extending this model to other 14-membered-ring compounds to determine the generality and predictive power of this approach.

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Disilene Complexes of Molybdenum and Tungsten

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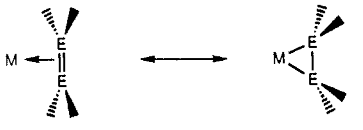
The stabilization afforded by coordination to transition metals has been exploited to prepare complexes of many reactive species that would otherwise have only brief lifetimes. Stable complexes of species such as carbon monosulfide,[1] benzynes,[2] and anti-Bredt olefins,[3] for example, have been isolated and characterized. Recently several researchers have explored the stabilization of unsaturated silicon species such as silenes ($R_2Si{=}CR'_2$)[4-6] and disilenes ($R_2Si{=}SiR_2$)[7] through the formation of transition-metal complexes. We now report the synthesis of molybdenum and tungsten complexes of a relatively unhindered disilene, Si_2Me_4, and the single-crystal X-ray structure determination of the tungsten complex.

The bonding of a disilene to a metal center can be expected to be similar to that of an organic olefin, which is best described by the Dewar-Chatt-Duncanson model.[8] In this model, synergistic σ and π interactions between the olefin p–π and π^* orbitals and metal orbitals of appropriate symmetry lead to a continuum of possible structures bounded by species containing formal sp^2 and sp^3 centers ("olefin complexes" and "metallacyclopropanes") as shown below.



The realization that the strong preference for sp^3 hybridization at silicon should lead to significant metallacyclic character in a disilene complex suggested to us that the synthesis of such complexes could be approached in the context of forming an MSi_2 ring, for example, by reductive dehalogenation of a precursor containing an X-M-Si-Si-X fragment. An analogous strategy has been used by Bennett and co-workers to synthesize a nickel benzyne complex.[2d] In the present work, synthesis of the group 6 metallocene derivatives $Cp_2M(Cl)(SiMe_2SiMe_2Cl)$ (M = Mo, W; Cp ≡ η^5-C_5H_5) was accomplished by treatment of $\{Cp_2MHLi\}_4$[9] with $ClSiMe_2SiMe_2Cl$,[10] followed by chlorination of the hydride with CCl_4 (eq 1). Reduction of $Cp_2M(Cl)(SiMe_2SiMe_2Cl)$ with Riecke magnesium in THF yields complexes with the stoichiometry $Cp_2M(SiMe_2)_2$ (M = Mo, **1a**, 67%; W, **1b**, 60%).[11]

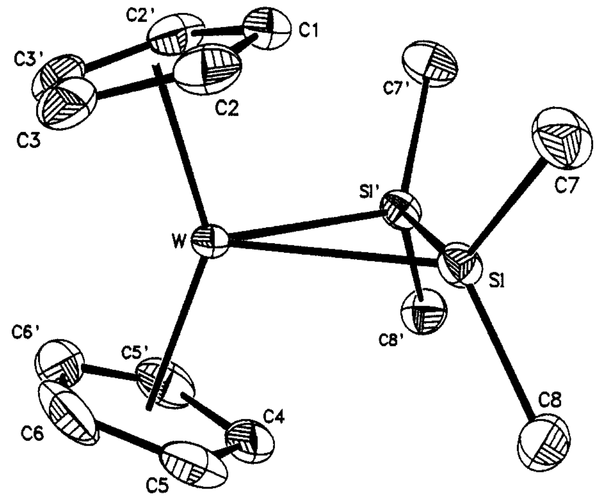
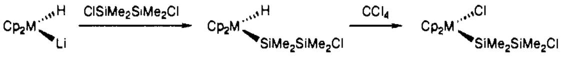
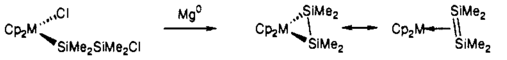


Figure 1. ORTEP drawing of $Cp_2W(SiMe_2)_2$ (**1b**) showing 30% probability thermal ellipsoids. Selected distances and angles: W-Si = 2.606 (2) Å; Si-Si' = 2.260 (3) Å; Si-C7 = 1.889 (8) Å; Si-C8 = 1.898 (9) Å; Si-W-Si' = 51.39 (6)°; W-Si-Si' = 64.30 (7)°; Si-Si-C7 = 124.0 (3)°; Si'-Si-C8 = 120.3 (3)°.



$$\mathrm{Cp_2M(H)(Li)} \xrightarrow{\mathrm{ClSiMe_2SiMe_2Cl}} \mathrm{Cp_2M(H)(SiMe_2SiMe_2Cl)} \xrightarrow{\mathrm{CCl_4}} \mathrm{Cp_2M(Cl)(SiMe_2SiMe_2Cl)} \tag{1}$$



$$\mathrm{Cp_2M(Cl)(SiMe_2SiMe_2Cl)} \xrightarrow{\mathrm{Mg^0}} \mathrm{Cp_2M}\overset{\mathrm{SiMe_2}}{\underset{\mathrm{SiMe_2}}{<|}} \longleftrightarrow \mathrm{Cp_2M}\leftarrow\overset{\mathrm{SiMe_2}}{\underset{\mathrm{SiMe_2}}{\|}} \tag{2}$$

Compounds **1a** and **1b** exhibit nearly identical spectroscopic properties. The ^1H NMR spectra are quite simple, consisting of two singlets in a 5:6 ratio at ca. δ 3.9 and 0.6 attributed to Cp and SiMe protons, indicating highly symmetrical structures. A single resonance is observed in the ^{29}Si NMR (DEPT) spectra (**1a**, δ -20.3; **1b**, δ -48.1, $^1J_{^{183}W-^{29}Si}$ = 50.7 Hz). The one-bond W-Si coupling constant in **1b** is quite small compared to those for other tungsten silyl complexes such as $Cp_2W(H)(SiMe_2Cl)$ (117.6 Hz), $Cp_2W(H)(SiMe_3)$ (84.2 Hz), and $Cp_2W(Cl)(SiMe_2SiMe_2Cl)$ (83.0 Hz), indicating that the W-Si bonding in **1b** involves a high degree of p character on the Si_2 fragment and a relatively small contribution from the silicon s orbitals.

Recrystallization of the tungsten analogue from hydrocarbon solvents yielded well-formed prisms suitable for single-crystal X-ray diffraction studies. The molecular structure of **1b** and selected metrical data are presented in Figure 1.[12] The molecule sits on a crystallographic mirror plane, which contains the tungsten atom and bisects the Si-Si vector and each of the Cp rings. The geometry at tungsten is typical for a bent metallocene complex. The two silicon atoms subtend an angle of 51.39 (6)° at tungsten, and the Cp ring centroid-tungsten-Cp ring centroid angle is

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(11) Satisfactory elemental analyses were obtained for all new compounds. Experimental details are included in the supplementary material.

(12) A crystal of **1b** ($C_{14}H_{22}Si_2W$, fw 430.35) measuring 0.32 × 0.30 × 0.23 mm enclosed in a glass capillary was mounted on an Enraf-Nonius CAD-4 diffractometer, and cell parameters were determined: monoclinic space group $P2/1m$ ($Z = 2$), with $\beta = 116.22$ (1)°, $a = 7.713$ (1) Å, $b = 13.178$ (2) Å, $c = 8.211$ (1) Å. A total of 1781 unique reflections were measured ($4° \leq 2\theta \leq 55°$), of which 1665 with $I > 3\sigma$ were used in the refinement (82 variables). Final agreement factors: $R_1 = 0.032$, $R_2 = 0.049$, and goodness-of-fit = 1.555. Full details of data collection and refinement are included in the supplementary material.

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142.7°. The W–Si bond length of 2.606 (2) Å is within the range of various estimates of the Si and W covalent radii (2.47–2.77 Å).[13,14] The experimental range for W–Si and Mo–Si bonds in seven structurally characterized silyl complexes is 2.389–2.669 Å (2.562-Å average).[15,16]

The Si–Si bond distance in **1b** is 2.260 (2) Å, a value that falls midway between the expected values for a single bond[17] (2.35 Å) and a double bond[18] (2.14 Å). However, unusual Si–Si distances have also been observed in other ESi_2 ring systems: E = O [2.227 (2) Å],[19] NR (2.232 Å),[20] CH_2 [2.272 (2) Å],[21] S [2.289 (2) Å],[22] Te (2.32 Å),[20] and SiR_2 (2.40 Å).[23] Among these main-group rings, however, the Si–Si distance decreases with increasing electronegativity and smaller size of the non-silicon atom. The extremely short Si–Si bond in **1b**, which contains a large electropositive tungsten atom, does not fit this trend and most probably results from partial Si–Si double bond character as described by the Dewar–Chatt–Duncanson model.

Another measure of disilene character in **1b** is the extent of pyramidalization at silicon. The angles subtended at each silicon by the methyl groups and the other silicon total 348.3°, between the 360° and 329.1° values expected for sp^2 and sp^3 hybridization. The planes containing the $SiMe_2$ fragments are bent away from the tungsten center by 30.2° from the "olefin" plane containing the two silicon atoms and perpendicular to the WSi_2 plane. Thus the silicons are somewhat pyramidal, but less so than found for carbon in ethylene complexes of low-valent early-transition metals ($Cp^*_2Ti(C_2H_4)$, 35°; $Cp^*Ta(CHCMe_3)(PMe_3)(C_2H_4)$, 34°).[24] Adverse nonbonded interactions with the Cp rings may increase the degree of nonplanarity at the silicon atoms. The C7–C3 (Cp–Me) separation is 3.30 Å, within the sum of the van der Waals radii (3.40 Å),[25] and the calculated closest H–H contact is ~2.0 Å. Steric interactions with the Cp rings may also be responsible for the small C7–Si–C8 angle of 104.0 (4)°.

Although **1b** is the first structurally characterized complex of its type, there have been two previous reports of mononuclear transition-metal disilene complexes. In 1987, West briefly described a compound formed by reaction of the stable disilene $Mes_2Si{=}SiMes_2$ (Mes ≡ 2,4,6-trimethylphenyl) with $(R_3P)_2Pt(CH_2{=}CH_2)$.[7a] More recently, Pham and West have reported the synthesis and spectroscopic characterization of two $(R_3P)_2Pt(R'_2SiSiR'_2)$ complexes (R = Ph, C_6H_{11}; R′ = *i*-Pr, Ph).[7b] In addition, Youngs and co-workers have prepared several binuclear platinum complexes in which the two metals are bound to opposite faces of a planar R_2SiSiR_2 fragment.[26]

In summary, the new complexes of the Si_2Me_4 ligand described in this report exhibit properties intermediate between disilene complex and disilametallacycle formalisms, analogous to the situation found in transition-metal complexes of organic olefins. The reaction chemistry of **1a** and **1b** is currently under investigation and will be described in future publications.

Acknowledgment. Financial support for this work was provided by the National Science Foundation and the Pew Science Program. D.H.B. also thanks the University of Pennsylvania Natural Science Association for a Young Faculty Award.

Supplementary Material Available: Description of synthetic procedures, X-ray data collection and refinement, and tables of positional parameters, anisotropic thermal parameters, and intramolecular bond angles and distances for **1b** (7 pages); table of final structure factor amplitudes for **1b** (6 pages). Ordering information is given on any current masthead page.

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(13) The covalent radius of silicon is 1.17–1.18 Å.[14a] The radii of tungsten and molybdenum have been variously estimated as 1.30–1.60 Å.[14a–d] It is assumed in the discussion that the radii of Mo and W are virtually identical.

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Oligonucleotides Containing Flexible Nucleoside Analogues

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In all forms of modern life, genetic information is stored in macromolecules having a pentose (ribose or deoxyribose) as the repeating unit. Because RNA molecules are the most plausible candidates for the first catalytic molecules,[1] and (entirely unrelatedly) as "antisense" oligonucleotides (both DNA and RNA) are potentially valuable for treating a wide range of intractable human diseases,[2] considerable effort has been devoted to the study of these molecules and their analogues.

Two conclusions are evident. First, ribose and deoxyribose ring systems are difficult to synthesize from simple precursors, especially under abiotic conditions.[3] Second, natural oligonucleotides are easily degraded biologically and, in the case of RNA, chemically. The first is problematical for models for the origin of life that postulate that RNA was the first self-replicating molecule; known abiotic reactions seem unable to produce sufficient ribose to permit the assembly of a self-replicating RNA molecule.[4] The second makes externally added antisense oligonucleotides largely unsuitable for controlling the expression of unwanted genes in vivo.

If carbon 2 is removed from the ribose ring system, an isosteric oligonucleotide analogue derived from glycerol can be envisioned (Scheme I, 4).[5] This "flexible" structure is attractive for several reasons. First, glyceronucleosides are (presumably) simpler to prepare than ribonucleosides under prebiotic conditions, and they

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