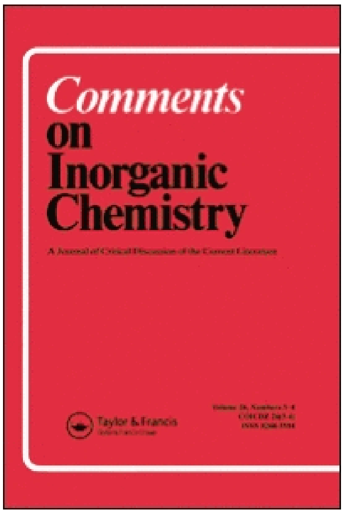

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The Role of Pauli Repulsion in Multiple Bonding: Structural Consequences and Energetic Implications

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The Role of Pauli Repulsion in Multiple Bonding: Structural Consequences and Energetic Implications

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The effect of Pauli repulsion in chemical bonding is discussed. Two types of effects are present, namely an interatomic as well as an intra-atomic Pauli repulsion. Those effects are responsible for the peculiarities encountered in chemical bonding involving heavier elements. Examples will be drawn from the analysis of multiple bonding.

Key Words: *Multiple bonding, Pauli repulsion, ethylene analogues, second-order Jahn–Teller distortion, isolobal analogy, Fischer carbenes.*

INTRODUCTION

Many concepts used for a qualitative description of chemical bonding that originated in the early days of theoretical chemistry have strictly been justified only for the first row elements. Contrary to common belief, many of these ideas cannot be generalized to the heavier elements. As for the concept of multiple bonding, experimental evi-

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dence underlining this fact was obtained early in this century. First attempts to synthesize compounds containing double bonded silicon proved unsuccessful.[1] In general, all experimental failures lead to the formulation of an empirical rule,[2] stating that elements having a principal quantum number greater than 2 do not form π_{pp} bonds amongst themselves or with other elements. It was only in the early eighties with the structural characterization of compounds containing Si = Si links[3] that this so-called "classical double bond rule" was overturned. However, many of the heavier analogues of ethylene possess trans-bent structures rather than a planar coordination around the group XIV atom,[4,5] indicating that the bonding is significantly different from that in the C = C case. The question was then posed whether these species could really be addressed as double bonded.[6]

Kutzelnigg[7] provided an explanation for the different bonding situation in heavier main group elements. He pointed out that the essential difference between first and higher rows is that the cores in the former contain only s-atomic orbitals, whereas the cores of the latter do at least include s- and p-atomic orbitals. One of the consequences is that for the first row atoms the s- and p-valence atomic orbitals are roughly located in the same region of space, whereas for the heavier atoms the p-atomic orbitals are much more expanded in space. This is a consequence of the Pauli exclusion principle in the sense that the valence orbitals must be orthogonal to the core. Further, the repulsive interaction between occupied orbitals of the two bond forming atoms will become of major importance for heavier elements. We call this effect interatomic Pauli repulsion, compared to the intra-atomic Pauli repulsion mentioned above.

In the following, we will discuss these ideas in connection with the heavier ethylene analogues, and we will expand our analysis to isolobal structures including transition metal fragments. We shall begin with a brief outline of our energy decomposition scheme.[8,9]

BOND ANALYSIS

We analyze the bonding energy in $R_nX = YR_m$ systems by the interaction of two fragments, XR_n and YR_m, which both possess the local equilibrium geometry of the final molecule and which both have an electronic structure suitable for double bonding. We call the energy associated with this process the bond snapping energy BE_{snap}. It can be decomposed into two main components, namely the steric repulsion term ΔE^0 and as the electronic interaction term ΔE_{int}:

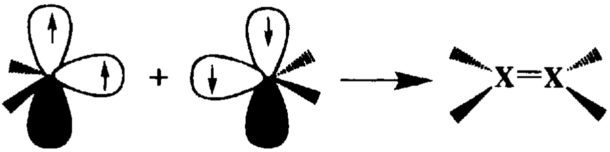
$$BE_{snap} = -[\Delta E^0 + \Delta E_{int}]. \tag{1}$$

ΔE^0 is in most cases dominated by the contribution of the interatomic Pauli repulsion, which is directly related to the two-orbital three or four electron interactions between occupied orbitals on both fragments. Whereas ΔE^0 is mostly destabilizing in nature, the term ΔE_{int} introduces the attractive orbital interactions between occupied and virtual orbitals on the two fragments.

The bond energy BE finally is obtained when the bond snapping energy is corrected by the preparation energy ΔE_{prep}:

$$BE = BE_{snap} - \Delta E_{prep}. \tag{2}$$

The preparation energy ΔE_{prep} represents the energy which is required to make the fragment ready for the formation of the bond. This step involves deformation of the ligand framework to the geometry in the final molecule and if required, the promotion energy from the electronic ground state to the electronic valence configuration.



SCHEME 1

To elucidate the role of the Pauli repulsion in chemical bonding, we analyze the bond snapping energy for ethylene, C_2H_4, and for planar disilene, Si_2H_4. Here, we consider the singlet coupling of two triplet fragments, Scheme 1, forming covalent σ as well as π bonds. Figure 1 shows BE_{snap} and its contributors ΔE^0 and ΔE_{int} as a function of X–X separation. For ethylene (Fig. 1a), we find that for C–C distances between 250 pm and 175 pm the bond snapping energy resembles the electronic interaction energy. The influence of the

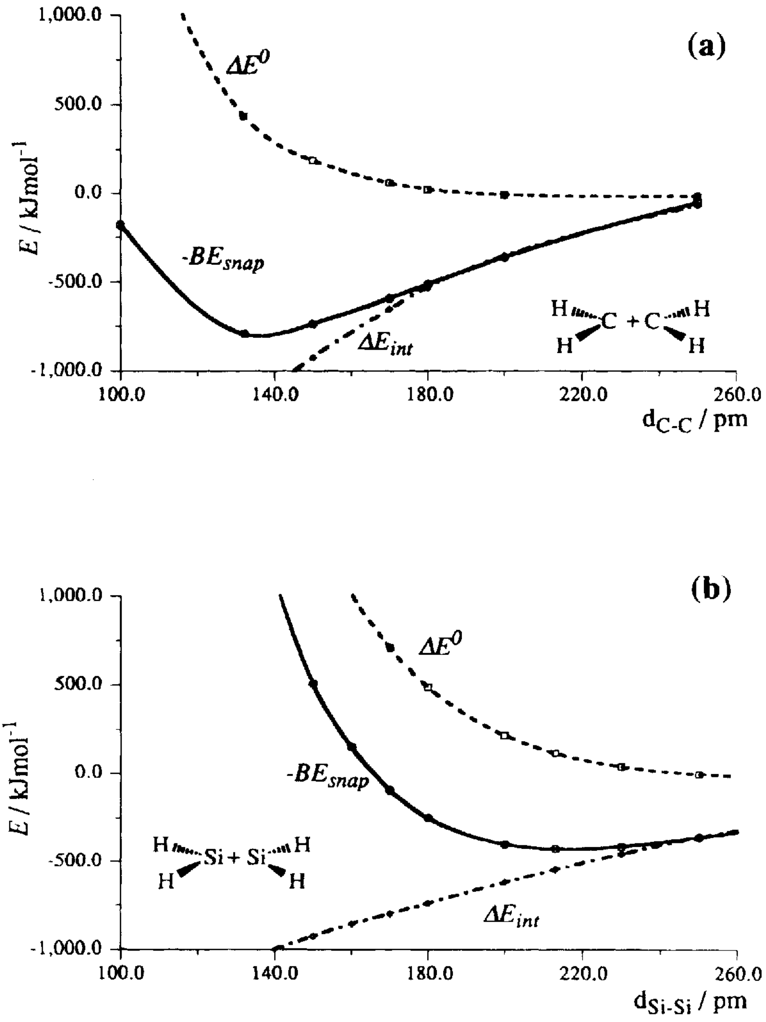


FIGURE 1 Orbital interaction energy (ΔE_{int}, dash-dotted lines), steric repulsion (ΔE^0, Dashed lines) and bond snapping energy ($-BE_{\text{snap}}$, solid lines) for $H_2X = XH_2$ systems as a function of X = X separation. (a) Ethylene. (b) Disilene.

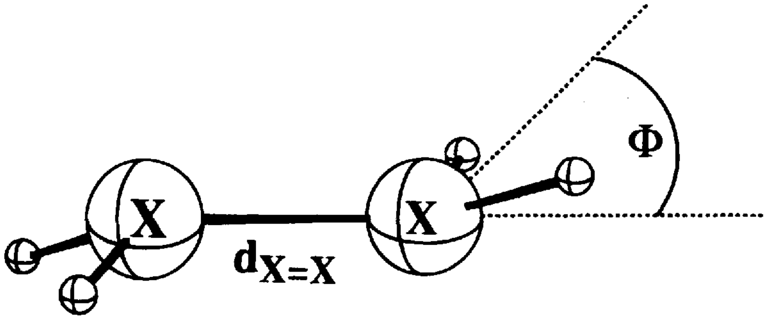


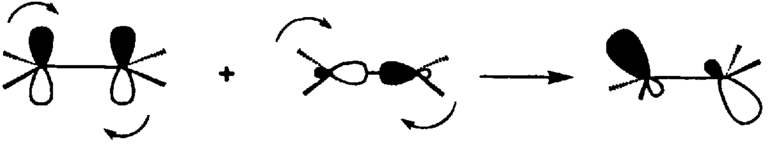
FIGURE 2 Trans-bent geometry of heavier ethylene homologues. Important structural parameters are the X–X bond length $d_{X=X}$ as well as the fold angle Φ.

steric repulsion term important for C–C separations r_{C-C} smaller than 150 pm and dominates for $r_{C-C} < 120$ pm. At the equilibrium bond distance of ethylene, we find a well-defined minimum on the energy surface with respect to the C–C bond distance. A different situation is observed for disilene (Fig. 1b). Due to the larger extent of the $3p_{Si}$ -orbitals compared to the $2p_C$ -orbitals, we already find a significant bonding interaction for a Si–Si distance of 250 pm. However, the bond snapping energy ΔE_{snap}, here is mainly influenced by steric interaction, which in turn is now determined by the two-orbital three-electron repulsive interaction between a 3p-valence orbital of one fragment with a 2p-core orbital of the other fragment. Under further contraction of the Si–Si bond, the stabilizing orbital interaction energy can no longer efficiently overcome the steric repulsion as in the case for ethylene. The Pauli repulsion becomes dominant for atom-atom distances smaller than about 190 pm. This now has two major consequences. The first result is the well-known fact that X–X bonds for heavier group XIV elements are significantly longer than typical C–C bonds. Secondly, the potential energy surface around the equilibrium Si–Si distance becomes very shallow, and the energetic difference between the double bonded equilibrium structure and a similar structure possessing a typical X–X single bond length is far smaller for disilene and other heavier ethylene analogues than it is for ethylene itself. For the heavier elements, the idea of a typical X–X double bond length has to be abandoned. For experimentally known Si = Si bond lengths we still find only relatively small variations between 214 and 216 pm,[4] whereas for the Ge = Ge case this range expands to 220 to 235 pm.[5] The X = X bond lengths in X_2R_4 systems becomes very sensitive to the nature of the ligands R.

To conclude this section, we briefly comment on orbital overlap and the bonding involving heavier elements. The longer bond distances as well as the weaker bond energies in compounds containing heavier elements are often explained by the nature of the *np* -orbitals involved in bonding. One commonly argues that the diffuse nature of the higher *p* orbitals is responsible for weaker bonds and longer bond distances, so as to maximize bonding orbital overlap. Whereas overlap arguments are very powerful in clarifying angular trends and thus in qualitatively predicting structures of molecules,[10] they are not suitable to explain trends in interatomic distances. Figure 1 indicates that the orbital interaction, which is directly related to the orbital overlap, does not alone determine the equilibrium geometry for the Si = Si bond. It is the interplay between ΔE^0 and ΔE_{int} which is important for a description of the bond. Whereas for ethylene the bond energy is mainly determined by the orbital interaction, we find for disilene and its heavier analogues the steric repulsion term to be dominant.

STRUCTURAL ALTERNATIVES: SECOND ORDER JAHN–TELLER DISTORTION

We now investigate the electronic structure of heavier X_2H_4 systems compared to ethylene. The most significant change is the energetic separation of the bonding π orbital and the antibonding σ^* orbital. Whereas for C_2H_4 these two orbitals differ in energy by 7.3 eV, this energy gap decreases for the Si, Ge, Sn and Pb analogues to 4.5 eV, 4.0 eV, 3.4 eV and 1.2 eV, respectively.[11] This now in turn has further structural consequences. If the energy gap is small enough, there might exist a geometric distortion which allows these orbitals to intermix,[12] leading to an overall stabilization of the X = X bond. It turns out that for X_2H_4 systems such a second order Jahn-Teller distortion is possible, leading from planar structures of D_{2h} symmetry to trans bent C_{2h} geometries, Fig. two, with pyramidal coordination around the X atom. Scheme 2 illustrates the orbital mixing under trans-bent distortion.[13]



SCHEME 2

Table I contains the important geometric parameters for planar and trans-bent X_2H_4 structures, as well as the barrier to planarity. All results presented for ethylene and its heavier analogues were obtained in density functional calculations.[11] We note that for all the systems, with the exception of ethylene, the trans-bent structure is favored over the planar geometry. Whereas for disilene the barrier to planarity is rather small, it increases when going down the period and shows for the diplumbene a significant value of 97 kJ/mol. The fold angle exhibits the same trend, and is steadily increasing when going to heavier elements. A frequency analysis reveals that all planar structures except that of ethylene represent transition states, with an imaginary frequency corresponding to the trans-bending vibrational mode. The other systems are true minima on the energy surface, possessing a spectrum of entirely real frequencies.

Of further interest is the fact that when going from the planar D_{2h} to the distorted C_{2h} structures, the X = X bond length increases.

TABLE I

Structural parameters and barriers to planarity for $H_2X = XH_2$ systems.

	Symmetry	$d_{X=X}$ (pm)	Φ (deg)	ΔE_p (kJ/mol)
C_2H_4	D_{2h}	132.3	0.0	
Si_2H_4	D_{2h}	212.7	0.0	
Si_2H_4	C_{2h}	215.0	36.1	7
Ge_2H_4	D_{2h}	220.5	0.0	
Ge_2H_4	C_{2h}	224.5	47.3	23
Sn_2H_4	D_{2h}	250.1	0.0	
Sn_2H_4	C_{2h}	256.9	51.0	31
Pb_2H_4	D_{2h}	269.3	0.0	
Pb_2H_4	C_{2h}	281.9	53.6	97

Since under trans-bending the substituents on one center now undergo larger steric interactions with the other center, the X = X bond becomes longer, leading to a reduction of this steric repulsion. Thus, trans-bending not only enhances ΔE_{int}, but also ΔE^0, and is therefore coupled with the X = X bond stretch.

We identified the small energy gap between the bonding π orbital and the antibonding σ^* orbital as the driving force of the second order Jahn–Teller distortion. This small energy gap is caused by two effects. First, the significantly longer X = X separation for the heavier systems compared to ethylene influences this orbital separation. As discussed above, this is an effect of the interatomic Pauli repulsion. Secondly, there are differences in the electronic structure of the bond forming triplet fragments. For methylene, the two singly occupied orbitals, which form the σ and π bonds in ethylene, are separated by 0.8 eV, whereas for silylene this value more than doubles and amounts to 1.7 eV. In fact, only CH_2 has a triplet ground state, whereas all heavier XH_2 fragments have a singlet ground state and need to be electronically promoted for bonding interaction. This fact has been explained by Kutzelnigg[7] in terms of an intra-atomic Pauli repulsion.

Also, Malrieu and Trinquier[14] utilized the value of the singlet–triplet splitting in evaluating conditions for trans-bending to occur.

BOND ENERGIES: σ AND π CONTRIBUTIONS

We now discuss the X = X double bond in more detail. Our bond analysis is presented in Table II. As mentioned above, we form the $H_2X = XH_2$ systems from two appropriately prepared $^3B_1$ carbenoids. Thus, for the heavier systems the preparation energy ΔE_{prep} will become of major importance for an assessment of the total bond energy. As shown in Table II, C_2H_4 requires only a small preparation energy, due to the rearrangement of the fragment geometry. For all other systems, ΔE_{prep} contributes significantly to the total bond energy, and becomes even more important than the steric repulsion term ΔE^0. The necessity for an electronic preparation explains the fact that in terms of bond dissociation the X = X double bond of the heavier systems appears to be weaker than the corresponding single bonds. As one might expect, the total bond energy and the bond

TABLE II

Bond analysis for $H_2X = XH_2$ systems. Energies are in kJ/mol.

		ΔE_{prep}	ΔE^0	ΔE_{int}	BE_{snap}	BE
C_2H_4	D_{2h}	13	437	−1230	794	781
Si_2H_4	C_{2h}	156	110	−544	434	278
Ge_2H_4	C_{2h}	200	123	−523	400	200
Sn_2H_4	C_{2h}	206	82	−424	342	136
Pb_2H_4	C_{2h}	303	73	−431	358	55

snapping energy for ethylene are much higher than those for the heavier systems. Further, the same can be observed for the absolute values of ΔE_{int}, and ΔE^0. However, if we look at the ratios of orbital interaction and steric repulsion, we find that for the heavier systems the ratio $\Delta E_{\text{int}}/\Delta E^0$ increases, indicating that minimization of ΔE^0 becomes more important than maximization of ΔE_{int}.

In order to obtain a value for the σ- and π-bond strengths, we further analyze the electronic interaction energy according to contributions from different symmetries. When analyzing the bonding in transbent systems, caution should be exercised using the terms σ and π. The characteristic feature of a π bond or orbital is that it has one and only one nodal plane or nodal surface which contains the bond axis.[15] In case of the trans-bent systems, however, this strict classification does not hold for the HOMO. Due to the mixing of the σ^* and π orbitals (Scheme 2), the resulting orbital contains contributions from atomic s-type basis functions, which change its nodal characteristics in a way that the X = X bond axis of the molecule no longer lies in the nodal plane of the orbital. However, this orbital is still strongly dominated by p-type basis functions, and transforms into the π orbital of the planar system. Therefore, we classify this contribution as π^σ bond, where our notation indicates a π-based orbital with σ contributions mixed in.

For planar systems, we can analyze the reaction $2XH_2 \rightarrow X_2H_4$ in C_{2v} symmetry. We can interpret the a_1 contribution of ΔE_{int} as the electronic interaction due to σ-bonding, $D_{\sigma,\text{int}}$, and the b_1 contribution as the electronic π-bond energy, $D_{\pi,\text{int}}$. Contributions from other irreducible representations are of minor importance and are not considered in our qualitative analysis. For the trans-bent systems, by taking $D_{\sigma,\mathrm{int}}$ and $D_{\pi,\mathrm{int}}$ from the elongated planar structures and using the change of electronic interaction energy under bending distortion, we can estimate values for $D_{\pi}{}^{\sigma}{}_{,\mathrm{int}}$ and $D_{\sigma}{}^{\pi}{}_{,\mathrm{int}}$, respectively. We call these bond strengths that are derived from the electronic interaction energy only, the intrinsic π or π^{σ} and the intrinsic σ or σ^{π} bond strength. The results of this analysis are gathered into Table III.

For the heavier ethylene homologues, both the σ^{π} and π^{σ}, bonds are weaker than the corresponding σ and π bonds in ethylene itself. This is, as we already have pointed out, a consequence of the enhanced Pauli repulsion. The weak double bond is certainly not due to a reduced π^{σ} interaction only. We are dealing with real double bonds, in which both σ^{π} and π^{σ} interactions are of importance. When going to heavier systems, the $\sigma^{\pi}/\pi^{\sigma}$ ratio decreases significantly compared to the σ/π ration in ethylene, indicating how the orbital mixing under trans-bending strengthens the π contribution. One could say that, with respect to the intrinsic bond strength values, the trans-bent systems possess even more double bond character than ethylene itself. However, the overall bond strength in these systems is mainly governed by the influence of Pauli repulsion and the preparation energy, which is the major cause for the weak link between the heavier atoms.

ISOLOBAL ANALOGIES

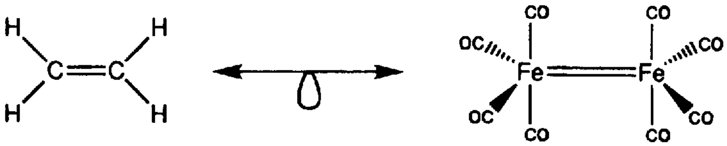
Having established the importance of Pauli repulsion in multiple bonding, we now expand our concepts from main group derivatives to transition metal fragments. We begin with a discussion of the

TABLE III

Intrinsic σ- and π-bond strengths in $H_2X = XH_2$ systems.

		D_{σ},$D_{\sigma}{}^{\pi}$ (kJ/mol)	D_{π},$D_{\pi}{}^{\sigma}$ (kJ/mol)	σ/π
C_2H_4	D_{2h}	875	315	2.78
Si_2H_4	C_{2h}	373	158	2.36
Ge_2H_4	C_{2h}	355	158	2.09
Sn_2H_4	C_{2h}	281	134	2.10
Pb_2H_4	C_{2h}	250	177	1.41

structure of $Fe_2(CO)_8$. This compound, which can be prepared by photolysis of $Fe_2(CO)_9$ in an Ar matrix, has generated some interest, especially with respect to the nature of the metal–metal bond. IR studies[16,17] suggest that the major product in the photolysis is a dibridged structure, similar to that of $Co_2(CO)_8$. However, experimental evidence was found for a second isomer, which seemed to correspond to an unbridged $Fe_2(CO)_8$ arrangement. A double bonded D_{2h} structure was proposed, according to Hoffmann's isolobal analogy.[18]



A density functional calculation on the Hoffmann structure revealed that the bond snapping ênergy for the Fe = Fe bond amounts to 206 kJ/mol. The same approach was taken as for the ethylene systems, namely analyzing the bond by coupling of two triplet C_{2v} fragments. This seems reasonable since $Fe(CO)_4$ is known to have a triplet ground state[19] and C_{2v} symmetry.[20] However, a further analysis of the electronic interaction energy showed that the intrinsic π bond strength in this system only is 46 kJ/mol, compared to 245 kJ/mol for the σ contribution. The π and σ^* orbitals are separated by only 3.2 eV, an even smaller gap than in the case for distannene. This all suggests that for this system a second order Jahn–Teller distortion might be favorable. Thus we investigated trans-bent alternatives of $Fe_2(CO)_8$, as shown in Fig. 3. If we allow for trans-bending, but freeze the angle $\langle$ Fe–C–O for the CO ligands which move towards a bridging position, we find a stabilization in energy of 35 kJ/mol. Further, 46 kJ/mol are gained when the angular restriction is lifted. A trans-bent C_{2h} arrangement seems indeed to be favored over the Hoffmann structure. Although two of the former equatorial CO ligands move towards a bridging position, the two Fe–C bond lengths are quite different. We find Fe–C separations of 179.3 pm and 246.6 pm, respectively. Thus, this structure has to be considered as unbridged rather than dibridged. Also of interest is the fact that the Fe = Fe bond shortens under trans-bending, in contrast to the $H_2X = XH_2$ systems discussed above. This indicates that there is some

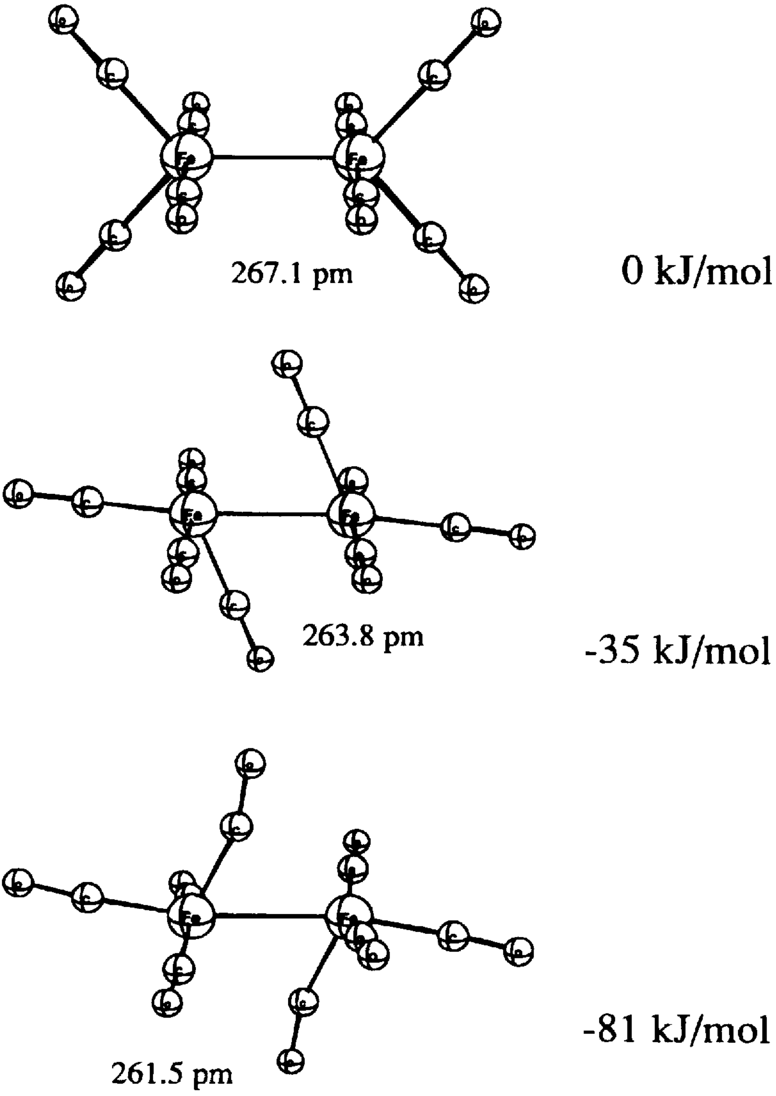
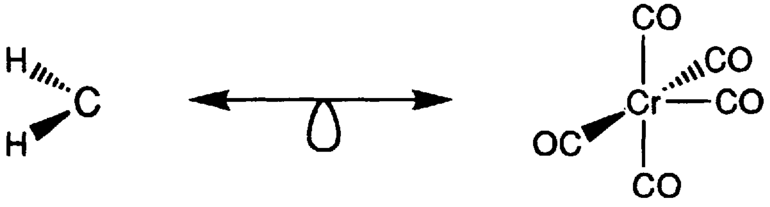


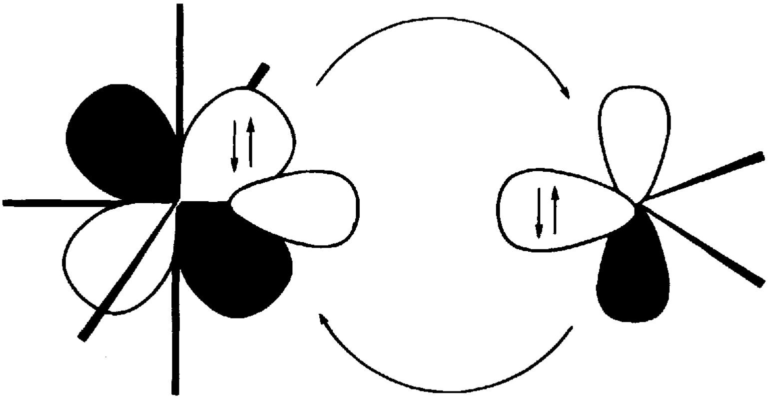
FIGURE 3 Different geometries for the unbridged $Fe_2(CO)_8$. A trans-bent distortion of the D_{2h} Hoffmann structure stabilizes the molecule.

stabilizing interaction between the bending CO ligands and the opposite Fe center.

Another common isolobal analogy[21] suggests that M(CO)$_5$ fragments involving group VI metals should compare to methylene:



Since (CO)$_5$Cr has a singlet ground state and a higher preparation energy than the methylene unit, a bond description involving σ donation to the metal and π back donation to the carbenoid fragment is most appropriate, Scheme 3.[22] Thus, we have a polar double bond with the σ contribution mainly localized at the ligand and the π contribution mainly localized at the metal center. This is also the main reason for the fact that now the appropriate σ^* orbital is too high in energy to allow for a stabilizing trans-bent distortion.



SCHEME 3

A density functional calculation was performed for a variety of Fischer carbenes and heavier derivatives.[23,24] To analyze the bonding in these systems, we introduce the concept of a reduced intrinsic σ bond strength $D'_{\sigma,\text{int}}$ by combining $D_{\sigma,\text{int}}$ and ΔE^0:

$$D'_{\sigma,\mathrm{int}} = D_{\alpha,\mathrm{int}} - \Delta E^0. \tag{3}$$

This definition can be justified by noting that the σ donation from the doubly occupied carbenoid orbital not only provides the major contribution to the orbital interaction energy, but also to the interatomic Pauli repulsion. The bond snapping energy now breaks down into σ and π contribution as

$$BE_{\mathrm{snap}} = D'_{\sigma,\mathrm{int}} + D_{\pi,\mathrm{int}}. \tag{4}$$

Results for Fischer carbenes and silylenes are presented in Fig. 4. It is noteworthy that all carbene based ligands, with the exception of CMe$_2$, show a higher π than a σ′ contribution, whereas all silylene based systems have a weak π bond around 70 kJ/mol, and have to

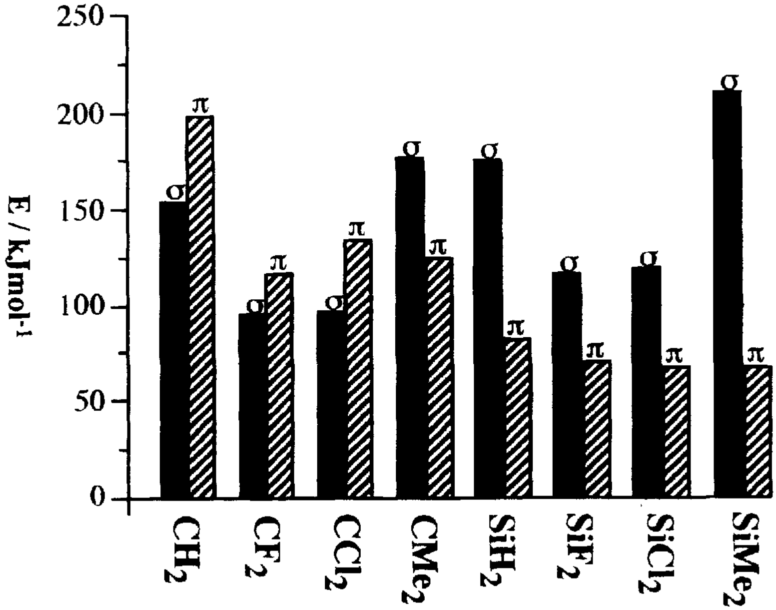


FIGURE 4 Reduced σ bond strengths and π bond strengths for various (CO)$_5$Cr = ER$_2$ systems.

be considered mainly as σ' donors. The main reason here is that for silicon based systems the orbital available for π back donation lies at higher energy than for the carbon based system. Consequently, the π orbitals of carbene systems are much more suitable for a back donation than that of heavier group XIV homologues.[24] The weak π bond affects the structures and the chemistry of silylene complexes. Most known Fischer type silylene compounds are obtained as donor stabilized species, with a Lewis base coordinated to the Si center.[25] Density functional calculations have shown that base coordination is energetically favored over π bonding.[23]

The trend continues that on going from metal carbenes and silylenes to the germanium and tin derivatives the bond energies are further decreasing. The intrinsic π bond energies in $(CO)_5Cr = EH_2$ systems as extracted from the orbital interaction energy amount to 202 kJ/mol, 82 kJ/mol, 72 kJ/mol and 51 kJ/mol for E = C, Si, Ge and Sn, respectively.[24] Also, when going down a transition metal triad, one observes, provided that relativistic effects are excluded, a steady decrease in the metal–ligand bonding energy. This has been shown using density functional theory for transition metal carbenes of group VI metals,[26] as well as for various transition metal carbonyls.[27,28] We consider the case of the group VI hexacarbonyls in more detail. The reason here for a weakening of the metal–ligand bond now is the core expansion at the metal centers. When going from the first row of transition metals to the higher rows, the energetic match between the valence metal d-orbitals and the π^* orbital at CO becomes less favorable, and the π bonding energy decreases.[28] The $D_{\sigma,\mathrm{int}}$ and $D_{\pi,\mathrm{int}}$ contributions could be enhanced considerably for any of the hexacarbonyls, but not without increasing ΔE^0 at the same time. What is of importance then for the relative strength of the M–CO bonds in $M(CO)_6$ again is the dependency[28] of $D_{\sigma,\mathrm{int}}$ and $D_{\pi,\mathrm{int}}$ a certain value of ΔE^0.

For bonds between two similar metal fragments, the core expansion at the metal center now stabilizes the metal–metal bond.[29] The 3d orbitals of the first row transition metals have about the same radial extent as the corresponding p and s core orbitals. Therefore, the bonding interaction between the d orbitals is accompanied by large steric repulsion due to the s and p core orbitals. When extending the core, the d orbitals become more diffuse so that good bonding interaction can be achieved for larger metal–metal separations. This effectively stabilizes the bond both with respect to ΔE^0 and ΔE_{int}. The dimetal octacarbonyls of group VIII metals may serve as an example. For the Hoffmann structure of $Fe_2(CO)_8$, we have found a bond snapping energy of 206 kJ/mol, with $D'_{\sigma,int} = 160$ kJ/mol and $D_{\pi,int} = 46$ kJ/mol. On going to $Os_2(CO)_8$, the bond is stabilized by roughly 100 kJ/mol, $BE_{snap} = 301$ kJ/mol. The intrinsic σ and π contribution now amount to $D'_{\sigma,int} = 193$ kJ/mol and $D'_{gp,int} = 108$ kJ/mol. The increase in the reduced σ bond strength is mainly caused by the reduction of ΔE^0.

CONCLUSION

To summarize our discussion, we would like to make a few final remarks. The peculiarities for heavier elements are mainly caused by steric repulsion effects. First, there is the interatomic Pauli repulsion between two bond forming atoms. For heavier elements, minimization of steric repulsion becomes dominant over maximization of orbital interaction. Second, the intra-atomic Pauli repulsion influences the electronic structure of the interacting fragments, leading to particular weak π contributions. The importance of Pauli repulsion in chemical bonding is not restricted to the case of multiple bonding, but constitutes a major theme in the bonding of heavier elements. Bonding as discussed for the first row elements should rather be looked at as the exception, rather than the rule.[7]

Acknowledgments

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