Ab Initio CASSCF Study of the Electronic Structure of the Transition-Metal Alkylidene-like Complexes Mo–M′H$_2$ (M′ = C, Si, Ge, and Sn)

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Abstract: A theoretical investigation of the electronic structure of the high-valent, transition-metal, alkylidene-like complexes MoM′H$_2$ (M′ = C, Si, Ge, and Sn) is reported. Based on ab initio calculations carried out at the complete active space multiconfiguration self-consistent field (CASSCF) level, the molecular structure of the ground state and some low-lying excited states have been determined. For M′ = C, Si, and Ge, the ground state has C_{2v} symmetry (state $^5B_1$) and corresponds to pairing each electron of the M′H$_2$ triplet $^3B_1$ with an electron of Mo (^7S). In the case of MoSnH$_2$, the lowest state is bent (C_s symmetry, state $^7A'$), the out-of-plane angle being 68°, and dissociates into SnH$_2$ ($^1A_1$) + Mo (^7S). Dissociation energies, potential energy profiles for the dissociation, harmonic force constants in terms of internal symmetry coordinates, and vibrational frequencies are reported. The comparison of these properties with those of their pentacarbonylated homologous (CO)$_5$M=M′H$_2$ shows that the carbene-like (Fischer) type of complexation is stronger than the alkylidene-like one (Schrock).

Introduction

Experimental and theoretical research on the electronic and geometric structure of transition-metal–carbenes and –alkylidenes is an active area in chemistry nowadays due to their potential activity in catalysis and in organic and organometallic synthesis.[1]

The nature of the metal–carbon double bond in organometallic compounds has been the focus of attention of several works, and this notion seems to be well established.[2,3] Typically two models of bonding have been proposed. Fischer-type complexes or metal–carbenes are usually 18-electron species and involve a "low-valent" metal fragment (e.g., (CO)$_5$Mo). The bond in this model can be understood as a σ-donor/π-acceptor relation from the singlet-state carbene.

Alkylidene or Schrock-type compounds[4] result when the metal fragment is "high-valent" (e.g., Cp$_2$TaR), and bonding with the CXY ligand is essentially a covalent double bond of the olefinic type. Formation of stable compounds is favored if the ground state of the CXY ligand is a triplet.

Substitution of the carbon atom in these complexes by an element of group 14, formally having similar bonding capabilities, leads to species L$_n$M=M′R$_2$ (M′ = Si, Ge, Sn, and Pb) in which a double bond between a transition metal and a main group metal appears. The chemistry of such hetero-bimetallic carbene-like complexes has been the subject of considerable research and has been summarized recently in excellent reviews.[5] However, the nature of such metal–metal double bond remains somewhat uncertain.

The electronic structure of the ground state ^7S of Mo atom is 5s^{1}4d^5, and, since the ground state of methylene is the triplet $^3B_1$,[6] naked Mo=CH$_2$ necessarily falls into the alkylidene category as shown in previous work on closely related transition-metal–methylene complexes.[7]

Electronic structure of naked Mo=M′H$_2$ (M′ = Si, Ge, Sn, and Pb) could be in principle rationalized on the grounds of their carbon parent; however, some striking points deserve a more careful analysis. First, the ground state of these M′H$_2$ ligands is not the triplet $^3B_1$ but the singlet $^1A_1$. Since singlet–triplet splitting ΔE_{s-t} is smaller (ΔE_{s-t} = 17–19,[8] 22,[8a,9] and 24[8a-10] kcal/mol for SiH$_2$, GeH$_2$, and SnH$_2$, respectively) than the excitation energy necessary to promote the Mo atom from its ground state toward its lowest excited state ^5D (lying 31.6 kcal/mol above[11]), an alkylidene-type structure of the double bond can also in principle be predicted. Second, theoretical and experimental studies of structures in which Si, Ge, and Sn are involved in the formation of a double bond have shown nonclassical distortions which have been related to the singlet–triplet splitting ΔE_{s-t}.[12]

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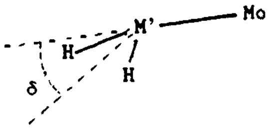
Table I. Definition of C_{2v} and C_s Internal Symmetry Coordinates for $MoM'H_2$[a]



C_{2v}	A_1	$S_1 = R$
		$S_2 = r_1 + r_2$
		$S_3 = \alpha_1 + \alpha_2 - \alpha_3$
	B_1	$S_4 = r_1 - r_2$
		$S_5 = \alpha_1 - \alpha_2$
	B_2	$S_6 = \delta$
C_s	A′	$S_1 = R$
		$S_2 = r_1 + r_2$
		$S_3 = \alpha_1 + \alpha_2 - \alpha_3$
		$S_4 = \delta$
	A″	$S_5 = r_1 - r_2$
		$S_6 = \alpha_1 - \alpha_2$

[a] $R = r_{MoM'}$; $r_1, r_2 = r_{M'H}$; $\alpha_1, \alpha_2 = \alpha_{HM'Mo}$; $\alpha_3 = \alpha_{HM'H}$.

For instance, in the series of compounds Si_2H_6,[12c,13] Ge_2H_6,[12c,14] Sn_2H_6,[10a,12c,15] and Pb_2H_6,[12c] the planar ethylene-like structure is less stable than the transbent one, arising from distortion of the double bond. Also, the possibility of nonclassical distortions in transition-metal complexes has been discussed and exemplified.[12a]

In a continuous effort devoted to elucidation of the structure of this type of multiple metal-metal bond, we have carried out a theoretical study of the molecular structure of a family of complexes showing a bond between a transition metal and an element of group 14.[16] In a previous paper,[17] a theoretical analysis of a series of Fischer compounds $(CO)_5Mo{=}M'H_2$ (M′ = C, Si, Ge, and Sn) was reported, and the dramatic difference between CH_2 and the rest of ligands was outlined. In the present paper we report ab initio CASSCF calculations of naked $Mo{=}M'H_2$ species with M′ being C, Si, Ge, and Sn. In this series, the carbon derivative has been included for the sake of comparison. Likewise, the lead homologue has not been considered since for this type of compound a large spin-orbit coupling is expected; this problem will be addressed elsewhere.[18] Effectively, as shown in a previous work,[19] tin derivatives would fall into the limit for which the noninclusion of spin-orbit effects, explicitly in the theoretical approach, does not modify substantially the conclusions about their structure.

Computational Details

Calculations were carried out at the MCSCF level of theory using the effective core potential (ECP) approximation to describe the inner core electrons. For the Mo and Ge atoms, Hay-Wadt's ECPs were used,[20] while for the C, Si, and Sn atoms, the pseudopotential approximation of Durand and Barthelat was chosen.[21] In the case of Mo and Sn, the pseudopotential accounts for relativistic effects (mass-velocity and Darwin corrections). The basis set for valence electrons was of double-ζ quality: in compacted notation, (3,3,4)/[2,1/2,1/3,1] for Mo;[20a] (3,3)/[2,1/2,1] for Ge;[20b] (4,4)/[3,1/3,1] for C, Si, and Sn.[21] On the heavy atoms a set of polarization d functions was also added (ζ = 0.6, 0.45, 0.25, and 0.20 for C, Si, Ge, and Sn, respectively). For hydrogen, the standard Huzinaga-Dunning (4s)/[2s] basis set was used.[22]

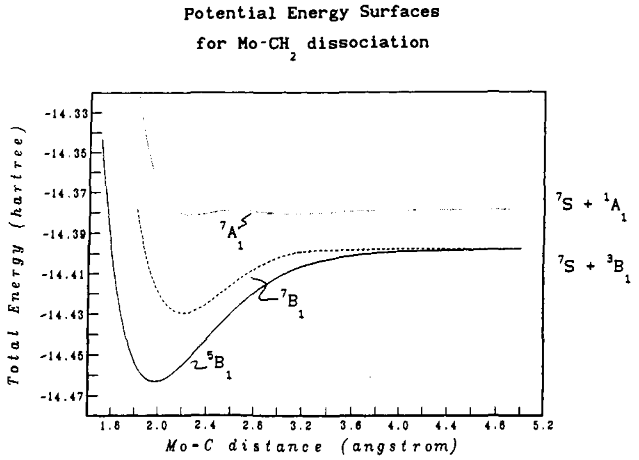


Figure 1. Potential energy profiles for dissociation of $MoCH_2$ into Mo + CH_2 fragments: $^5B_1$, $^7B_1$ → Mo (^7S) + CH_2 ($^3B_1$); $^7A_1$ → Mo (^7S) + CH_2 ($^1A_1$).

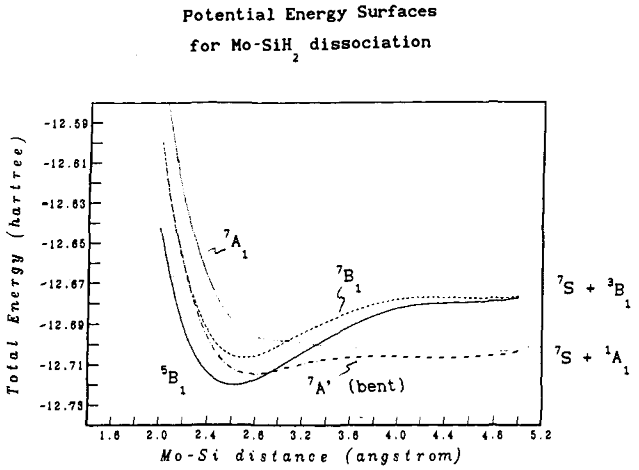


Figure 2. Potential energy profiles for dissociation of $MoSiH_2$ into Mo + SiH_2 fragments: $^5B_1$, $^7B_1$ → Mo (^7S) + SiH_2 ($^3B_1$); $^7A_1$, $^7A'$ → Mo (^7S) + SiH_2 ($^1A_1$).

The valence space used consisted of the four orbitals that are more directly involved in formation of the Mo=M′ double bond and also the rest of the Mo atom valence shell to account for spin-coupling effects. The orbitals selected were the pair sp_σ, p_π of the $M'H_2$ ligand and the 5s and 4d set of Mo. The active space was, thus, eight electrons distributed over eight orbitals, the wave function being of the CASSCF type.[23] The number of configurations was 180, 18, 21, and 39 corresponding to $^5B_1$, $^7A_1$, $^7B_1$ (C_{2v}), and $^7A'$ (C_s) states. In the calculations without symmetry there were 720 CSF's for the quintuplet and 63 CSF's for the septets.

Molecular geometries were optimized using standard analytical gradient techniques under C_{2v} or C_s constraint, with residual forces being less than 10^{-4} hartree/bohr. Stationary points were then characterized by computation and further diagonalization of the matrix of second derivatives F^x in a Cartesian coordinate representation. In order to obtain a set of physically meaningful force constants in terms of internal symmetry coordinates (Table I), the F^x matrix was transformed using the

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Table II. Total Energies[a] E, Dissociation Energies[b] DE, $^5B_1$–$^7B_1$ Splitting[b] ΔE, and Geometries[c] for MoM′H_2 Complexes

	E	DE	ΔE	$r_{MoM'}$	$r_{M'H}$[d]	$\alpha_{HM'H}$[d]	δ
MoCH_2							
$^5B_1$	−0.46317	41.0	20.9	1.9705	1.0891	114.3	0.0
$^7B_1$	−0.42990	20.1		2.2084	1.0866	113.1	0.0
limit $^7S + {}^3B_1$	−0.39778				1.0762	128.6	
limit $^7S + {}^1A_1$	−0.37832				1.1033	102.1	
MoSi_2							
$^5B_1$	−0.72019	27.3	8.5	2.6174	1.4877	107.2	0.0
$^7B_1$	−0.70659			2.7010	1.4859	107.2	0.0
limit $^7S + {}^3B_1$	−0.67673				1.4763	118.2	
$^7A'$	−0.71474	7.2		2.7873	1.5035	99.5	53.3
limit $^7S + {}^1A_1$	−0.70330				1.5154	93.3	
MoGe_2							
$^5B_1$	−0.62706	26.1	7.9	2.6602	1.5495	106.3	0.0
$^7B_1$	−0.61452			2.7404	1.5483	106.3	0.0
limit $^7S + {}^3B_1$	−0.58546				1.5355	118.3	
$^7A'$	−0.62556	3.8		2.9107	1.5766	97.1	61.5
limit $^7S\ {}^1A_1$	−0.61943				1.5864	93.2	
MoSn_2							
$^5B_1$	−0.27564	26.6	6.6	2.8028	1.7436	105.2	0.0
$^7B_1$	−0.26508			2.8606	1.7429	105.1	0.0
limit $^7S + {}^3B_1$	−0.23317				1.7286	116.7	
$^7A'$	−0.28057	3.7		3.0810	1.7763	95.3	68.0
limit $^7S + {}^1A_1$	−0.27471				1.7801	92.7	

[a] Hartrees. Shifted by 14 hartrees in the carbon derivative and by 12 hartrees in the rest of the series. [b] In kcal/mol. [c] Angstroms and degrees. See Table I for definition of δ. [d] The values $r_{M'H}$ and $\alpha_{HM'H}$ reported in the entries of limits correspond to optimized geometries of M′H_2 ligands at CASSCF level. The singlet–triplet splitting of M′H_2 at this level of theory is 12.2, −16.7, −21.3, and −26.1 kcal/mol for M′ = C, Si, Ge, and Sn, respectively.

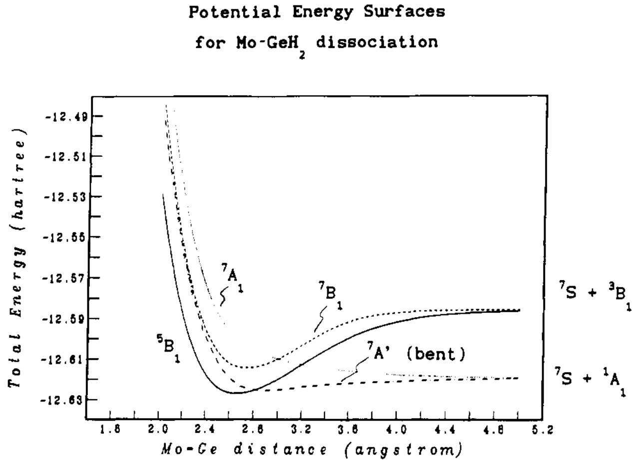


Figure 3. Potential energy profiles for dissociation of MoGeH_2 into Mo + GeH_2 fragments: $^5B_1$, $^7B_1 \rightarrow$ Mo (^7S) + GeH_2 ($^3B_1$); $^7A_1$, $^7A' \rightarrow$ Mo (^7S) + GeH_2 ($^1A_1$).

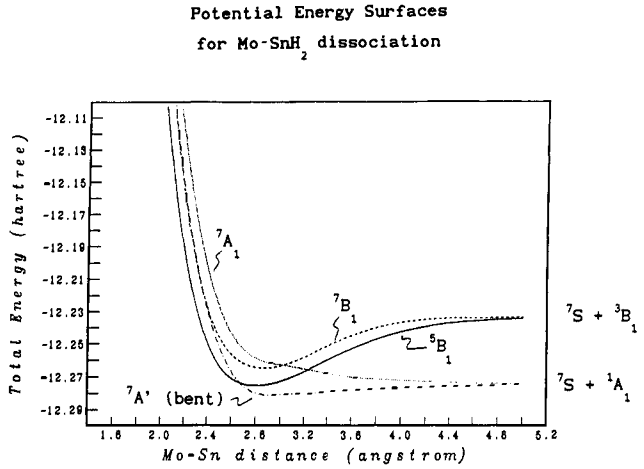


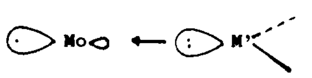
Figure 4. Potential energy profiles for dissociation of MoSnH_2 into Mo + SnH_2 fragments: $^5B_1$, $^7B_1 \rightarrow$ Mo (^7S) + SnH_2 ($^3B_1$); $^7A_1$, $^7A' \rightarrow$ Mo (^7S) + SnH_2 ($^1A_1$).

B matrix. All calculations were performed using the HONDO-7 system of programs.[24]

Results

In a similar way as that stated for ion $CrCH_2^+$,[7a] the interaction between the ^7S ground state of molybdenum atom ($S = 3$) and the triplet $^3B_1$ of the M′H_2 ligand ($S = 1$) leads to three possibilities of spin combinations: the quintet $^5B_1$ corresponding to pairing each electron of M′H_2 with an electron of Mo, thus forming one σ bond and one π bond; the septet $^7B_1$ state with a σ bond but no π bond; and the third possibility, the high-spin $^9B_1$ state which formally has no bond (since it gives place to a repulsive curve,[7b] it will not be considered here).

On the other hand, when the M′H_2 ligand is in the $^1A_1$ singlet state (ground state for SiH_2, GeH_2, and SnH_2), the state arising from interaction with the ^7S Mo state is the $^7A_1$ resulting from a σ donation of the lone pair of M′H_2 to the Mo atom



Total energies and optimized geometrical parameters related with these states are collected in Table II. In Figures 1–4, the potential energy curves corresponding to dissociation of MoM′H_2 into Mo (^7S) + M′H_2 ($^3B_1$ or $^1A_1$), for M′ = C, Si, Ge, and Sn, are reported.

MoCH_2. As can be seen from Figure 1, the $^5B_1$ state lies lower than $^7B_1$, the splitting between these states being 20.9 kcal/mol. Both the ordering and the splitting are in agreement with the results found for the equivalent states of $CrCH_2^+$. The Mo–C bond distance in the $^5B_1$ ground state is found to be 1.970 Å. There are no experimental data available for MoCH_2, but our results agree with other related systems. Thus, the Mo–C bond length calculated for the complex $(CO)_5Mo{=}CH_2$ is 1.985 Å,[17] and a typical experimental value for this double bond distance is 2.06 Å.[5a] It is worth noting that the latter values correspond to Fischer-type compounds. Other theoretical values involving closely related transition metals are, for instance: R(Cr—C) = 1.91 Å (in $CrCH_2^+$ [7b]), R(Mn—C) = 2.01 Å (in the isoelectronic $MnCH_2^+$ [7d], and R(Nb—C) = 1.87 Å (in $NbCH_2^{2+}$ [7f]). On the other hand, the H–C–H bond angle, 114°, is close to that of ethylene (117.6°) in agreement with a sp²-hybridized center. Concerning the dissociation energy, our value, deduced with respect

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Table III. Vibrational Analysis for $MoM'H_2$ States $^5B_1$

		$MoCH_2$	$MoSiH_2$	$MoGeH_2$	$MoSnH_2$
		Force Constants[a]			
A_1	f_{11}	1.9886	0.8360	0.8146	0.7640
	f_{22}	5.8098	3.0031	2.6882	2.3877
	f_{33}	0.4932	0.4571	0.4625	0.4285
	f_{21}	0.0955	0.0355	0.0318	0.0339
	f_{31}	−0.0195	0.0370	0.0554	0.0514
	f_{32}	−0.1559	−0.0843	−0.0908	−0.0733
B_1	f_{44}	5.7681	2.9716	2.6633	2.3681
	f_{55}	0.1281	0.1223	0.1100	0.1062
	f_{54}	0.1102	0.0520	0.0601	0.0568
B_2	f_{66}	0.1651	0.0780	0.0905	0.0679
		Frequencies[b]			
A_1	ω_1 M'–H str	3197	2276	2139	2012
	ω_2 HM'H bend	1454	981	934	797
	ω_3 Mo–M' str	520	249	181	155
B_1	ω_4 M'–H str	3290	2287	2136	2008
	ω_5 HM'H bend	462	319	282	245
B_2	ω_6 wag	716	309	305	230

[a] In mdyn/Å. [b] In cm^{-1}.

Table IV. Vibrational Analysis for $MoM'H_2$ States $^7B_1$

		$MoCH_2$	$MoSiH_2$	$MoGeH_2$	$MoSnH_2$
		Force Constants[a]			
A_1	f_{11}	1.5020	0.8455	0.8361	0.7916
	f_{22}	5.8911	3.0247	2.7024	2.3900
	f_{33}	0.5173	0.4574	0.4644	0.4305
	f_{21}	0.0537	0.0014	0.0035	0.0098
	f_{31}	0.0762	0.0312	0.0478	0.0451
	f_{32}	−0.1695	−0.0833	−0.0934	−0.0756
B_1	f_{44}	5.8516	2.9967	2.6819	2.3760
	f_{55}	0.1756	0.1220	0.1142	0.1049
	f_{54}	0.1008	0.0511	0.0563	0.0523
B_2	f_{66}	0.0230	−0.3947	−0.4526	−0.7340
		Frequencies[b]			
A_1	ω_1 M'–H str	3222	2285	2145	2013
	ω_2 HM'H bend	1469	983	936	799
	ω_3 Mo–M' str	456	250	184	158
B_1	ω_4 M'–H str	3312	2297	2144	2011
	ω_5 HM'H bend	539	318	288	244
B_2	ω_6 wag	262	694i	682i	755i

[a] In mdyn/Å. [b] In cm^{-1}.

Table V. Vibrational Analysis for $MoM'H_2$ States $^7A'$

		$MoSiH_2$	$MoGeH_2$	$MoSnH_2$
		Force Constants[a]		
A'	f_{11}	0.5693	0.3547	0.2599
	f_{22}	2.7953	2.4197	2.1568
	f_{33}	0.8772	1.0905	1.1957
	f_{44}	0.4136	0.5822	0.6905
	f_{21}	−0.0211	−0.0296	−0.0221
	f_{31}	−0.0509	−0.0675	−0.0517
	f_{41}	0.0798	0.1059	0.0898
	f_{32}	−0.1304	−0.1341	−0.0891
	f_{42}	0.1481	0.1525	0.1226
	f_{43}	−0.4739	−0.6890	−0.8238
A''	f_{55}	2.7723	2.4047	2.1441
	f_{66}	0.1588	0.1488	0.1283
	f_{65}	0.0445	0.0413	0.0364
		Frequencies[b]		
A'	ω_1 M'–H str	2201	2032	1914
	ω_2 HM'H bend	1010	974	843
	ω_3 wag	387	339	269
	ω_4 Mo–M' str	203	114	86
A''	ω_5 M'–H str	2205	2028	1909
	ω_6 HM'H bend	351	319	262

[a] In mdyn/Å. [b] In cm^{-1}.

Table VI. Calculated Mo–M' and M'–H Bond Orders for $MoM'H_2$ Complexes

		$MoCH_2$	$MoSiH_2$	$MoGeH_2$	$MoSnH_2$
Mo–M'	$^5B_1$	1.4471	1.0214	0.9325	0.9361
	$^7B_1$	0.8640	0.8794	0.8132	0.8418
	$^7A'$		0.6941	0.5311	0.4350
M'–H	$^5B_1$	0.9359	0.9578	0.9255	0.9137
	$^7B_1$	0.9364	0.9613	0.9276	0.9161
	$^7A'$		0.9496	0.9508	0.9305

to the limit $^7S + {}^3B_1$, is DE = 41 kcal/mol, close to that computed for $CrCH_2^+$ (DE = 49 kcal/mol).

Both the quintet $^5B_1$ and the septet $^7B_1$ are true minima on the potential energy surface as shown by their vibrational analysis reported in Tables III and IV. In the $^7B_1$ state the Mo–C bond length is 2.208 Å, thus 0.24 Å larger than that of the ground state. The force constant associated with the Mo–C bond also appears to be lowered by 0.48 mdyn/Å (24%), while the dissociation energy is 20.1 kcal/mol. Also, the Mo–C bond order[25] decreases from 1.447 to 0.864 (Table VI). All these results are in agreement with loss of the π bond in the septet state.

Finally the $^7A_1$ state shows an extremely flat curve without a real minimum, while in $CrCH_2^+$ ion[7a] the corresponding $^6A_1$ carbenic state shows a stationary point at 2.32 Å. This discrepancy can be accounted for by the larger σ-donation from the carbene toward the Cr^+ cation than toward the Mo atom.

$MoSiH_2$, $MoGeH_2$, and $MoSnH_2$. Under C_{2v} constraint, the behavior of the molybdenum–alkylidene-like complexes is similar to that of $MoCH_2$. Thus the ground state is the quintet $^5B_1$; the septet $^7B_1$ lies higher, although the splittings between these states diminish down the group (8.5, 7.9, and 6.6 kcal/mol for M' = Si, Ge, and Sn, respectively) and are significantly lower than that of $MoCH_2$ (20.8 kcal/mol). The $^7A_1$ carbenic states are also repulsive, but now they cross the $^5B_1$ and $^7B_1$ states because of inversion of the relative stability of the singlet with respect to the triplet in the isolated ligand $M'H_2$ (see Figures 2–4 and compare them with Figure 1).

In all cases, $^5B_1$ states are always true minima on the potential energy hypersurfaces (Table III). The Mo–M' bond length increases from 2.617 Å (Si) to 2.803 Å (Sn) according with the trends observed from experiment (typical Mo–M' bond distances in Fischer-type compounds are R(Mo–Si) = 2.48 Å, R(Mo–Ge) = 2.50 Å, and R(Mo–Sn) = 2.63 Å). Force constants associated with the Mo–M' bond undergo a similar evolution, decreasing from $f_{\text{Mo-Si}}$ = 0.836 mdyn/Å to $f_{\text{Mo-Sn}}$ = 0.764 mdyn/Å. These results can be accounted for by the increasingly diffuse nature of the M' s and p orbitals which leads to a less effective overlap with Mo orbitals and, therefore, to a weakening of the bond. Dissociation energies DE from these states are close to each other (in kcal/mol: 27.3 (Si), 26.1 (Ge), and 26.6 (Sn)), but all of them are considerably lower than that of $MoCH_2$. The low values of the $f_{\text{M-M'}}$ force constants and dissociation energies DE compared with those of $MoCH_2$ ($f_{\text{Mo-C}}$ = 1.989 mdyn/Å, DE = 41.0 kcal/mol) show that bonding capabilities of the $M'H_2$ ligand are significantly diminished with respect to methylene.

In the $^7B_1$ states, the Mo–M' bond lengths follow the same trend as those of the quintets, namely a lengthening down the group, and, as in $MoCH_2$, they are larger than for the quintets. However, comparing the increments in the Mo–M' bond distance arising from excitation of the $^5B_1$ states toward the $^7B_1$ ones, for $MoCH_2$ it was 0.24 Å, while for the other compounds they are less than 0.1 Å. This low lengthening of the interatomic distances suggests that Mo–M' bonding in the $^7B_1$ and $^5B_1$ states is quite similar. In other words, since, as discussed above, there is no π bond in $^7B_1$ states, it seems that in $^5B_1$ states only the σ bond is efficient and the π bond is almost negligible. These ideas are confirmed by examination of the Mo–M' bond orders (Table VI) and $f_{\text{Mo-M'}}$ stretch force constants (Table IV). Thus, while going from the quintet to the septet in $MoCH_2$, the bond order decreases by 0.583

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[25] Villar, H. O.; Dupuis, M. *Chem. Phys. Lett.* **1987**, *142*, 59 and references therein.

(40%), the lowering in the rest of the series being only 0.10–0.14 (10–13%). In its turn, the f_{Mo-C} force constant decreases by 24%, while in the rest of the series the $f_{Mo-M'}$ force constants do not change significantly (in fact, they rise slightly). All these considerations are in agreement with the essential difference between bonding capability of methylene with respect to silylene, germylene, and stannylene ligands as stated above. In fact, taking into account the values of the force constants and bond orders, it would seem more reasonable to compare the quintets states of the Si, Ge, and Sn derivatives with the septet $^7B_1$ of $MoCH_2$.

Although all these considerations about structural similarities of these compounds are interesting enough, probably the most important difference with respect to the carbon derivative is due to the fact that the $^7B_1$ states are not true minima on the potential energy surfaces. Examination of Table IV shows that in these compounds there is one imaginary frequency whose associated normal coordination corresponds to a wagging displacement of hydrogen atoms out of the molecular plane (defined by angle δ in Table I).

Geometry optimization of the septets without C_{2v} constraint leads to structures which have C_s symmetry and are considerably distorted from the planarity, the angles δ being 53.3°, 61.4°, and 68.0° for M′ = Si, Ge, and Sn, respectively. It is worth noting that the distortion degree correlates with the out-of-plane angle found in, for instance,[12b] disilene, Si_2H_4 (33–36°), digermene, Ge_2H_4 (38–40°), and distannene, Sn_2H_4 (46–50°), which in turn has been related to the energy gap between the singlet and the triplet $\Delta E_{s\text{-}t}$ of the fragment $M'H_2$. This topic has been treated by several authors,[12] but, as far as we can ascertain, this is the first time that such distortion has been reported for a bond in which the partner of the $M'H_2$ moiety is a naked transition metal. In the present case there is, however, a qualitative differentiating aspect since usually such nonclassical distortions are found in *double* bonds, but in the septets there is formally *only* a σ bond. This result makes clear that these out-of-plane deformations are not necessarily related to double bonds but to the character of the atom or group to which the $M'H_2$ fragment is bonded.

Analysis of the nature of the wave function associated with these $^7A'$ states reveals that they arise from a mix of $^7B_1$ and $^7A_1$ (going from C_{2v} toward C_s symmetry group, both species have $^7A'$ symmetry and thus the mix is allowed). For technical reasons, only the lowest $^7A'$ state of each compound has been considered in the present work. This mix causes two main effects (Figures 2–4). First, the equilibrium Mo–M′ bond distance is found to be higher as a consequence of incorporating the repulsive character of the carbenic-type states $^7A_1$. Bond lengths are decidedly large (2.787, 2.911, and 3.081 Å) and $f_{Mo-M'}$ force constants are considerably decreased with respect to $^7B_1$ states (33%, 58%, and 67% for M′ = Si, Ge, and Sn, respectively; see Tables IV and V). Also, the charge transfer from the Mo atom to $M'H_2$ in these species is lower than that in $^7B_1$ states as observed in their Mulliken population analysis.[26] Second, as a consequence of the avoided crossing, there is a stabilization of the $^7A'$ state with respect to its parent $^7B_1$. This gain of energy leads to a lowering of the splitting between the quintet and the septet which, on the other hand, decreases down the group. For M′ = Si and Ge, there are no more consequences, but for $MoSnH_2$ the sign of the splitting changes and the septet $^7A'$ lies lower than the quintet $^5B_1$. In other words, at this level of calculation the ground state of the $MoSnH_2$ complex is no longer planar (C_{2v}) but bent (C_s). The stabilization of $^7B_1$ states, due to the mixing with the $^7A_1$ ones, also offers a model for understanding the distortion observed in $^7A'$ states. After mixing, $^7A'$ states incorporate some possibility (through its $^7A_1$ component) of back-donation from a singly occupied orbital of Mo atom toward the empty p_π orbital of the $M'H_2$ fragment. The Mo–M′ bond in this state has, therefore, some multiple character, and a mechanism of nonclassical distortion is then possible. Notice, however, that in the present case the starting driving force appears to be the avoided crossing instead of the multiple bond.

Dissociation energies of septet $^7A'$ states with respect to the limit $^7S + {}^1A_1$ are 7.2, 3.8, and 3.7 kcal/mol for Si, Ge, and Sn, respectively. Taking into account the low stability of this type of bond, the question is whether or not compounds with a Mo–M′ formal single bond without additional stabilizing factors can be isolated.

Carbene versus Alkylidene Type of Complexation. Let us compare in this section structural properties of the series of carbene-like or Fischer-type compounds $(CO)_5Mo{=}M'H_2$ with that of alkylidene-like or Schrock-type compounds $Mo{-}M'H_2$. For the first element of the series, M′ = C, the Mo–C bond length in both types of complexes are sensitively similar (1.97–1.98 Å). This behavior can be assumed to be an exception since, as we have already shown for the rest of the series, the bond distances here calculated appear to be somewhat larger than those calculated at an equivalent level of theory in the compounds $(CO)_5Mo{=}M'H_2$, M′ = Si, Ge, and Sn. This lengthening of the Mo–M′ bond distance suggests a weakening of the bond strength in the alkylidene series and is clearly confirmed by the values of the associated $f_{Mo-M'}$ force constants. Thus, starting with $Mo{-}CH_2$, carbonylation of the transition metal–alkylidene to give $(CO)_5Mo{=}M'H_2$ causes a considerable enhancement of f_{Mo-C} (from 1.98 to 3.2 mdyn/Å). In the remaining elements of the series the changes in $f_{Mo-M'}$ are not so dramatic, but the force constant is always higher in the carbene-like series: $f_{Mo-M'}$ = 1.27, 1.13, and 0.90 mdyn/Å for M′ = Si, Ge, and Sn, respectively. These values are to be compared with those reported in Table III for ^5B states. These considerations make clear that, as far as the Mo–M′ bond strength is concerned, the Fischer type of complexation is more efficient than the Schrock one. This conclusion is specially true when M′ = C, as the effect is much more noticeable.

A similar trend is observed when dissociation energies DE are compared. In the carbene-like series $(CO)_5Mo{=}M'H_2$, DE values obtained from the dissociation curves computed at an equivalent level of calculation were 76.5, 47.2, 40.6, and 40.8 kcal/mol for M′ = C, Si, Ge, and Sn. Compared with those reported in Table II, it appears clear that the binding energy in the alkylidene-like series is almost half that of the carbene-like series.

Finally, let us compare the role played by the metallic fragments Mo and $(CO)_5Mo$ as far as their predisposition to binding $M'H_2$ is concerned. As stated in the Introduction, the $M'H_2$ ligand, singlet or triplet, coordinates a Mo atom or (pentacarbonyl)molybdenum(0) fragment, which in its turn can be in low- or high-spin states. For the Mo atom, the high-spin ground state ^7S is more stable than the lowest state, having a lone pair necessary to bind the $M'H_2$ ligand following a Fischer model (the state ^5D), by 31.6 kcal/mol.[11] Therefore, even for the less favored partner (SnH_2, $\Delta E_{s\text{-}t}$ = 24 kcal/mol), the ^7S–$^3B_1$ alkylidene-type of complexation if preferred. In its turn, the singlet state of $(CO)_5Mo$ is calculated to be 41.4 kcal/mol more stable than the triplet;[27] therefore, the singlet–singlet carbene-like coupling should be preferred even for methylene, for which the singlet lies 9.1 kca/mol above the triplet.[6] In other words, the preferred type of complexation in the compounds examined here is governed by the larger low–high spin difference (in absolute value) found in the transition-metal fragment with respect to the singlet–triplet splitting in the $M'H_2$ ligand.

Conclusions

In this work ab initio CASSCF calculations of the ground state and some low-lying excited states of alkylidene-type compounds $MoM'H_2$, (M′ = C, Si, Ge, and Sn) are reported.

In all cases studied, the electronic state $^5B_1$, corresponding to a formal $\sigma + \pi$ double bond, is a true minimum on the potential energy hypersurface relative to ground-state fragments. Both dissociation energies of states $^5B_1$ in Mo (^7S) + $M'H_2$ ($^3B_1$) and force constants $f_{MoM'}$ decrease down the group. For the carbon derivative they are noticeably higher than for the rest of the series,

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[26] Mulliken population analyses are given as supplementary material. For instance, in the case of $MoSnH_2$, the Mo total population increases from 5.76 ($^7B_1$) to 5.84 ($^7A'$).

[27] Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1576.

showing that bonding capabilities of silylene, germylene, and stannylene are considerably lower than those of methylene.

The electronic states $^7B_1$, corresponding to species with a formal σ bond, lie above the $^5B_1$ states, and the $^5B_1$–$^7B_1$ splitting diminishes regularly down the group. With the exception of $MoCH_2$, the septets $^7B_1$ are first-order stationary points with an imaginary frequency associated with a wagging displacement of hydrogen atoms out of the molecular plane. Full optimization of these species leads to C_s structures (states $^7A'$) considerably distorted from planarity. This anomalous behavior of the transition metal–metal bond increases down the group and is related to nonclassical distortions observed in the series of compounds Si_2H_6, Ge_2H_6, and Sn_2H_6. Because of such distortion, the ground state of the heaviest element of the series, $MoSnH_2$, is found to be bent (C_s, state $^7A'$) instead of planar (C_{2v}, state $^5B_1$).

Finally, comparison of naked $MoM'H_2$, with their pentacarbonylated homologous $(CO)_5Mo{=}M'H_2$, reveals that, as far as Mo–M′ bond strengths and dissociation energies are concerned, the Fischer-type of complexation is stronger than the Schrock one.

Note Added in Proof. After this paper was submitted for publication, we found out the work reported by Cundari and Gordon[28] on the nature of the transition-metal–silicon double bond in which geometries and force constants of charged species $CrM'H_2^+$ (M′ = Si, Ge, and Sn) were also reported. The results and trends observed are in agreement with those found in the present work.

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Supplementary Material Available. Mulliken population analysis for all states of $MoM'H_2$ complexes are only available on request from the author (11 tables).

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UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations

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Abstract: A new molecular mechanics force field, the Universal force field (UFF), is described wherein the force field parameters are estimated using general rules based only on the element, its hybridization, and its connectivity. The force field functional forms, parameters, and generating formulas for the full periodic table are presented.

I. Introduction

Parameters and functional forms are the vital infrastructure of molecular mechanics and dynamics force fields. One of the most important uses of molecular dynamics and energy minimization is the estimation of structures for new molecules. Unfortunately, the popular force fields, based on the classic work in the field,[1a-z] are limited to particular combinations of atoms, for example, those of proteins, organics, or nucleic acids.[1aa-ff] Progress has been made toward development of force fields which could, in principle, be extended to the entire periodic table though systematic procedures for obtaining the parameters have not been presented.[2,3] Further, the angle bend function used in these standard force fields (harmonic in θ) has the wrong shape to describe angular distortion approaching 180° for a nonlinear molecule. This functional form cannot describe the dynamics of inorganic materials such as zeolites which have equilibrium angles of ~150° and distort thermally to 180° with barriers to inversion of ~1 kcal/mol.[4a] In order to facilitate studies of a variety of atomic associations, we have developed a new force field using general rules for estimating force field parameters based on simple relations. This set of fundamental parameters is based only on the element, its hybridization, and connectivity. We refer to this new force field as a Universal force field (UFF). The angular distortion functional forms in UFF are chosen to be physically reasonable for large amplitude displacements. The force field functional forms and parameters are discussed in section II. Results for select organic, main group inorganic, and transition metal complex structures are provided in section III. Reference compounds used to obtain covalent radii for the elements are

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