rings A and E must therefore be at C-2 of ring A with a free hydroxyl at C-3 in calichemicin γ_1^1. Similar experiments were carried out on the tetraacetate of **11**, confirming that, in **11**, both C-2A and C-3A bear free hydroxyls.

In this report we have shown calichemicin γ_1^1 to consist of four glycosidic units, a hexasubstituted benzene moiety, and an undefined $C_{18}H_{16}NO_4S_3$ unit. The exact configuration of the ethylamino sugar (ring E) is presently unknown; work is in progress to synthesize both of the enantiomers of **5** for optical activity comparison. In the following paper we assign the structure of the calichemicin aglycon ($C_{18}H_{17}NO_5S_3$).[11]

Acknowledgment. We thank J. K. Manning and L. Barbieri for technical assistance and V. Dean for optical rotation measurements.

Supplementary Material Available: Table of ^{13}C NMR chemical shifts of **1-3**, **5**, **7**, **9**, and **11**, ^1H NMR spectra of **1**, **2**, and **11**, summary of crystal data, computer-generated perspective drawing with atom numbering scheme, and table of the atomic positional and thermal parameters of **6** (8 pages). Ordering information is given on any current masthead page.

(10) ^1H NMR chemical shifts of ring A protons determined by ^1H-^1H COSY experiments. **2**: δ 4.62 (1A), 3.62 (2A), 4.04 (3A), 2.31 (4A), 3.74 (5A). **13**: 5.66 (1A), 3.63 (2A), 5.49 (3A), 2.68 (4A), 3.80 (5A).
(11) The calichemicin aglycon is defined as ($C_{18}H_{16}NO_4S_3$)-OH.

Calichemicins, a Novel Family of Antitumor Antibiotics. 2. Chemistry and Structure of Calichemicin γ_1^1

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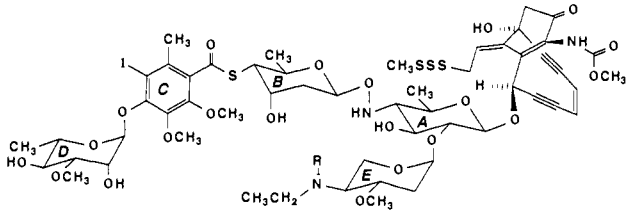
Received February 12, 1987

The structures of a number of methanolysis products of calichemicin γ_1^1 ($C_{55}H_{74}IN_3O_{21}S_4$), a potent antitumor antibiotic, are reported in the preceding paper. These degradation studies show calichemicin γ_1^1 to consist of four glycosidic units, a fully substituted iodothiobenzoate moiety, and an undefined $C_{18}H_{17}NO_5S_3$ aglycon.[1] Evidence is presented in the present paper which defines the structure of the aglycon and allows us to assign calichemicin γ_1^1 the structure **1**, containing the unprecedented bi-



1 calichemicin γ_1^1, R = H
2 *N*-acetylcalichemicin γ_1^1, R = CH_3CO

cyclo[7.3.1]tridec-9-ene-2,6-diyne system, a unique N-O glycosidic linkage, and a methyl trisulfide moiety. Interestingly, the enediyne system can be readily triggered to aromatize via a free radical intermediate[2] by cleavage at the methyl trisulfide moiety. This aromatization process may be responsible for the remarkable DNA damaging effects of the calichemicins and is probably related to the reaction of neocarzinostatin with thiols.[3]

(1) Lee, M. D.; Dunne, T. S.; Siegel, M.; Chang, C. C.; Morton, G. O.; Borders, D. B. *J. Am. Chem. Soc.*, preceding paper in this issue.
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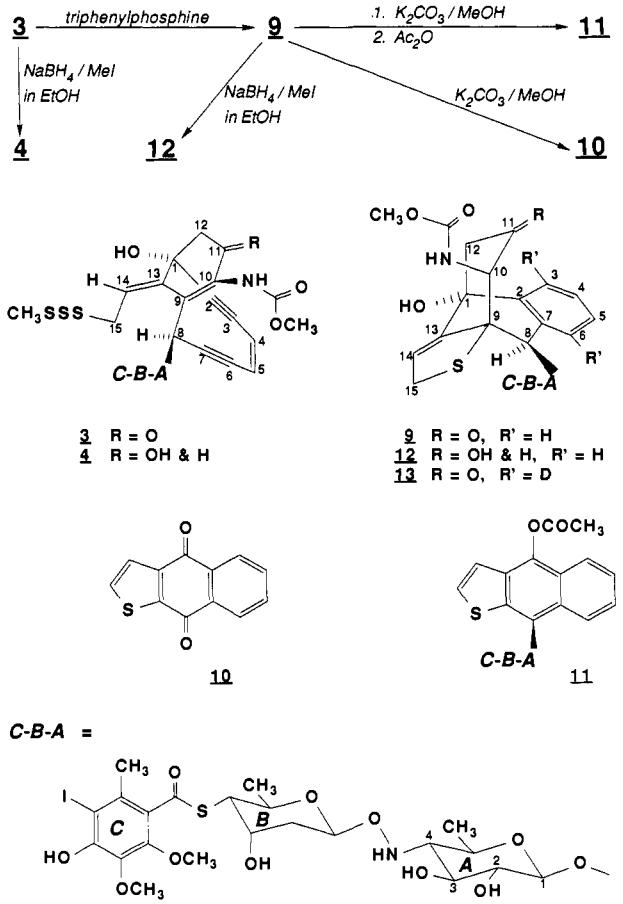
Scheme I



Extensive NMR studies including ^1H-^1H COSY, ^{13}C DEPT, and ^1H-^{13}C correlation were carried out on **1**, its mono-*N*-acetyl derivative **2**,[1] and the pseudoaglycon **3**.[1] These spectral studies showed that the aglycon of calichemicin γ_1^1 contained two methyl groups (δ_H 2.52, δ_C 22.8, C-15-SSSCH$_3$; δ_H 3.77, δ_C 53.6, C-10-NHCOOCH$_3$),[4] a vinyl ABX system (A δ_H 5.89, δ_C 122.4, CH-4; B δ_H 5.81, δ_C 123.9, CH-5; X δ_H 6.27, δ_C 71.2, CH-8; J_{AB} = 9.5 Hz, J_{BX} = 1.4 Hz),[5] an isolated =CH-CH$_2$- spin system (δ_H 6.45, δ_C 127.5, $^3J_{HCCH}$ = 9.8, 5.3 Hz, CH-14; δ_H 3.87, 4.12, δ_C 39.1, CH$_2$-15),[6] an isolated methylene (δ_H 2.84, 3.22, δ_C 53.5, $^2J_{HCH}$ = 16.8 Hz, CH$_2$-12), and an α,β-unsaturated ketone (δ_C 191.8, C-11; IR 1680 cm^{-1}). These structural units accounted for 14 of the protons and nine of the carbons of the aglycon ($C_{18}H_{17}NO_5S_3$). The remaining nine carbons (δ_C 72.5, 83.9, 87.5, 98.7, 100.4, 130.6, 136.3, 140.7, and 154.3) did not bear protons.

Treatment of **3** (Scheme I) with $NaBH_4$/EtOH in the presence of methyl iodide gave dihydropseudoaglycon **4** ($C_{40}H_{49}IN_2O_{15}S_4$, FABMS weak M + K at *m/z* 1091 and M + Na at *m/z* 1075; δ_H 2.17 dd, 2.73 dd, δ_C 45.7, $^2J_{HCH}$ = 13.7 Hz, CH$_2$-12; δ_H 4.75 m, δ_C 66.8, CH-11, $^3J_{HCCH}$ = 6.3, 4.4 Hz), establishing the connectivity between the α,β-unsaturated ketone and the isolated

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(4) The NMR data of the aglycon portion of **1-3** are practically identical. Since there is much less signal overlap in the spectra of **3**, the chemical shifts and coupling constants (except for the ABX system) observed in **3** are reported here.
(5) The chemical shifts and coupling constants observed for **2** are reported for the ABX system. The AB portion of the ABX system in **3** collapses into a two-proton singlet; the BX interaction can still be observed in ^1H-^1H COSY experiment.
(6) The chemical shifts of the methylene protons was determined by ^1H-^1H COSY experiment.

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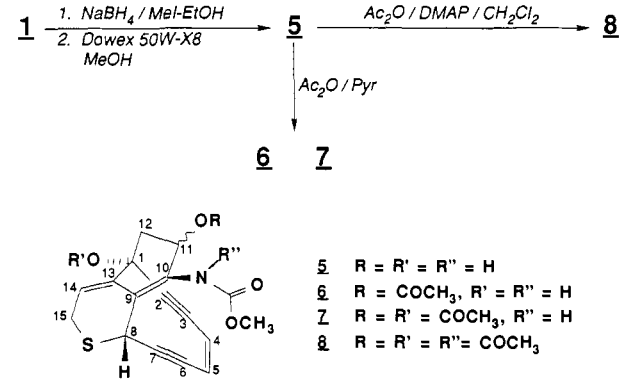
Scheme II



methylene and the presence of a substituent on the α carbon of the α,β-unsaturated ketone.[7] Methanolysis (Dowex 50W-X8, H^+ form, Scheme II) of dihydrocalichemicin γ_1^I (prepared from calichemicin γ_1^I by the $NaBH_4$/EtOH/MeI method) gave modified dihydroaglycon **5** [$C_{17}H_{15}NO_4S$, FABMS weak $(M - H)^-$ at m/z 328; UV λ_{max}^{MeOH} 239 (ϵ 3200), 267 nm (ϵ 3000); IR (KBr) 2190, 1710, 1520 cm^{-1}] instead of the expected **4**. Extensive NMR studies showed that **5** has lost the methyl group at δ_H 2.52 (δ_C 22.8) while the rest of the dihydroaglycon moiety remained intact. However, significant changes in chemical shifts were observed for the =CH—CH_2— spin system and the X of the vinyl ABX system. Careful analysis of the NMR data of **5** suggested the presence of a =CH—CH_2—S—CH— moiety in a six-membered ring, establishing the connectivity between the =CH—CH_2— spin system and the vinyl ABX system in **5**.[8] Compound **5** was converted (Scheme II) to its monoacetate **6**, diacetate **7**, and triacetate **8**,[9] demonstrating the presence of three exchangeable protons in **5**. The large downfield shift (0.6 ppm) of one of the methylene protons in **7** (δ_H 3.25, dd) and **8** (δ_H 3.30, dd) revealed the presence of a tertiary hydroxyl group α to the methylene of the $CH_2CH(OH)$ unit. The chemical shifts of four of the quaternary carbons (86.1, 87.6, 99.7, and 102.0 ppm) in **5** and the IR band at 2190 cm^{-1} (weak) suggested the presence of conjugated acetylenes which will be discussed further below.

In an attempt to elucidate the nature of the three sulfur atoms in the aglycon, calichemicin γ_1^I was treated with triphenylphosphine in CH_2Cl_2. An aromatized derivative containing four contiguous aromatic protons was obtained concomitant with triphenylphosphine sulfide and methyl mercaptan.[10] Due to the complexity of the NMR spectra of this compound, the pseudoaglycon **3** ($C_{40}H_{47}IN_2O_{15}S_4$, Scheme I) was treated with excess triphenylphosphine in CH_2Cl_2/CH_3OH (2:1) and the corresponding aromatized compound **9** ($C_{39}H_{47}IN_2O_{15}S_2$, HRFABMS M + Na Δ 1.0 mmu) was isolated. The absence of both the carbon resonances (83.9, 87.5, 98.7, 100.4 ppm) of the conjugated acetylenes and the proton resonances (5.89, 5.81 ppm) of the ABX system suggested that these subunits were converted to the new aromatic ring (δ_H 7.61 d, δ_C 124.1, CH-3; δ_H 7.36 m, δ_C 130.7, CH-4; δ_H 7.25 m, δ_C 128.8, CH-5; δ_H 7.35 m, δ_C 132.3, CH-6) of **9**. Long-range ^1H–^{13}C correlation (COLOC)[11] experiments revealed interactions through multiple bonds between δ_H 3.70 (s, 3 H, δ_C 52.8, OCH_3) and δ_C 157.1 as well as between δ_C 157.1 and δ_H 5.06 (d, 1 H, coupled to an exchangeable doublet at δ_H 5.38, $^3J_{HCNH}$ = 8.5 Hz; δ_C 69.2, d), suggesting the presence of a $CH_3OCONHCH$ moiety.[12] The existence of the carbamate group was confirmed by the IR absorption at 1710 and 1520 cm^{-1} for **5**.

Treatment of **9** with methanolic K_2CO_3 (30 min) afforded naphtho[2,3-*b*]thiophene-4,10-dione (**10**, Scheme I), which was also isolated from the acid hydrolysates of *N*-acetylcalichemicin γ_1^I. Sequential treatment of **9** with methanolic K_2CO_3 (5 min) and excess acetic anhydride trapped the intermediate of the above conversion as **11**. Compound **11** ($C_{36}H_{40}INO_{13}S_2$, HRFABMS M + K Δ 2.7 mmu) crystallized in the asymmetric triclinic space group $P\bar{1}$; its structure, including the absolute configuration, was determined by X-ray crystallography.[13] Structure **11** established the unusual N–O glycosidic linkage between rings A and B, the glycosidic linkage of ring A to the aglycon portion of **9**, and the basic carbon skeleton of the aglycon portion of **9**. Nuclear Overhauser difference experiment carried out on **9** showed a strong NOE between δ_H 4.83 (d, J = 8.1 Hz, H-1A) and the two protons at δ_H 4.60 (s, H-8) and δ_H 7.35 (m, H-6), establishing the proximity of ring A to the methine carbon at δ_C 80.1 (δ_H 4.60), and prompted us to assign the chemical structure of **9**. The connectivity between C-10 and C-11 was suggested by ^1H–^{13}C COLOC experiments and confirmed by ^1H–^1H COSY analysis of the dihydro derivative (**12**) of **9**.[14]

The methyl group at δ_H 2.52 (δ_C 22.8) was missing in **9**; however, the molecular formula of **9** differed from **3** by the elements of CS_2. In order to locate the three newly acquired protons in **9**, the conversion of **3** to **9** by triphenylphosphine was carried out in CD_2Cl_2/CD_3OD (2:1). Compound **13** was obtained with deuterium incorporated at the para positions (C-3 and C-6) of the new aromatic ring.[15] No deuterium incorporation was observed when the same reaction was carried out in CH_2Cl_2/CD_3OD, suggesting a free radical mechanism for the aromatization. The deuterium labeling pattern of **13** necessitated the existence of the benzene-1,4-diyl diradical as an intermediate of the reductive aromatization and argued the presence of an enediyne system in **3**.[2] The chemical structure of **3** was assigned on the basis of the structure of **9**, the reductive aromatization process discussed above, the formation of both triphenylphosphine sulfide and methyl mercaptan during the aromatization, and the structural information obtained for **4** and **5**. The complete structure of calichemicin γ_1^I was assigned as **1** on the basis of the structure of **3** and the structure of **13** in the preceding paper.

The conversion of **3** to **9** necessitates the loss of the $SSCH_3$ moiety and the concomitant Michael addition of the thiolate to C-9. Release of strain at the bridgehead (C-9) allows the formation of the 1,4-diradical which abstracts hydrogen radical from the solvent to afford **9**.[2,15] On reduction of the $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl (cf. dihydrocalichemicin γ_1^I), the corresponding thiolate displaces the glycosidic linkage at C-8 to give **5**. Assuming an S_N2 displacement, the stereochemistry at C-8 of the intact calichemicin γ_1^I may be inferred. Preliminary CD study on **1** suggests

(7) (a) The carbonyl resonance at δ_C 191.8 disappeared in **4**; the intensity of the 1680-cm^{-1} IR band in **4** was reduced to half of that in **3**. (b) Omitting the MeI led to decomposition since compound **3** was extremely sensitive to base. Treatment with $NaBH_3CN$ under a variety of conditions failed to convert **3** to **4**.

(8) NMR data of =$CHCH_2SCH$— in **5**: δ_H 6.09, δ_C 117.0 (CH-14); δ_H 3.30, 3.60, δ_C 24.5 (CH_2-15); $^3J_{HCCH}$ = 4.3, 4.3 Hz, $^2J_{HCH}$ = 17.7 Hz; δ_H 4.70, δ_C 30.7 (CH-8); $^4J_{HCSCH}$ = 1.2 Hz, J_{BX} = 1.4 Hz. A change in the substitution pattern for the carbon (C-8) associated with the X-proton, possibly from O to S, was inferred by the large upfield shift of this carbon (δ_C 67.3 in **4**, δ_C 30.7 in **5**). A small coupling of 1.2 Hz between the X-proton (δ_H 4.70) and one of the methylene protons of the =$CHCH_2$— unit suggested that these two units were joined via a sulfide linkage in **5**.

(9) High-resolution EIMS data m/z 311.0626 ($C_{19}H_{17}NO_5S$), 353.0713 ($C_{21}H_{19}NO_6S$), and 395.0837 ($C_{23}H_{21}NO_7S$) were obtained for the M–HOAc ions derived from **6**, **7**, and **8**, respectively.

(10) (a) Harpp, D. N.; Gleason, J. G. *J. Am. Chem. Soc.* **1971**, *93*, 2437–2445. (b) Harpp, D. N.; Ash, D. K. *J. Chem. Soc., Chem. Commun.* **1970**, 811–812.

(11) (a) Lee, M. S.; Repeta, D. J.; Nakanishi, K.; Zagorski, M. G. *J. Am. Chem. Soc.* **1986**, *108*, 7855–7856. (b) Kessler, H.; Griesingie, C.; Zarboch, J.; Foosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331–336. (c) Kessler, H.; Griesingie, C.; Lauty, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 444–445.

(12) Mallams, A. K.; Puar, M. S.; Rossman, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3938–3940.

(13) The X-ray analysis was carried out by Molecular Structure Corporation, College Station, TX 77840. Compound **11** crystallized in the triclinic space group $P\bar{1}$, with one molecule of **11** and two molecules of chloroform per unit cell; see supplementary material.

(14) Two- and three-bond interactions were observed (cf. COLOC experiment of **9**) between the proton at δ 5.06 (H-10) and the carbons at δ 73.0 (C-9), 80.1 (C-8), and 199.8 (C-11) as well as between the proton at δ 4.60 (H-8) and the carbons at δ 73.0 (C-9), 143.3 (C-13), 132.3 (C-7), and 140.3 (C-2), further confirming the structural assignment of **9**.

(15) The third new proton in **9** was enolizable (H-10) and the deuterium label was lost during the reaction workup and the crhomatographic purification of **13**.

the configuration of the aglycon portion of the molecule to be as drawn.[16]

Acknowledgment. We thank Professors K. L. Rinehart, Jr., K. Nakanishi, and C. Townsend and Dr. N. Colthup for helpful discussions; J. K. Manning and L. Barbieri for technical assistance; and M. Pastel for GCMS identification of methyl mercaptan.

Supplementary Material Available: Tables of ^{13}C NMR shifts of **3–5** and **9**, summary of crystal data, computer-generated perspective drawing with atom numbering scheme, and table of the atomic positional and thermal parameters of **11** (7 pages). Ordering information is given on any current masthead page.

(16) (a) Liu, H.-W.; Nakanishi, K. *J. Am. Chem. Soc.* **1982**, *104*, 1178–1185. (b) A negative first and positive second Cotton effect (311 nm, $\Delta\epsilon$ −370; 272 nm, $\Delta\epsilon$ +370) was observed for calichemicin γ_1^1, suggesting a negative chirality of the enediyne/dienone chromophoric system as drawn.

Reversible Stereospecific Extrusion of Ethylene from a 1,2-Diosmacyclobutane. Determination of Stereochemistry by Liquid-Crystal NMR

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In a reaction analogous to the desorption of an olefin from a metal surface, (μ-1,2-ethanediyl)octacarbonyldiosmium[1] (**1**) undergoes facile ethylene loss. As **1** is related to cyclobutane by the isolobal analogy[2] between $Os(CO)_4$ and CH_2, the loss of ethylene from **1** can be compared to the fragmentation of cyclobutane into two ethylenes—a classic example of a reaction "forbidden" by orbital symmetry as a concerted process. One would, therefore, expect the loss of ethylene from **1** to be forbidden as a concerted process[3] and to occur by a diradical mechanism leading to loss of stereochemistry. We now report that, to the contrary, the loss of ethylene from **1** is stereospecific.

Elegant experimental studies of $[2_\pi + 2_\pi]$ thermal cycloreversions[4] in organic systems have demonstrated that the most sensitive stereochemical test for diradical intermediacy is the observation of retention or loss of stereochemistry at a primary radical center.[5] A sensitive test for diradical intermediacy in the fragmentation of **1** is thus the observation of retention or loss of stereochemistry in the evolution of ethylene from **1**-*3,4*-d_2. It seemed likely that stereochemically pure *cis*- and *trans*-**1**-*3,4*-d_2 would be available from the reaction of $Na_2[Os_2(CO)_8]$[1a,7] (**2**) with *meso*- and *dl*-ethanediyl-*1,2*-d_2 bis(trifluoromethanesulfonate)[8] (**3**), respectively, on the assumption that the reaction would occur with inversion at both chiral centers and therefore with retention of their relative stereochemistry.

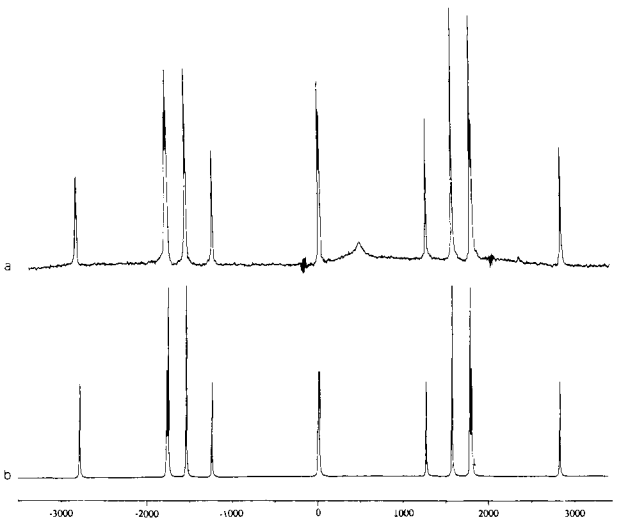
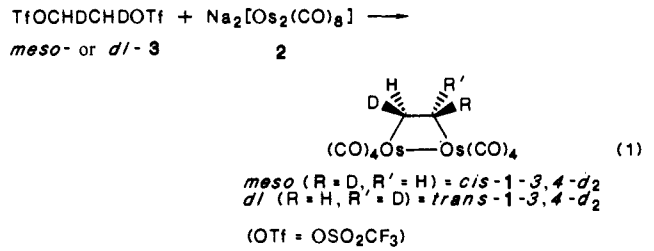
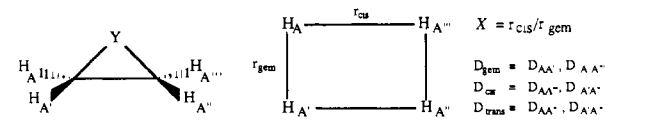


Figure 1. ^1H NMR spectrum, 200 MHz, of partially oriented **1**: (a) experimental, <3.0 wt% **1** in E. Merck, Licristal TNC-1565, t = 23 °C, 660 scans, sweep width = 15 kHz; (b) calculated, D_1 = −520.5 Hz, D_2 = −934.4 Hz, D_3 = +418.5 Hz.



Determination of both the stereochemistry (cis or trans) and stereochemical purity of **1**-*3,4*-d_2 poses an interesting spectroscopic problem, for which the dipolar couplings observable in liquid-crystal ^1H NMR spectra[9] provide a unique solution. The magnitude of this coupling is directly dependent on the magnetic moments of the nuclei and on the degree of molecular orientation, and is inversely dependent on r^3, where r is the internuclear separation. The C_{2v} symmetry of **1**[10] means that two parameters are required to describe its orientation;[9d] the observed dipolar couplings in such a four-spin system are, therefore, not a simple function of relative internuclear distance. However, in a four-proton system of this symmetry a useful relationship (eq 2) has

$$D_{trans} = (X^2 + 1)^{-5/2}[D_{cis}X^5 + D_{gem}] \quad (2)$$



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(2) (a) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (c) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(3) (a) Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370. (b) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergstr., 1971.

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(7) Hsu, L.-Y.; Bhattacharyya, N.; Shore, S. G. *Organometallics* **1985**, *4*, 1483.

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(10) Although the diosmacyclobutane ring of **1** is puckered in the solid state,[1a] a single, sharp ^1H NMR signal is observed down to −90 °C, reflecting a very low inversion barrier and justifying the assumption of effective C_{2v} symmetry in the liquid-crystal experiments.

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