Organometallics **2004,** *23,* 2944−2948

Where Are the Hydrogen Atoms in $[(\eta^5\text{-}C_5H_5)(PH_3)_2W(H_2SiMe_2)]^+$? A Theoretical Study

Krishna K. Pandey,*,[†,‡] Matthias Lein,[‡] and Gernot Frenking*,[‡]

School of Chemical Sciences, Devi Ahilya University Indore, Indore, India 452017, and Fachbereich Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

Received January 13, 2004

Quantum-chemical DFT calculations of the tungsten silylene complex $[Cp(PH_3)_2W(H_2SiMe_2)]^+$ have been carried out with the aim to elucidate the structure and bonding situation of the molecule. The W−$SiMe_2$ interactions have been examined with an energy decomposition analysis. The geometry optimization with the constraint of C_s symmetry gives a classical dihydride structure as the lowest-lying energy minimum form. Four other structures which have up to two bridging hydrogen atoms are only <5 kcal/mol higher in energy than the classical form. The results suggest that the model complex $[Cp(PH_3)_2W(H_2SiMe_2)]^+$ and the real complex $[Cp^*(dmpe)W(H)_2SiMe_2][B(C_6F_5)_4]$, which was synthesized by Tilley, have a very fluxional $W(H_2SiMe_2)$ moiety, which makes it meaningless to classify the structure as classical or nonclassical. The energy decomposition analysis indicates that, in all binding modes, $W \rightarrow SiMe_2$ π-back-donation is very weak. The silylene complex should therefore be considered as a $W(d^2)$ compound, where the formal oxidation state of the metal is +4.

Introduction

The characterization of transition-metal σ complexes has attracted much attention in recent years, due to their role in the oxidative-addition and reductive-elimination steps occurring in a wide variety of catalytic processes.[1] Since the report of the first nonclassical dihydrogen complex[2] in 1984, numerous examples of dihydrogen[3] and silane[4] complexes have been reported. The transformation of a coordinated dihydrogen molecule into a dihydride is a key problem in the field of transition-metal-mediated hydrogen activation, where silylene and silane complexes play an important role.[1] In this context, the recent synthesis and X-ray diffraction study of the silylene complex $[Cp^*(dmpe)W(H)_2SiMe_2][B(C_6F_5)_4]$ (**I**) by Mork and Tilley,[5] which has a transition metal with a low d^n configuration, is of particular interest because the positions of the hydrogen atoms in complex **I** could not be determined. The X-ray structure contains two independent cation−anion pairs in the asymmetric unit. The Si−W−P bond angles in one cation, **Ia**, are nearly identical, while in the other cation, **Ib**, they are quite different. The latter study is also relevant for the search of transition-metal base-free silylene[5,6] and η^2-silane complexes,[1,4b,e,7] which are important because of their practical applications in synthesis and catalysis and also because their structure and bonding situation is a challenging topic in transition-metal chemistry.

Theoretical calculations have been carried out to substantiate the presence of η^2-dihydrogen[3g,8] and η^2-silane[4d,g−i,9] coordination to a metal center in many transition-metal complexes. It has been suggested that the lengthening of the H−Si bond in metal−η^2-HSi

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[†] Devi Ahilya University Indore.

[‡] Philipps-Universität Marburg.

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10.1021/om049964f CCC: $27.50
Publication on Web 05/05/2004

complexes is due to its low-lying σ^* orbital. Hence, a stable complex which exhibits a truly nonclassical H−Si bonding situation can be expected when there is only weak back-bonding. As pointed out by Frenking et al.,[10] there is a danger in the uncritical use of the frontier orbital model for explaining chemical bonding, because other factors such as electrostatic interactions and Pauli repulsions may also play a significant role. If **I** is a W(IV) complex, it would have a d^2 configuration at the metal and back-bonding should be strong. However, if **I** is a W(VI) complex, the metal configuration would be d^0 and back-bonding should be very weak. Therefore, it is possible that **I** could be the first complex which has a metal−η^2-H_2SiMe_2 moiety. Mork and Tilley reported that, on the basis of the ^{1}H NMR T_1 relaxation experiments, the hydride ligands in the silylene dihydride complexes appear to be classical in nature.[5] The chemical behavior of **I** showed, however, that the compound reacts in a chameleon-like way. The reaction with 1 equiv of pyridine forms the isolable complex $[Cp^*(dmpe)W(H)_2SiMe_2(py)][B(C_6F_5)_4]$, which is a typical reaction for a late-metal silylene complex. In contrast, the reaction of **I** with MeCl produces Me_3SiCl, formally by insertion of Me_2Si into the C−Cl bond, while the osmium silylene complex $[Cp^*(Me_3P)_2OsSiMe_2][B(C_6F_5)_4]$ reacts with alkyl chlorides to form $[Cp^*(Me_3P)_2OsSiMe_2Cl][B(C_6F_5)_4]$.[5]

To shed some light on the structure of **I**, we carried out quantum-chemical calculations using gradient-corrected DFT methods of the model compound $[Cp(PH_3)_2W(H_2SiMe_2)]^+$ (**II**). We report about the equilibrium geometries of isomeric forms of **II** and the theoretically predicted ^{29}Si NMR chemical shifts. We also present a theoretical analysis of the metal−ligand bonding situation.

Theoretical Methods

The calculations were performed at the nonlocal DFT level of theory using the exchange functional of Becke[11] and the correlation functional of Perdew[12] (BP86). Scalar relativistic effects have been considered using the ZORA formalism.[13] Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations. Triple-ζ basis sets augmented by two sets of polarization functions have been used for all the elements.[14] The $(n-1)s^2$ and $(n-1)p^6$ core electrons of the main-group elements and $(1s2s2p3s3p3d4s4p4d)^{46}$ core electrons of tungsten were treated by the frozen-core approximation.[15] An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to present the Coulomb and exchange potentials accurately in each SCF cycle.[16] The vibrational frequencies have been calculated using numerical second derivatives. The calculations of the ^{29}Si NMR chemical shifts were carried at the BP86/GIAO level of theory using quadruple-ζ basis sets augmented by four sets of polarization functions. All calculations were carried out using the program package ADF-2002.01.[17]

The bonding interactions between the fragments $[Cp(PH_3)_2W(H)_2]^+$ and $SiMe_2$ have been investigated using the energy decomposition analysis (EDA) of ADF, which is based on the methods of Morokuma[18] and Ziegler and Rauk.[19] According to the EDA, the bond dissociation energy ΔE between two fragments such as $[Cp(PH_3)_2W(H)_2]^+$ and $SiMe_2$ is partitioned into several contributions that can be identified as physically meaningful entities. First, ΔE is separated into the two major components ΔE_{prep} and ΔE_{int}:

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \tag{1}$$

Here, ΔE_{prep} is the energy that is necessary to promote both fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state that they have in the combined molecule. ΔE_{int} is the interaction energy between the two fragments in the molecule. The interaction energy, ΔE_{int}, can be divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \tag{2}$$

ΔE_{elstat} describes the classical electrostatic interaction between two fragments, which is usually attractive. The second term in eq 2, ΔE_{Pauli}, gives the repulsive interactions between the fragments due to the fact that two electrons with the same spin cannot occupy the same region in space. The term comprises the four-electron destabilizing interactions between occupied orbitals. ΔE_{Pauli} is calculated by enforcing the Kohn−Sham determinant of the molecule, which results from superimposing both fragments, to obey the Pauli principle through antisymmetrization and renormalization. The stabilizing orbital interaction term ΔE_{orb} is calculated in the final step of the energy analysis when the Kohn−Sham orbitals relax to their optimal form. This last term can be further partitioned into contributions by the orbitals that belong to different irreducible representations of the point group of the system. It has been suggested that the ratio $\Delta E_{elstat}/\Delta E_{orb}$ may be used to estimate the covalent and electrostatic character of the bond.[10] Further details about the method have been described in the recent literature.[20]

Results and Discussion

We optimized the geometry of the model compound **II** with the constraint of C_s symmetry using different starting structures for the optimization. Six different structures, **IIa**−**f**, were found as stationary points on the PES. The calculated structures are shown in Figure 1. Table 1 gives the most important bond lengths and

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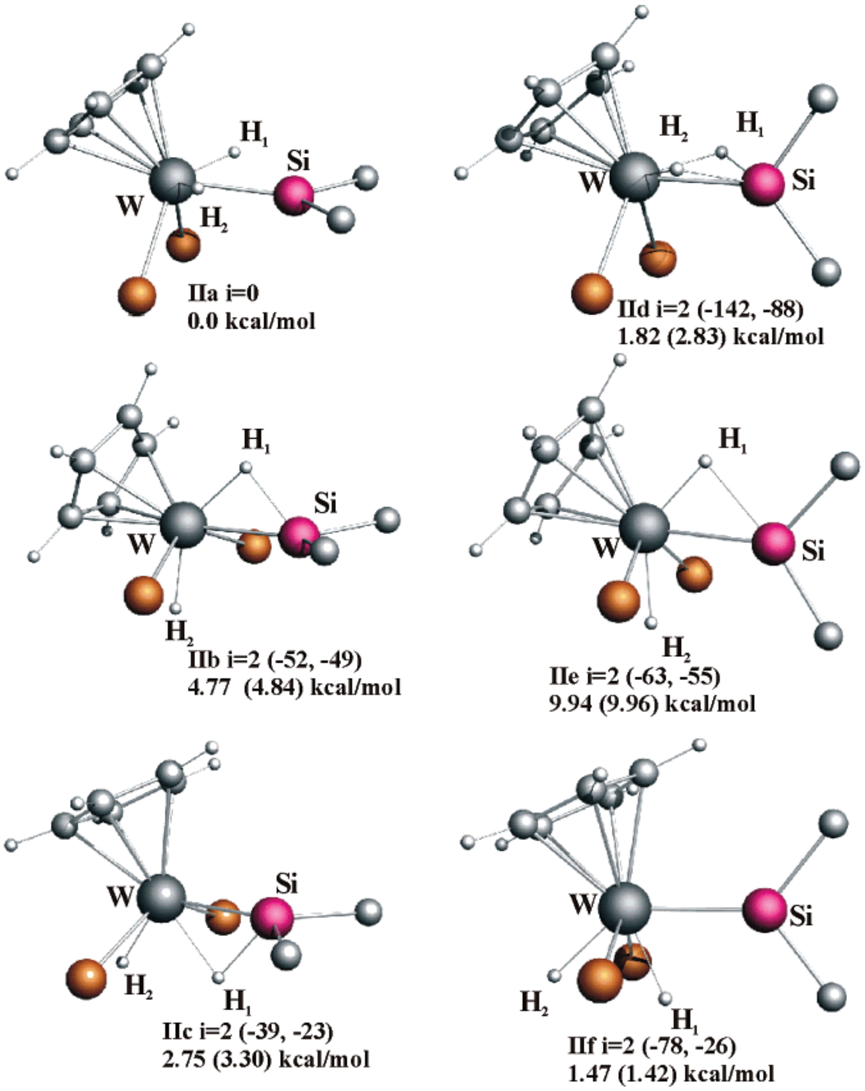

Figure 1. Optimized structures (BP86/TZ2P) of the model complexes **IIa**−**f**, showing the number of imaginary frequencies *i* (cm^{-1}) and relative energies (kcal/mol). ZPE-corrected relative energies are given in parentheses.

bond angles of **IIa**−**f** and the experimental values of the two forms **Ia** and **Ib**.

The energetically lowest lying form of the model compound **IIa** is a silylene complex which has two classical W−H hydride bonds above the $SiMe_2$ ligand pointing toward the Cp ring (Figure 1). Structure **IIa** is a minimum on the PES ($i = 0$). The geometry optimizations of other starting structures with the same arrangement of the silylene ligand with respect to the Cp and PH_3 ligands, but with a different orientation of the hydride ligands, gave **IIb** and **IIc** as stationary points. Both structures are second-order saddle points ($i = 2$) on the PES. However, both forms are only 4.77 kcal/mol (**IIb**) and 2.75 kcal/mol (**IIc**) higher in energy than **IIa**. Both forms have one η^2-bonded hydrogen atom bridging the silylene ligand and the tungsten atom. Structure **IIc** has the classical hydride ligand and the η^2-bonded hydrogen atom on the same site of the $SiMe_2$ ligand plane, while **IIb** has the hydrogen atoms on opposite sites. The small energy differences between the energy minimum structure **IIa** and the nonclassical forms **IIb** and **IIc** suggest that there is a large hydrogen atom fluxionality in compound **II**.

The significant hydrogen fluxionality in **II** is further corroborated when the structures of **IId**−**f** are considered where the $SiMe_2$ ligand is rotated 90° about the W−Si bond. Figure 1 shows that structures **IId** and **IIf** are only 1.82 and 1.47 kcal/mol higher in energy, respectively, than **IIa**. The former structure has two η^2-bonded hydrogen atoms bridging the silylene ligand and the tungsten atom, while the latter form has two classical W−H hydride bonds. It is only structure **IIe** which has one classical and one bridging hydrogen atom that is somewhat higher (9.94 kcal/mol) in energy than **IIa**. Note that all structures **IId**−**f** are second-order saddle points ($i = 2$) on the PES. We want to emphasize that the present level of theory does not exclude the possibility that the relative energies of the structures and the nature of the stationary point on the PES for **IIa**−**f** change at higher levels of theory, because the energy differences are very small. This should not change the main conclusion of the paper, because the BP86/TZ2P level of theory has been proven to be quite reliable for the calculation of transition-metal compounds.[24] The important point of the present calculations is the finding that the energy differences between classical and nonclassical hydride complexes having

Table 1. Selected Optimized Geometrical Parameters[a] and Hirshfeld Charges for $[(\eta^5\text{-}C_5H_5)(PH_3)_2W(H)_2(SiMe_2)]^+$

	exptl[b]		calcd					
	Ia	**Ib**	**IIa**	**IIb**	**IIc**	**IId**	**IIe**	**IIf**
r(W,Si)	2.358(2)	2.354(2)	2.414	2.485	2.407	2.412	2.440	2.442
r(W,P)	2.475(2)	2.487(2)	2.474	2.434	2.447	2.442	2.424	2.445
	2.476(2)	2.431(3)						
$r(W,H_1)$			1.711	1.730	1.847	1.788	1.708	1.735
$r(W,H_2)$			1.711	1.855	1.749	1.788	1.755	1.717
$r(W,C_{Cp})_{av}$	2.347(8)	2.365(8)	2.354	2.338	2.343	2.342	2.379	2.365
r(Si,C)	1.861(9)	1.84(1)	1.889	1.890	1.886	1.877	1.894	1.886
	1.877(9)	1.88(1)				1.882	1.890	1.902
$r(Si,H_1)$			2.116	3.195	1.725	1.770	1.945	2.370
$r(Si,H_2)$			2.116	1.671	3.611	1.770	2.783	3.873
$a(W,H_1,Si)$			77.4	50.5	35.4	85.3	83.5	71.1
$a(W,H_2,Si)$			77.4	89.5	84.7	85.3	60.1	25.7
a(Si,W,P)	97.77(7)	97.37(9)	92.8	80.1	91.5	97.8	80.8	92.7
	97.00(8)	108.6(1)						
a(W,Si,C)	130.8(3)	130.2(4)	127.5	127.9	127.8	129.4	126.9	127.8
	126.7(3)	125.6(4)				122.0	127.2	127.5
W			0.11	0.14	0.12	0.11	0.13	0.11
Si			0.33	0.32	0.33	0.39	0.33	0.32
$SiMe_2$			−0.01	0.06	0.03	0.17	−0.01	−0.06
H_1			−0.06	−0.09	−0.05	−0.05	−0.07	−0.07
H_2			−0.06	−0.05	−0.09	−0.05	−0.08	−0.09

[a] Distances (r) are given in Å and angles (a) in degrees. [b] Reference 5.

zero, one, or two η^2-bonded hydrogen atoms bridging the silylene ligand and the tungsten atom are very small. Thus, even if an X-ray structure analysis or an NMR spectrum would give a classical hydride structure, the complex might react like a compound which has a nonclassical bonding situation, because of the significant hydrogen fluxionality which is predicted by the calculations. Note that the calculated bond lengths and bond angles of **IIa** are in good agreement with the experimental values of **Ia** and **Ib** (Table 1). The good agreement, which could be interpreted that **I** has a classical dihydride structure with a silylene ligand, is deceptive, because the nonclassical forms are close in energy. We want to point out that in a recent theoretical study of silylene complexes $[(dhpe)Pt(SiHR_2)]^+$ by Lledos, Eisenstein, and co-workers[4g] it was also found that classical and nonclassical forms are very close in energy.

We searched for other energy minimum structures besides **IIa** which might exist on the PES. To this end, we used slightly distorted geometries of the C_s forms **IIb**−**f** as the starting points for geometry optimization without symmetry constraint (C_1). The optimizations either gave the C_s structures as a result of the geometry optimization or they converged to structure **IIa**. Inspection of the imaginary modes showed that the associated vectors indicate a rotation of the CH_3 or PH_3 groups which deviate slightly from local C_{3v} symmetry. The imaginary modes are *not* associated with movement of the hydridic hydrogen atoms or rotation of the silylene group. We think that the small imaginary frequencies which are calculated by numerical second derivatives of the energy with respect to the coordinates are an artifact of the mathematical procedure caused by the flat potential energy surface for rotation of the CH_3 or PH_3 groups and that structures **IIb**−**f** are true energy minima.

Table 2. Calculated ^{29}Si NMR Chemical Shifts (in ppm) of TMS and Compounds IIa−f at the BP86/GIAO/QZ4P//BP86/TZ2P level

	TMS	**IIa**	**IIb**	**IIc**	**IId**	**IIe**	**IIf**
σ	319.7	−42.9	56.8	−74.2	−18.8	−48.6	−142.0
δ[a]	0.0	362.6	262.9	393.9	338.5	368.3	461.7

[a] Relative to TMS.

To identify the structure which is observed experimentally, we calculated the ^{29}Si NMR chemical shifts of **IIa**−**f** and compared the theoretically predicted values (Table 2) with the experimental result for **I,** δ 314 ppm.[5] The theoretical data for **IIa**−**f** in Table 2 are within the range of 263−462 ppm. Previous calculations of silicon compounds have shown that calculated ^{29}Si NMR chemical shifts using the GIAO approach are in very good agreement with experimental values.[22] However, the calculations were performed for normal silicon compounds in the oxidation state +IV. The accuracy of GIAO values for the ^{29}Si NMR signal of a silylene ligand might not be as good as for silicon compounds which have a normal bonding situation. A theoretical study of experimental and theoretical (GIAO) ^{29}Si NMR signals in stable silylenes showed that the calculations overestimate the downfield shift by 20−30 ppm.[23] It is possible that the calculated values for **IIa**−**f** are also somewhat too high. The calculated values for **IIb** (263 ppm) and for **IIf** (462 ppm) are beyond the range of the experimental value, 314 ppm. The theoretical value for the energy minimum structure **IIa** (363 ppm) would be in reasonable agreement with the reported data if it is assumed that the calculation overestimates the deshield-

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Table 3. Energy Decomposition Analysis of $[(\eta^5\text{-}C_5H_5)(PH_3)_2W(H)_2(SiMe_2)]^+$ Using the Fragments $[(\eta^5\text{-}C_5H_5)(PH_3)_2W(H)_2]^+$ and $SiMe_2$[a]

term	IIa	IIb	IIc	IId	IIe	IIf
ΔE_{int}	−94.2	−93.3	−94.0	−100.9	−87.5	−80.3
ΔE_{Pauli}	227.3	299.3	280.6	410.9	251.2	175.9
ΔE_{elstat}[b]	−187.8	−209.5	−214.9	−260.7	−191.5	−159.1
	(58.4%)	(53.4%)	(57.4%)	(50.9%)	(56.5%)	(62.1%)
ΔE_{orb}[b]	−133.7	−183.1	−159.7	−251.0	−147.2	−97.1
	(41.6%)	(46.6%)	(42.6%)	(49.1%)	(43.5%)	(37.9%)
A′[c] (σ)	−122.1	−170.3	−146.3	−209.9	−120.5	−73.6
	(91.3%)	(93.0%)	(91.6%)	(83.6%)	(81.9%)	(75.8%)
A″[c] (π)	−11.7	−12.9	−13.4	−41.2	−26.7	−23.4
	(8.7%)	(7.0%)	(8.4%)	(16.4%)	(18.1%)	(24.2%)

[a] The energy values are given in kcal/mol. [b] The value in parentheses gives the percentage contribution to the total attractive interactions. [b] The value in parentheses gives the percentage contribution to the total orbital interactions.

ing as in stable free silylenes, but also the theoretical values for **IIc**−**e** would still be in the range of the experimental value.

Should the classical silylene complex be considered as a d^2 complex where the tungsten-based electrons are not invoked in the metal−silylene interactions, or is there a significant W→SiMe$_2$ π-back-donation which means that the metal has a formal d^0 configuration? What is the difference among the W−SiR$_2$ interactions in the structures **IIa**−**f**? Detailed information is available from the results of the EDA calculations which are given in Table 3.

The EDA result shows that the W−SiMe$_2$ attractive interactions in **IIa**−**f** have an electrostatic character slightly higher than the covalent character. The ΔE_{orb} term in the energy minimum structure **IIa** contributes 41.6% of the total attraction. The orbital term has a slightly higher weight in the other forms, except in **IIf**, but it is always <50%. Note that the absolute value of ΔE_{orb} in **IId** is rather large because of the doubly hydrogen bridged structure, which has also the largest Pauli repulsion (Table 3). We want to point out that the atomic partial charges which are given in Table 1 are deceptive for estimating electrostatic interactions between bonded atoms. The calculated charges for W and Si are positive. A naïve interpretation would suggest that there should be electrostatic repulsion between the silylene ligand and the metal in the complexes **IIa**−**f**. The electronic charge at the atoms is highly nonisotropic in most molecules. The silicon atom in silylenes SiR$_2$ has a σ electron pair. Even in SiF$_2$, the positively charged Si carries a *local area of negative charge* concentration in the σ direction which causes SiR$_2$ species to behave like a Lewis base. A similar situation has recently been described for group 13 diyl complexes $(CO)_m$TM−ER (E = B through Tl) where the electrostatic attraction between TM and E comes from the local negative charge of the overall positively charged atom E and the local charge depletion of the overall negatively charged atom TM.[10]

The most important information of the EDA results comes from the breakdown of the ΔE_{orb} term into the contributions of the a′ (σ) and a″ (π) orbitals. Table 3 shows that the π-contribution to the W−SiMe$_2$ bonding in the classical energy minimum structure **IIa** is rather small (8.7%). This means that the silylene ligand binds mainly as an σ-donor and that the π-back-bonding is relatively weak. This is in agreement with a recent energy decomposition analysis of tungsten complexes (CO)$_5$W−EH$_2$ (E = C − Pb), which show that only when E = C is there a significant π-bonding, while the π-contributions in the heavier analogues are rather small.[21]

Table 3 shows that the other structures **IIb**−**f** exhibit also rather small W−SiMe$_2$ π-back-bonding contributions. The largest absolute value is found for structure **IId** (41.2 kcal/mol). However, the relatively strong π-contribution does not come from genuine W→SiMe$_2$ π-back-donation through interactions with the metal d(π) electrons but rather from the doubly bridging W−H bonds. Note that the relative contributions of the π-back-bonding in the complexes **IId**−**f**, where the silylene group is rotated by 90°, are somewhat larger (16.4−24.2%) than in the complexes **IIa**−**c** (7.0−8.7%) but the σ bonding is still the dominant contribution to the ΔE_{orb} term.

After this work was completed, a joint experimental and theoretical study was published about the structure of the hydrido(hydridosilylene)tungsten complexes [Cp′(CO)$_2$(H)W=Si(H){C(SiMe$_3$)$_3$}], where Cp′ = Cp*, η^5-C$_5$Me$_4$Et.[25]

Summary

The geometry optimization of the tungsten silylene complex $[Cp(PH_3)_2W(H_2SiMe_2)]^+$ with the constraint of C_s symmetry gives the classical dihydride structure **IIa** as the lowest lying energy minimum form. Four other structures, **IIb**−**d**,**f**, which have up to two bridging hydrogen atoms, are <5 kcal/mol higher in energy than **IIa**. The results suggest that the model complex **II** and the real complex **I**, which was synthesized by Tilley, have a very fluxional W(H$_2$SiMe$_2$) moiety which makes it meaningless to classify the complex as a classical or nonclassical silylene compound. The energy decomposition analysis indicates that, in all binding modes, W→SiMe$_2$ π-back-donation is very weak. The silylene complex should therefore be considered as a W(d^2) compound where the formal oxidation state of the metal is +4.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. K.K.P. thanks the Alexander von Humboldt Foundation for a research fellowship. Excellent service by the Hochschulrechenzentrum of the Philipps-Universität Marburg is gratefully acknowledged. Additional computer time was provided by the HLRS Stuttgart and HHLRZ Darmstadt.

Supporting Information Available: Table with the Cartesian coordinates of the optimized structures of **IIa**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049964F