

This is seen readily when the effective temperatures from metastable dissociation of proton-bound dimers are considered. The largest effective temperature is observed when the dimer is made up of a primary alcohol proton-bound to a secondary alcohol and the smallest when only secondary alcohols are used. These findings are interpreted as a consequence of different geminal substitution patterns of alcohols affecting the vibrational states of the proton-bound dimer and hence providing an entropic factor which

operates together with the enthalpic product stability factor on which the kinetic method is based. As the results show, it is possible to avoid this difficulty and obtain precise gas-phase acidities by using alcohols of the same structural types as reference compounds.

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Electronic Structure of the Transition-Metal–Carbene-like Complexes $(\text{CO})_5\text{Mo}=\text{M}'\text{H}_2$ ($\text{M}' = \text{C}, \text{Si}, \text{Ge}, \text{and Sn}$). A Theoretical Study Based on ab Initio CASSCF Calculations

Antonio Márquez and Javier Fernández Sanz*

Contribution from the Department of Physical Chemistry, Faculty of Chemistry, University of Sevilla, E-41012, Sevilla, Spain. Received June 10, 1991

Abstract: A theoretical study of the bond between a transition metal and an element of group 14 is reported. Based on quantum-mechanical calculations carried out at Hartree–Fock SCF and CASSCF levels, the molecular structure of the series $(\text{CO})_5\text{Mo}=\text{M}'\text{H}_2$, $\text{M}' = \text{C}, \text{Si}, \text{Ge}, \text{and Sn}$, has been determined. The $\text{Mo}=\text{M}'$ double-bond structure corresponds to the well-known sp_σ -donor/ p_π -acceptor scheme, which becomes less efficient for the heavier terms of the series. Evolution of geometrical parameters is discussed and found in excellent agreement with experimental trends. In particular, the lowering of the $\text{H}=\text{M}'\text{—H}$ bond angle is well described and appears to be related to the different mix of the M' s and p orbitals. Dissociation energies, potential energy profiles for the dissociation process yielding $(\text{CO})\text{Mo}_5$ and $\text{M}'\text{H}_2$, rotational barriers of the $\text{M}'\text{H}_2$ ligand around the 4-fold axis of the $(\text{CO})\text{Mo}_5$ fragment, and force constants associated to the $\text{Mo}=\text{M}'$ bond stretch are also reported.

Introduction

The nature of the metal–metal bond in heterobi- or heteropolymetallic complexes has been a topic of growing interest in the last few years. The reactivity and potential activity of these compounds in organometallic synthesis are the subject nowadays of considerable work, both experimental and theoretical.¹ From a structural viewpoint, the main interest is constituted by the exciting properties of the metal–metal bond. Among dinuclear compounds, those showing a bond between a transition metal and a metal of group 14 fall into a special category. For instance, transition-metal–tin compounds are in fact heterodinuclear species, but they can be seen as a special type of organometallic complex in which a carbon atom has been replaced by tin. Therefore, it seems reasonable to assume an a priori rationalization of their structural properties on the grounds of their carbon parents.

Since the work of Marks^{2,3} in 1971, the chemistry of divalent germanium, tin, and, to a lesser extent, silicon and lead homologues of metal carbenes $\text{L}_n\text{M}=\text{M}'\text{XY}$, has been the subject of considerable experimental work and has been summarized in excellent review articles.⁴ In spite of all this experimental work, the nature of these metal–metal bonds remains somewhat uncertain, in particular as far as the metal–metal double-bond features are concerned.

Metal–carbon double bonding in metallic carbenes has focused the attention of several theoretical works and the notion seems

to be well established.⁵ Thus, the structure of naked transition-metal carbenes has been carefully analyzed,⁶ and experimental data of their thermochemistry are also available.⁷ For obvious technical reasons, theoretical calculations on more realistic compounds in which the transition metal has its coordination capabilities fulfilled (typically carbonyl derivatives $(\text{CO})_n\text{M}=\text{CXY}$) are scarce^{6a,8} and often based on the approximated Fenske–Hall method.⁹ In fact, only a few numbers of Cr, Mo, Ni, and Fe carbonyl carbenes have been examined at an ab initio level of

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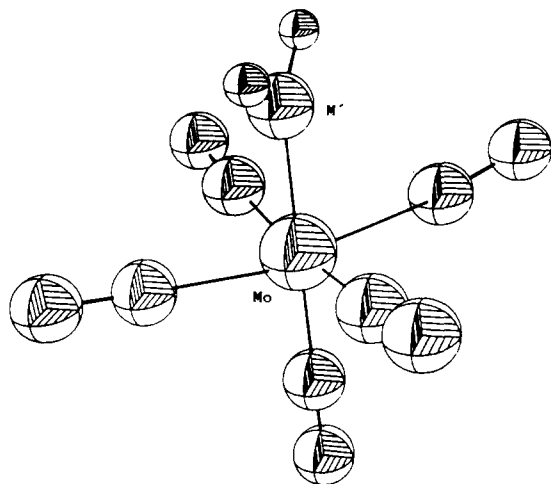
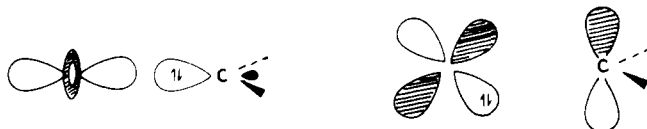


Figure 1. Molecular geometry of the staggered $(\text{CO})_5\text{Mo}=\text{M}'\text{H}_2$ complexes. Their eclipsed conformers are obtained by rotating the $\text{M}'\text{H}_2$ ligand 45° around the C_4 axis of the $(\text{CO})_5\text{Mo}$ fragment.

theory. Indeed, and for the same reasons, these calculations have been carried out using uncorrelated wave functions or a limited MCSCF method. In particular, the bond structure of (pentacarbonyl)chromium (or molybdenum) carbenes correspond to the so-called Fischer-type complexes,^{5,10} which are 18-electron species and have the metal in a low oxidation state. The bond in these compounds can be understood as a singlet-state carbene donating the σ electron pair to the metal fragment with a corresponding amount of back-donation from the metal to the vacant π orbital of methylene.



Concerning the bond between a transition metal and heavier elements of group 14, Nakatsuji et al. reported¹¹ an ab initio RHF calculation on a silylene-chromium complex showing its Fischer-type nature, although when compared with its carbon homologue, the double-bond strength was found to be considerably lower. As far as we can ascertain, ab initio calculations on germanium and tin homologues have never been reported.¹²

Interest in knowledge of this type of multiple metal-metal bond structure has led us to perform a theoretical study¹³ of the molecular structure of a family of complexes showing a bond between a metal transition and an element of group 14. In this paper, the first of a series, we report ab initio CASSCF calculations on species modeling the bond between a (pentacarbonyl)molybdenum(0) fragment and a silylene, germylene, or stannylene ligand (general formula $(\text{CO})_5\text{MoM}'\text{R}_2$, with M' being C, Si, Ge, and Sn; for the sake of comparison the carbene homologue has also been considered).¹⁴

The Model. In the first accurate calculation on a carbonyl transition-metal carbene, Spangler et al.^{6a} modeled the R groups by hydrogen atoms, $(\text{CO})_3\text{NiCH}_2$. This model was later criticized^{8b} by arguing that, as stated above, in a Fischer-type complex, a σ bond is formed by donation of the lone pair of the singlet-state

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(14) Although $\text{M}=\text{PbRR}'$ derivatives have been prepared (see, for instance: Herrmann, W. A. *Chem. Ber.* **1989**, *112*, 445), plumbylens have not been considered in this work because of the large spin-orbit coupling expected for these compounds.

Table I. Selected Geometrical Parameters of the 1-4 Optimized Structures^a

	1	2	3	4
$R_{(\text{Mo}-\text{M}')}$	2.0202	2.4809	2.5623	2.6515
	1.9855 ^b	2.4643 ^b	2.5305 ^b	2.6255 ^b
$R_{\text{Mo}-\text{C}_{\text{eq}}}$	2.1151	2.1156	2.1142	2.1099
$R_{\text{Mo}-\text{C}_{\text{ax}}}$	2.1987	2.1204	2.1014	2.1001
$R_{\text{C}-\text{O}_{\text{eq}}}$	1.2282	1.2316	1.2311	1.2313
$R_{\text{C}-\text{O}_{\text{ax}}}$	1.2287	1.2301	1.2312	1.2303
$R_{\text{M}'-\text{H}}$	1.0915	1.4877	1.5542	1.7490
$\alpha_{\text{H}-\text{M}'-\text{H}}$	107.0	100.2	99.4	98.7
$\alpha_{\text{M}'\text{MoC}_{\text{eq}}}$	86.1	89.5	89.7	89.4
$\alpha_{\text{MoCO}_{\text{eq}}}$	172.6	179.2	179.4	178.4
$\tau_{\text{M}'\text{MoCO}_{\text{eq}}}$	5.2	17.3	22.4	8.4

^a Bond distances in angstroms and bond angles in degrees.

^b Obtained from CASSCF calculations.

carbenic fragment (1A_1) to the metal. Since the ground state of CH_2 is the triplet 3B_1 ,¹⁵ a model in which the R substitute stabilizes the singlet with respect to the triplet would be preferable. Thus, the carbenic ligand has often been modeled by $\text{CH}(\text{OH})$. However, in the case of SiH_2 , GeH_2 , and SnH_2 , the relative position of the triplet and the singlet is reversed, the singlet 1A_1 being more stable than the triplet 3B_1 by 17-19,¹⁶ 23-23,^{16a,17} and 22-24^{16a,18} kcal/mol, respectively. In principle, one can choose as model either $\text{M}'\text{H}(\text{OH})$ or $\text{M}'\text{H}_2$ (mixed models are not valuable since the presence of the hydroxyl affects the π system significantly). In order to save computer time and facilitate the analysis, we have chosen for the present calculations the model $(\text{CO})_5\text{MoM}'\text{H}_2$ both in its eclipsed and staggered conformations (Figure 1).

Since one of our main goals is to get a reliable comparison of the relative $\text{Mo}=\text{M}'$ bond strengths, these structures have been fully optimized at ab initio Hartree-Fock level instead of taking an averaged experimental geometry. In order to obtain a deeper understanding of the electronic structures of the $\text{Mo}=\text{M}'$ double bond, a subsequent CASSCF optimization of the $\text{Mo}-\text{M}'$ interatomic bond distance has also been performed.

Computational Details

Ab initio Hartree-Fock calculations were undertaken using the effective core potential (ECP) approximation to describe the inner core electrons. For the Mo and Ge atoms, the Hay-Wadt ECPs were used.¹⁹ For the C, O, Si, and Sn atoms, the pseudopotential approximation of Durand and Barthelat was chosen.²⁰ In the case of Sn, the pseudopotential accounts for relativistic effects (mass and Darwin corrections). The basis set for valence electrons was of double- ζ quality for the $\text{Mo}-\text{CH}_2$ fragment and minimal for the CO ligands. More specifically, the basis set in compacted notation was (3,3,4)/[2,1/2,1/3,1] for Mo;^{19a} (3,3)/[2,1/2,1] for Ge;^{19b} (4,4)/[3,1/3,1] for C, Si, and Sn;²⁰ and (4,4)/[1,1] for C (CO ligand) and O. On the heavy atoms of the $\text{M}'\text{H}_2$ ligand, a set of polarization d functions was also added ($\zeta = 0.6, 0.45, 0.25$, and 0.20 for C, Si, Ge, and Sn, respectively). For hydrogen, the standard Huzinaga-Dunning (4s)/[2s] basis set was used.²¹

Electron correlation effects were introduced into the wave function using the CASSCF method.²² The correlated electrons were the four

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Table II. Most Important Configurations in the CASSCF Expansion of the Wave Function

struct	configuration	coeff
1	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi)^2$	0.942
	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi^*)^2$	0.173
	$(d_{x^2-y^2})^2(\sigma)^2(\pi)^2(d^*_{yz})^2$	-0.113
	$(d_{yz})^2(\sigma)^2(\pi)^2(d^*_{x^2-y^2})^2$	-0.106
	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^1(\pi)^1(\sigma^*)^1(\pi^*)^1$	-0.098
2	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi)^2$	0.956
	$(d_{yz})^2(\sigma)^2(\pi)^2(d^*_{x^2-y^2})^2$	-0.099
	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi^*)^2$	-0.096
	$(d_{x^2-y^2})^2(\sigma)^2(\pi)^2(d^*_{yz})^2$	-0.091
3	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi)^2$	0.952
	$(d_{yz})^2(\sigma)^2(\pi)^2(d^*_{x^2-y^2})^2$	-0.098
	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi^*)^2$	-0.092
	$(d_{x^2-y^2})^2(\sigma)^2(\pi)^2(d^*_{yz})^2$	-0.092
	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi)^2$	0.956
4	$(d_{x^2-y^2})^1(d_{yz})^1(\sigma)^2(\pi)^2(d^*_{x^2-y^2})^1(d^*_{yz})^1$	0.102
	$(d_{x^2-y^2})^1(d_{yz})^2(\sigma)^2(\pi)^1(d^*_{x^2-y^2})^1(\pi^*)^1$	0.104
	$(d_{x^2-y^2})^2(d_{yz})^2(\sigma)^2(\pi^*)^2$	-0.093

of the $Mo=M'$ double bond (σ and π components) and the rest of the d electrons of the molybdenum atom. The orbitals selected were the 5s and 4d set of Mo and the pair sp_{σ}, p_{π} of M' . The active space was, thus, 8 electrons and 8 MOs (1764 CSFs).

Molecular geometries were fully optimized at RHF level using an analytical gradient technique under C_{2v} constraint, with residual forces being less than 10^{-4} hartree/bohr. Keeping the rest of the geometrical parameters frozen, the interatomic $Mo-M'$ distance was then optimized at the CASSCF level by using numerical differentiation. All the calculations were performed using the HONDO-7 package.²³

Results and Discussion

Molecular Structure and Wave Functions. In Table I, the equilibrium geometries computed for the four structures $s-(CO)_5Mo=M'H_2$, 1, $M' = C$; 2, $M' = Si$; 3, $M' = Ge$; and 4, $M' = Sn$, are reported. We will start this section with $Mo-M'$ bond lengths; however, due to the lack of experimental data a preliminary discussion is in order. There are a large number of stable carbenes of the group 6 elements (Cr, Mo, W). From these structural data, the $Mo=C$ double bond length is estimated to be ~ 2.06 Å.^{5b} There are no structural data for the $Mo=Ge$ and $Mo=Sn$ double bond but there are for the Cr and W derivatives. Thus, typical bond distances for $Cr=Ge$ and $W=Ge$ are²⁴ 2.367 and 2.632 Å. To choose 2.50 Å as averaged value for $Mo=Ge$ seems reasonable. Likewise a mean "experimental" value for the $Mo=Sn$ bond length of 2.63 Å would arise from the observed $Cr=Sn$ (2.562 Å) and $W=Sn$ (2.702 Å).²⁵ This estimation agrees with the observed value for the $Mo-Sn$ single bond^{4b} (2.66–2.89 Å). When the theoretical values are compared with the "experimental" ones,²⁶ a general close agreement can be observed. At the RHF level, the computed bond lengths are somewhat larger than the experimental with the exception of 1. This exception can be understood, bearing in mind that the averaged value for the $Mo=C$ bond distance has been deduced from complexes in which the carbon atom is substituted by a π donor group, and thus, the π carbenic system is relatively more extended toward the substitute with weakening of the π_{MoC} bond.

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Table III. Mulliken Population Analysis for Compounds 1–4

		1	2	3	4
		SCF/CAS	SCF/CAS	SCF/CAS	SCF/CAS
Mo	s	0.279/0.285	0.242/0.245	0.253/0.257	0.225/0.229
	p_{σ}	0.150/0.150	0.151/0.148	0.142/0.142	0.215/0.213
	total p	0.107/0.102	0.099/0.100	0.087/0.092	0.167/0.169
	d_{σ}	0.369/0.449	0.327/0.363	0.311/0.347	0.355/0.391
	d_{π}	1.204/1.098	1.384/1.345	1.388/1.348	1.410/1.432
	total d	4.726/4.605	4.867/4.791	4.858/4.778	4.937/4.862
M'	s	5.112/4.993	5.206/5.137	5.198/5.127	5.329/5.258
	p_{σ}	1.334/1.297	1.298/1.293	1.553/1.549	1.471/1.468
	p_{π}	1.208/1.127	1.124/1.103	0.921/0.906	0.881/0.868
	total p	0.406/0.620	0.146/0.187	0.131/0.164	0.105/0.134
	total d	2.768/2.887	2.110/2.136	1.811/1.837	1.712/1.734
	total	0.120/0.115	0.176/0.176	0.194/0.193	0.089/0.088
C_{ax}	total	4.222/4.299	3.583/3.696	3.557/3.578	3.271/3.290
C_{eq}	total	3.863/3.884	3.863/3.876	3.870/3.885	3.870/3.885
O_{ax}	total	3.874/3.881	3.873/3.887	3.877/3.891	3.879/3.894
O_{eq}	total	6.351/6.347	6.353/6.350	6.357/6.355	6.356/6.354
H	total	6.359/6.352	6.362/6.360	6.362/6.359	6.363/6.361
		0.762/0.772	1.026/1.022	1.032/1.027	1.102/1.098

When the $Mo=M'$ bond distance is compared in the series 1–4, the first effect observed is the progressive increasing of this value from 2.02 Å for 1 to 2.65 Å for 4. Electron correlation diminishes this parameter by about 0.02–0.04 Å, the $Mo=C$ being the bond distance most affected. Such a shortening of the equilibrium bond lengths due to the effects of the nondynamical electron correlation has already been observed^{18a,27} and can be understood by analyzing the CASSCF wave function and the electron redistribution introduced into the system. With this aim, the coefficients of the most important configurations in the CASSCF wave function have been reported in Table II. Whatever M' is, the reference determinant clearly predominates, although for 1, the associated coefficient (0.942) is somewhat lower than for the rest of the compounds (0.952–0.956). Disregarding the reference configuration, the most important contributions are inner d correlation and $\pi_{MoM'}$ intrabond. For 1, the $(\pi^0)(\pi^*)^2$ configuration shows a coefficient of 0.173. The effect caused by this configuration is a lowering of the ionic component of the π_{MoC} bond since the π^*_{MoC} orbital has a larger contribution of the $p_{\pi}(C)$ with respect to the $d_{\pi}(Mo)$. Consequently, there is an enhancement of the back-donation from the $d_{\pi}(Mo)$ orbital toward the $p_{\pi}(C)$ one, leading to a stronger π_{MoC} bond. With respect to 2–4, the inner d correlation is similar to that of 1; however, the diexcitation $(\pi^0)(\pi^*)^2$ is found to contribute in less degree, and thus, the shortening in the $Mo=M'$ bond length is smaller.

Another interesting geometrical variation concerns the $H-M'-H$ angle, which in going from 1 to 4 decreases from 107° to 98° . This variation has already been reported from experiment,^{4a,24,25} and typical values are 108 – 114° (C), 103° (Ge), and 98° (Sn). It has been suggested that this evolution may be accounted for either by decreasing the steric hindrance down this series or by lowering the M' p atomic function contribution to the σ hybrid orbitals of the $M'H_2$ group (formally sp^2). Since the steric effects are negligible in our model, our calculations prove unambiguously the later hypothesis to be essentially correct.

A more detailed analysis of the differences in the electronic structure of the compounds 1–4 can be obtained from the Mulliken populations reported in Table III. Although using Mulliken population absolute values has been questioned, the fact that both the basis set and molecular structures are similar leads to reliable comparisons.²⁸ Following the bond scheme outlined above for a Fischer-type complex, the σ bond is a donation of an electron pair of the $M'H_2$ ligand to a metallic sd_{σ} vacant orbital, while the π bond corresponds to the back-donation from a d orbital of the metal toward the p_{π} vacant orbital of the ligand. More or less to the same extent, both the σ and the π bonds are polarized

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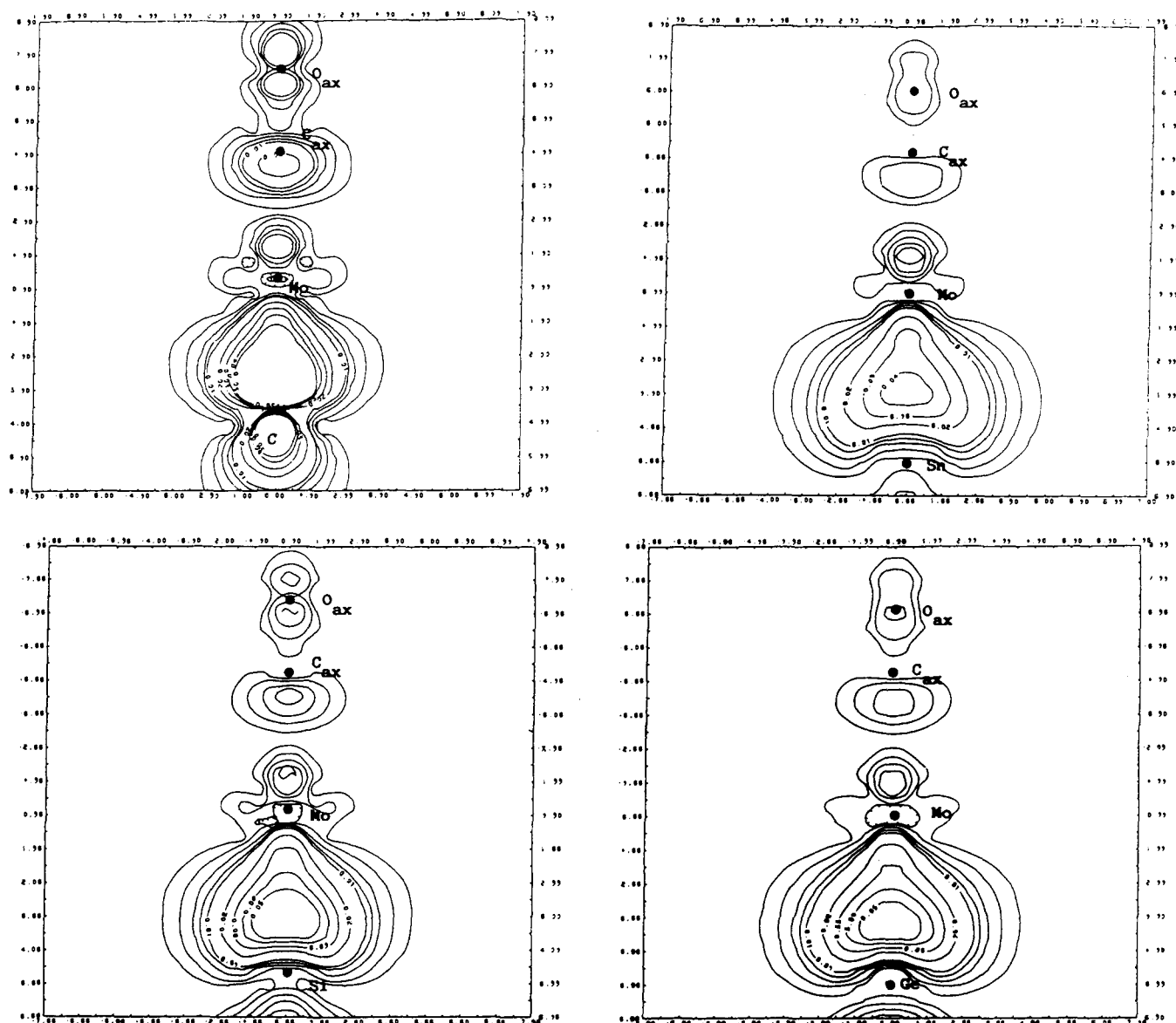


Figure 2. Isodensity contours for the σ bond of $(\text{CO})_5\text{Mo}-\text{M}'\text{H}_2$ compounds: (a) $\text{M}' = \text{C}$, (b) $\text{M}' = \text{Si}$, (c) $\text{M}' = \text{Ge}$, and (d) $\text{M}' = \text{Sn}$.

toward the ligand and the metal, respectively. This scheme agrees with the Mulliken populations of Table III, although significant dependence on the nature of M' is found. Thus, the population of the $\text{Mo } d_x$ orbital increases going from 1 to 4. Concomitantly, the population of the $\text{M}' p_x$ orbitals lowers. This behavior can be easily understood by taking into account the increasing diffuse nature of the $p_x(\text{M}')$ orbital which leads to a less effective overlap with the $d_x(\text{Mo})$ one and, therefore, to a weakening of the π bond. This lesser back-donation explains why, in complexes of the type $\text{L}_n\text{M}=\text{M}'\text{XY}$, the $\text{M}'\text{XY}$ ligand still has a certain character of a Lewis acid and features easy addition of a neutral base to yield adducts of the type $\text{L}_n\text{M}=\text{M}'\text{XY}\leftarrow\text{B}$.

Although individual fluctuations in populations of the orbitals involved in the $\sigma_{\text{MoM}'}$ bond are found, the overall population for both Mo and M' remains rather similar in the series. Taking for M' the set of s and p_x orbitals, one can observe that while the population of the latter decreases, that of the s orbital increases. However, when we go from 1 to 4, the lowering in the $\text{HM}'\text{H}$ bond angle reveals, as mentioned above, a diminution in the mix of s and p orbitals. In other words, through the series, the p contribution to the orbital bearing the $\text{M}'\text{H}_2$ lone pair lowers; therefore, the participation of the s orbital in the $\sigma_{\text{MoM}'}$ bond raises. Thus, although the Mulliken population of the $s + p_x$ set is almost the same, in the heavier terms of the series, the larger contribution of the s orbital, nondirectional, reduces the Lewis acid character

of the $\text{M}'\text{H}_2$ ligand faced to the $(\text{CO})_5\text{MO}$ fragment.

In order to get an easier view of the differences in the bonding of these compounds, plots of isodensity contours for the σ and π bonds are reported in Figures 2 and 3. In 1, Figure 2a, the $sp_x(\text{C})$ orbital has a large contribution to the σ bond, which is compact and causes an important charge transfer toward the $4d_x(\text{Mo})$ orbital. In Figure 2b-d, the sp_x orbital becomes less directional and more diffuse and a poorer charge transfer is observed. When concern turns to the π bond, Figure 3a shows how the similar spatial extension of the $p_x(\text{C})$ and $d_x(\text{Mo})$ orbitals leads to an efficient overlap and considerable charge transfer. In the heavier terms of the series, Figure 3b-d, the continuous increase in the size of the p_x orbitals decreases the overlap and, therefore, weakens the bond. It is worth noting that, whatever M' is, the Fischer-type model of bonding is well suited.

Focusing attention now on the structure of the $(\text{CO})_5\text{Mo}$ fragment, one can see that whatever M' is, the distances $\text{Mo}-(\text{CO})_{\text{eq}}$ are always similar ($\approx 2.11 \text{ \AA}$) while the $\text{Mo}-(\text{CO})_{\text{ax}}$ ones decrease slightly from 1 to 4. The largest difference found is passing from 1 to 2 (0.07 \AA). On the other hand, while in 2-4 the distances $\text{Mo}-(\text{CO})_{\text{ax}}$ and $\text{Mo}-(\text{CO})_{\text{eq}}$ are almost similar, in 1, the distance $\text{Mo}-(\text{CO})_{\text{ax}}$ is significantly larger than the $\text{Mo}-(\text{CO})_{\text{eq}}$ one. These variations suggest that (i) the π -acceptor/ σ -donation ratio for the CH_2 ligand is higher than that of SiH_2 , GeH_2 , and SnH_2 . (ii) Since both CH_2 and $(\text{CO})_{\text{ax}}$ compete for

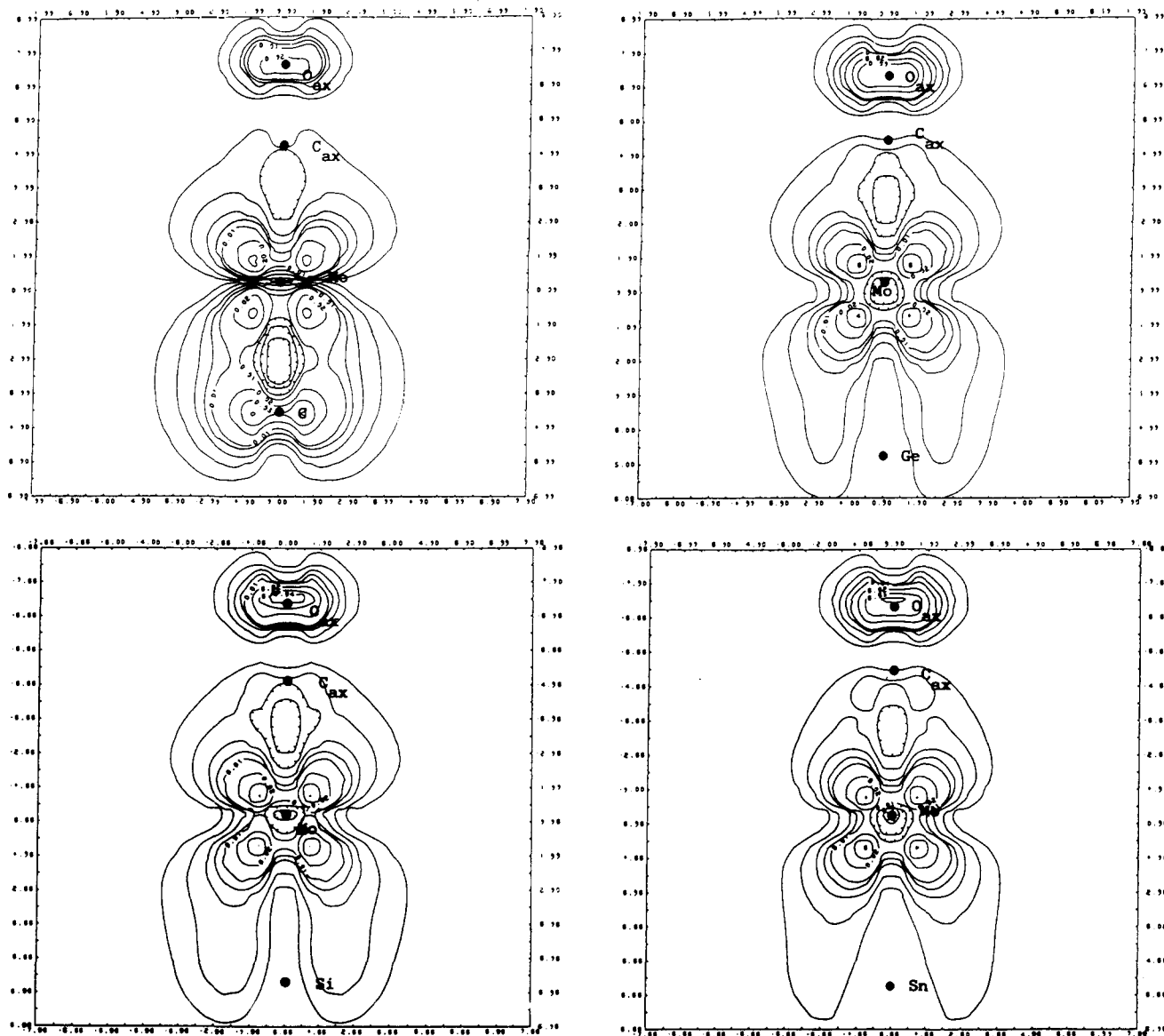


Figure 3. Isodensity contours for the π bond of $(\text{CO})_3\text{Mo}=\text{M}'\text{H}_2$ compounds: (a) $\text{M}' = \text{C}$, (b) $\text{M}' = \text{Si}$, (c) $\text{M}' = \text{Ge}$, and (d) $\text{M}' = \text{Sn}$.

the same electron pair, the former is a better π acceptor than the latter.

Another interesting structural aspect is shown by the fact that the $\text{M}'\text{-Mo-C}_{\text{eq}}$ bond angles are smaller than 90° . This "umbrella effect" has been observed experimentally^{4b,29} and explained on the grounds of a solid-state package. However, the results of our calculations show the presence of interactions between the equatorial carbonyls and the $\text{M}'\text{H}_2$ ligand leading to a such distortion.

Dissociation Energies, $\text{Mo}=\text{M}'$ Bond Strengths, and Rotational Barriers. In Table IV, the energetics for 1-4 and their eclipsed rotational isomers (the series 1'-4') are summarized. Dissociation energies (DE) have been calculated from the CASSCF potential curves reported in Figure 4. During dissociation, each fragment can split off as a triplet $|\sigma^1\pi^1|$ or a singlet $|\sigma^2\pi^0| + \lambda|\sigma^0\pi^2|$. In the processes reported in Figure 4, whatever M' is, after dissociation, both the metallic fragment and the $\text{M}'\text{H}_2$ ligand are singlet states, in agreement with earlier studies. The dissociation energy for 1 is calculated to be 76.5 kcal/mol. This value is higher than that reported by Taylor and Hall^{8b} for the $(\text{CO})_3\text{Mo}=\text{CH}(\text{OH})$ complex (60 kcal/mol). There are three main reasons for this difference: (i) The level of calculation used by these authors corresponds to a full CI among the $\sigma^2\pi^2\sigma^*\pi^*$ system. As we have

Table IV. Total Energies (au), Dissociation Energies (DE, kcal/mol), Rotational Barriers (ΔE , kcal/mol), and Harmonic Force Constants (f , mdyn/Å) for the $\nu_{\text{MoM}'}$ Stretch

	RHF		CAS SCF		
	E_{total}	ΔE_r	E_{total}	ΔE_r	f DE
1	-119.728 964		-119.834 178		3.234 76.53
1'	-119.729 191	0.48	-119.814 190	0.75	
2	-118.033 223		-118.128 558		1.270 47.22
2'	-118.033 708	0.30	-118.129 155	0.37	
3	-117.939 399		-118.034 782		1.132 40.64
3'	-117.939 556	0.10	-118.034 982	0.12	
4	-117.596 623		-117.692 433		0.898 40.83
4'	-117.596 950	0.21	-117.692 922	0.12	

already noted, the effect of electron correlation is to reinforce the double bond by lowering the ionic component of the bond. Since our CI is more extended, this lowering is somewhat larger. (ii) The substitution of one hydrogen by a hydroxyl in the CH_2 ligand stabilizes the singlet state of the carbenic fragment, and therefore, the barrier for dissociation decreases. (iii) Our geometrical structures have been optimized. The same reasons account also for the difference between our DE for 2 (47.2 kcal/mol) and that

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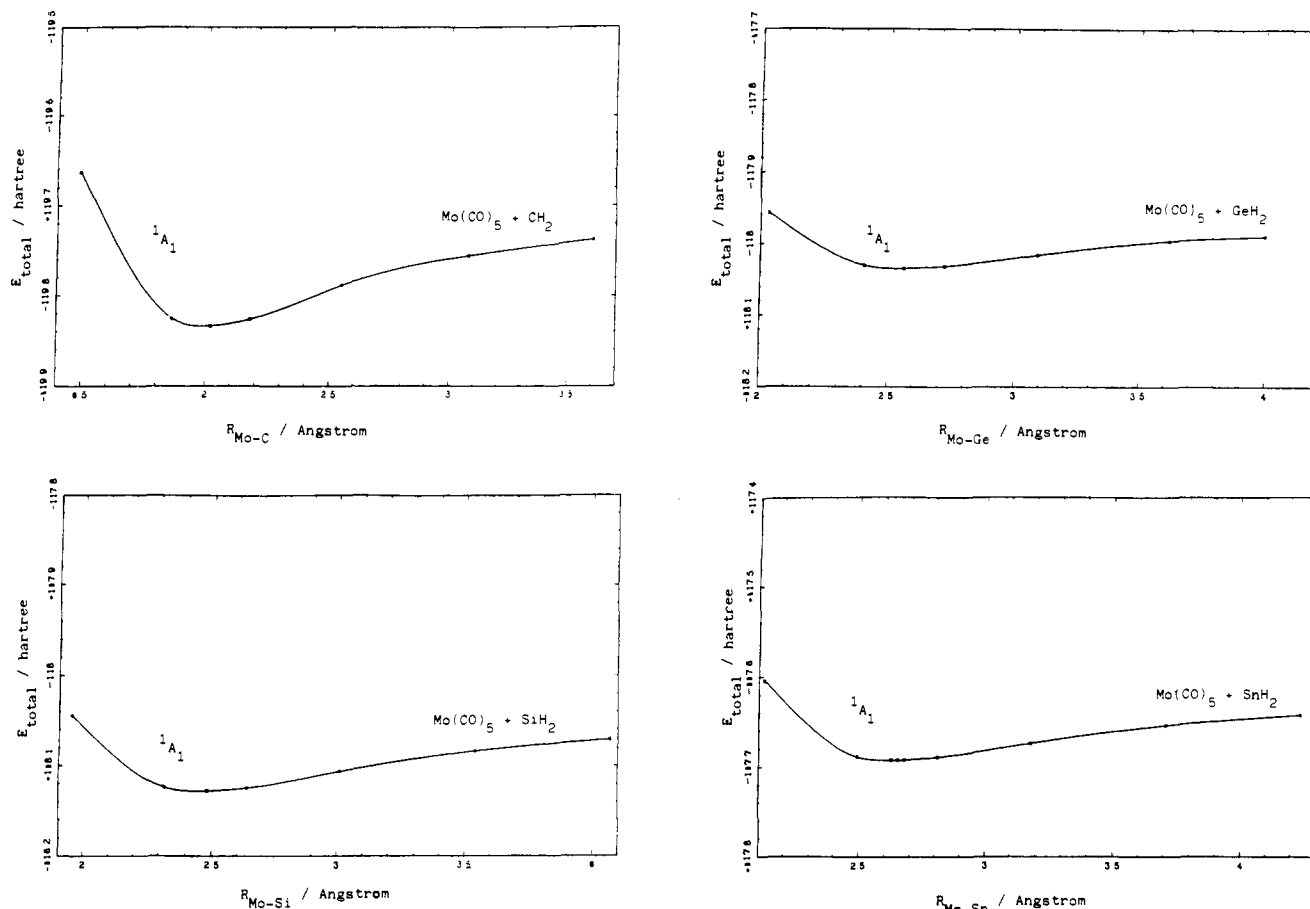


Figure 4. Potential energy curves for the dissociation of $(\text{CO})_5\text{Mo}=\text{M}'\text{H}_2$ into $(\text{CO})_5\text{Mo}$ and $\text{M}'\text{H}_2$ singlet fragments obtained from CASSCF calculations.

calculated by Nakatsuji et al.¹¹ for $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ (29.6 kcal/mol).

On the other hand, the most striking point emerging from Table IV is the clear difference between the dissociation energy of 1 and that of 2-4. DE diminishes along the series according to the discussion of the precedent section with the exception of 4, which is slightly higher than 3 (this difference appears to be very small and meaningless). However, the gap observed between 1 and 2 is considerable (almost 30 kcal/mol) and, in our opinion, cannot be accounted for only by the fact that dissociation of 1 leads to an excited state of CH_2 while 2-4 dissociate always into $\text{M}'\text{H}_2$ ground states. This idea is confirmed by examination of the force constants associated with the $\text{Mo}=\text{M}'$ stretch vibration. For 1, the force constant ($f_{\text{Mo-C}} = 3.234 \text{ mdyn/\AA}$) is almost 3 times that of 2 ($f_{\text{Mo-Si}} = 1.270 \text{ mdyn/\AA}$). From this value, a regular lowering of the force constant is observed ($f_{\text{Mo-Ge}} = 1.132 \text{ mdyn/\AA}$, $f_{\text{Mo-Sn}} = 0.898 \text{ mdyn/\AA}$). These results evidence a noticeable change in the coordination capabilities of the $\text{M}'\text{H}_2$ ligand passing from 1 to 2-4 and would explain why silylene-, germylene-, and stannylene-metal transition derivatives are difficult to isolate. This relatively low strength of the bond together with the fact that for 2-4 the M' center is positive charged (the mean charge is ~ 0.5 ; see Table III) agrees with the experimentally observed trend in the sense that usually the compounds obtained incorporate Lewis base, $((\text{CO})_5\text{Mo}-\text{M}'\text{R}_2 \leftarrow \text{B})$.

Finally, when the relative energies of the rotational conformers are considered, one can observe that, whatever the level of calculation, the staggered conformation is less stable than the eclipsed one although the difference is small. The rotational barriers are, thus, low and the trend is to decrease going from 1 to 4. The value found at the RHF level for 1 (0.48 kcal/mol) is close to that reported by Nakatsuji et al.^{8a} for the related compound $(\text{CO})_5\text{Cr}=\text{CH}(\text{OH})$ and increases slightly at the CASSCF level. For 2-4, the barriers are almost half of 1 and do not depend significantly on the level of calculation. Due to these low rotational

barriers, one can conclude that the rotation of the $\text{M}'\text{H}_2$ ligand around the 4-fold metallic fragment axis is essentially free, mainly for the heavier terms of the series.

Conclusions

In this paper, a theoretical ab initio study on the electronic structure of the bond between a transition metal and an element of group 14 is reported. This is the first comparative analysis on the double bond properties of the series of compounds methylene-, silylene-, germylene-, and stannylene(pentacarbonyl)Mo(0).

Their equilibrium molecular structures have been optimized at the RHF level for both the staggered and eclipsed conformers. Going down the group, the $\text{Mo}=\text{M}'$ bond distance lengthens according to chemical intuition. Electron correlation, incorporated through CASSCF calculations, shortens the bond length, and we have argued that this effect is due to a lowering of the ionic character of the bond caused by the relatively large contribution of the $(\pi)^0(\pi^*)^2$ configuration. Compared with the available experimental data, the predicted values show a mean deviation of 1.6%.

The $\text{H}-\text{M}'-\text{H}$ bond angle decreases going from methylene to stannylene derivatives in excellent agreement with the observed trend, and our calculations show that this behavior is a consequence of the different mix of the s and p orbitals of M' instead of a steric interaction.

Our calculations also account for the umbrella effect, demonstrating that such an effect is not due to solid package requirements but to interactions between the $\text{M}'\text{H}_2$ ligand and the equatorial carbonyls.

The analysis of the wave function shows that the Fischer-type model of bonding is well-suited whatever M' is although the increasing diffuse character of the s and p orbitals of M' leads to a less efficient overlap with the Mo d orbitals and, therefore, to a weakening of the bond both for the σ and π components. Indeed, with the exception of the methylene derivative, the M'

atom is noticeably positively charged, explaining why these types of compounds are rarely isolated except as ylides. These considerations suggest that the chemical properties of species where $M' = \text{Si, Ge, and Sn}$ are quite different from their carbene parents.

This suggestion is also confirmed by the dramatic difference found in the dissociation energies and force constant associated with $\text{Mo}=\text{M}'$ bond strength between the carbene derivative and the rest of the compounds.

Finally, when the relative energy of the staggered and eclipsed conformers is examined, the conclusion is that the rotation of the $\text{M}'\text{H}_2$ group is practically free.

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Low-Lying Electronic Excited States of Buckminsterfullerene Anions

Fabrizia Negri, Giorgio Orlandi,* and Francesco Zerbetto

Contribution from Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via F. Selmi 2, 40126 Bologna, Italy. Received July 8, 1991

Abstract: We report Pople–Pariser–Parr (PPP) calculations of the energies of the lowest electronically excited states of six C_{60} anions ranging from the monoanion to the hexaanion. Multiplicities up to septet are included. The results for the monoanion are compared with the existing absorption spectrum. The stability of various anions and the possibility of obtaining them by electrochemical reduction are discussed. In most of the species studied, we find a remarkable density of electronic levels close to the electronic ground state. This density is due to the existence, in neutral C_{60} , of a triply degenerate lowest unoccupied molecular orbital (LUMO), together with a close-lying LUMO+1 of the same degeneracy.

1. Introduction

Fullerene compounds have very recently been isolated,¹ and fullerrite can now be considered one of the phases of carbon. It is made by molecules containing from 60 up to possibly several hundred carbon atoms, which shape themselves in the form of pentagons and hexagons to build spheroids. The archetype of these compounds is the highly symmetric C_{60} cluster, or Buckminsterfullerene (Bf), in which 12 pentagons and 20 hexagons are arrayed in the highest possible symmetry on the surface of a sphere.² The characterization of the physical and chemical properties of these molecules is now in progress and promises to yield remarkable results. Among other data that are presently becoming available, a particularly fascinating achievement was the reported electron transport, or conductivity, that C_{60} , and to a lesser extent C_{70} , show upon doping with alkali metals.³ Shortly after a communication on this subject was published,³ the same laboratory reported a transition temperature to superconductivity of 18 K for the potassium-doped Bf crystal.⁴ Very recently, two subsequent editorial comments⁵ have reported a dramatic increase of this transition temperature, which is presently claimed to be 42 K for the rubidium and thallium dopants and 57 K for the iodine dopant. To date, such a temperature is the highest for an organic material. The nominal composition of the sample that showed the higher conductivity was M_3C_{60} . This is possibly to be related to the crystal structure of C_{60} , which has a face-centered cubic packing with two vacant tetrahedral sites of radius 1.12 Å and one octahedral site of radius 2.06 Å.³ These sites can ac-

commodate three alkali atoms, and the addition of a fourth atom modifies the original crystal lattice⁶ and possibly hinders the electron transport from one molecule to the other. Alternatively, the highest conductivity of the K_3C_{60} composition samples may be due to the different electronic structure of the various anions. Thus, a question to be addressed here is whether one can explain the trend observed in the conductivity and possibly offer suggestions on how to improve on the results of refs 3 and 4. The availability of the visible and near-infrared absorption spectrum of the C_{60}^- anions⁷ is another reason that prompted us to study these compounds.

Recently, we reported the vibrational frequencies of C_{60} together with the magnitude of the Jahn–Teller distortion in its monoanion.⁸ After the publication of some of the C_{60} and C_{70} vibrational frequencies,^{9,10} we calculated, with an upgraded QCFF/PI^{11,12}

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