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.

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

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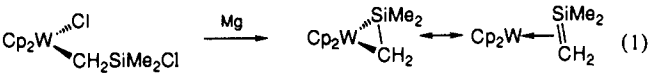
Received April 12, 1990

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 ($^1J_{^{183}W\text{-}^{29}Si}$ = 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 ($^1J_{^{183}W\text{-}C}$ = 28.5 Hz, $^1J_{C\text{-}H}$ = 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, $^1J_{C\text{-}H}$ = 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

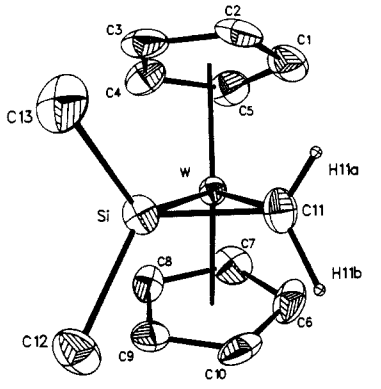


Figure 1. ORTEP drawing of $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$ (**1**) showing 30% probability thermal ellipsoids. Hydrogen atoms on the Cp and methyl groups are omitted for clarity. Selected distances (Å) and angles (deg): W-Si = 2.534 (2); W-C11 = 2.329 (7); Si-C11 = 1.800 (8); Si-C12 = 1.896 (9);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

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(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, $J_{W\text{-}C}$ = 28.5, J_{CH} = 137 Hz); ^{29}Si NMR (DEPT) δ -15.66 ($J_{W\text{-}Si}$ = 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.

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(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.

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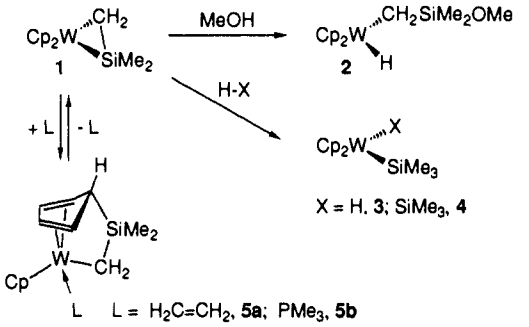
Scheme I



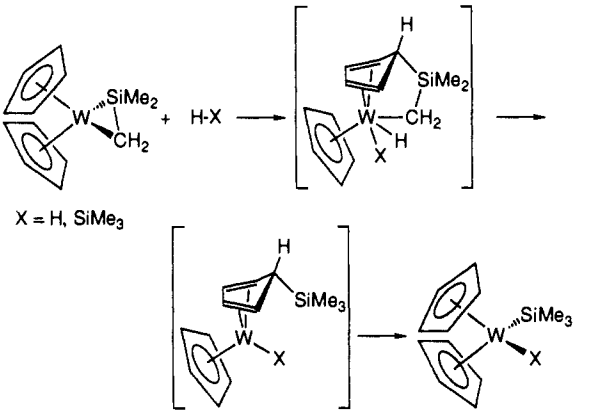
presumably be attributed to partial Si–C double bond character. The silene Si–C distance in this tungsten complex is very similar to values found in silene complexes of ruthenium (1.78 (2) Å)[2a] and iridium (1.810 (6) Å),[2b] despite the different coordination environments at the metals and substituents on silicon in the three compounds.

Preliminary studies indicate that **1** is highly reactive toward a variety of reagents under mild conditions (Scheme I). Methanolysis of **1** in benzene results in cleavage of the W–Si bond to produce $Cp_2W(H)(CH_2SiMe_2OMe)$ (**2**).[14] In contrast, **1** reacts with nonpolar reagents such as hydrogen and trimethylsilane at 25 °C to yield quantitatively $Cp_2W(H)(SiMe_3)$ (**3**)[15] and $Cp_2W(SiMe_3)_2$ (**4**),[16] the products of W–C bond cleavage.

Treatment of **1**, an 18e⁻, coordinatively saturated complex, with donor ligands such as C_2H_4 and PMe_3 at 25 °C results in the formation of η^4:η^1-$C_5H_5SiMe_2CH_2$ complexes in which the donor ligand occupies a coordination site on tungsten generated by migration of the silene silicon to the Cp ring (**5a**,**b**; L = C_2H_4, PMe_3). Surprisingly, this transformation is completely reversible. An equilibrium mixture of **5a** and **1** (ca. 4:1) is formed in benzene solution under 4 atm of ethylene, and removal of the ethylene atmosphere results in quantitative conversion back to **1**. Compound **5a** has been characterized by ^1H, ^{13}C, and 2-D (COSY) NMR.[17] Related migration of silicon ligands to Cp rings has been observed in several metal silyl complexes, generally following ring deprotonation.[18] The reverse migration of alkyl groups from endo-substituted η^4-C_5H_5R complexes has also been observed.[19] Compound **5b** is less labile than **5a**, although it also reverts to **1** in the absence of PMe_3 at 65 °C in benzene solution. Compound **5b** has been isolated in 90% yield and fully characterized.[20] The structure of **5b** has been conclusively established by a single-crystal X-ray diffraction study, the results of which will be reported in a future publication.[21]

Although reaction of **1** with H_2 or Me_3SiH could proceed via concerted addition across the W–C bond[22] or through a 16e⁻ η^3-Cp intermediate,[23] the formation of **5a**,**b** suggests an interesting alternative in which H–X oxidative addition (X = H, $SiMe_3$) occurs at the 16e⁻ center in an η^4-Cp intermediate generated by silene to ring migration (Scheme II). Reductive elimination of the C–H bond would yield an η^4-*endo*-$C_5H_5SiMe_3$ complex, and silyl-group migration back to tungsten would then yield the observed products.

Scheme II



Acknowledgment. Financial support of this work by the National Science Foundation (Grant No. CHE-8808161) is gratefully acknowledged. D.H.B. also thanks the University of Pennsylvania Natural Science Association for a Young Faculty Award.

Supplementary Material Available: Description of synthetic procedures and spectroscopic data for all new compounds, details of X-ray data collection and refinement for **1**, and tables of positional parameters, anisotropic thermal parameters, and intramolecular distances and angles for **1** (9 pages); listing of final structure factor amplitudes for **1** (7 pages). Ordering information is given on any current masthead page.

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(14) $Cp_2W(H)(CH_2SiMe_2OMe)$ (**2**): ^1H NMR δ 4.17 (Cp), 3.42 (OMe), 0.19 ($SiMe_2$), −0.74 (CH_2), −11.33 (W–H, J_{W-H} = 72 Hz); $^{13}C\{^1H\}$ NMR δ 78.80 (Cp), 49.76 (OMe), 0.20 ($SiMe_2$), −42.15 (CH_2, J_{W-C} = 58 Hz).

(15) Jiang, Q.; Koloski, T. S.; Berry, D. H., manuscript in preparation.

(16) $Cp_2W(SiMe_3)_2$ (**4**): ^1H NMR δ 3.87 (Cp), 0.40 ($SiMe_3$). Anal. Calcd for $C_{16}H_{28}Si_2W$: C, 41.74; H, 6.13. Found: C, 41.87; H, 5.95.

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(20) (η^4:η^1-$C_5H_5SiMe_2CH_2$)W(Cp)(PMe_3) (**5b**): ^1H NMR δ 5.43 (m, 1 H, C_5H_5Si), 4.74 (m, 1 H, C_5H_5Si), 3.95 (Cp, d, J_{P-H} = 3.1 Hz), 3.89 (m, 1 H, C_5H_5Si), 2.22 (m, 1 H, C_5H_5Si), 1.06 (m, 1 H, C_5H_5Si), 0.86 (d, J_{P-H} = 7.9 Hz, 9 H, PMe_3), 0.55 (dd, J_{P-H} = 4.4 Hz, J_{H-H} = 11.6 Hz, 1 H, $SiCH_2$), 0.47 (s, 3 H, SiMe), 0.36 (s, 3 H, SiMe), 0.10 (t, J_{P-H} = J_{H-H} = 11.6 Hz, 1 H, $SiCH_2$); ^{29}Si NMR (DEPT) δ 27.91 (d, J_{Si-P} = 4.0 Hz). Anal. Calcd for $C_{16}H_{27}PSiW$: C, 41.57; H, 5.89. Found: C, 40.74; H, 5.74.

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Synthesis and Structure of an *in*-Phosphaphane: Enforced Interaction of a Phosphine and an Aromatic Ring

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A major theme of cyclophane chemistry is the study of functional-group interactions resulting from enforced mutual proximity. Lone-pair electrons are frequently brought into contact with benzene rings in the heterophanes,[1] and the pyridinophane **1** is perhaps the most extreme example of this sort.[2] Its crystal structure shows the pyridine to be perpendicular to the benzene ring,[2b] and the basicity of the pyridine is substantially reduced;[2c]

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