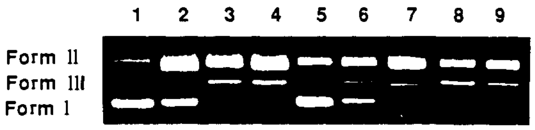
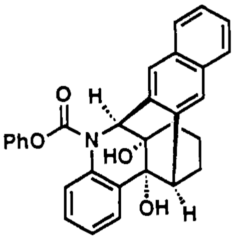


Figure 2. Supercoiled DNA interaction with selected model compounds. ΦX174 DNA was incubated for 48 h at 37 °C with compounds **14**, **1b**, **2b**, **22**, **1c**, **2c**, **1a**, and A (the corresponding N-protected sulfone of **1a**) in buffer (50 mM Tris·HCl, pH 8.5) and analyzed by electrophoresis (1% agarose gel, ethidium bromide stain). Lane 1: DNA control. Lane 2: **14** [10.0 mM]. Lane 3: **1b** [10.0 mM]. Lane 4: **2b** [10.0 mM]. Lane 5: **22** [10.0 mM]. Lane 6: **1c** [10.0 mM]. Lane 7: **2c** [10.0 mM]. Lane 8: **1a** [0.1 mM]. Lane 9: A [1.0 mM]. Key: I, form I DNA; II, form II DNA; III, form III DNA.

observed for the starting benzene diyne (**12**) and cycloaromatized product (**23**). In contrast, however, the naphthalene diyne **20** produced, upon acid-induced Bergman cycloaromatization, the anthracene derivative **24** (49% yield), which exhibited, as expected, strong and characteristic UV and fluorescence profiles. These profiles were distinct from those of its precursor [UV (EtOH), **20**, λ_{max} (log ϵ) 304 (3.47), 294 (4.01), 284 (4.26), 267–240 (4.53–4.55), 214 (4.50) nm; **24**, λ_{max} (log ϵ) 390 (3.74), 369 (3.78), 351 (3.66), 333 (3.45), 318 (3.20), 267–244 (4.43–4.46), 215 (4.43) nm; fluorescence (EtOH, 1 μM, excitation at 260 nm), **20**, λ_{max} 435, 412, 393, 374, 357 nm; **24**, λ_{max} 520, 466, 442, 413, 392 nm, see Figure 1]. Figure 1 shows the fluorescence spectra of **20** and **24**, demonstrating the striking and potentially useful differences between the arene diyne **20** and its Bergman cyclization product **24**.



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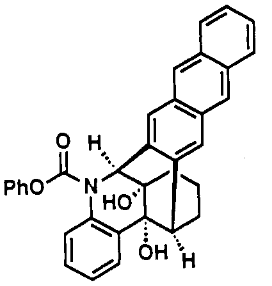

24

Epoxides **1b** and **1c** (Scheme I) were generated from their corresponding precursors **14** and **22** by treatment with DBU in benzene, and although rather labile, they exhibited enhanced stability relative to the parent epoxide **1a**.[7b] Treatment of **1b** and **1c** with silica gel in wet benzene led smoothly to the *cis*-diols **2b** and **2c**. The benzene diyne **2b** was stable enough to be detected by TLC and ^{1}H NMR spectroscopy but cyclized readily on standing at ambient temperatures [half-life (t/2) in THF-d_8 at 20 °C, ca. 2.5 h]. On the other hand, the naphthalene diyne **2c** exhibited enhanced stability compared to **2b** and could be purified by chromatography and characterized by the usual means. Its half-life (t/2) in THF-d_8 at 37 °C was determined by ^{1}H NMR spectroscopy to be ca. 44 h. Thus, the energy gains in forming the cycloaromatized products from these (ar)enediynes were approximately reflected in their observed rates of cyclization.

Compounds **1b**, **1c**, **2b**, **2c**, **14**, and **22** exhibited significant DNA-cleaving activity when incubated with supercoiled ΦX174 at pH 8.5 at 37 °C (Figure 2). Noteworthy in these experiments is the diminished activity of these arene diynes toward DNA relative to the enediyne **1a**, which is in line with their chemical and steric profiles. Compounds **14** and **22** exhibited potent anticancer activities against a variety of cell lines such as Molt-4 leukemia [IC$_{50}$ ca. 10^{-7} M for **14** and IC$_{50}$ ca. 10^{-8} M for **22**].[12]

The described designed molecules or modified analogues may serve as tools in following the reactions and distributions of enediyne-type agents both in vitro and in vivo. In addition, modulation of the enediyne reactivity toward Bergman cyclization allowed for the first time the isolation of *cis*-diol systems of the dynemicin A type. Finally, the powerful anticancer properties of these systems endow them with considerable therapeutic potential.

Acknowledgment. We thank Drs. Dee H. Huang and Gary Siuzdak of The Scripps Research Institute for the NMR and mass spectroscopic assistance. This work was financially supported by the National Institutes of Health and The Scripps Research Institute.

Supplementary Material Available: A listing of selected spectroscopic data for compounds **1b**, **1c**, **2b**, **2c**, **12**, **14**, **20**, **22**, **23**, and **24** (7 pages). Ordering information is given on any current masthead page.

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[12] We thank Dr. W. Wrasidlo of The Scripps Research Institute for these assays.

Organosamarium-Mediated Synthesis of Bismuth Bismuth Bonds: X-ray Crystal Structure of the First Dibismuth Complex Containing a Planar $M_2(\mu\text{-}\eta^2{:}\eta^2\text{-}Bi_2)$ Unit

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Increased interest in p-block chemistry in the past few years has led to many advances in the synthesis and reaction chemistry of main-group elements and complexes. One of the more challenging synthetic problems in this area is the controlled construction of molecules containing bonds between the heavier p-block elements, which have lower bond strengths than their lighter congeners. For example, in group 15, RE=ER compounds (E = P, As, Sb, Bi) containing unsupported multiple bonds are known for phosphorus and arsenic,[1] but analogous antimony and bismuth species have been observed only when stabilized by transition-metal carbonyl anions.[2-8] Compounds containing E–E single bonds involving the heavier congeners in group 15 are known, but can be accessed by only a few synthetic routes: by reduction of the elements to form Zintl ions,[9,10] by incorporation into transition-metal carbonyl clusters,[11-14] and by reduction of R_3E and R_2EX

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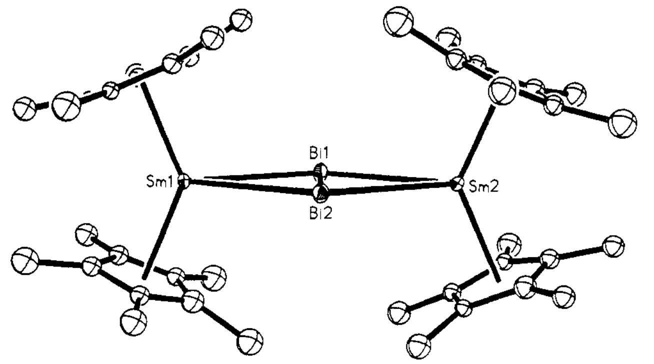

Figure 1. ORTEP diagram of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ (**1**) with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (deg) are as follows: Sm(1)–Bi(1), 3.265 (1); Sm(2)–Bi(1), 3.283 (1); Sm(1)–Bi(2), 3.291 (1); Sm(2)–Bi(2), 3.311 (1); Sm(1)–Bi(1)–Sm(2), 129.6 (1); Sm(1)–Bi(2)–Sm(2), 127.6 (1); Bi(2)–Bi(1)–Sm(1), 64.7 (1); Bi(2)–Bi(1)–Sm(2), 64.9 (1); Bi(1)–Bi(2)–Sm(1), 63.7 (1); Bi(1)–Bi(2)–Sm(2), 63.9 (1).

to form $R_2E–ER_2$ compounds.[15-18]

We report here a new way to synthesize complexes of the heavy group 15 elements containing EE bonds using the divalent organosamarium complex $(C_5Me_5)_2Sm$.[19,20] Recent studies of the reactivity of this bent metallocene have shown that this complex can provide surprising results with a variety of substrates.[21-26] In surveying the reactivity of $(C_5Me_5)_2Sm$, we have found that it reacts with $BiPh_3$ to provide a new route to dibismuth compounds and the first example of a planar $M_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ unit.

$BiPh_3$ reacts with 2 equiv of $(C_5Me_5)_2Sm$ upon mixing in benzene, toluene, or cyclohexane to form a red-brown solution.[27] Removal of solvent gave a mixture which could be separated by differential solubility in hexane and toluene. The hexane-soluble portion was found by ^1H NMR spectroscopy to contain biphenyl and $(C_5Me_5)_2SmPh$ (benzene and cyclohexane reactions) or $(C_5Me_5)_2Sm(CH_2Ph)$ (toluene reaction).[28,29] The ^1H NMR spectrum of the toluene-soluble product contained a single resonance consistent with the presence of a C_5Me_5 ligand in a Sm(III) complex, but it was not structurally definitive. An X-ray crystallographic study[30] was necessarily initiated to identify this product, and it was found to be $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ (**1**), Figure 1. The overall reaction in benzene or cyclohexane is shown in eq 1.

$$4(C_5Me_5)_2Sm + 2BiPh_3 \rightarrow [(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2) + 2PhPh + 2(C_5Me_5)_2SmPh \qquad (1)$$

Complex **1** is the first example of a dibismuth complex in which the Bi_2 moiety coordinates to two metals in a planar side-on bonding mode, and it is also the first dibismuth complex of an f element. The samarium and bismuth atoms are coplanar to within 0.0027 Å. The average Sm–C(C_5Me_5) distance, 2.72 (2) Å, is typical of the range of values found for eight-coordinate trivalent samarium complexes containing two C_5Me_5 rings[24] and is significantly smaller than the observed range for eight-coordinate divalent samarium complexes.[19,24,31] The formally dianionic dibismuth unit in **1** has a Bi–Bi distance of 2.851 (1) Å. This value is shorter than typical Bi–Bi single bond distances, which are generally greater than 2.99 Å: $Ph_2BiBiPh_2$, 2.990 (2);[17] $Bi_2Os_4(CO)_2$, 3.017 (2) Å;[13] $[Bi_2CoFe_2(CO)_{10}]^-$, 3.092 (2).[11] It is also shorter than the 2.936 (2) and 2.941 (2) Å distances in Bi_4^{2-}, which is assigned a bond order of 1.25.[32] The Bi–Bi distance in **1** can also be compared with the distances in the following complexes, which are thought to contain some multiple bonding between the bismuth atoms: $[W(CO)_5]_3Bi_2$, 2.818 (3);[3] $[(MeC_5H_4)Mn(CO)_2]_3Bi_2$, 2.813;[4] $W_3(CO)_{13}Bi_3Me$, 2.796 (1);[6] and $[(MeC_5H_4)Mo(CO)_2]_2Bi_2$, 2.838 (1) Å.[5] In the first two examples, the neutral Bi_2 fragments are thought to be six-electron donors; in the latter two examples, they are considered to be four-electron donors.

The composition of **1** is analogous to that of the crystallographically characterized dinitrogen complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**2**).[21] The structures of **1** and **2** differ, however, in that the four C_5Me_5 ring centroids in **1** define a square plane, whereas a tetrahedral arrangement of the four ring centroids is present in **2**. This is reasonable since the average Sm–Bi bond distance in **1**, 3.29 (2) Å, is much longer than the 2.36 (1) Å average Sm–N bond distance in **2**. There is no steric need for a tetrahedral arrangement of C_5Me_5 rings in **1**.[33] The 0.93-Å difference in Sm–Bi and Sm–N average distances can be compared to differences in calculated radii of these elements, which range from 0.76 to 0.95 Å.[34] Note that in **2** the dinitrogen unit is also formally a dianion, but its short 1.088 (12) Å bond distance is very close to that of free dinitrogen, 1.0975 Å.[35] In contrast, the Bi–Bi distance in the $(Bi_2)^{2-}$ unit in **1** is not unusually short. In previously reported transition-metal complexes, the electron contribution of the dibismuth unit to the metal has been rationalized on the basis of the 18-electron rule.[3-6] The situation is less clear in **1** since (a) the samarium center does not follow an 18-electron rule, (b) trivalent $(C_5Me_5)_2Sm$ units are known to bind one to three additional electron pairs,[20,26,36] and (c) the planarity of the Sm_2Bi_2 unit makes it impossible for two perpendicular Bi_2 π orbitals to point to both metals. The exact nature of bonding

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(27) Addition of a toluene solution of $BiPh_3$ (56 mg, 0.127 mmol) to a green toluene solution of $(C_5Me_5)_2Sm$ (107 mg, 0.254 mmol) causes an immediate color change to red-brown. Removal of solvent after 30 min and extraction with hexane leaves a yellow-brown solution and **1**, as a red-brown solid (49 mg, 60%). Addition of THF to the hexane solution, removal of solvent, and NMR analysis in C_6D_6 shows the presence of biphenyl and $(C_5Me_5)_2Sm(CH_2Ph)(THF)$.[28,29] Recrystallization of **1** from toluene gives crystals suitable for X-ray crystallography. Anal. Calcd for $C_{40}H_{60}Sm_2Bi_2$: C, 38.14; H, 4.80; Sm, 23.88; Bi, 33.18. Found: C, 37.86; H, 4.75; Sm, 23.75; Bi, 32.90. ^1H NMR (C_6D_6, 25 °C): 1.63 s. IR (KBr): 2958 m, 2902 s, 2857 s, 1439 m, 1376 m, 1083 m, 1018 m, 803 m cm^{-1}.

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(30) Complex **1** crystallizes from toluene in space group $P2_1$ with unit cell constants at 173 K of a = 13.045 (2) Å, b = 10.9608 (12) Å, c = 15.306 (2) Å, β = 114.07 (1)°, V = 1998.2 (5) Å^3, and D_{calcd} = 2.093 g cm^{-3} for Z = 2. Least-squares refinement of the model based on 3684 reflections ($|F_o| > 6.0\sigma(|F_o|)$) converged to a final R_F = 3.5%.

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will require further study of **1** and related species. The generality of this reaction is being explored.

Acknowledgment. We thank the National Science Foundation for support for this research. Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: ORTEP diagrams and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters for **1** (16 pages); table of observed and calculated structure factor amplitudes for **1** (18 pages). Ordering information is given on any current masthead page.

Novel Radical Cyclization of *N*-Aziridinyl Imines

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Despite the synthetic usefulness of radical cyclization reactions,[1] the cyclization pathway is mainly limited to 5-exo closure along with somewhat less efficient 6-exo and 6-endo closure due to stereoelectronic and geometric reasons.[2] A fundamentally new approach for the formation of five- and six-membered-ring radicals from acyclic precursors was sought, and we report here an unprecedented radical cyclization using 2-phenyl-*N*-aziridinyl imines which we believe has considerable synthetic potential for the formation of carbon–carbon bonds. Our approach is outlined in Scheme I and is based on three factors along with the original Eschenmoser reaction.[3] First, alkyl radicals are known to add to oxime ethers.[4] Second, β-fragmentation of three-membered rings is a facile process due to the relief of ring strain.[5] Third, consecutive β-fragmentations via ejection of styrene and nitrogen are expected to be fast processes.[6]

Our initial study focused on the use of the *N*-aziridinyl imines as radical acceptors. *N*-Aziridinyl imines were prepared in 60–80% yield by treatment of aldehydes and ketones in ethanol with a pentane solution of 1-amino-2-phenylaziridine at 0 °C, and a mixture of syn and anti isomers was used. **CAUTION!** *1-Amino-2-phenylaziridinium acetate is explosive, and proper precautions should be taken whenever it is used.*[7] Treatment of the bromide **1a** (Table I) with n-Bu$_3$SnH (2.0 equiv) and AIBN (0.1 equiv) in benzene (0.01 M in the bromide) at 80 °C for 4 h afforded 30% of **2a** along with 33% of the *N*-aziridinylpiperidine.[8] Under the same conditions, the use of the phenyl selenide **1b** obviated the problem of intramolecular N-alkylation and gave **2a** in 75% yield. **1c** was cleanly cyclized to **2c**, and there was no evidence of the N-alkylated product. As shown in Table I, radical cyclization of **3**, **5a**, and **7a** using structurally different radical precursors proceeded smoothly, yielding the cyclized products in high yields.[9,10] Similarly, the keto hydrazones **5b** and

Scheme I

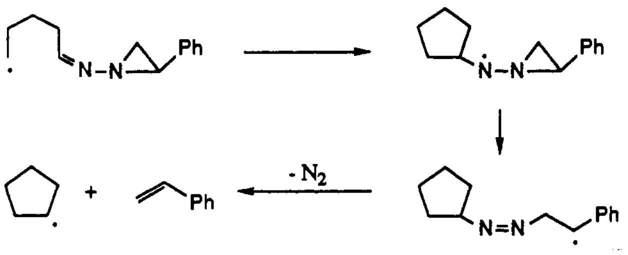
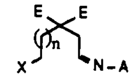
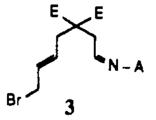
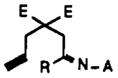
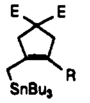
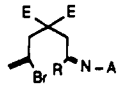
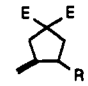


Table I. Radical Cyclization of 2-Phenyl-*N*-aziridinyl Imines

substrate[a]	time, h	product (yield, %)
		
1a: n=1, X=Br	4	**2a** (30)
1b: n=1, X=SePh	2	**2a** (75)[b]
1c: n=2, X=Br	2	**2c** (85)
 **3**	4	 **4** (89)
		
5a: R=H	3	**6a** (84)
5b: R=CH$_3$	3	**6b** (96)
		 
7a: R=H	4	**8a** (87/13)[c] **9a** (67)
7b: R=CH$_3$	6	**8b** (94/6)[c] **9b** (92)

[a] E = COOEt, A = 2-phenyl-*N*-aziridinyl group. [b] Nine percent of the reduction product was obtained. [c] The ratio was determined by ^{1}H NMR analysis and refers to **8a**/**9a** and **8b**/**9b**, respectively.

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[7] CAUTION! After preparation of 1-amino-2-phenylaziridinium acetate (approximately 10-g scale) by the known procedure (Muller, R. K.; Joos, R.; Felix, D.; Schreiber, J.; Wintner, C.; Eschenmoser, A. *Org. Synth.* **1976**, *55*, 114), it exploded during storage at room temperature, causing minor injuries. The cause of the explosion is unclear at present. Thus, it is desirable to use a pentane solution of 1-amino-2-phenylaziridine for the preparation of *N*-aziridinyl imines.

[8] The byproduct was 1-(2′-phenylaziridinyl)-4,4-bis(ethoxycarbonyl)piperidine. Furthermore, it was obtained in 75% yield without the formation of **2a** when **1a** was treated with n-Bu$_3$SnH in refluxing benzene for 4 h without the addition of AIBN. ^{1}H NMR (300 MHz, CDCl$_3$, –50 °C): δ 1.19 (t, 3 H, J = 7.1 Hz), 1.21 (t, 3 H, J = 7.1 Hz), 1.89 (t, 2 H, J = 11.5 Hz), 2.10 (d, 1 H, J = 4.5 Hz), 2.15 (d, 1 H, J = 7.64 Hz), 2.28–2.51 (m, 4 H), 2.72 (dd, 1 H, J = 4.8, 7.9 Hz), 3.08–3.11 (m, 2 H), 4.12 (q, 2 H, J = 7.1 Hz), 4.16 (q, 2 H, J = 7.1 Hz), 7.16–7.32 (m, 5 H). IR (NaCl): 2952, 1733, 1452, 1367, 1246, 1129 cm^{-1}. HRMS (M$^+$): calcd for C$_{19}$H$_{26}$O$_4$N$_2$ 346.1892, found 346.1877.

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