Nature of the Transition Metal-Silicon Double Bond

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The nature of the metal-silicon double bond is investigated using ab initio wavefunctions. Electron correlation is specifically included in the calculations at the FORS-MCSCF (full optimized reaction space multiconfiguration self-consistent field) level of theory. Silylene complexes of the form MSiH₂⁺, containing metals from the first transition series (M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni), are chosen for this study. An analysis of the bonding and electronic structure among the silylene complexes is presented. The silylene complexes are compared to representative carbene analogues, MCH₂⁺, and to CrGeH₂⁺ and CrSnH₂⁺.

Introduction

Organometallic chemistry has been a profitable area of research for many years.¹ Chemistry at the interface of the transition-metal and main group disciplines, in particular transition metal–silicon chemistry, has received increased attention recently.² Transition metal–Si complexes have been implicated as intermediates in important reactions such as hydroisolation,³ silane polymerization,⁴ and chemical vapor deposition of transition-metal silicides.⁵ Complexes with a transition metal–carbon double bond occupy a position of importance in chemistry due to their putative intermediacy in many significant reactions.⁶ The first examples of complexes with transition metal–silicon double bonds, silylene complexes, have been reported recently.⁷ These complexes include coordinatively saturated complexes (e.g., THF, pyridine, or MeCN) coordinated to the Lewis bases (e.g., THF, pyridine, or MeCN). Coordination of analogous type I and type II complexes in the gas-phase is the focus of the present theoretical research. For the sake of comparison, first-row, transition metal carbene complexes (e.g., germylenes, stannylenes, and plumbylenes).²d,e The few silylene complexes which are known include coordinatively saturated complexes (e.g., [Cp(Ph₂P─C₅H₃)_2Ru(SiR₃)⁺]⁺ in solution phase and coordinatively unsaturated ions (e.g., FeSiH³⁺) in the gas phase.⁹

It is the purpose of this research to probe the nature of the bonding in simple silylene complexes of the form MSiH₂⁺ using high level, ab initio wavefunctions (including electron correlation). Silylene complexes, MSiH₂⁺ (M = Ti, V, Cr, Fe, Co, Ni), have been studied experimentally using ion-beam techniques.⁷ Highly accurate wavefunctions, including the effects of electron correlation, allow for a reliable description of the nature of the transition metal–Si double bond and provide a reference with which to compare future calculations on coordinatively saturated silylene complexes. Metals from the first transition series (Sc, Ti, V, Cr, Mn, Fe, Co, Ni) are the focus of the present theoretical research. For the sake of comparison, first-row, transition metal carbene complexes, MCH₂⁺, are investigated at comparable levels of theory. The homologous series of CrEH₂⁺ (E = C, Si, Ge, and Sn) complexes are also included in this study.

In contrast to the large number of characterized carbene complexes,⁶ structurally characterized silylene complexes are rare.²⁶,²⁷ Surprisingly, numerous examples of the higher homologues of silylenes have been reported (i.e., germynes, stannylenes, and even plumbylenes).²⁷ The few silylene complexes which are structurally characterized possess Lewis bases (e.g., THF, pyridine, or MeCN) coordinated to the Si atom.²⁷æ From the notation of Petz,²⁷ these compounds are referred to as type II complexes. This is to distinguish them from type I complexes which have no coordinated base. Comparison of analogous type I and type II germylene and silylene complexes reveals minor perturbations in the geometry upon coordination of the base: the metal-ligand bond lengths by a small amount (<0.1 Å) and the coordination about the ligated atom remains approximately trigonal planar.²⁷ The metal–ligand bond lengths in type II complexes remain smaller than "normal" single bond values.²⁷ All the silylenes (as well as germynes and stannylenes) which have been reported are low valent complexes. In this respect, the silylenes and their higher homologues are more like the "Fischer-type" carbene complexes. To our knowledge, no high-valent silylene complexes (i.e., the Si analogue of "Schrock-type" carbones) has been isolated. High-valent, silylene complexes have been proposed as reactive intermediates in silane polymerization by group IVB (Ti, Zr, and Hf) catalysts.⁴⁴

Calculations

The calculations described herein employ the GAMESS ab initio quantum chemistry package.⁴ Effective core potentials (ECPs) and valence basis sets are used for the transition metals and all main group elements other than C and H.⁵ The C and H atoms are described at the all-electron level employing the 6-31G basis set. The C, Si, Ge, and Sn bases are augmented with a d polarization function (ξ_C = 0.800 for C; ξ_Si = 0.450 for Si; ξ_Ge = 0.246 for Ge; ξ_Sn = 0.183 for Sn). Electron correlation is incorporated using the FORS-MCSCF (full optimized reaction space multiconfiguration self-consistent field) method.¹⁰ The

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References

Figure 1. Schematic diagram showing the geometry, Cartesian axes, FORS-MCSCF wavefunction, states studied and calculated vibrational data for the MSHt+ complexes in this study. The ground state term is enclosed in brackets.

FORS-MCSCF wavefunction includes electron correlation by creating all possible electronic configurations (configuration state functions or CSFs) which can be generated by distributing the active electrons within the active MOs. The molecular orbitals (MOs) which comprise the CSF are optimized as is the contribution each CSF makes to the total FORS-MCSCF wavefunction. The active electrons and active orbitals for the MEHt (E = C, Si, Ge, or Sn) calculations are those associated with the metal-ligand double bond and nonbonding electrons located on the metal.

Stationary points on the potential energy surfaces (PESs) are located using the methods of Baker. Geometry optimizations for all electronic states of interest are carried out at the FORS-MCSCF level employing the basis sets described above. All complexes are optimized within the constraints of C3v symmetry. The Cartesian axes employed are shown in Figure 1. The force constant matrix, obtained from finite differences of analytically determined gradients, was calculated at all stationary points in order to confirm that the geometry corresponds to a minimum (i.e. all positive force constants) on the potential energy surface.

The selection of an active space is a critical factor in a FORS-MCSCF calculation. With the small, symmetrical ions chosen for this study, extra flexibility can be built into the wavefunction while still maintaining computational tractability. If the MSiHt+ complex is considered to be comprised of M* and SiH* fragments, an obvious choice of active spaces is the 3d and 4s AOs of the former and the nonbonding MOs (σSi and πSi) of the latter. Bringing these components together (under C3v symmetry) yields an eight orbital active space: (σMSi(1a1)πMSi*(2b1)σSi(3a1)πSi*(3b2)). The (u1) and (u*) are nonbonding metal MOs. The first three of these are derived from the d(xy), d(zy), and d(xz) AOs, respectively, while the latter (σ1) is a combination of the 4s and 3d1 AOs of the metal ion. The metal–silicon σ bonding and antibonding MOs are in-phase and out-of-phase combinations, respectively, of the 3dσ MO of the metal ion and the π nonbonding MO of the SiH1 fragment. The metal–silicon πMSi and πMSi* are in-phase and out-of-phase combinations, respectively, of the 3dx2−y2 and 4pAOs of the metal ion into any of the active space MOs. The number of active electrons is 4 for SiSHt* and increases by one for each successive transition metal so that NiSiHt* has 11 active electrons. The active spaces for the MCHt+, CrGeHt+, and CrSnHt+ complexes are selected in an identical fashion. The various states (1a1, 2a1, or 3a1) chosen for geometry optimizations of the silylene complexes are given in Figure 1. For MCHt+, CrGeHt+, and CrSnHt+ only that state with the same symmetry as the calculated ground state of the silylene analogue was investigated. Various MCHt+ complexes have been studied using ab initio techniques and the reader is referred to the original literature12 for a more detailed discussion of these.

The contributions from the various resonance structures which describe the metal–silicon double bond are calculated using the MC/LMO/CI (multiconfiguration/localized molecular orbital/configuration interaction) procedure. The MC/LMO/CI procedure described in detail elsewhere and will only be briefly summarized here.13 This procedure has been used previously to characterize the metal–carbon double bond in alkylidene complexes14 as well as main-group species.10 The MC/LMO/CI procedure consists of three steps. In step 1, a FORS-MCSCF calculation is carried out using the active electrons and active orbitals described above. In step 2, the MCSCF natural orbitals which describe the metal–ligand multiple bond are localized with the Boys procedure15 to yield “AO-like” MOs, σE, πE, and σF. The “AO-like” MOs are predominantly located on either the metal or ligand end of the metal–ligand bond. The metal nonbonding molecular orbitals (NBOs) are already localized and are, therefore, not submitted to further localization. In step 3, configuration interaction (CI) with an active space comprising of the “AO-like” MOs and metal NBOs is used to generate all possible resonance structures.

Results and Discussion

a. FORS-MCSCF Wavefunction for MSiHt+ . The FORS-MCSCF wavefunctions for the silylene complexes can be conceptually partitioned into four subspaces: core, metal–silicon σ bond, metal–silicon π bond, and metal nonbonding MOs, |(core*)2(σE*)2(πE*)2(δ1,δ2,πE,σF)⟩.

I. Core. The core subspace is occupied by core electrons (largely removed by the use of ECPs) and valence MOs which are expected to be well described at the Hartree–Fock level and play a little role in the ME bond (e.g., the Si–H bonding MOs 3a1 and 2b1). The only nonvalence electrons included in the present calculations are the eight electrons in the 3s and 3p AOs of the transition metal. In all species studied here the 3s and 3p orbitals comprise the four lowest energy MOs (1a1, 2a1, 1b1, and 1b2). The core orbitals are each assumed to have an occupation number of two in setting up the FORS-MCSCF equations. However, the core orbitals are not "frozen" in a FORS-MCSCF calculation, since they change in response to the active orbitals being optimized.

II. Metal–Silicon σ and π. The next two subspaces, (σE*)2 and (πE*)2, are those needed to describe the metal–silicon double bond. One would expect these two pairs of MOs (4a1 and 7a1; 2b1 and 3b1) to be occupied by a total of two electrons each. In other words, CSFs generated by the "excitation" of an electron(s) from the σ and π subspaces into the metal NBOs (or vice versa) will

Transition Metal–Silicon Double Bond


have a small contribution to the FORS-MCSCF wavefunction. The FORS-MCSCF calculations on the silylene complexes support this contention. Configurations which correspond to correlation within the metal–silicon α and σ manifolds account for the great majority (99%), depending on the particular metal) of the ground state FORS-MCSCF wavefunction. It is these MOs that will largely determine the nature of the metal–silicon interaction. Thus, it is these orbitals with which we will be primarily concerned.

iii. Metal Nonbonding. The final subspace is comprised of nonbonding MOs primarily located on the metal: δi, δσ, πi, σi. For the complexes in this study, the number of nonbonding electrons ranges from 0 (Sc) to 7 (Ni). Electronic states of different symmetries are obtained by rearranging the electrons in the nonbonding subspace. The state of maximum multiplicity that can be obtained by placing the nonbonding electrons into these four nonbonding MOs was chosen for the present investigation. All of the states considered are obtained by removing one electron to account for the positive charge, one to participate in the π bond, and one to participate in the σ bond leaves five d electrons to be distributed among the four nonbonding MOs. This leads to a multiplicity of four.

As an example of M+ /SiH2 interaction, consider the reaction of Co+ with SiH2. The 3F (d5) ground state of Co+ is 9.9 kcal mol−1 below the 3F (d6)1,14. The reaction of Co+ in either of these states with SiH2 (1B 1 or 1A 1) can be envisioned pictorially as in equation 1a. The reaction in equation 1a is a coupling of Co+ and triplet silylene; the second reaction, eq 1b, is a coupling of Co+ and singlet silylene. In either case there are six electrons remaining in the nonbonding space, giving rise to possible singlet and triplet states for CoSiH2+. For example, the CSF (δi,δσ,π,σ,δi) possesses B2 symmetry as does the CSF (δσ,δσ,π,σ,δσ). The B2 FORS-MCSCF wavefunction for CoSiH2++ will be a linear combination of these and other B2 symmetry CSFs (384 in total). The high-spin, triplet states of CoSiH2++ are much lower in energy than the 1A 1 state (40 kcal mol−1 at the MCSCF level). The various excited triplet states of CoSiH2++ are approximately 1–4 kcal mol−1 above the 1B 2 ground state. The states chosen for the FORS-MCSCF geometry optimization of the other MSiH2+ complexes were selected in an analogous fashion and are listed in Figure 1 along with the calculated ground state (in brackets).

b. Geometries of MSiH2+. The geometric results, metal–silicon bond length and H–Si–H angle, for the calculated ground state silylene complexes are summarized in Table I. The Si–H equilibrium bond length is 1.47 ± 0.01 Å for all the silylenes studied. Small differences in the geometries of the various silylene complexes occur upon changing the state symmetry. Since the only difference between these states is the occupation of the metal NBMOS, minor geometric perturbations are expected. The vibrational frequencies and force constants for the MSi bond are listed in Figure 1 for the ground state. In order to compare metal–silicon multiple bonding with the more familiar carbon case, the minimum energy geometries of the carbene analogues, MCH2+ (M = Sc to Ni) were also determined at the FORS-MCSCF level. Multiply bonded chromium complexes, CrEH2+ (E = C, Si, Ge, and Sn) were included since coordinatively saturated analogues of most of these have been reported.26,34,4,6 The geometries of these complexes are collected in Table I.

and must be carried out when comparing metrical data from coordinatively saturated, type II silylenes with calculated values for MSiH2+ complexes. Zybi1 and Muller have reported MSi bond lengths of 2.29 and 2.43 Å for (CO)5FeSi(O-t-Bu)-HMPA (and (CO)5FeSi(O-t-Bu)-HMPA), respectively.7c The calculated bond lengths are 2.31 Å (B1, FeSiH2+), and 2.45 Å (B2, CrSiH2+), respectively. The TiSiH2+ (A1) bond length is 2.52 Å. Ziegler and Harrod have calculated a value of 2.43 Å for Cp2TiSiH2+ at a lower level of theory. The calculated bond lengths for CrGeH2+ (B2) and CrSnH2+ (B2) are slightly longer than those reported for the type I complexes (CO)5CrGe(SMe3)+, and (CO)5CrSn(CH(SiMe3))2+.8 The MCH2+ equilibrium geometries calculated here are in excellent agreement with values previously reported at the all-electron level.12 This agreement between all-electron and pseudopotential calculations further demonstrates the utility of the latter in the determination of geometries for transition-metal complexes.

The metal–silicon bond lengths of the MSiH2+ complexes decrease upon proceeding from the early to the late transition metals (Figure 1). The only anomaly is MnSiH2+ (B2). These trends parallel those seen in other coordinatively unsaturated cations such as M2+(E=CH, MCH3+) and (MH2)5.9 The decrease in bond lengths is consistent with the smaller ionic and covalent radii as one goes from Sc to Ni. The metal–silicon force constant remains fairly constant as one proceeds from ScSiH2+ to CrSiH2+ (Figure 1) but varies quite markedly for the later transition metal silylene complexes. The atypically long and weak bonds in Mn complexes have been attributed to the significant loss of exchange interactions that accompanies the coupling of two electrons in the high-spin, 7S state of Mn++.14 Note that the calculated force constant for TiSiH2+ (A1, 1.33 mdyn Å−1) is comparable to that of CrSiH2+ (B2, 1.30 mdyn Å−1) and nearly as large as that of FeSiH2+ (B2, 1.53 mdyn Å−1). The latter two complexes have characterized, coordinatively saturated analogues while the former has been proposed as an intermediate in silane polymerization.16

How do the silylene complexes compare to other multiple bond compounds?18 As expected, the silylene complexes have quite weak bonds (as demonstrated qualitatively by the calculated metal–silicon force constants) when compared to other multiply bonded species—main group or transition metal. The metal–silicon force constants average 0.0200 mdyn Å−1, with those for the first half of the series clustered around 1.30 mdyn Å−1. The corresponding stretching frequencies are 323 and 343 cm−1, respectively.

<table>
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<td>111</td>
<td>1.98</td>
</tr>
<tr>
<td>VCH2+ (B2)</td>
<td>1.08</td>
<td>112</td>
<td>1.96</td>
</tr>
<tr>
<td>CrCH2+ (B2)</td>
<td>1.08</td>
<td>115</td>
<td>1.92</td>
</tr>
<tr>
<td>MnCH2+ (B2)</td>
<td>1.08</td>
<td>118</td>
<td>2.03</td>
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<tr>
<td>FeCH2+ (B2)</td>
<td>1.07</td>
<td>117</td>
<td>1.96</td>
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<td>1.08</td>
<td>116</td>
<td>1.90</td>
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<tr>
<td>CrGeH2+ (B2)</td>
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<td>1.69</td>
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<td>2.67</td>
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*The geometry optimizations in Table I were calculated at the FORS-MCSCF level of theory using the basis sets and active space distributed in the text. The state symmetries at which the optimizations were carried out are also specified.

TABLE II: Natural Orbital Occupation Numbers (NOON) for MSiH$_2^*$

<table>
<thead>
<tr>
<th>complex</th>
<th>NOON$^a$ (σ$_{MSi}$)</th>
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<th>NOON- (σ$^*_i$)</th>
<th>NOON- (σ$^*_MSi$)</th>
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</tr>
<tr>
<td>NiSiH$_2^*$</td>
<td>1.96</td>
<td>1.97</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$^a$The calculations were performed at the minimum energy geometry for the ground state indicated in Figure 1. $^b$The natural orbital occupation number (NOON) were calculated from the FORS-MCSCF wavefunction using the basis set, active MOs, and active electrons described in the text.

These values are much lower than those for the CC bond in olefins. For example, $k_{EC}$ for ethylene is calculated to be 8.2 mdyn Å$^{-1}$ at the FORS-MCSCF ($\sigma$ $\pi$ $\pi^*$ active space) level of theory.$^{16}$ The main group ethylene analogues H$_2$ECH$_2$ have calculated $k_{EC}$ in mdyn Å$^{-1}$, of 3.3 (E = Si), 3.9 (E = Ge), and 3.0 (E = Sn) at the same level of theory. These values are slightly larger than those calculated for the homonuclear ethylene analogues, H$_2$E:H$_2$, 2.6 (E = Si), 2.3 (E = Ge), and 1.7 (E = Sn). The carbene complexes, MCH$_2^+$, have calculated $k_{EC}$ in the range of 2.00–3.00 mdyn Å$^{-1}$. Although the relationship between force constants and dissociation energies is only qualitative, this level of theory predicts relative double bond strengths, based on calculated force constants, to be CC > EC > EE, MC > MSi.

For the homologous series of CrEHC: (B) complexes the calculated CrE force constants decrease slightly as E becomes heavier: 1.30 mdyn Å$^{-1}$ (CrSiH$_2^+$), 1.22 mdyn Å$^{-1}$ (CrGeH$_2^+$), and 1.06 mdyn Å$^{-1}$ (CrSnH$_2^+$). It is interesting to note the smaller force constants, and presumably weaker bond, for the germylene and stannylene in light of the fact that chromium-germylene and chromium-stannylene complexes (type I) have been structurally characterized, but a type I chromium–stannylene complex has not. This suggests two possibilities. First, it may be that bond strengths in coordinatively unsaturated ions cannot be directly compared with coordinatively saturated (type I) complexes. The second possibility is that the instability of the stannylene is a result of kinetic and not thermodynamic (i.e. bond strength) factors.

c. Electronic Structure of MSiH$_2^*$. The MC/LMO/CI (multiconfiguration/localized molecular orbital/configuration interaction) procedure describes the chemical bond in terms of the resonance structures which contribute to it. The resonance structures are denoted using the (jkl) notation, where the i, j, k, and l are the occupation numbers of the "AO-like" MOs $\pi_i$, $\pi_j$, $\pi_k$, and $\pi_l$, respectively. Thus, the configuration [2020] corresponds to a resonance structure with a dative ligand-to-metal $\sigma$ bond and a metal-to-ligand $\pi$ backbond. Similarly, [1111] corresponds to a resonance structure with covalent $\sigma$ and $\pi$ electrons. These two bonding schemes are represented as M$=$E ([2020]) and M$=$E ([1111]) and are referred to as the $\sigma$-dative/$\pi$-backbond and all-covalent resonance structures, respectively. The $\sigma$ bond is described by the bottom arrow or line; the $\pi$ bond is described by the upper arrow or line. The terms dative, covalent and backbond are used in their usual sense. A dative configuration, $\sigma$ or $\pi$, has two electrons located on the ligand "AO-like" MO while the metal counterpart is vacant. A backbond configuration has the opposite occupation of the "AO-like" MOs. A dative interaction is indicated by an arrow pointing toward the metal, while a backbond interaction is represented by an arrow pointing toward the ligand. The covalent interaction is indicated by a straight line.

In the Hartree–Fock (HF) approximation the $\sigma$ and $\pi$ bonding MOs are assumed to have an occupation number of 2.0. The closer the natural orbital occupation number (NOON) is to 2.0, the better the MO is described at the HF level. The calculated NOON values for the metal–silicon $\sigma$ and $\pi$ MOs are listed in Table II. The NOON for the $\sigma$ bond is approximately constant and nearly 2.0, except for MnSiH$_2^+$. Even for MnSiH$_2^+$, the NOON is 1.88. The NOON for the $\pi_{MSi}$ bonding MO decreases toward the center of the first transition series and then increases as it approaches the end of the series.$^{17}$ Indeed, there is considerable $\pi$ diradical character for all MSiH$_2^+$ species, except for M = Co and Ni. Thus, while the $\sigma$ space in the complexes is described reasonably well at the Hartree–Fock level, the same is not the case for the $\pi$ space. So, except for Mn little accuracy may be lost (and a large reduction in the number of CSFs gained) by removing $\sigma_{MSi}$ and $\sigma_{MSi}^*$ from the FORS-MCSCF active space. FORS-MCSCF geometry optimization of the silylenes with an active space comprised of the metal–silicon $\pi$ MOs and the metal NBMOs show little change in calculated properties when compared to those in Figure 1. Since MnSiH$_2^+$ has the largest $\sigma^*$ NOON, this molecule exhibits a modest (0.07 Å) decrease in the MnSi bond length when the metal–silicon $\sigma$ MOs are excluded from active space. In summary, the metal–silylene complexes,

(16) Gordon, M. S.; Cundari, T. R. Unpublished results. These calculations were carried out using the same ECPs for the main-group elements (and all electron basis set for C and H) as employed for the calculation of the MEH$_4^+$ complexes in this study. The active electrons are those involved in the double bond between the two heavy elements in E$_2$H$_4$ (D$_2$): the active space comprises the $\pi_{1r}$, $\pi_{2r}$, $\pi^*_{1r}$, and $\pi^*_{2r}$. As for the transition metals described in this paper, the wavefunctions are of the FORS-MCSCF type.

(17) For comparison, the NOON values in ethylene are 1.98 for $\pi_{1C}$ and 1.92 for $\pi_{2C}$. At the other extreme in the main-group ethylene analogues is Si$_2$H$_4$. NOON($\pi_{1Si}$) = 1.97; NOON($\pi_{2Si}$) = 1.79.
energy than others. Those with two electrons each in the described at the single determinant level.

**TABLE III:** MC/LMO/CI Results for Silylene Complexes

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</table>

*The contribution made by the various resonance structures (given in percentage terms) to the ground state were calculated using the MC/LMO/CI method with the basis sets described in the text.* 4 The configuration (or resonance structure) is denoted by the \( i\rangle j\rangle k\rangle l\rangle \) notation, where \( i, j, k, \) and \( l \) are the occupation numbers of the "AO-like" MOs \( \psi_{\alpha}, \psi_{\beta}, \psi_{\mu}, \) and \( \psi_{\nu} \), respectively. The occupation numbers of the metal nonbonding MOs are not given. *This is the sum of the nine prime resonance structures.* 4 The diagonal and off-diagonal one-matrix elements are denoted by \( \gamma \).

at least in these coordinatively unsaturated examples, cannot be described at the single determinant level.

One expects that some resonance structures will be higher in energy than others. Those with two electrons each in the \( \sigma \) and \( \pi \) manifolds will be the most favorable resonance structures (using the \( i\rangle j\rangle k\rangle l\rangle \) notation, \( i+l \) and \( j+k \) must both be equal to 2). In this way, the molecule avoids contributions from resonance structures with weaker one-electron and three-electron bonds. It is satisfying that the MC/LMO/CI method supports this view.

The nine resonance structures with two-center/two-electron bonds account for the vast majority (94% to >99%) of the ground-state wavefunction (Table III and Figures 2-4). The remaining contributions are split between resonance structures with one- and three-electron bonds and resonance structures which correspond to transfer of an electron from either of the \( \sigma \) or \( \pi \) manifolds into a metal NBMO. The MC/LMO/CI data for MSHt are listed in Table III and shown graphically in Figure 2. The analogous data for the carbene and CrEHt complexes are plotted in Figures 3 and 4, respectively.

The character of the natural orbitals (and the resonance contributors) change markedly as the metal is varied in the silylene complexes. The silylenes show more variation than the carbene complexes (Figure 3) and much more than the CrEHt complexes (Figure 4). The CrEHt complexes are almost invariant to modification of the ligand.

The distribution of resonance structures which describe the metal-silicon double bond, as obtained from the MC/LMO/CI procedure, concurs with the natural orbital analysis of the metal-silicon double bond. The percent contributions of the various resonance contributors to MSHt are plotted in Figure 2. Figure 2a shows the individual contributions of each resonance structure; Figure 2b is plotted in terms of area, so that a larger area signifies a more important resonance structure. The contribution from the (2020) configuration remains fairly constant at less than 10% for the early silylenes but increases rapidly for MnSiHt (2B1g) and the later silylenes until it becomes the most dominant configuration resonance contributor for CoSiHt (2B1g) and NiSiHt (2A1g) (Figure 2a). This \( \sigma \)-dative/\( \pi \)-backbond resonance structure, Ni≡Si, accounts for almost 62% of the ground state wavefunction of NiSiHt (2A1g) or nearly 3 times as much as any other resonance structure! The [1111] resonance structure moves in an opposite direction to [2020]. For ScSiHt (2A1g), the all-covalent resonance structure, Sc≡Si, contributes 43.1% to the overall description of the scandium-silicon double bond. Figure 2b clearly shows how the [1111] configuration decreases as [2020] begins to dominate the description for the later silylene complexes. The contributions of all the other resonance structures are relatively constant across the series. This change in the dominant resonance contribution correlates with a decrease in the \( d \) orbital energies as one proceeds from left to right across the periodic table. This decrease results from a contraction in the orbitals, due to an increase in the metal.
effective nuclear charge, and results in a σ bond which is more polarized toward the metal and a compensatory π backbond.

The carbene complexes (Figure 3) show a much smaller change in the resonance structure contributions when compared to the analogous silylene complexes. The two most important contributions even at the extreme right of the first transition series are the covalent ([11111]) and σ-ylide ([2110] or M = E) for the MCH$_2^+$ complexes. There is some variation in the relative importance of these two configurations, but not nearly as much as in the silicon analogues. Likewise, the [2020] configuration does not rise as far to dominate the description of NiCH$_2^+$ as it does for NiSiH$_2^+$.

Thus, it is more accurate to describe the double bond with the M = E resonance structure for the later, electron-rich silylenes than it is for their carbene counterparts.

Figures 2a and 3a demonstrate that the contribution from the σ-ylide ([2110]) remains fairly constant at ~37% for MCH$_2^+$ and ~30% for MSiH$_2^+$, despite the changes in the metal. The σ-ylide possesses the dative σ bond of the σ-dative/π-backbond resonance structure and the covalent π bond of the all-covalent resonance structure. So, the σ-ylide can make significant contributions to the description of both the metal-silicon and metal-carbon double bonds despite the changes in the electronic environment. For the early carbenes, the [2110] and [1111] make nearly equal contributions and account for roughly 70% of the total ground-state wavefunction. The [2020] configuration makes a contribution of less than 10% to ScCH$_2^+$ (A$_1$). Thus, for the early transition metals, the silylenes and carbenes are described to a large extent by the same resonance structures, [2110] and [1111]. The [1111] configuration is roughly 10% higher than the [2110] configuration for the early MSH$_2^+$ complexes while the situation is reversed (i.e. [2110] greater than [1111]) for the early carbene complexes. Thus, a limiting description of MSH$_2^+$ for the early silylenes would be a triplet silylene low-spin coupled to M$^+$ (as in eq 1b) while the later silylenes correspond to the coordination of singlet silylene to M$^+$ (as in eq 1a).

Summary

This paper deals with the effects of changing the metal on the nature of the transition metal-silicon double bond in the ion-beam complexes MSH$_2^+$. The important conclusions to be gathered from this research include the following.

1. The MSH$_2^+$ complexes have significantly weaker bonds (as estimated by calculation of the MS force constant) than their MCH$_2^+$ counterparts. For the homologous series CrEH$_2^+$(E = C, Si, Ge, Sn) the silylene complex has a calculated force constant greater than those of germylene and stannylene. This suggests that type I silylenes are reasonable synthetic targets.

2. An accurate description of the bonding in these complexes necessitates the inclusion of electron correlation effects. The FORS-MCSCF data lead to the reasonable conclusion that the metal-silicon σ bond is better described at the Hattrée–Fock level than is the metal-silicon π bond. The latter requires a multiconfigurational wavefunction to describe the diradical character. The conclusions drawn by Carter and Goddard for carbene complexes are consistent with this point.

3. The MC/LMO/CI data show that the early transition metal silylenes, e.g. ScSiH$_2^+$, are dominated by the [1111] (all-covalent or M=E) and [2110] (σ-ylide or M = E) resonance structures, with the [2020] (σ-dative/π-backbond or M = E) resonance structure making a small contribution. The late transition metal silylenes, e.g. NiSiH$_2^+$, are dominated by the [2020] and to a lesser extent the [2110] configurations. The plot of the MC/LMO/CI data in Figure 2 clearly illustrate how one description of the nature of the transition metal–silicon double bond is transformed into the other.

Acknowledgment

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Reactions and Photochemistry of Chromium and Molybdenum with Molecular Hydrogen at 12 K

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Cr and Mo have been cocondensed with molecular hydrogen in Kr and Ar matrices at 12 K. Both chromium and molybdenum atoms were found to insert into the H–H bond upon absorption of UV light (320–380 nm) to form MH$_2$ (M = Mo, Cr). The symmetric and antisymmetric stretching frequencies have been identified for both CrH$_2$ and MoH$_2$ and the bond angles are estimated to be 118 ± 5° and 110 ± 5° for CrH$_2$ and MoH$_2$, respectively, from the relative intensities of the antisymmetric and symmetric stretching modes. The stretching force constants of CrH$_2$ and MoH$_2$ are determined to be 1.64 and 1.86 mdyn/Å. A geometry of slightly unequivalent M–H bonds for MHD (M = Cr and Mo) is suggested. A molecular hydrogen adduct, CrH$_2$(H$_2$), is found in reactions with excess hydrogen. Photolysis of the matrices which contain appreciable CrH$_2$ (H$_2$) with light of 520 nm < λ < 580 nm leads to the formation of CrH$_4$. In the molybdenum reactions, MoH, MoH$_3$, and possibly MoH$_4$ were identified as products of UV photolysis as well.

Introduction

The study of the dihydrogen complexes, both in solutions and in low-temperature matrices, has been an active area, due to their important roles in homogeneous and heterogeneous hydrogenation catalysis. The most well studied systems have been complexes of group VI (Cr, Mo, and W) metals which contain γ-H$_2$ together with various ligands, such as PR$_3$, Cp, and CO$_2$ etc. The γ-H$_2$