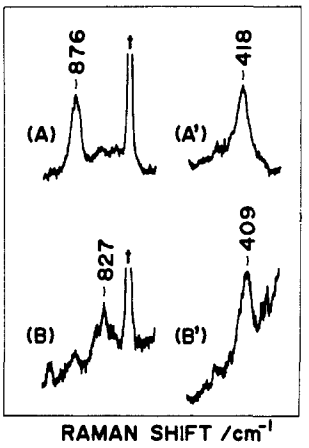


Figure 3. Resonance Raman spectra in the 1000–800 and 500–350-cm^{-1} regions of the O_2 adduct of **1** at −80 °C in a spinning cell: (A and A') $^{16}O_2$ adduct; (B and B') $^{18}O_2$ adduct. Excitation, 676 nm, 20 mW. Exposure time, 3.2 s. Number of scans, 100. The spectra were observed with a Kr^+ ion laser and an OMA-III system. Peaks marked by a dagger are due to solvent (toluene).

removal of the MeCN molecule in **2** to recover **1** is effected upon the evacuation of the solid sample under vacuum. Thus, **1** is a five-coordinate species (a N_3O_2 ligand donor set) having one open coordination site.

Figure 2 explores the interaction between **1** and dioxygen. A solution of **1** in toluene (trace A) shows no characteristic absorption band in the visible region under an argon atmosphere. Bubbling of dioxygen into the solution at −20 °C causes an immediate color change from pale yellow to dark green, giving rise to a strong band at 679 nm (trace B), which disappears upon bubbling with argon (trace C). A second treatment with dioxygen reproduces the characteristic band at 679 nm, whose intensity is almost the same as that of the initial one (trace D). These results clearly demonstrate reversible binding of dioxygen to **1**.

Resonance Raman spectra of the oxygenated complex in toluene excited at 676 nm were observed at −80 °C with a spinning cell (1800 rpm). The results are shown in Figure 3, where the spectra of $^{16}O_2$ (A and A') and $^{18}O_2$ derivatives (B and B') are displayed. The 876- and 418-cm^{-1} bands of the $^{16}O_2$ derivative are downshifted to 827 and 409 cm^{-1}, respectively, in the $^{18}O_2$ derivative, although a small amount of the $^{16}O_2$ derivative is present as a contaminant in spectrum B. The magnitude of the frequency shifts is in reasonable agreement with the values expected on the basis of diatomic approximation (50 and 15 cm^{-1}, respectively). Accordingly, the 876- and 418-cm^{-1} bands are assigned to the O–O and Fe–O_2 stretching vibrations, respectively. These Raman bands were not observed upon blue and green excitation, implicating that the 679-nm absorption arises from a charge-transfer transition between dioxygen and iron. Although the O–O stretching is slightly higher than that of oxyhemerythrin (845 cm^{-1}),[10] it is located in a frequency region typical for peroxo transition-metal complexes.[11,12] In fact, the manometric measurement of the O_2 uptake at −78 °C is 0.5 mol/mol of **1**,[13] implying the formation of a peroxo-bridged binuclear iron(III) complex.[14]

One of the striking features of **1** is its inertness toward CO. The toluene solution of **1** saturated with CO does not give any IR absorption band ascribed to a coordinated CO at room temperature. This is in contrast to the CO binding ability of the iron(II) porphyrin complexes. However, this is consistent with hemerythrin, which yields no stable CO adduct. Consequently, **1** can mimic, at least in part, the structure and function of nonheme iron containing oxygen transport proteins.

Acknowledgment. We thank Prof. Y. Ishimura and Dr. R. Makino of Keio University for low-temperature measurements of electronic spectra and Prof. Y. Fukuda of Ochanomizu University for magnetic susceptibility measurements. We appreciate the kind editing of this manuscript by Dr. J. K. Bashkin of Monsanto. Supports for this research from the Ministry of Education, Science and Culture, Japan (62430018 and 01607003), are gratefully acknowledged. N.K. is also grateful to Kawakami Memorial Foundation for financial support.

Supplementary Material Available: Tables S-I–S-V of crystallographic details, atomic coordinates including hydrogens and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles for **2** (10 pages); Table S-VI of observed and calculated structure factors for **2** (12 pages). Ordering information is given on any current masthead page.

(10) (a) Kurtz, D. M., Jr.; Duward, F. S.; Klotz, I. M. *J. Am. Chem. Soc.* **1976**, *98*, 5033. (b) Richardson, D. E.; Emad, M.; Reem, R. C.; Solomon, E. I. *Biochemistry* **1987**, *26*, 1003. (c) Shiemke, A. K.; Loehr, T. M.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1986**, *108*, 2437.

(11) μ-Peroxo binuclear iron porphyrin complexes do not give a Raman line due to ν(O–O): Paeng, I. R.; Shiwaku, H.; Nakamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 1995. However, for the Fe^{3+}–O_2^{2-} side-on complex, an IR band due to O–O stretching is reported at 806 cm^{-1}: McCandlish, E.; Miksztal, A. R.; Nappa, M.; Sprenger, A. Q.; Valentine, J. S.; Stong, J. D.; Spiro, T. G. *Ibid.* **1980**, *102*, 4268.

(12) A few peroxo iron complexes whose structures were confirmed by resonance Raman spectroscopy are as follows. (a) Fe–(O_2): Ahmad, S.; McCallum, J. D.; Shiemke, A. K.; Appelman, E. H.; Loehr, T. M.; Sanders-Loehr, J. *Inorg. Chem.* **1988**, *27*, 2230 (ν(O–O), 815 cm^{-1}). (b) Fe–(O_2)–Fe: Sawyer, D. T.; McDowell, M. S.; Spencer, L.; Tsang, P. K. S. *Ibid.* **1989**, *28*, 1166 (ν(O–O), 882 cm^{-1}). (c) Fe_2–(O_2)–Fe_2: Micklitz, W.; Bott, S. G.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372 (ν(O–O), 853 cm^{-1}).

(13) The consumed amount of dioxygen was determined with a closed vacuum system equipped with a manometer. The measurements were performed with cooling of the solution at −78 °C. Comparison of the pressure decrease with blank experiments showed that 0.666 mmol of **1** in 20 mL of toluene reacts with 0.314 mmol of dioxygen.

(14) The other possibilities that the adduct is a mononuclear peroxo iron complex or an asymmetric binuclear complex, in which the peroxide ion coordinates to one side iron, are not excluded at the present stage.

Macrolactams: A New Class of Antifungal Agents

Vinod R. Hegde,*[1a] Mahesh G. Patel,[1a] Vincent P. Gullo,[1a] Ashit K. Ganguly,[1b] Olga Sarre,[1b] and Mohindar S. Puar[1c]

Departments of Microbial Products, Chemical Research, and Molecular Spectroscopy
Schering-Plough Research, Bloomfield, New Jersey 07003

Andrew T. McPhail*

Department of Chemistry
P. M. Gross Chemical Laboratory
Duke University, Durham, North Carolina 27706

Received March 5, 1990

Various structural classes of compounds such as macrolides, peptides, nucleosides, polyenes, heterocycles, etc. exhibit antifungal activity. Recently, during our efforts to pursue novel antifungals,[2] we have isolated members of a new class of potent antifungal agents[3,4] which comprise a 14-membered macrocyclic lactam ring attached to a sugar. Structure elucidation of members of this novel class of compounds proved difficult owing to the absence of similar compounds in the literature as well as to the presence of a multiple number of saturated carbon atoms. Sch 38516 (**1**), produced by *Actinomadura vulgaris* subsp. *lanata*,[5,6] is a representative member

(1) (a) Microbial Products Department. (b) Chemical Research Department. (c) Molecular Spectroscopy Department.

(2) Detailed assay procedures were presented at the 1987 Annual SIM meeting held at Baltimore, MD, Aug 8–14, 1987: Lotvin, J. A.; Smith, E. B.; Shaw, K. J.; Ryan, M. J., PS #12.

(3) Four papers on these macrolactams were presented at the 28th ICAAC meeting held at Los Angeles, CA: Paper No. 305–308, Oct 1988.

(4) Manuscripts detailing taxonomy, fermentation, isolation, and structures are in preparation.

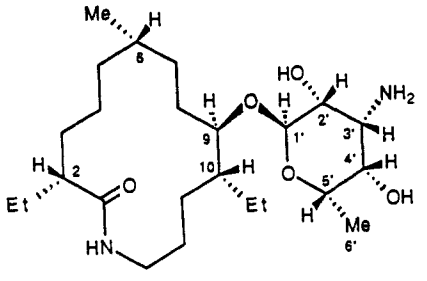
(5) The producing microorganism was obtained from a soil sample collected in Missouri.

(6) A manuscript detailing the taxonomy, fermentation, and isolation is in preparation.

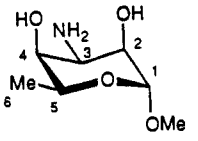
0002-7863/90/1512-6403$02.50/0

of this new class. It is active against *Candida* sp. (MIC 0.91 μg/mL) and dermatophytes (MIC >80.6 μg/mL).[7]

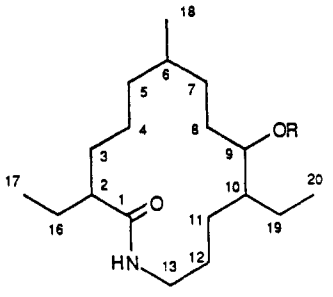
The mixture of antifungal compounds containing **1** was obtained by extraction of the fermentation broth from *A. vulgaris* with 1-butanol followed by precipitation of the complex in an ether–hexane mixture. Separation and purification of **1** from this complex was achieved by preparative HPLC on silica gel,[8] and **1** was isolated as a white crystalline solid {mp 156–160 °C, $[\alpha]^{26}_D$ −6.7° (DMSO, *c* 0.5)}. Compound **1** is basic in nature and ninhydrin positive. High-resolution FAB mass measurements established the molecular formula as $C_{24}H_{46}N_2O_5$. The IR spectrum[9] of **1** contained bands characteristic of NH and amide functions while the UV spectrum showed only end absorptions. Examination of the ^{1}H NMR spectrum[10] revealed that **1** contained two primary (δ 0.75 and 0.80) and two secondary (δ 0.81 and 1.18) methyl groups and several methylenes and methines and also indicated the presence of a sugar with an anomeric proton at δ 4.8. Consistent with the molecular formula, the ^{13}C NMR spectrum[11] contained signals for 24 carbon atoms. Four methyl groups, ten methylenes, nine methines, and one quaternary carbon center were indicated by ^{13}C APT experiments.



1



2



3 R = H

4 R = Ac

5 R = sugar - $NHSO_2C_6H_4$-*p*Br

Methanolysis of **1** yielded a methyl glycoside **2**, with 4-epi mycosamine type relative stereochemistry,[12] in addition to an aglycon **3**, which still possessed the amide functionality.[13] The structure of the aglycon was established by 2D(^{13}C–^{13}C) chemical shift correlation studies[14] of its monoacetate **4**.[15]

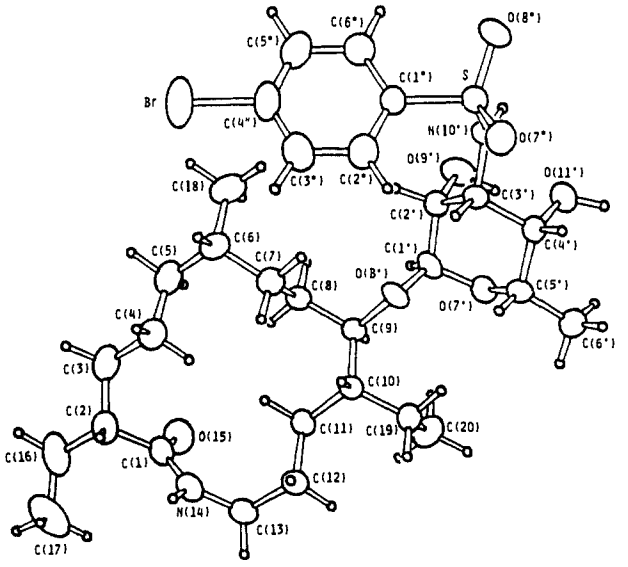


Figure 1. ORTEP diagram showing the atom-numbering scheme and solid-state conformation of **5**; small circles represent hydrogen atoms.

The complete structure and absolute stereochemistry of **1** were established by X-ray crystal structure analysis[16,17] of the *p*-bromobenzenesulfonamide derivative **5**. A view of the solid-state conformation of **5** is provided in Figure 1. The aglycon is a unique macrocyclic lactam with a 14-membered ring analogous to macrocyclic lactones. It is devoid of functionality except for the ring amide and the hydroxy group linked to the sugar. Stereochemical assignments at the carbon centers are 2*R*, 6*S*, 9*R*, and 10*R*. The macrocyclic ring has a rectangular [3434]-type[18] conformation which may be converted into a form similar to that corresponding to the minimum energy conformation of cyclotetradecane[19] by simply rotating the NH–CO moiety around the C_1–C_2 and C_{13}–N_{14} bonds so that the carbonyl oxygen atom is oriented on the β-face of the ring rather than on the α-face as in **5**. Configurations at the sugar carbon centers are 1*R*, 2*R*, 3*R*, 4*S*, and 5*S*, and thus **5** is an α-glycoside derived from a novel amino sugar, 3-amino-3,6-dideoxy-L-talopyranose, which has been

(7) The in vitro geometric mean minimum inhibitory concentration (MIC) of Sch 38516 was determined against seven strains of *Candida* and six strains of dermatophytes.

(8) Purified on a Waters Associates Prep. 500 A instrument, using their silica gel cartridge; eluting solvent: methylene chloride–methanol–triethylamine, 95:5:0.25 (TLC: Analtech, silica gel GF plates, R_f = 0.12]. Activity was monitored by inhibition of *Candida* growth, and the purity was determined by thin-layer chromatography.

(9) IR bands at 3430, 3340, 2940, 1645, 1550, 1460, and 1055 cm^{-1}.

(10) ^{1}H NMR[Varian XL-400, $CDCl_3$ + CD_3OD (1:1)]: δ 0.75 (t, *J* = 7.0 Hz, CH_3), 0.8 (t, *J* = 7.0 Hz, CH_3), 0.81 (d, *J* = 7 Hz, CH_3), 1.18 (d, *J* = 6.5 Hz, CH_3), 0.9–1.7 (CH_2 and CH), 1.92 (m, 1 H), 2.95 (dt, *J* = 12, 1 Hz, 1 H), 3.4 (m, 1 H), 3.55 (m, 1 H), 4.8 (d, *J* = 1 Hz, 1 H), 6.7 (br, exchangeable, 1 H).

(11) ^{13}C NMR ($CDCl_3$ + CD_3OD): (ppm) 176.8 (C_1), 49.8 (C_2), 32.8 (C_3), 24.3 (C_4), 33.5 (C_5), 30.5 (C_6), 24.5 (C_7), 20.7 (C_8), 76.0 (C_9), 40.3 (C_{10}), 24.5 (C_{11}), 27.3 (C_{12}), 38.2 (C_{13}), 26.0 (C_{16}), 11.5 (C_{17}), 19.8 (C_{18}), 19.8 (C_{19}), 8.3 (C_{20}) for the aglycon; (ppm) 97.1 ($C_{1'}$), 72.6 ($C_{2'}$), 47.6 ($C_{3'}$), 71.4 ($C_{4'}$), 67.2 ($C_{5'}$), and 16.0 ($C_{6'}$) for the sugar.

(12) ^{1}H NMR ($CDCl_3$) of **2**: δ 1.17 (d, *J* = 7 Hz, $C_{5'}$-CH_3), 1.97 (s, $COCH_3$), 2.18 (s, $COCH_3$), 2.20 (s, $COCH_3$), 3.4 (s, OCH_3), 4.13 (dq, *J* = 7, 1 Hz, $C_{5'}$-H), 4.69 (dt, *J* = 8, 4 Hz, $C_{3'}$-H), 4.76 (d, *J* = 1 Hz, $C_{1'}$-H), 4.82 (dd, *J* = 4, 1 Hz, $C_{2'}$-H), 5.12 (dd, *J* = 4, 1 Hz, $C_{4'}$-H), 5.76 (br d, *J* = 8 Hz, NH).

(13) Compound **3** has IR bands at 3300, 2950, 1635, 1545, 1450, 1370, 1235, 910, and 710 cm^{-1}.

(14) Mareci, T. H.; Freeman, R. *J. Magn. Reson.* **1982**, *48*, 158–163.

(15) Aglycon monoacetate **4**: ^{1}H NMR ($CDCl_3$) δ 0.8 (t, *J* = 7 Hz, CH_3), 0.82 (d, *J* = 7 Hz, CH_3), 0.85 (t, *J* = 7 Hz, CH_3), 1.0–1.7 (CH_2 and CH), 1.9 (m, C_7-H), 2.0 (s, $COCH_3$), 2.9 (m, NCH), 3.75 (m, NCH), 4.8 (m, C_9-H), 5.6 (br, NH); ^{13}C NMR ($CDCl_3$) (ppm) 175.79 (C_1), 49.80 (C_2), 33.30 (C_3), 23.34 (C_4), 33.69 (C_5), 31.10 (C_6), 27.32 (C_7), 26.31 (C_8), 76.60 (C_9), 41.08 (C_{10}), 24.99 (C_{11}), 26.21 (C_{12}), 38.85 (C_{13}), 26.81 (C_{16}), 12.29 (C_{17}), 20.85 (C_{18}), 21.24 (C_{19}), 10.18 (C_{20}), 21.46 ($COCH_3$), 170.78 (*C*OCH_3).

(16) Crystal data for **5**: $C_{30}H_{49}BrN_2O_7S$, *M* = 661.71, orthorhombic, space group $P2_12_12_1$, No. 19, *a* = 13.880 (1) Å, *b* = 43.197 (3) Å, *c* = 5.360 (1) Å (from 25 orientation reflections, 37° < θ < 44°), *V* = 3213 (1) Å^3, *Z* = 4, d_{calcd} = 1.368 g cm^{-3}, μ(Cu Kα radiation, λ = 1.5418 Å) = 27.2 cm^{-1}. Crystal dimensions: 0.11 × 0.11 × 0.50 mm. Intensity data (*hkl*, 3849 reflections, θ_{max} = 75°) were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, graphite monochromator; ω–2θ scans). The crystal structure was solved by the heavy-atom approach. Full-matrix least-squares refinement of non-hydrogen atom positional and anisotropic temperature factor parameters, with hydrogen atoms included at their calculated position, converged (maximum shift 0.02σ) at *R* = 0.040 (R_w = 0.055, GOF = 1.48). Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package.

(17) The absolute configuration of **5** was established during the course of the least-squares parameter refinement by incorporating the imaginary contributions to the anomalous dispersion terms into the structure factor calculations at a late stage in the analysis (*R* = 0.042, R_w = 0.059). For parameters corresponding to the absolute configuration represented by structure **5**, *R* = 0.044 and R_w = 0.061 were significantly lower than those for parameters of the mirror image (*R* = 0.051, R_w = 0.073).

(18) For nomenclature describing cycloalkane ring conformations, see: Dale, J. *Acta Chem. Scand.* **1973**, *27*, 1115–1129.

(19) Saunders, M. *J. Am. Chem. Soc.* **1987**, *109*, 3150–3152.

found thus far only in this class of compounds.

Although there are several reports of mixed lactone-lactam antibiotics[20] and a reported polyenic macrocyclic lactam, stubomycin (hitachimycin),[21] to our knowledge Sch 38516 and the related compounds represent a new macrolactam family of compounds. Other members of this class and their biosynthesis will be discussed elsewhere.

Acknowledgment. We thank Mr. A. King for isolating sufficient quantities of material and Dr. B. N. Pramanik for mass spectral data.

Supplementary Material Available: Tables of crystallographic data, fractional atomic coordinates, thermal parameters, bond lengths and angles, and torsion angles for **5** (11 pages); tables of observed and calculated structure factor amplitudes for **5** (21 pages). Ordering information is given on any current masthead page.

(20) (a) Ganguly, A. K. *Antibiotics: Isolation, Separation and Purification*; Weinstein, M. J., Wagman, G. H., Eds.; Elsevier: Amsterdam, 1978; pp 39-68. (b) Brufani, M. *Topics in Antibiotic Chemistry*; Sammes, P. G., Ed.; Ellis Horwood: Chichester, England, 1977; Vol. 1, pp 91-212. (c) Viridenomycin: Hasegawa, T.; Kamiya, T.; Henmi, T.; Iwasaki, H.; Yamatodani, S. *J. Antibiot.* **1975**, *28*, 167-175.

(21) Omura, S.; Nakagawa, A.; Shibata, K.; Sano, H. *Tetrahedron Lett.* **1982**, *23*, 4713-4716.

Structure and Reactivity of $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$, a Tungsten Silene Complex

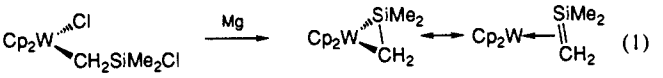
Timothy S. Koloski, Patrick J. Carroll, and Donald H. Berry*,[1]

Department of Chemistry and Laboratory for Research on the Structure of Matter University of Pennsylvania Philadelphia, Pennsylvania 19104-6323

Received April 12, 1990

Remarkable progress has been made over the last two years in the synthesis of stable transition-metal complexes of unsaturated silicon ligands. In 1988 Tilley and co-workers reported the first stable silene complexes, $(C_5Me_5)Ru(PR_3)(H)(\eta^2\text{-}R'_2Si{=}CH_2)$.[2] More recently, stable mononuclear complexes of disilenes have been prepared by Pham and West[3] and by our research group,[4] and binuclear disilene complexes have been prepared by Youngs and co-workers.[5] Unlike stable free silenes and disilenes which require extremely bulky substituents to prevent dimerization, the stabilization afforded by coordination to transition metals has allowed the isolation of complexes of relatively unhindered silenes and disilenes. We have recently extended our method of preparation of stable disilene complexes to the synthesis of a silene complex, and we now describe the structure of $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$ (**1**, $Cp \equiv \eta^5\text{-}C_5H_5$) and its reactions with methanol, hydrogen, trimethylsilane, and donor ligands.

Silene complex **1**[6] was prepared in 86% isolated yield by the reductive dechlorination of $Cp_2W(Cl)(CH_2SiMe_2Cl)$[7] with magnesium in dimethoxyethane (eq 1). The ^1H NMR spectrum of **1** consists of three singlets in the ratio 10:6:2 corresponding to equivalent sets of Cp, SiMe, and CH_2 protons, respectively.



(1)

A single resonance is observed at δ -15.7 in the ^{29}Si NMR (DEPT) spectrum ($^1J_{^{183}W-^{29}Si}$ = 57.1 Hz). The one-bond W-Si coupling constant is small compared to those of tungsten silyls studied in our laboratory (83.0-117.6 Hz) and is similar to that reported for the analogous tungsten disilene complex (50.7 Hz).[4] The ^{13}C NMR spectrum of **1** reveals a resonance for the methylene carbon at δ -41.09 ($^1J_{^{183}W-C}$ = 28.5 Hz, $^1J_{C-H}$ = 137 Hz). The W-C coupling constant is substantially smaller than those observed in normal tungsten-carbon single bonds (43-89 Hz).[8] The low degree of s-orbital character in the bonds to tungsten in **1** implied by the small W-Si and W-C couplings is consistent with the metal interacting principally with the p-π orbitals of a silaolefinic fragment.[9] However, the small C-H coupling of the methylene carbon argues for a greater degree of metallacyclic character in **1** than in the analogous molybdenocene ethylene complex, $Cp_2Mo(\eta^2\text{-}C_2H_4)$ (^{13}C: δ 11.8, $^1J_{C-H}$ = 153 Hz).[10]

An ORTEP drawing of the structure of **1** determined from a single-crystal X-ray diffraction study is shown in Figure 1.[11] The W-Si (2.534 (2) Å) and W-C11 (2.329 (7) Å) bond lengths are not unusual compared with those in structurally characterized tungsten silyls and alkyls. However, the silene Si-C bond length of 1.800 (8) Å lies between typical Si-C single bond (1.87-1.91 Å)[12] and Si-C double bond (1.70-1.76 Å)[13] distances, which can

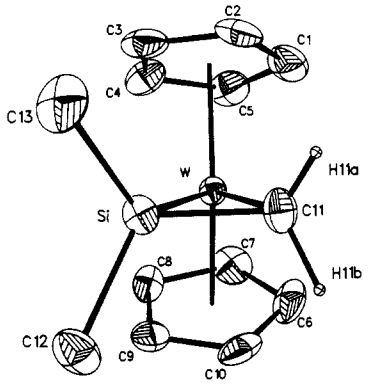


Figure 1. ORTEP drawing of $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$ (**1**) showing 30% probability thermal ellipsoids. Hydrogen atoms on the Cp and methyl groups are omitted for clarity. Selected distances (Å) and angles (deg): W-Si = 2.534 (2); W-C11 = 2.329 (7); Si-C11 = 1.800 (8); Si-C12 = 1.896 (9); Si-C13 = 1.877 (9); Si-W-C11 = 43.2 (2); W-Si-C11 = 64.30 (7); C11-Si-C12 = 124.0 (3); C11-Si-C13 = 120.3 (3); C12-Si-C13 = 103.7 (5); H11a-C11-H11b = 117.

(1) Alfred P. Sloan Fellow, 1990-1992.

(2) (a) Campion, B. K.; Heyn, R.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558. (b) Campion, B. K.; Heyn, R.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 4079.

(3) (a) Pham, E. K.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667-7668. (b) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517.

(4) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 452.

(5) (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068-4070. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577-578. (c) Anderson, A. B.; Shiller, P.; Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2320.

(6) $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$ (**1**): ^1H NMR δ 3.94 (Cp), 0.45 ($SiMe_2$), -0.63 (CH_2); $^{13}C\{^1H\}$ NMR δ 74.42 (Cp), -1.48 ($SiMe_2$), -41.09 (CH_2, J_{W-C} = 28.5, J_{CH} = 137 Hz); ^{29}Si NMR (DEPT) δ -15.66 (J_{W-Si} = 57.1 Hz). Anal. Calcd for $C_{13}H_{18}SiW$: C, 40.43; H, 4.70. Found: C, 40.38; H, 4.65.

(7) $Cp_2W(Cl)(CH_2SiMe_2Cl)$ was prepared in 72% yield from the reaction of $[Cp_2WHLi]_4$ with $ClSiMe_2CH_2Cl$. Anal. Calcd for $C_{13}H_{18}Cl_2SiW$: C, 34.16; H, 3.97. Found: C, 34.27; H, 4.10. The assignment of the structure as $Cp_2W(Cl)(CH_2SiMe_2Cl)$ rather than $Cp_2W(Cl)(SiMe_2CH_2Cl)$ is based on the large W-C coupling (61 Hz, δ -26.1) in the ^{13}C NMR spectrum and the absence of an observable W-Si coupling in the ^{29}Si spectrum (δ 45.9). Full details are included in the supplementary material.

(8) Mann, B. E.; Taylor, B. F. In *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; pp 41, 185.

(9) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(10) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507.

(11) A crystal of **1** ($C_{13}H_{18}SiW$) measuring 0.28 × 0.25 × 0.18 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, and cell parameters were determined: orthorhombic space group $P2_12_12_1$ (Z = 4), with a = 7.446 (1) Å, b = 8.352 (1) Å, c = 20.156 (2) Å, and V = 1253.6 (4) Å^3. A total of 2128 unique reflections were measured ($4° \le 2\theta \le 55°$), of which 1695 with $I > 3\sigma$ were used in the refinement (136 variables). All non-hydrogen atoms were refined anisotropically. The methylene hydrogens were located, but their positional parameters could not be successfully refined. At least one hydrogen on each methyl group was located, and all other hydrogen atom positions were calculated. Final agreement factors: R_1 = 0.025, R_2 = 0.033, and goodness of fit = 1.012. Full details of data collection and refinement are included in the supplementary material.

0002-7863/90/1512-6405$02.50/0