Table I. Some Physical Properties of Cyclic and Acyclic Ethynylene Polysilanes

compd	mp, °C	^{1}H NMR,[a] ppm	^{13}C NMR,[a] ppm	^{29}Si NMR,[a] ppm	Raman (IR),[b] cm^{-1}	UV, nm (log ϵ)
2	55-56	0.17 (6 H, s), 0.23 (12 H, s), 0.24 (12 H, s)	−7.57, −3.46, −2.81, 115.67, 116.39	−45.61, −35.77, −34.21	2091.5 (2080)	226.5 (4.21), 236 sh (4.03)
1	139	0.25 (24 H, s)	−3.07, 119.46	−33.62	2082.4	242 sh (3.97), 250 (4.13)
3	64-65	0.34 (12 H, s), 0.35 (6 H, s)	−3.13, −1.11, 126.70, 132.25	−26.85, 1.57	2042.0	243 sh (3.64), 251 (3.70), 260 sh (2.41)
4[c]	44-44.5	0.05 (18 H, s),[d] 0.24 (12 H, s)[d]	−3.20, −0.07, 111.62, 116.91	−38.17, −19.08	2097.5 (2100)	223 (4.03), 230 (4.06)

[a] In $CDCl_3$. [b] In *n*-hexane. [c] $Me_3Si-C{\equiv}C-SiMe_2SiMe_2-C{\equiv}C-SiMe_3$. [d] In CCl_4.

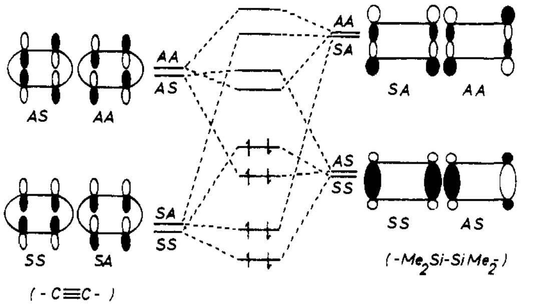

Figure 1. Qualitative molecular orbital diagram of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (**1**).

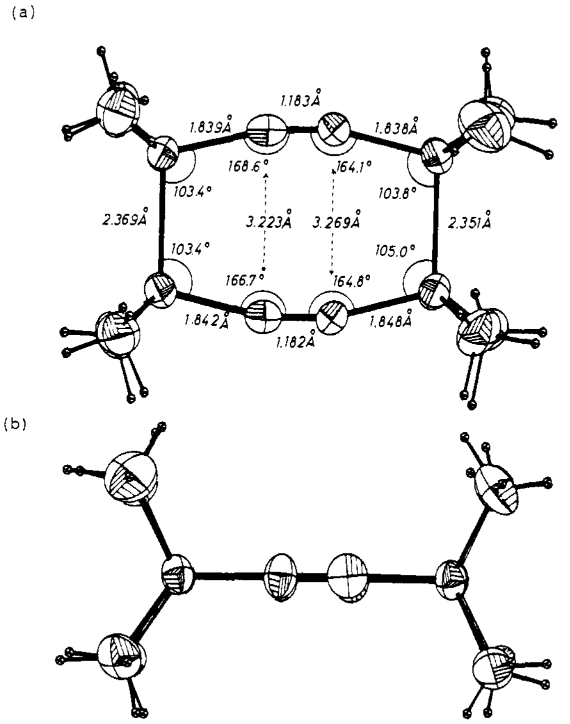

Figure 2. Molecular structure of **1**: (a) ORTEP view with appropriate data of bond lengths and angles; (b) side view.

shift in the UV spectra for **1** and **3**. Thus, **1** shows an absorption maximum at 250 nm (ϵ 13,400).

Two major factors, i.e., ring strain and σ–π conjugation, may be considered to account for the UV shift. However, judging from ^{13}C NMR data of acetylene units, the ring strain of **1** is not very significant; i.e., only a 2.55 ppm shift is observed for the ^{13}C NMR chemical shift of the sp carbon of **1** in comparison with **4**. Moreover, the molecular structure of **1** as determined by X-ray crystallography (Figure 2)[7] demonstrates rather little distortion in both disilane and acetylene units. Therefore, the enhanced bathochromic shift in the UV spectra of **1** should primarily be caused by the unique electronic structure of **1**, in which the HOMO is raised due to extensive σ–π mixing.[8]

The carbon–carbon triple bonds of **3** are very much distorted as judged by ^{13}C NMR. Thus ^{13}C NMR chemical shifts of the triple bond appeared with large low-field shifts at 126.70 and 132.25 ppm. These values are rather close to those of 1,2-bis(trimethylsilyl)ethylenes.[9] Therefore, the bond order of the triple bond of **3** decreases considerably.[10] Correspondingly, the C≡C stretching frequencies (Raman) decreased in the order of **2** > **1** > **3**.[11]

Registry No. 1, 85263-68-9; **2**, 85442-77-9; **3**, 85442-78-0; **4**, 85442-79-1; 1,2-diethynyl-1,1,2,2-tetramethyldisilane, 54773-31-8; 1,3-dichlorohexamethyltrisilane, 812-36-2.

Supplementary Material Available: ORTEP view of the structure of **1** and tables of crystal data, bond angles, bond lengths with estimated deviations, final atomic coordinates and isotropic temperature factors for hydrogen atoms, final anisotropic factors of non-hydrogen atoms, and observed and calculated structure factors (17 pages). Ordering informations is given on any current

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(7) Crystal data for **1**, $C_{12}H_{24}Si_4$ (fw 280.68), are as follows: monoclinic *Pc*; a = 7.676 Å; b = 6.348 Å; c = 19.909 Å; β = 111.908°; V = 900.157 Å; Z = 2; number of reflections 1707; D_{calcd} = 1.035 g cm^{-3}; R = 0.0441. Since the X-ray crystallographic determination of **1** revealed several interesting facts, we will report the experimental details as well as the structural parameters in a forthcoming paper.

(8) A referee pointed out that the σ–π mixing of a sort proposed for **1** should take place equally well in **2**. However, this is highly unlikely, since the HOMO of trisilane is composed of the antibonding combination of two δ(Si–Si) orbitals, which requires the SA combination of the two acetylene π orbitals for conjugation (Figure 1) as a logical consequence. The SA combination of two acetylene π orbitals cannot conjugate with the HOMO of disilane, so that cyclic through-conjugation observed for **1** does not exist for **2**. Indeed, the UV spectrum of **2** can be reconstructed almost perfectly simply by adding the spectra of **4** and octamethyltrisilane.

(9) Block, H.; Seidl, H. *J. Organomet. Chem.* **1968**, *13*, 87. For a discussion of ^{13}C NMR and UV spectra of polysilylethylenes: Sakurai, H.; Tobita, H.; Nakadaira, Y. *Chem. Lett.* **1982**, 1251.

(10) The ^{29}Si NMR chemical shifts of **3** are also anomalous. We will discuss the structure and reactions of **3** in detail later.

(11) All new compounds in this report gave correct elemental analyses and exact mass spectra.

A Stereorational Synthesis of Optically Active *trans*-Cycloalkenes and [10.10]Betweenanene

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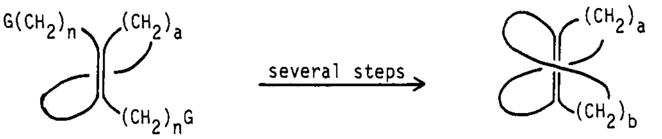
Early studies on medium-ring *trans*-cycloalkenes contributed significantly to perceptions of transannular effects,[1] restricted rotation,[2] and molecular chirality.[3] More recently the discovery of new biologically active unsaturated macrocyclic natural products[4] has underscored the importance of fundamental work on large-ring *trans*-cycloalkenes. Several years ago we described the synthesis of [10.10]betweenanene (II, *a* = *b* = 10), a novel fused-ring macrocyclic trans olefin, by a route involving ring closure of a bis(ω-functionalized)-1,2-disubstituted-*trans*-cyclododecene (I, *a* = 10, *n* = 4, G = CO_2Me).[5] The difficult accessibility of such *trans*-cycloalkenes has heretofore hampered our extension of this approach to functionalized and optically active betweenanenes. We now detail (1) an attractive new synthetic route to optically active *trans*-cycloalkenes of known absolute configuration and (2) an application of this route to the synthesis of (+)-(*R*)-[10.10]betweenanene of high optical purity.



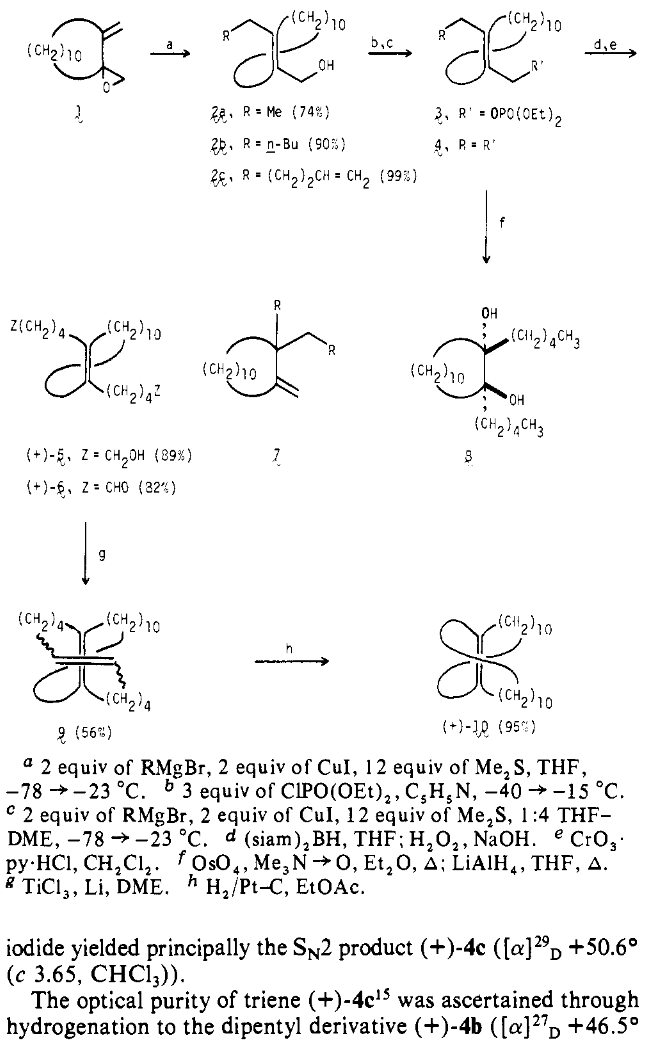
I

II

Treatment of 2-methylenecyclododecanone[6] with lithiodimethylsulfonium methylide in THF[7] afforded the epoxide **1** (Scheme I). This epoxide reacted smoothly with a 1:1 Grignard reagent–cuprous iodide complex in dimethyl sulfide–tetrahydrofuran at low temperature[8] via an S_N2' pathway[9] to give the trans-product **2** (over 98% on the basis of ^1H NMR analysis). The racemic 4-pentenyl derivative **2c** was oxidized by the Sharpless stoichiometric procedure[10] in methylene chloride at −23 °C for 10 min (!) to afford the corresponding epoxy alcohol[11] and recovered (*R*)-cyclododecenylcarbinol[12,13] (+)-**2c** ($[\alpha]^{29}{}_D$ +54.6° (*c* 4.28, $CHCl_3$)) of 95% optical purity (78% yield) on the basis of ^1H Eu(facam)$_3$ NMR shift studies.[14]

Reaction of phosphate **3b** with the previously employed butylmagnesium bromide–copper iodide reagent[8] in tetrahydrofuran–1,2-dimethoxyethane afforded the S_N2 product **4b** along with a lesser amount of the S_N2' product **7b** (~6:1) in over 90% yield. The optically active 4-pentenyl system **3c** gave similar results. Treatment with 3-butenylmagnesium bromide–copper iodide yielded principally the S_N2 product (+)-**4c** ($[\alpha]^{29}{}_D$ +50.6° (*c* 3.65, $CHCl_3$)).

Scheme I



[a] 2 equiv of RMgBr, 2 equiv of CuI, 12 equiv of Me_2S, THF, −78 → −23 °C. [b] 3 equiv of $ClPO(OEt)_2$, C_5H_5N, −40 → −15 °C. [c] 2 equiv of RMgBr, 2 equiv of CuI, 12 equiv of Me_2S, 1:4 THF–DME, −78 → −23 °C. [d] $(siam)_2BH$, THF; H_2O_2, NaOH. [e] $CrO_3\cdot$py·HCl, CH_2Cl_2. [f] OsO_4, $Me_3N\rightarrow O$, Et_2O, Δ; $LiAlH_4$, THF, Δ. [g] $TiCl_3$, Li, DME. [h] H_2/Pt–C, EtOAc.

The optical purity of triene (+)-**4c**[15] was ascertained through hydrogenation to the dipentyl derivative (+)-**4b** ($[\alpha]^{27}{}_D$ +46.5° (*c* 2.16, $CHCl_3$)) followed by hydroxylation[16] to the diol (−)-**8** ($[\alpha]^{27}{}_D$ −45.7° (*c* 2.0, $CHCl_3$), mp 75–77 °C). Precisely measured additions of Eu(facam)$_3$[14] to racemic diol (±)-**8** (mp 104–105.5 °C) caused virtual disappearance of the carbinol carbon (δ 79.3) and effected pronounced shifting and eventual splitting of the methylene signals.[17] The optically active sample of diol (−)-**8** showed shifted but unsplit methylene peaks, while a synthetic mixture of 80% (−)-**8** and 20% (±)-**8**, similarly treated, exhibited the shifted and split peaks of the racemic sample but with areas of 90:10 rather than 50:50. We therefore judge the optical purity of (−)-**8** to be better than 90%.

The optical properties of [*a.b*]betweenanenes have held our interest for a number of years.[5] Nakazaki prepared (−)-(*R*)-[8.8]betweenanene (II, *a* = *b* = 8)[18] of 0.5% optical purity estimated by comparison of its optical rotation with that of *trans*-cyclooctene.[19a] We have found larger ring *trans*-cycloalkenes to have substantially lower molecular rotations than

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(1) For background material see the excellent review on the stereochemistry of many-membered rings: Sicher, J. *Prog. Stereochem.* **1962**, *3*, 210–13.

(2) Binsch, G.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 5157–62. Cope, A. C.; Gamellin, C. R.; Johnson, H. W., Jr.; van Auken, T. V. *J. Am. Chem. Soc.* **1963**, *85*, 3276–79.

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(4) For example, macrolides: Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 585–90. Cembranolides: Weinheimer, A. J.; Chang, C. W. J.; Matson, J. A. *Fortschr. Chem. Org. Naturst.* **1979**, *36*, 286–387. Ansamycin antibiotics: Kupchan, S. M.; et al. *J. Am. Chem. Soc.* **1972**, *94*, 1354–5. Macrocyclic tetronic acids: Mallams, A. K.; Puai, M. S.; Rossman, R. R. *Ibid.* **1981**, *103*, 3938–40.

(5) Cf.: Marshall, J. A.; Black, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 7581–3. Marshall, J. A. *Acc. Chem. Res.* **1980**, *13*, 213–8.

(6) Gras, J.-L. *J. Org. Chem.* **1981**, *46*, 3738–41. Kruizinga, W. H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 5183–9.

(7) The reagent is prepared from trimethylsulfonium iodide in 4:1 HMPA–THF via addition to low halide methyllithium at −23 °C.

(8) Cf.: Fujisawa, T.; Sato, T.; Kawara, T.; Ohashi, K. *Tetrahedron Lett.* **1981**, *22*, 4823–6.

(9) (a) Anderson, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 4978–9. (b) Herr, R. W.; Johnson, C. R. *Ibid.* **1970**, *92*, 4979–81. (c) For an excellent review, see: Magid, R. M. *Tetrahedron* **1980**, *36*, 1901–30. (d) For recent applications in cyclohexane systems see: Marino, J. P.; Jaën, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3165–72 and references therein.

(10) Martin, U. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.*, **1981**, *103*, 6237–40.

(11) For a previous application of the Sharpless methodology to cyclodecenylcarbinols see: Marshall, J. A.; Flynn, K. E. *J. Am. Chem. Soc.* **1982**, *104*, 7430–5. These epoxidations are among the fastest yet reported for the Sharpless reaction.

(12) The rules for assigning absolute configuration to *trans*-cycloalkenes are delineated in Cahn et al.: Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–416.

(13) The assignment of absolute configuration is based upon the Sharpless model for allylic alcohol epoxidations: Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974–6.

(14) Facam is 3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato. Cf.: Kime, K. A.; Sievers, R. E. *Aldrichimica Acta* **1977**, *10*, 54–62.

(15) The organocopper coupling could proceed via a pathway involving allylic radicals. Rotation about the C-1/C-2 bond would effect cis/trans isomerization while jump rope rotation[5] would cause racemization.

(16) Castwells, J.; Meakins, G. D.; Swindells, R. *J. Chem. Soc.* **1962**, 2917–24.

(17) The spectra were measured with an IBM NR-80 spectrometer at initial sample concentrations of 0.60 M ($CDCl_3$). Data acquisition over at least 10^4 scans was carried out for each sample.

(18) Nakazaki, M.; Yamamota, K.; Maeda, M. *J. Chem. Soc., Chem. Commun.* **1980**, 294–5.

(19) (a) Cope, A. C.; Ganellin, C. R.; Johnson, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3192–3. (b) Cf.: Marshall, J. A.; Konicek, T. R.; Flynn, K. E. *J. Am. Chem. Soc.* **1980**, *102*, 3287–8. Most of our *trans*-cycloalkene *hydrocarbons* show molecular rotations between [φ] = 140 and 200°. *trans*-Cyclooctene has a molecular rotation of 500°.

trans-cyclooctene.[19b] However, the presence of two mutually reinforcing chiral ring elements in betweenanenes might conceivably cause enhanced molecular rotations relative to simple *trans*-cycloalkenes. It was therefore of interest to prepare a sample of optically pure [10.10]betweenanene (**10**).[5]

Hydroboration–oxidation of triene (+)-**4c** afforded the diol (+)-**5** ($[\alpha]^{29}_{D}$ +30.3° (*c* 3.00, $CHCl_3$)), which was oxidized to the dialdehyde (+)-**6** ($[\alpha]^{28}_{D}$ +77.1° (*c* 2.62, $CHCl_3$)) in 82% yield with pyridinium chlorochromate.[20] Cyclization with activated titanium by McMurry's method[5,21] gave diene **9**, a 4:1 mixture of trans and cis isomers according to GLC and NMR analysis. Hydrogenation afforded (+)-(*R*)-[10.10]betweenanene (**10**) ($[\alpha]^{29}_{D}$ +46.9° (*c* 1.16, $CHCl_3$), mp 85–88 °C).

The absolute configuration of (+)-**10** follows from the known enantioselectivity of the Sharpless epoxidation and from the CD curves of both **10** and its monocyclic precursor (+)-**4c**. Both showed negative Cotton effects in agreement with the assigned (*R*) configuration.[22] The optical purity of these samples is estimated to be greater than 90% on the basis of the ^{13}C NMR analysis of diol (−)-**8**.

Thus, [10.10]betweenanene (**10**) possesses a molecular rotation ($[\phi]$ = 140°) comparable with simple 1,2-disubstituted *trans*-cycloalkenes.[19] Evidently, the two chiral ring elements are not optically reinforcing at the sodium D line.[23] It seems likely that smaller ring betweenanenes could show enhanced rotations as a consequence of ring strain analogous to *trans*-cyclooctene. We hope to resolve this point in due course.

Acknowledgment. We are deeply grateful to Dr. A. R. Garber for his counsel and expert assistance in the planning and execution of the critical ^{13}C NMR experiments. We appreciate the help of Professor John Dawson with the CD measurements. The able assistance of James Peterson is acknowledged for providing samples of several key intermediates. Support for this work was provided by the National Science Foundation through research Grant CHE-8026013.

Supplementary Material Available: Listing of spectral and physical data for **1**, (±)-**2a**, (±)-**2b**, (±)-**2c**, (+)-**2c**, (*R*)-**3c**, (+)-**4b**, (+)-**4c**, (+)-**5**, (+)-**6**, (±)-**8**, (−)-**8**, (*R*)-**9**, and (+)-**10** (4 pages). Ordering information is given on any current masthead page.

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[22] Scott, A. I.; Wrixon, A. D. *Tetrahedron* **1970**, *26*, 3695–715 (see pp 3706–9).

[23] The CD spectra of triene (+)-7c and (+)-[10.10]betweenanene showed molecular ellipticity values of $[\theta] = -1.88 \times 10^4$ and -2.86×10^4, respectively.

Ruthenium and Osmium Thiolate Compounds

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Although the chemistry of iron–thiolate[1-3] and iron–sulfide–thiolate[4] compounds is extensive, the analogous chemistry of ruthenium and osmium complexes has not been established.[5] Herein we report the synthesis, structure, and properties of the first polythiolate complexes of ruthenium and osmium.

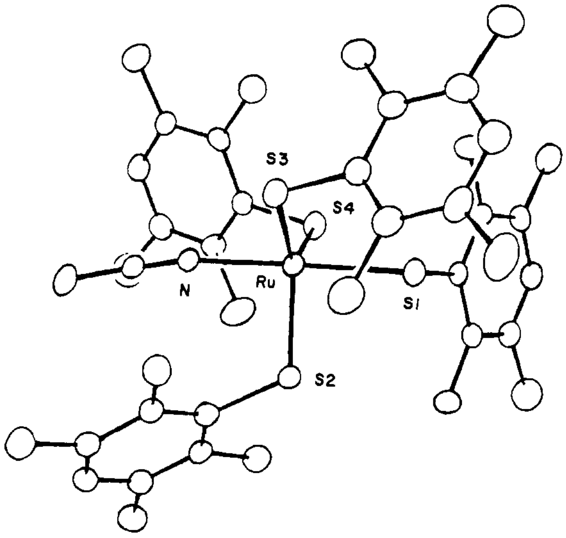

Figure 1. Structure of $Ru(SC_{10}H_{13})_4(CH_3CN)$; selected bond lengths (Å): Ru–S1, 2.383 (1); Ru–S2, 2.196 (2); Ru–S3, 2.219(2); Ru–S4, 2.212 (2); Ru–N 2.096 (5).

The reaction of $[RuCl_4(CH_3CN)_2](Et_4N)$[12] or $OsCl_3$ with 4 equiv of the lithium salt of 2,3,5,6-tetramethylbenzenethiolate[13] and a 0.5 equiv of 2,3,5,6-tetramethylphenyl disulfide[14] in refluxing methanol–acetonitrile (2:1) solutions for 6 h under nitrogen produces upon cooling 80–95% isolated yields of $Ru(SC_{10}H_{13})_4(CH_3CN)$ (**1**) or $Os(SC_{10}H_{13})_4(CH_3CN)$ (**2**), respectively. Methylene chloride solutions of **1** are red-orange [λ_{max} (ϵ_M) 281 nm (17 000), 306 (sh) (13 600), 377 (32 500)]; solutions of **2** are yellow-green [λ 260 nm (sh) (18 300), 334 (23 500)].

An X-ray crystallographic study of $Ru(SC_{10}H_{13})_4(CH_3CN)$,[15] Figure 1, shows the five ligands to be coordinated to the ruthenium in a trigonal bipyramidal[16] arrangement with the acetonitrile

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[2] Lane, R. W.; Ibers, J. A.; Frankel, R. B.; Papaefthymiou, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 84–98.

[3] Millar, M.; Lee, J. F.; Koch, S. A.; Fikar, R. *Inorg. Chem.* **1982**, *21*, 4105–4106.

[4] Berg, J. M.; Holm, R. H. In "Iron–Sulfur Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1982; pp 1–66 and references therein.

[5] Molecular ruthenium and osmium compounds possessing predominately metal–sulfur interactions have been limited to complexes of the bidentate ligands SacSac,[6] 1,1-dithiolate,[7] and 1,2-dithiolene.[8] Complexes of the type $[Ru(NH_3)_5(L)]^{n+}$, where L is a range of sulfur donors including thiolate, have been well characterized.[9] Polymeric $Ru(SR)_2$ and $Ru(SR)_3$ have been mentioned.[10,11]

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[14] In the absence of the disulfide, $Ru(SC_{10}H_{13})_4(CH_3CN)$ is acquired in about 45% yield under the same conditions.

[15] $Ru(SC_{10}H_{13})_4(CH_3CN)$ crystallizes from ethanol in the monoclinic space group $P2_1/c$ with a = 18.706 (3) Å, b = 11.637 (2) Å, c = 19.223 (4) Å, β = 93.02 (1)°, V = 4179 (2) Å^3, Z = 4. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by using normal Patterson and difference Fourier methods. The hydrogens whose positions were located or calculated were used in the structure factor calculations but were not refined. Final least-squares refinement gave R = 0.037 and R_w = 0.050 for 3751 reflections with $|F_o| > 3\sigma(|F_o|)$.

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