inversion at the germanium atom is heavily biased in favor of one diastereomer.

The potential of 3 to serve as a Lewis acid has been demonstrated in two intramolecular pericyclic reactions of aldehydes. The first is the intramolecular ene reaction of 3-methylcitronellal (**5**;[23] Scheme II). Treatment of **5** with **3** at room temperature (1.0 equiv/5 min or 0.1 equiv/24 h) resulted in the cyclization to a 68:32 mixture of *trans*-**6** and *cis*-**6**.

In an extension of the intramolecular [4 + 2] cycloaddition of α,β-unsaturated aldehydes with vinyl sulfides reported from these laboratories,[24] we examined the utility of **3** as a reagent for the closure of enals (*E*)-**7** and (*Z*)-**7** (Scheme III). Thus, treatment of (*E*)-**7** (as a 66:34 *E*/*Z* mixture of vinyl sulfides) with 1.0 equiv of **3** cleanly produced the trans fused cyclohexapyran (*trans*-**8**) in 63% yield (95% based on available *E*-vinyl sulfide; the *Z*-vinyl sulfide remained unreacted). Interestingly, the *Z* enal (66:34 *E*/*Z* mixture of vinyl sulfides) cyclized as expected to the cis fused cyclohexapyran (*cis*-**8**) but also produced the cyclobutane **9**.[25] Prolonged treatment of **9** with **3**

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[18] To a -78 °C solution of **3** (0.90 mmol) in diethyl ether (4 mL) was added *n*-butyllithium (0.99 mmol). The mixture was warmed to room temperature, and the solvent was removed under vacuum to give the crude lithium germanate as a white foamy solid. A solution of tetraethylammonium bromide (1.125 mmol) in CH_2Cl_2 (4 mL) was added to a suspension of the lithium germanate in CH_2Cl_2 (3 mL). The pale yellow solution was stirred for 2 h and filtered and the solvent removed under vacuum to give a white solid. Recrystallization of the crude product from acetone/chloroform gave the tetraethylammonium germanate **4b** as colorless needles (382 mg, 57%): mp 175-178 °C; ^1H NMR (acetone-d_6) 8.27 (d, J = 7.4 Hz, 2 H, H-C(3)), 7.52 (br d, J = 7.0 Hz, 2 H, H-C(6)), 7.21-7.38 (m, 4 H, H-C(4), H-C(5)), 3.48 (q, J = 7.3 Hz, 8 H, NCH_2), 1.61 (m, 1 H, H-C(1″)), 1.37 (tt, J = 7.3, 1.8, 12 H, $NCCH_3$), 1.20-1.15 (m, 5 H, H-C(1″), H-C(2″), H-C(3″)), 0.75 (t, J = 7.3, 3 H, H-C(4″)); ^{13}C NMR (acetone-d_6) 144.44 (C(2)), 140.91 (C(6)), 136.28 (C(4)), 128.53 (C(5)), 126.27, 126.10 (2 q, $^1J_{C-F}$ = 290 Hz, CF_3-C(2′)), 125.30 (C(3)), 82.99 (septet, $^2J_{C-F}$ = 27.4 Hz, C(2′)), 52.91 (NCH_2), 27.88 (C(1″)), 26.84 (C(2″)), 25.43 (C(3″)), 14.09 (C(4″)), 7.52 ($NCCH_3$); ^{19}F NMR (acetone-d_6) -73.90, -73.94 (A_3B_3, J_{F-F} = 7.8 Hz). Anal. ($C_{30}H_{37}F_{12}NO_2Ge$) C, H, N, F.

[19] X-ray crystal structure of **4b**: orthorhombic space group $Pna2_1$; a = 18.819 (5) Å, b = 19.547 (4) Å, c = 9.151 (5) Å; V = 3366 (4) Å^3; Z = 4; d_{calcd} = 1.468 g/cm^3. A colorless, transparent, platelike crystal (0.1 × 0.3 × 0.3 mm) was cut from a larger crystal and mounted with epoxy on a thin glass fiber. Out of a possible 3962 unique reflections, 2307 were considered to be observed at the $2.58\sigma(I)$ significance level. The structure was solved by heavy-atom methods; the correct position for germanium was deduced from a Patterson map. Atomic parameters for the anion and cation were refined in separate blocks, non-hydrogen atoms were refined with anisotropic thermal parameters, and a group isotropic thermal parameter for idealized hydrogen atoms was refined for each ion. Final residuals: R = 0.046, R_w = 0.043.

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converted the cyclobutane into the pyran, thus demonstrating the kinetic preference for the [2 + 2] pathway in this series.[26] Clearly, 3 is a mild Lewis acid, as these cyclizations proceeded rapidly at −78 °C with $BF_3{\cdot}OEt_2$. Nonetheless, the potential for rationally designed improvements in coordinating ability and catalytic activity have been clearly demonstrated in the superior Lewis acidity of 3 compared to that of 1. Indeed, whereas 1 was shown to coordinate 4-(dimethylamino)benzaldehyde at low temperature,[11c] it displayed no activity as a Lewis acid in these reactions. Recently, however, Martin has reported the use of 1 as a Lewis acid catalyst in the reduction of carbonyl groups with a hydridosilicate.[27]

The synthesis and reactions of chiral, nonracemic organogermanium complexes as well as further applications of strain release Lewis acidity will be the subject of future reports.

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Supplementary Material Available: Preparation details and full characterization data for 3 and **4a–d**, along with listings of crystal data, positional and thermal parameters, bond lengths and angles, torsional angles, and van der Waals contacts and ORTEP diagrams and unit cell packing figures for 3 and **4b** (42 pages); tables of structure factors for 3 and **4b** (20 pages). Ordering information is given on any current masthead page.

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Nickel-Catalyzed Cross Couplings of Dithioacetals with Me_3SnCH_2MgI. A Possible β-Trimethylstannide Elimination[†]

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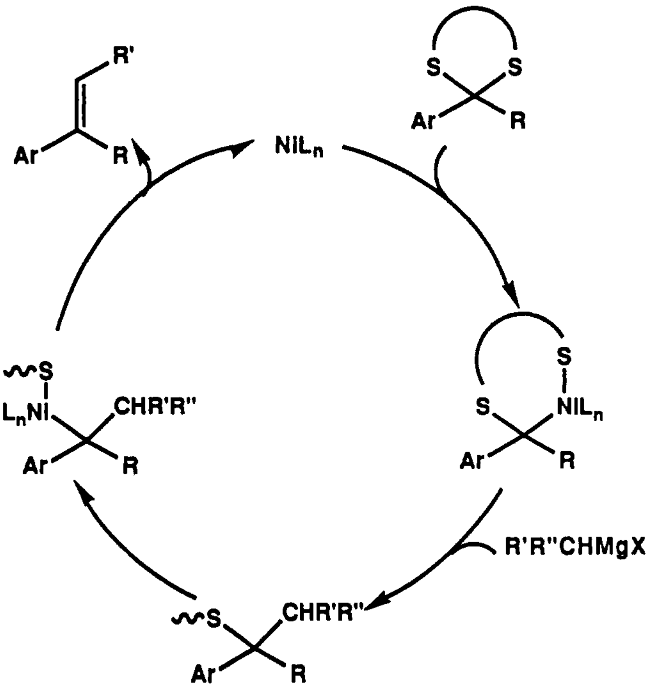
Summary: $NiCl_2(PPh_3)_2$-catalyzed cross coupling reactions of benzylic dithioacetals with Me_3SnCH_2MgI give arylethenes in good yields. The reaction may proceed preferentially via a possible β-trimethylstannide elimination.

β-Elimination of an organometallic species is extremely important in transition-metal-catalyzed reactions.[1] We recently reported several useful nickel-catalyzed cross-coupling reactions of Grignard reagents with dithioacetals.[2,3] Various evidence suggests that the mechanism of this catalytic process may involve the first formation of a carbon–carbon bond followed by an elimination step (Scheme I).[3a,4] When Me_3SiCH_2MgCl is employed, the reaction gives a facile synthesis of allyl-[3b] and vinylsilanes.[3c,d,h] In these cases, β-hydride elimination is apparently more favorable than β-elimination of a Me_3Si group.[5] Since the carbon–tin bond is weaker than the carbon–silicon bond,[6] it seems conceivable that the β-trimethylstannyl group might undergo facile elimination during the course of the catalytic reactions. We have tested this viewpoint and now describe one such elimination reaction in the nickel-catalyzed cross-coupling reac-

Scheme I



(R' = H, Alkyl, or Me_3Si, R" = H or Me_3Sn)

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[†] Dedicated in memory of the late Professor J. K. Stille.

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