is likely formed when *cis*-1-ethoxy-1-buten-3-yne, $HC{\equiv}CCH{=}CH(OMe)$, is reacted with 1 to give the paramagnetic, TBP acetylide $[(PP_3)Fe\{C{\equiv}CCH{=}CH(OMe)\}]BPh_4$ (7)[15] as the butadiene $H_2C{=}CHCH{=}CH(OMe)$ is quantitatively liberated. Under H_2 this reaction is also catalytic, selectively hydrogenating the C–C triple bond.

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[15] 7: IR (Nujol mulls) 2015 cm^{-1} (w), $\nu(C{\equiv}C)$, 1615 cm^{-1} (m), $\nu(C{=}C)$, 1270 cm^{-1} (s), $\nu(C{-}O{-}C)$; $\mu_{eff} = 3.36\ \mu_B$; ESR silent. Anal. Calcd for $C_{71}H_{67}BFeOP_4$: C, 75.68; H, 5.99; Fe, 4.96. Found: C, 75.53; H, 5.92; Fe, 4.89.

Synthesis and Structure of Novel Antimony Thiametallacycles†

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Summary: The first examples of a new class of main-group metallacycles, 4,5-didehydro-2-thiastibolanes, have been synthesized. These compounds were prepared via transmetalation from zirconocene metallacycles. The X-ray crystal structures of the 1-chloro-4,5-dimethyl-4,5-didehydro-2-thiastibolane (**4a**) and the 1-bromo-4,5-diphenyl-4,5-didehydro-2-thiastibolane (**5b**) are reported.

Recently a dramatic resurgence of interest in the organometallic chemistry of the main group elements has occurred. To a large degree this renewed activity derives from the utility of main-group compounds in fields such as ceramics,[1] electronic[2] and thermochromic materials,[3,4] and marine antifouling compounds.[5] The development of general, efficient synthetic methods for the preparation of hitherto inaccessible main-group organometallics should greatly enhance progress in many of these fields. In this communication, we report the preparation and characterization of a new class of main-group metallacycle, 4,5-didehydro-2-thiastibolanes, via a transmetalation from zirconium.[6]

We recently reported the synthesis and a study of the reactivity of the thioformaldehyde complex of zirconocene.[7] In particular, metallacycles **2** can be prepared by treatment of either thioformaldehyde complex **1a** or **1b** with an alkyne. Following the precedent of Fagan and Nugent,[6] exposure of benzene suspensions of the thiazirconacycles to 1 equiv of $PhSbCl_2$ or SbX_3 (X = Cl, Br) results in the rapid and quantitative (by ^1H NMR) formation of the corresponding antimony metallacycles **3**–**5** and zirconocene dichloride. With the exception of **3b**, the compounds may be isolated in good yield by the removal of benzene in vacuo, extraction with hexanes/ether (ca. 10:1), and chromatography on alumina III or anhydrous $MgSO_4$.[8] The formation of **3b** can be observed by ^1H NMR,[9] and the compound is indefinitely stable either in solution or as a solid in the presence of Cp_2ZrCl_2. However, all attempts to remove Cp_2ZrCl_2 have either failed or resulted in the decomposition of **3b**. Metallacycles **3a**, **4**, and **5** are all air-stable solids and may be stored indefinitely in a dry atmosphere.

Compounds **4b** and **5c** were characterized by single-crystal X-ray diffraction studies,[10] and the ORTEPs are shown in Figures 2 and 3. Compound **4b** is polymeric in the crystalline state. The structure consists of a single stibacycle per asymmetric unit cell. However, the antimony and sulfur atoms of the molecule are mutually bound to the sulfur and antimony atoms of a neighboring molecule (contact distance 3.1 Å), affecting a seesaw geometry about the antimony atoms of the dimeric unit. An additional S–Sb close contact of approximately 3.5 Å gives rise to a puckered net of Sb–S parallelograms in the *ac* plane of the unit cell (see Figure 2b). The geometry about the antimony atom can best be described as a square pyramid with the long contact lying in the basal plane of the unit and the axial position occupied by an intermolecular carbon atom C(3). The sulfur atom of each stibacycle is puckered 0.26 Å out of the plane defined by Sb, C(1), C(2), and C(3) in the direction of the second antimony atom to which it is bound.

The structure of compound **5c** consists of a centrosymmetric dimer. The intermolecular Sb–S distances are in

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† Dedicated to our friend and colleague Professor Dietmar Seyferth on the occasion of his 60th birthday.

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[8] Compounds **3a**, **4a**, and **5a** were purified by chromatography on alumina III; compounds **4b**,**c** and **5b**,**c** were purified by chromatography on anhydrous $MgSO_4$.

[9] ^1H NMR (300 MHz, C_6D_6): δ 6.98 (dt, J = 7, 1 Hz, 1 H), 6.74 (dt, J = 7, 1 Hz, 1 H).

[10] X-ray data for **4b**: crystals from toluene-d_8 at room temperature; a colorless prism of **4b** (0.15 mm × 0.18 mm × 0.18 mm) was mounted on a glass fiber; data were collected at 23 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.7169$ Å; orthorhombic, space group *Pbca*; $a = 11.541$ (2) Å, $b = 19.104$ (3) Å, $c = 7.3483$ (8) Å; $V = 1620.2$ (8) Å^3; $Z = 8$; d(calcd) = 2.11 g/cm^3. A total of 1682 reflections were collected (ω–2θ scan) to 2θ of 50.0°. The structure was solved by direct methods (SHELXS-86). Anisotropic refinement of all non-hydrogen atoms by full matrix least squares (fixed hydrogen parameters, $d_{C'-H} = 0.95$ Å) resulted in $R = 0.036$ and $R_w = 0.042$. X-ray data for **5c**: crystals from toluene at −20 °C; a colorless block of **5c** (0.65 mm × 0.65 mm × 0.65 mm) was mounted on a glass fiber; data were collected at 23 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.7169$ Å; monoclinic, space group *C*2/*c*; $a = 18.805$ (2) Å; $b = 7.566$ (1) Å, $c = 24.416$ (2) Å; $V = 3358$ (1) Å^3; $Z = 8$; d(calcd) = 1.982 g/cm^3. A total of 2575 unique reflections were collected (ω–2θ scan) to 2θ of 48.8°. The structure was solved by direct methods (SHELXS-86). Non-hydrogen atoms were refined anisotropically with the exception of the solvate presumed to be toluene (vide infra): $R = 0.043$ and $R_w = 0.051$. The solvate (occupancy = 0.5) was highly disordered about the crystallographic 2-fold axis. The model used evenly distributed the toluene molecule about the 2-fold axis with the symmetry element passing through the ortho and meta carbons. Seven peaks from the difference Fourier map were assigned a total scattering power equivalent to three carbon atoms. This model precluded the location of the methyl carbons because of the large number of sites over which they were distributed.

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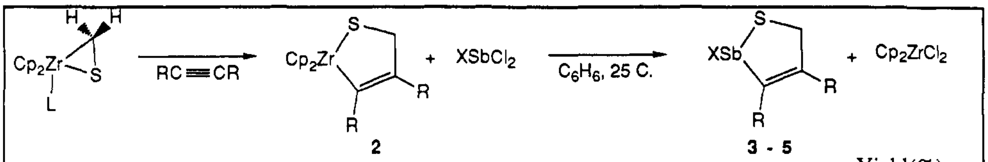
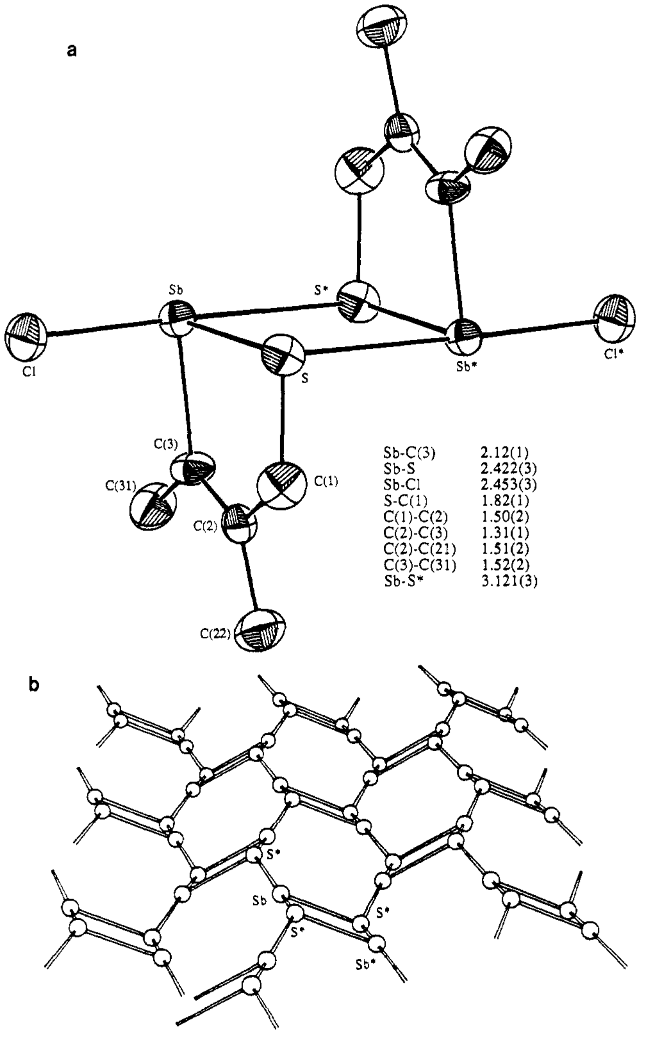


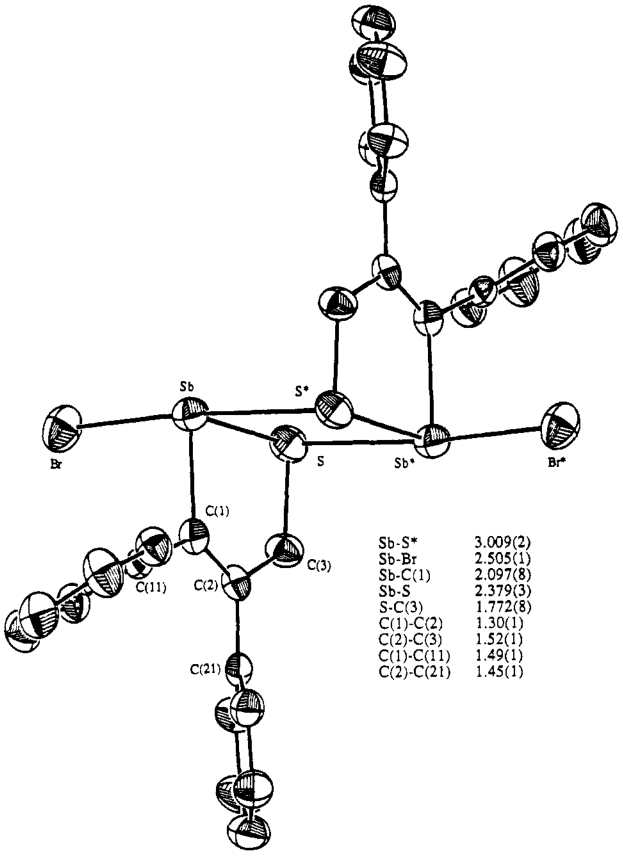
							Yield(%)
				3a	X = Ph	R = H	86
1a	L = PMe$_3$	**2a**	R = H	**3b**	X = Cl	R = H	100*
1b	Ligand free, generated *in situ*	**2b**	R = Me	**4a**	X = Ph	R = Me	84
		2c	R = Ph	**4b**	X = Cl	R = Me	80
				4c	X = Br	R = Me	90
				5a	X = Ph	R = Ph	85
				5b	X = Cl	R = Ph	80
				5c	X = Br	R = Ph	83

Figure 1. All yields are isolated except that with an asterisk, which was determined by ^1H NMR.



Sb-C(3)	2.12(1)
Sb-S	2.422(3)
Sb-Cl	2.453(3)
S-C(1)	1.82(1)
C(1)-C(2)	1.50(2)
C(2)-C(3)	1.31(1)
C(2)-C(21)	1.51(2)
C(3)-C(31)	1.52(2)
Sb-S*	3.121(3)

Figure 2. (a) ORTEP diagram of the dimeric unit of **4b** with selected bond distances (Å). Selected bond angles (deg): S–Sb–C(3) = 83.9 (4), C(1)–S–Sb = 97.1 (4), S–Sb–Cl = 95.9 (1), Cl–Sb–C(3) = 95.1 (3). Intermolecular angles: Cl–Sb–S* = 174.3 (1), S–Sb–S* = 89.1 (1). (b) Packing diagram of **4a** showing the propagation of Sb_2S_2 parallelograms through the *ac* plane of the unit cell; all other atoms omitted for clarity.



Sb-S*	3.009(2)
Sb-Br	2.505(1)
Sb-C(1)	2.097(8)
Sb-S	2.379(3)
S-C(3)	1.772(8)
C(1)-C(2)	1.30(1)
C(2)-C(3)	1.52(1)
C(1)-C(11)	1.49(1)
C(2)-C(21)	1.45(1)

Figure 3. ORTEP diagram of **5c** with selected bond distances (Å). Selected bond angles (deg): Sb–S–C(3) = 95.8 (3), S–Sb–C(1) = 86.7 (2), S–Sb–Br = 101.74 (6), C(1)–Sb–Br = 93.2 (2). Intermolecular angles: Sb–S–Sb* = 96.75 (7), S–Sb–S* = 83.25 (7).

good agreement with those of the dimeric unit of **4b**; however, there is no third close contact. As in **4b**, the sulfur atom is perturbed out of the plane (0.24 Å) defined by the other atoms of the metallacycle. The torsional angles defined by the plane of metallacycle and the phenyl substituents at C(1) and C(2) are 103.7 (8)° and 43 (1)°, respectively. There is also one-half molecule of toluene per unit cell. The solvent molecule sits on a C_2 axis and exhibits what appear to be two independent disorders. A meta disorder along the C_2 axis is superimposed on a translational disorder bisected by the axis.[11]

Solution molecular weight determinations indicate that the compounds are monomeric in benzene solution.[12] The ^1H NMR, ^{13}C NMR, and analytical data are all fully consistent with the proposed structures.[13] The diastereotopic

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(11) A decay of in the intensity standards was observed with time (18.0%). The decay in intensity was sufficient that only data to 45° in 2θ was used in the structural determination. The presummed culprit for the decay was the gradual loss of solvent from the crystal.

(12) (a) Compounds **3a**, **4a**,**b**, and **5c** were subjected to solution molecular weight determinations as described elsewhere.[12b] The concentration range for the molecular weight determinations was 0.0560 to 0.1700 M. (b) Bercaw, J. E.; Burger, B. J. Vacuum Line Techniques for Handling Air-Sensitive Organometallic Compounds. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 79–102.

(13) All new compounds were characterized by ^1H NMR, ^{13}C NMR, IR, combustion analysis, and/or high-resolution mass spectrometry. Details are available in the supplementary material.

methylene protons of the three 1-phenyl-substituted metallacycles **3a**, **4a**, and **5a** appear as a pair of well-resolved doublets in the room-temperature ^{1}H NMR. No significant broadening of the signal occurs on warming to 90 °C. In contrast, the diastereotopic methylene protons of the 1-halo-substituted metallacycles **3b**,**c**, **4b**,**c**, and **5b**,**c** undergo a concentration-dependent exchange reaction. In sufficiently dilute solution ($M \leq 0.015$), the diastereotopic protons of these compounds appear as well-resolved doublets at room temperature; the spectra are virtually identical in the methylene region with the spectra of the phenyl-substituted metallacycles. We attribute the fluxional behavior exhibited by the halometallacycles to a reversible halide exchange reaction. This conclusion is supported by crossover experiments between **4c** and **5b** which indicate that a rapid halide exchange is occurring in solution.[14]

Investigations of the properties and reactivity of these and related main-group metallacycles are in progress.

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Supplementary Material Available: An experimental section containing the preparation and spectroscopic characterization of compounds, crystallographic data and procedures, ORTEP diagrams of **4a** and **5c**, tables of bond distances and angles, tables of final positional and thermal parameters, and tables of least-squares planes (37 pages); listings of structure factors (20 pages). Ordering information is given on any current masthead page.

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[14] A full analysis of the fluxional behavior and reactivity of these compounds will be reported in a full paper.

Polymeric Organosilicon Systems. 5. Synthesis of Poly[(disilanylene)butenyne-1,4-diyls] with Highly Conducting Properties

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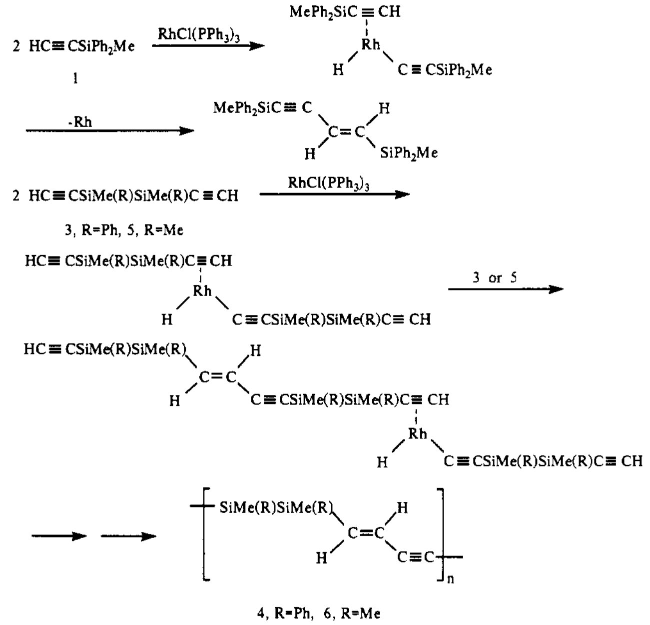
Summary: The reaction of 1,2-diethynyl-1,2-dimethyl-1,2-diphenyl- and 1,2-diethynyltetramethyldisilane with a catalytic amount of RhCl(PPh$_3$)$_3$ in toluene at room temperature afforded the respective poly[(disilanylene)butenyne-1,4-diyls]. Treatment of the films of these polymers with SbF$_5$ vapor gave the conducting films.

Scheme I



During the course of our investigation on the C-H bond activation of ethynylsilanes by a transition metal complex,[1-3] we have found that treatment of 1,2-diethynyldisilanes with a catalytic amount of RhCl(PPh$_3$)$_3$ readily affords a new type of polymers, poly[(disilanylene)butenyne-1,4-diyls], in which the alternate arrangement of a disilanylene unit and an enyne group is found regularly in the polymer backbone. The advantage of this route is that no alkali-metal condensation is involved in all processes.

First, we investigated the reaction of an ethynyl-substituted monosilane with a rhodium catalyst. Thus, when a mixture of ethynylmethyldiphenylsilane (**1**) and a 5 mol % of RhCl(PPh$_3$)$_3$ in toluene was stirred at room temperature for 24 h, (*E*)-1,4-bis(methyldiphenylsilyl)-1-buten-3-yne (**2**) was obtained in 94% yield (Scheme I). No regio- and stereoisomers were detected in the reaction mixture by either GLC or spectrometric analysis. All spectral data obtained for **2** were identical with those of an authentic sample reported previously.[1]

Interestingly, the reaction of 1,2-diethynyl-1,2-dimethyldiphenyldisilane[4] (**3**) with a rhodium catalyst gave poly[(1,2-dimethyldiphenyldisilanylene)butenyne-1,4-diyl] (**4**) with high molecular weight.[5] The diethynyldisilane **3** used as the starting monomer could readily be obtained by the reaction of ethynylmagnesium bromide prepared from acetylene and ethylmagnesium bromide, with 1,2-dichloro-1,2-dimethyldiphenyldisilane in THF. When a mixture of 2.051 g (7.1 mmol) of **3** and 2 mol % of RhCl(PPh$_3$)$_3$ in 10 mL of toluene was stirred under an argon atmosphere at room temperature for 2 days, a viscous brown solution that has no insoluble substances was obtained. The solution was poured into ethanol, and the

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[4] Compound **3**: bp 138–140 °C (1.0 mmHg); mp 34–36 °C; IR $\nu_{C\equiv C-H}$ 3280, $\nu_{C\equiv C}$ 2040 cm^{-1}; ^{1}H NMR (δ in CCl$_4$) 0.48, 0.54 (6 H, s, MeSi), 2.56 (2 H, s, HC$\equiv$C), 7.2–7.8 (10 H, m, phenyl ring protons). Anal. Calcd for C$_{18}$H$_{18}$Si$_2$: C, 74.42; H, 6.24. Found: C, 74.35; H, 6.10.

[5] Compound **4**: mp 90–95 °C; ^{1}H NMR (δ in CCl$_4$) 0.47 (6 H, br s, MeSi), 5.93 (1 H, d, $J = 19$ Hz, olefinic proton), 6.66 (1 H, d, $J = 19$ Hz, olefinic proton), 6.87–7.91 (10 H, m, phenyl ring protons); ^{13}C NMR (CDCl$_3$) δ −5.7, −5.4, −3.9, −3.8 (MeSi), 91.2, 91.3, 91.5, 91.6, 109.81, 109.84, 109.9 (C$\equiv$C), 125.8, 125.9 (C=C), 127.86, 127.93, 127.97, 128.1, 129.3, 134.4, 134.5, 134.6, 134.7, 134.8, 134.9 (phenyl ring carbons), 142.5, 142.8 (C=C); IR $\nu_{C\equiv C}$ 2146 cm^{-1}; UV (film) λ_{max} 294 nm.

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