Information about the disposition of the ring systems relative to one another and to other parts of calicheamicin can in principal be obtained from interresidue NOEs. Calicheamicin is an extended molecule and more than one atom intervenes between monosaccharides in several of the linkages, so in practice few interresidue NOEs are observed in the ROESY spectra. The strong NOEs between E1 and A2, and E3 and R14, and the weak NOE from A1 to R8 in both $CDCl_3$ and CD_3OD help define two of the glycosidic linkages and the orientation of the rearranged aglycon to the oligosaccharide. The fact that the NOEs are similar in these different solvents suggests that the molecule is rigid in this region. Such an interpretation is consistent with studies showing that torsional oscillations of glycosidic linkages to secondary alcohols tend to be confined to narrow regions of conformational space.[10-12] Thus, not only are the individual sugars in oligosaccharides rigid, but many of the glycosidic linkages are conformationally restricted as well.

Perhaps the most interesting feature in the calicheamicin oligosaccharide is the N–O linkage between the A and B rings; N–O linkages are quite rate in oligosaccharides. Obviously, the N–O bond could play a role in hydrogen bonding to polar functionalities in the minor groove. It may also be an important structural element that enforces an extended conformation in the central portion of the molecule. Studies by others on hydroxylamine derivatives show that rotation and inversion barriers around N–O bonds can be high, as much as 15 kcal/mol in some instances.[13] However, even at −50 °C, the resonance lines of the A- and B-ring protons in the vicinity of the N–O linkage of calicheamicin do not show signs of slow exchange in either $CDCl_3$ or CD_3OD. Although the temperature studies are equivocal because we do not know either the barrier height or the population distribution around the N–O bond, the results could indicate that there is a preferred conformer of the N–O bond. The existence of a weak NOE between B1 and the A6 methyl group and the fact that the protons in the vicinity of the N–O linkage resonate at almost identical frequencies in all three solvents strongly support this interpretation.

Finally, it is worth noting that these studies were carried out in organic solvents because neither calicheamicin ϵ nor calicheamicin γ^1 is soluble in water at millimolar concentrations. In fact, the calicheamicin oligosaccharide is remarkably hydrophobic—all the sugars are 6-deoxy[14] and there are only four free hydroxyls. It is likely that this hydrophobicity plays a significant role in DNA binding.

In conclusion, NMR studies indicate that the calicheamicin oligosaccharide is substantially preorganized. The ability to adopt a rigid, extended conformation makes oligosaccharides potentially ideal DNA binders. The calicheamicin oligosaccharide may provide insight into additional features necessary to design oligosaccharide-based DNA-binding molecules. In particular, the N–O linkage and the notable hydrophobicity may be important design elements.

Acknowledgment. We thank Dr. George Ellestad and Dr. Wei-Dong Ding (Lederle Laboratories) for a generous gift of both calicheamicin γ^1 and ϵ. This work was supported by The Parenteral Drug Association Foundation for Pharmaceutical Sciences (fellowship for S.W.), the Searle Scholars Program/The Chicago Community Trust, and funds from an ONR Young Investigator Award (to D.K.).

Supplementary Material Available: A table of ^1H NMR chemical shifts, coupling constants, and NOEs for the oligosaccharide portion of calicheamicin ϵ (1 page). Ordering information is given on any current masthead page.

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(14) 6-Deoxy sugars are common in DNA-binding oligosaccharides. Two other examples are chromomycin and mithramycin.

Enantioselective Total Synthesis of a Protosterol, 3β,20-Dihydroxyprotost-24-ene

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Received May 11, 1990

The enzymic cyclization of 2,3-oxidosqualene[1] in sterol biosynthesis is considered to form a primary tetracyclic skeleton (protostane, fusidane), which must undergo rearrangement before common sterols such as lanosterol, the precursor of cholesterol, can be produced.[2] We report herein the first direct total synthesis of the protosterol system, specifically protostenediols **1a** and **1b**, which are of biosynthetic interest, by an effective and enantiospecific route.[3]

Enone **2**[4] and 2-methyl-1,3-cyclohexanedione were converted to the Michael coupling product (Et_3N in dimethoxyethane at 23 °C),[5] which underwent enantioselective aldol cyclization[6] with 1 equiv of (*S*)-phenylalanine and 0.5 equiv of (+)-camphorsulfonic acid in dimethylformamide at 23 °C for 24 days to form **3** [77% yield, 95% ee as determined by ^1H NMR analysis in C_6D_6 with added shift reagent Eu(hfc)$_3$ (Aldrich Co.)]. Recrystallization from ether at −20 °C afforded pure (*S*)-(+)-enedione **3**; $[\alpha]^{23}_D$ + 110.3° (*c* = 4, $CHCl_3$), mp 67–68 °C, 81% recovery. Position-selective and stereoselective annulation of **3** was effected by the following sequence: (1) addition of **3** to a premixed solution of potassium hexamethyldisilazide and Et_3B (1.1:1) in THF at −78 °C, warming to −25 °C, and reaction at −25 °C with diethyl 3-iodopropynephosphonate[7] for 2 h to afford (after sgc) the desired monoalkylation product (86%); (2) hydration of C≡C to give a β-ketophosphonate using 1 equiv of $HgCl_2$ and 1.5 equiv of pyridine in aqueous THF at 23 °C for 36 h; and (3) cyclization of the crude product with 2 equiv of Cs_2CO_3 in THF at 23 °C for 16 h to give stereospecifically the pure tricyclic enone **4** (72%). Reduction of **4** with lithium trisiamylborohydride in THF at −40

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(4) Saucy, G.; Koch, W.; Muller, M.; Furst, A. *Helv. Chim. Acta* **1970**, *53*, 964–973. We found it preferable to prepare **2** from methyl 5-oxoheptanoate (Reinheckel, H.; Gensike, R. *J. Prakt. Chem.* **1968**, *37*, 214–224) by ketalization (ethylene glycol, tosic acid, C_6H_6 at reflux, 96%), reduction of COOMe to CHO (*i*-Bu_2AlH, hexane–toluene, −78 °C, 98%), reaction with H_2C=CHMgBr in THF at 0 °C (99%), and Swern oxidation to **2** (oxalyl chloride, DMSO, Et_3N in CH_2Cl_2, 84%).

(5) Abbreviations used herein: THF, tetrahydrofuran; sgc, silica gel chromatography; MOM, methoxymethyl; TBS, *tert*-butyldimethylsilyl; TES, triethylsilyl.

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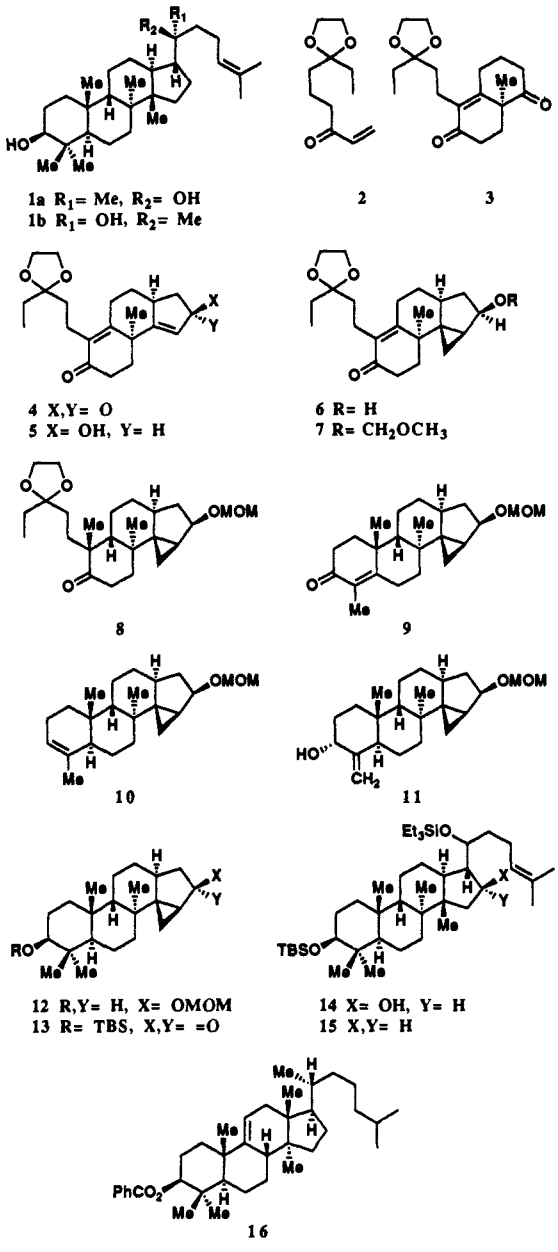
(7) Poss, A. J.; Belter, R. K. *J. Org. Chem.* **1987**, *52*, 4810–4812.

0002-7863/90/1512-6429$02.50/0

Chart I



°C afforded the 16β-alcohol **5** (77%),[8a] which was selectively converted to **6** (66%)[8a] by treatment with 1 equiv of *n*-BuLi in ether at −20 °C followed by 15 equiv of ICH_2ZnI[9] in ether at 23 °C for 12 h. The methoxymethyl ether **7**[8] was prepared from **6**, $C_6H_5NMe_2$, and CH_3OCH_2Br at 20 °C for 1 h (94% after sgc). Reduction of **7** with 4 equiv of Li in 1:1 THF–liquid NH_3 containing 1.1 equiv of H_2O at −40 °C for 3 min, addition of 2 equiv of isoprene (to destroy excess Li) and 15 equiv of CH_3I at −70 °C, and reaction at −70 °C for 1 h gave, after warming to −35 °C, quenching with H_2O, extractive isolation, sgc, and recrystallization, 70% of tetracyclic ketone **8**;[8a] mp 73–74 °C, $[\alpha]^{23}_D$ −39.7° (*c* = 1.8, $CHCl_3$).[10] Deketalization of **8** (0.02% HCl in 250:1 acetone–H_2O at 23 °C for 20 h) and aldol closure (1% KOH in 1:1 CH_3OH–H_2O at reflux for 6 h) gave pentacyclic enone **9**;[8a] mp 103–104 °C, $[\alpha]^{23}_D$ +148.3° (*c* = 1.2, $CHCl_3$), 95%.

The crucial generation of the trans A/B fusion was effected by using the following novel sequence: (1) reduction of the carbonyl group of **9** with sodium borohydride in THF–CH_3OH at 0 °C for 1 h to form the corresponding 3β-alcohol, mp 113–114 °C (100%); and (2) reaction of the 3β-ol with 10 equiv of *p*-toluenesulfonylhydrazide in CH_3NO_2 at 4 °C for 24 h to form a solution of the corresponding 3α-hydrazine derivative, which was warmed with 5% NaOAc–HOAc at 50 °C for 30 min to afford, after isolation and sgc, a crystalline mixture (>98%) containing 78% of the desired olefin **10**[11] (product of [3,3] sigmatropic rearrangement of a Δ^4-olefinic 3α-hydrodiazene (α-N=NH) intermediate).[12] The mixture was epoxidized (monoperoxyphthalic acid in CH_2Cl_2 in the presence of pH 7 buffer at 4 °C with stirring) and purified by sgc to give a single A/B trans 3α,4α-epoxide (76% overall from **9**), mp 90 °C (dec), which upon reaction with 4.5 equiv of methylmagnesium isopropylcyclohexylamide[13a] in ether–toluene at 4 °C for 12 h afforded allylic alcohol **11**: mp 115–117 °C; $[\alpha]^{23}_D$ +64.2° (*c* = 1.5, $CHCl_3$), 97% yield.[8] Oxidation of **11** (periodinane,[13b] CH_2Cl_2, 23 °C, 1 h) gave the corresponding ketone, which was reduced by addition to 4 equiv of Li and 1.1 equiv of H_2O in 1:1 THF–NH_3 (−40 °C, 3 min) and methylated by sequential treatment with isoprene (1 equiv) and CH_3I (6 equiv, 30 min) to afford a 4,4-dimethyl-3-keto compound; $[\alpha]^{23}_D$ +130.2° (*c* = 1, $CHCl_3$), 67%. Further reduction with $NaBH_4$ in THF–CH_3OH at 0 °C gave alcohol **12**;[8a] mp 88–90 °C, $[\alpha]^{23}_D$ +17.9° (*c* = 1, $CHCl_3$), 95% yield. Transformation of **12** to the ketone **13**[8] was accomplished by the following sequence: (1) silylation [*tert*-butyldimethylsilyl chloride (TBSCl)–imidazole–DMF at 50 °C for 12 h, 98% yield]; (2) MOM ether cleavage (3.5 equiv of diphenylbromoborane[14] in CH_2Cl_2 at −40 °C for 10 min, 94% yield); and (3) oxidation (2.5 equiv of pyridinium chlorochromate on Al_2O_3[15] in CH_2Cl_2 at 23 °C for 5 h, 95%). Ketone **13** was converted to the 20-norprotostene **14** by the following sequence: (1) deprotonation with *i*-Pr_2NLi in THF at −15 °C, addition of 5-methyl-4-hexenal[16] at −40 °C, then reaction at −15 °C for 30 min, and silylation in situ with $Et_3SiOSO_2CF_3$–Et_3N at −50 to +23 °C to provide the silylated aldol product (87%) as a 20:1 mixture of diastereomers at C(20); and (2) reduction with 13 equiv of Li in 1:1 THF–NH_3 containing 10 equiv of H_2O at −50 °C for 40 min to give, after quenching with aqueous NH_4Cl at −60 °C, alcohol **14** (92%). Alcohol **14** was deoxygenated at C(16) by Ireland's process:[17] (1) deprotonation of OH (*n*-BuLi, THF, −20 °C), and phosphorylation with 2 equiv of $(Me_2N)_2POCl$ at 23 °C for 2 h; and (2) removal of THF and reduction with Li in $EtNH_2$–*t*-BuOH at 0 °C for 30 min to form **15** (79%). Tetracyclic intermediate **15** was transformed into the pure protosterols **1a** and **1b** as follows: (1) selective cleavage of Et_3Si using 1% CF_3CO_2H in 5:1 THF–H_2O at 23 °C for 3 h (95% yield); (2) oxidation of the 20-hydroxyl function to give a 20-ketone (5 equiv of pyridinium chlorochromate on Al_2O_3 in CH_2Cl_2 at 20 °C for 5 h, 93% yield); (3) methylation at C(20) with 3.2 equiv of CH_3MgBr in ether at 0 °C for 30 min followed by sgc to give the 3-TBS derivatives of **1a** (69%, silica gel TLC R_f 0.38 in 1:3 ether–hexane, oil) and **1b** (30%, silica gel TLC R_f 0.29 in 1:3 ether–hexane, mp 124–126 °C); and (4) desilylation with dry Bu_4NF in THF at 50 °C for 10 h to give quantitatively pure **1a** (colorless oil, $[\alpha]^{23}_D$ +4.0° (*c* = 0.35,

(8) (a) Stereochemistry was confirmed by complete analysis of ^1H NMR spectra using 2D NMR correlation; (b) Some key NOE data follow (from ^1H–^1H COSY and NOEDS at 500 MHz in $CDCl_3$). For **7**: 11α-H to 13α-H (+10.4%), 16α-H to 13α-H (+6.6%), 16α-H to 15α-H (+5.3%). For **11**: 13α-H to 8α-CH_3 (+3.8%), 5α-H to 8α-CH_3 (+12%), 10β-CH_3 to 9β-H (+4%). For **14**: 16α-H to 20-H (+1.6%), 20-H to 16α-H (+2.1%).

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$CHCl_3$), R_f 0.27 in 2:1 ether-hexane) and **1b** (mp 156-157 °C, $[\alpha]^{23}_D$ +8.1° (c = 0.8, $CHCl_3$), R_f 0.25 in 2:1 ether-hexane).[18,19] Protostenediols **1a** and **1b** were separately converted to the corresponding 3-benzoyl-24,25-dihydro derivatives and treated with BF_3 at -78 °C in CH_2Cl_2 for 15 min. Each gave cleanly a 1:1 mixture of dihydroparkeol benzoate (**16**) and the C(20) diastereomer, which was separated by silica gel TLC ($AgNO_3$). The dihydroparkeol benzoate produced by rearrangement from **1a** or **1b** was found to be identical with an authentic sample of **16**.[20] The conversion of **1a** or **1b** to **16** confirms the successful synthesis of **1a** and **1b**. This synthesis contains a number of noteworthy steps including (1) enantioselective and efficient generation of **3**, (2) selective annulation of **3** to **4**, (3) use of the 14,15β-methylene group as a precursor of the 14β-methyl group and also as a control element for the specific introduction of the 17α side chain, (4) use of the allyl diazene rearrangement for generating the trans A/B (B-boat) arrangement, and (5) efficient elaboration of the A-ring substructure.[21]

Supplementary Material Available: Full spectral data on compounds **2-16** as well as other synthetic intermediates (32 pages). Ordering information is given on any current masthead page.

(18) Assignment of stereochemistry at C(20) in **1a** and **1b** is based on comparison of the ^{13}C NMR spectra with those of dammarenediols I and II. See: Asakawa, J.; Kasai, R.; Yamasaki, K.; Tanaka, O. *Tetrahedron* **1977**, *33*, 1935-1939. Tanaka, O.; Nagai, M.; Ohsawa, T.; Tanaka, K.; Kawai, K. *Chem. Pharm. Bull.* **1972**, *20*, 1204-1211.

(19) For a partial synthesis of a protostenediol (**1b**) from fusidic acid, see: Immer, H.; Huber, K. *Helv. Chim. Acta* **1971**, *54*, 1346-1360.

(20) Synthesized from cycloartenol as described by: Shimizu, N.; Itoh, T.; Saiito, M.; Matsumoto, T. *J. Org. Chem.* **1984**, *49*, 709-712.

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Induced Internal Electron Transfer Reactivity of Tetrathioperrhenate(VII): Synthesis of the Interconvertible Dimers $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$ and $[Re_2(\mu\text{-}SS_2CNR_2)_2(S_2CNR_2)_3][O_3SCF_3]$ (R = Me, *i*-Bu)

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Received March 19, 1990

Rhenium sulfides, e.g., ReS_2 and Re_2S_7, have long been recognized for their hydrogenation and dehydrogenation reactivity.[1] Periodic trends in catalytic hydrodesulfurization (HDS) reveal rhenium sulfur systems to have high activity.[2] However, discrete, soluble rhenium sulfur species have not received as much attention as have group VI sulfide systems.[3] The tetrathiometalate anions of V, Mo, and W (VS_4^{3-}; MoS_4^{2-}; WS_4^{2-}), which possess fully oxidized (d^0) metal centers and fully reduced (S^{2-}) sulfide ligands, undergo internal redox upon reacting with external oxidants.[4] In these reactions bound sulfide ions (S^{2-}) serve as the reductant forming disulfide (S_2^{2-}) concomitant with reduction of the metal center. Conspicuously, ReS_4^- is the only soluble tetrathiometalate whose chemistry in this regard has not been explored. Here we report that tetraalkylthiuram disulfide, acting as an *oxidant*, induces a dramatic and unprecedented 3e$^-$ *reduction* of the Re(VII) center of ReS_4^-. Moreover, the resultant Re(IV)-Re(IV) dimer, $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$ (**1**), undergoes induced internal electron transfer in the presence of tetraalkylthiuram disulfide and a Lewis acid, leading to the Re(III)-Re(III) dimer $Re_2(\mu\text{-}SS_2CNR_2)_2(S_2CNR_2)_3^+$ (**2**), which contains two trithiocarbamate ligands. The interconversion of **1** and **2** involves induced redox in both directions and can be effected with high regioselectivity.

The reaction of red-violet $[Et_4N][ReS_4]$[5] with tetraalkylthiuram disulfides in acetonitrile gives green products with the general formula $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$ (**1**; R = Me, **1a**; *i*-Bu, **1b**). Tetraalkylthiuram disulfides, conventionally used as *oxidants*, in this reaction induce a 3e$^-$ internal *reduction* of the Re(VII) metal center to give the neutral Re(IV) dimer. The coordinated sulfide (S^{2-}) serves as the reductant for both the tetraalkylthiuram disulfide and the Re(VII). Elemental sulfur is produced, presumably from coordinated sulfide. Analytical and spectroscopic data[6] are consistent with the formulation $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$.

Dark green rectangular crystals were obtained by layering hexane over a THF solution of **1b** at -20 °C. The single-crystal X-ray diffraction study[7] of **1b** reveals a crystallographically centrosymmetric dinuclear structure (Figure 1) containing distorted edge-shared bioctahedra.[8] Each rhenium atom is coordinated to two bridging sulfide and two chelating dithiocarbamate ligands. The Re-Re distance is short, 2.546 (1) Å, with the Re

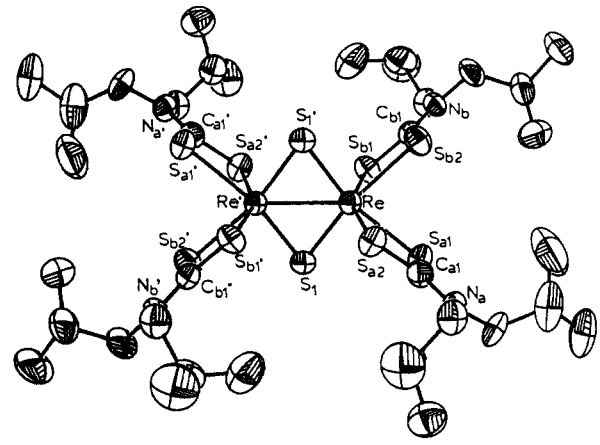

Figure 1. A perspective drawing of $Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4\cdot 2OC_4H_8$ (**1b**) (OC_4H_8 not shown) with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. For clarity, the carbon atoms of the isobutyl groups are not labeled.

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(5) Müller, A.; Diemann, E.; Rao, V. V. K. *Chem. Ber.* **1970**, *103*, 2961-2971. Müller, A.; Krebs, B. *Naturwissenschaften* **1966**, *53*, 178-179. Müller, A.; Krickemeyer, E.; Bogg, H.; Penk, M.; Rehden, D. *Chimia* **1986**, *40*, 50-52. Complex **1a** is synthesized from a 1:1 mole ratio of $[Et_4N][ReS_4]$ and $(S_2CNMe_2)_2$ in acetonitrile at 25 °C for 18 h. The green product is isolated by filtration and washing with acetonitrile and ether, giving **1a** in 70% yield.

(6) Anal. Calcd for **1b**: C, 34.48; H, 5.79; N, 4.47; S, 25.57; Re, 29.70. Found: C, 34.49; H, 5.82; N, 4.49; S, 26.05; Re, 29.48. FAB-MS displayed parent ion peaks and fragmentation patterns corresponding to the dinuclear formulation. Infrared spectra (KBr pellet): bands at 420-440 and 330-350 cm^{-1} suggesting a bridging Re-S unit and no band attributable to S-S stretching. UV-vis spectra had low-energy bands at 750 and 650 nm. ^1H NMR (22 °C, $CDCl_3$, 360 MHz): δ 2.843 (s, 1), 3.358 (s, 1).

(7) Data collection and structure refinement by Crystalytics Co., Lincoln, NE. **1b** crystal data: $Re_2(\mu\text{-}S)_2(S_2CN(i\text{-}Bu)_2)_4\cdot 2OC_4H_8$, monoclinic, $P2_1/c$, (No. 14), a = 11.084 (2) Å, b = 13.815 (3) Å, c = 19.945 (4) Å, β = 92.23 (2)°, Z = 2, V = 3052 (2) Å^3, D_{calcd} = 1.522 g cm^{-3}. The structure was refined (301 parameters) to R_1 = 0.043, R_2 = 0.051, 3268 independent reflections. Bond distances (Å): Re-Re', 2.546 (1); Re-S_{a1}, 2.511 (3); Re-S_{a2}, 2.430 (3); Re-S_1, 2.275 (3). Bond angles (deg) of Re_2S_2 core: Re-S_1-Re', 68.1 (1); S_1-Re-S_1', 111.9 (1); S_{a1}-Re-S_{a2}, 70.6 (1).

(8) Cotton, F. A. *Polyhedron* **1987**, *6*, 667-677.

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