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parentheses. In almost all cases, the agreement is excellent, although much of the agreement is the result of the method of choosing transition states. Nonetheless, several of the results were obtained without adjustment of parameters, and the overall agreement inspires our confidence in the geometries, bonding parameters, and the reaction coordinate.

The results support the presumption of an E1cB-like E2 mechanism for the Hofmann elimination from (2-phenylethyl)-trimethylammonium ions; they also support Thornton's predictions of substituent effects on transition-state structure. The leaving group and α-D_2 kinetic isotope effects lend strong support to the importance of differential solvation of the reactant and transition state and of the necessity of considering the role of solvent in interpreting leaving group KIE.

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Ring Strain in Cyclopropane, Cyclopropene, Silacyclopropane, and Silacyclopropene

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Abstract: The strain energy in four three-membered rings is calculated by using the appropriate isodesmic reactions. Calculations with and without d functions on the heavy atoms indicate that while these polarization functions tend to reduce ring strain, the addition of d orbitals has little effect on the predicted *trends*. While introduciton of unsaturation drastically increases the strain in the carbon system (cyclopropane → cyclopropene), this is not the case for silicon (silacyclopropane → silacyclopropene). As a result cyclopropane and cyclopropene are predicted to be the least and most strained rings, respectively.

Ring strain is a concept which is frequently used to rationalize instability and reactivity of small cyclic compounds. Recently, a novel quantitative measure of ring strain has been proposed.[1] This method makes use of *isodesmic reactions* in which the number of bonds of each type is formally conserved on going from reactants to products. The use of isodesmic reactions is particularly useful in quantum chemistry since the effect of correlation error is expected to be minimal in such reactions. As a result, one can use Hartree–Fock-level energy differences with some degree of confidence.

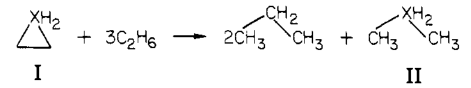
In this paper the ring strain in cyclopropane, cyclopropene, silacyclopropane, and silacyclopropene is examined by using ab initio molecular orbital calculations. Cyclopropane and cyclopropene have been studied before[1] and are included here for internal consistency. While semiempirical[2–4] and ab initio[5] calculations have been carried out on the silicon rings, no attempt has been made to evaluate the strain in these rings or, more importantly, their ring strain relative to the hydrocarbon analogues. In view of the apparent stability of the silicon-containing rings,[6] such a comparison is clearly of interest.

The methodology used in the calculations is summarized in the Methodology section, while the results of the ring strain calculations are presented and discussed in the Results and Discussion section. To aid the latter discussion approximate quadratic force fields have been generated for the four rings, and these are also presented in the Results and Discussion section.

Methodology

Two separate basis sets have been used in these calculations. All geometry optimizations were performed by using the 3-21G basis set developed recently.[7,8] Because split valence basis sets are known[9] to overestimate ring strain, the geometry optimizations were followed by single point 6-31G*[9,10] calculations at the final geometries. Addition of polarization functions appears to give a proper accounting of strain.[9] The geometry optimizations and force field calculations were carried out with the use of the HONDO system of programs.[11]

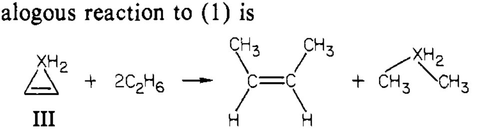
The isodesmic reaction used to measure strain in the saturated rings is



(1)

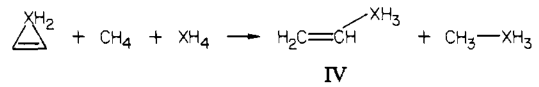
where X may be C or Si. In eq 1 the strained XH_2 and CH_2 groups on the left are replaced by their unstrained counterparts on the right. The addition of ethane provides the appropriate number of methyl groups.

The appropriate reaction for the unsaturated rings is less clear. The analogous reaction to (1) is



(2)

in which a strained XH_2 and substituted ethylene are replaced by their unsubstituted analogues. However,[1] the use of eq 2 is somewhat ambiguous since it measures, in addition to ring strain, the stabilization or destabilization effect due to the proximity of the XH_2 and unsaturated moieties. An isodesmic reaction which corrects this problem is



(3)

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(1) J. D. Dill, A. Greenberg, and J. F. Liebman, *J. Am. Chem. Soc.*, **101**, 6814 (1979).

(2) P. R. Jones and D. D. White, *J. Organomet. Chem.*, **154**, C33 (1978).

(3) P. R. Jones and D. D. White, *J. Organomet. Chem.*, **181**, 399 (1979).

(4) M. C. Bohm and R. Gleiter, *J. Chem. Soc., Perkin Trans. 2*, 443 (1979).

(5) J.-C. Barthelat, G. Trinquier, and G. Bertrand, *J. Am. Chem. Soc.*, **101**, 3785 (1979).

(6) R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, **98**, 3715 (1976).

(7) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980).

(8) M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *J. Am. Chem. Soc.*, submitted.

(9) P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **16**, 217 (1972).

(10) M. S. Gordon, *Chem. Phys. Lett.*, submitted.

(11) H. F. King and M. Dupuis, *J. Comput. Phys.*, **21**, 144 (1976); M. Dupuis and H. F. King, *Inter. J. Quantum Chem.*, **11**, 613 (1977); *J. Chem. Phys.*, **68**, 3998 (1978).

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Table I. Calculated Geometries for X = C[a]

parameter	I[e]	II[f]	III[g]	IV[h]	*cis*-2-butene[i]
R(XH)	1.073 (1.083)	1.085 (1.096)	1.074 (1.087)	1.082[b] (1.085)	1.079[b] (1.095)
				1.085[c] (1.098)	1.085[c] (1.095)
R(XC)	1.516 (1.512)	1.540 (1.526)	1.523 (1.515)	1.509 (1.506)	1.508 (1.497)
R(CC)	1.516 (1.512)		1.282 (1.300)	1.316 (1.340)	1.318 (1.350)
R(CH$_1$)		1.084 (1.089)		1.074 (1.081)	1.076 (1.090)
R(CH$_2$)	1.073 (1.083)	1.084 (1.094)	1.060 (1.070)	1.075 (1.091)	
R(CH$_3$)				1.076 (1.090)	
α(HXH)	114.61 (114.0)	107.50 (106.1)	114.84 (114.7)	108.44[d] (109.0)	
α(CXC)	60.0 (60.0)	111.24 (112.4)	49.78		
α(H$_1$CX)		111.33 (111.8)	145.44 (149.9)		
α(H$_2$CX)	117.89	110.29 (110.6)			
α(H$_1$CH$_2$)		108.08 (108.1)		116.61 (118.0)	
α(H$_2$CC)	117.89			121.75 (120.5)	
α(H$_3$CC)				119.52 (119.0)	118.01 (117.3)
α(CCX)				124.88 (124.3)	127.69 (126.7)
α(H$_A$XC)				111.49 (111.2)	112.73
α(H$_B$XC)				110.42	111.09

[a] Bond lengths in Å, angles in deg. Numbering system is shown in Figure 1. Experimental values in parentheses. [b] In-plane hydrogen. [c] Out-of-plane hydrogen. [d] H(in-plane)–X–H(out-of-plane). [e] R. J. Butcher and W. J. Jones, *J. Mol. Spectrosc.*, 47, 64 (1973). [f] D. R. Lide, *J. Chem. Phys.*, 33, 1514 (1960). [g] P. H. Kasai, R. J. Myers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, 30, 512 (1959). [h] I. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, 17, 207 (1973). [i] S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, 34, 231 (1970). Numbering system same as for propene.

Table II. Calculated Geometries for X = Si[a]

parameter	I	II[e]	III	IV[f]
R(XH)	1.475	1.494 (1.483)	1.480	1.492[b] (1.475)
				1.491[c]
R(XC)	1.892	1.916 (1.867)	1.869	1.895 (1.853)
R(CC)	1.563		1.324	1.320 (1.347)
R(CH$_1$)		1.086 (1.095)		1.074 (1.097)
R(CH$_2$)	1.075	1.086 (1.095)	1.067	1.073 (1.097)
R(CH$_3$)				1.077 (1.094)
α(HXH)	115.43	107.25 (107.8)	111.62	109.14[d] (108.7)
α(CXC)	48.79	112.45 (111.0)	41.49	
α(H$_1$CX)		110.39	154.30	
α(H$_2$CX)	118.93			
α(H$_1$CH$_2$)		108.16 (108.0)		115.46 (119.1)
α(H$_2$CC)	116.08			122.36 (120.6)
α(H$_3$CC)				118.52 (118.0)
α(CCX)				124.72 (122.9)
α(H$_A$XC)				110.11
α(H$_B$XC)				110.10

[a] Bond lengths in Å, angles in deg. Numbering system is shown in Figure 1; experimental values in parentheses. [b] In-plane hydrogen. [c] Out-of-plane hydrogen. [d] H(in-plane)–X–H(out-of-plane). [e] L. Pierce, *J. Chem. Phys.*, 34, 498 (1961). [f] J. M. O'Reilly and L. Pierce, *J. Chem. Phys.*, 34, 1176 (1961).

Table III. Total Molecular Energies (hartree)

molecule	3-21G//3-21G	6-31G*//3-21G[c]
hydrogen	−1.12295[a]	−1.12295
methane	−39.97688[a]	−40.19517
silane	−289.68698[b]	−291.22455
ethane	−78.79395[a]	−79.22862
methylsilane	−328.52612[b]	−330.27116[d]
cyclopropane	−116.40118	−117.05829
cyclopropene	−115.16200	−115.82198
silacyclopropane	−366.13428	−368.08617
silacyclopropene	−364.92998	−366.88998
propane	−117.61328	−118.26332
propene	−116.42400	−117.07140
dimethylsilane	−367.36568	−369.31756
vinylsilane	−366.15362	−368.11112
cis-2-butene	−155.24392	−156.10768

[a] From ref 7. [b] From ref 8. [c] This notation indicates a 6-31G* calculation at a 3-21G geometry. [d] 6-31G*//4-31G.

Table IV. Strain Energies (kcal/mol)

	ΔE(3-21G//3-21G)		ΔE(6-31G*//3-21G)	
reaction	X = C	X = Si	X = C	X = Si
1	−35.6	−47.8	−28.7	−45.3
2	−67.3	−57.6	−57.6	−49.0
3	−64.1	−53.9	−55.0	−45.5

However, in this case the groups are not strictly conserved. Both reactions 2 and 3 are conisdered below.

Results and Discussion

The optimized 3-21G geometries for the hydrocarbons and silanes are listed in Tables I and II, respectively. The geometries for ethane,[7] silacyclopropane,[10] and vinylsilane[10] have been reported previously. The latter two are repeated in Table II for the sake of comparison. The numbering system for all structures is shown in Figure 1.

The structures of all five hydrocarbons have been determined experimentally, and the agreement between experiment and theory is quite good. Particularly satisfying are the correct predictions of a decrease in CC bond length in cyclopropane relative to propane and the absence of delocalization shortening in the cyclopropene CC single bond relative to cyclopropane. The corresponding shortening in propene relative to propane is 0.02 Å. The shorter CC double bond length in cyclopropene relative to propene is also reproduced, as are all of the trends in bond angles.

The structures of the silicon-containing rings have not yet been determined experimentally. The calculated geometries for the unstrained silanes are in good agreement with experiment, although the Si–C bond lengths are predicted to be somewhat too long. The latter is apparently corrected by the addition of polarization functions.[5,12] The calculated structure of silacyclopropene is similar to that predicted by Barthelat et al.[5] Some interesting differences appear in the silane trends, relative to those discussed above. While the Si–C bond length in silacyclopropane is predicted to be shorter than that in dimethylsilane, in analogy with the corresponding hydrocarbons, this bond is found to shorten as much in the strained system (III) as in the unstrained system (IV) when adjacent unsaturation is introduced. This implies that some delocalization stabilization exists in silacyclopropene, and this should stabilize the silicon system relative to cyclopropene. Note also that in contrast with the corresponding hydrocarbons, the C═C double bond length is about the same in silacyclopropene and vinylsilane. This is further evidence of the delocalization effect mentioned above. However, no evidence is found for an unusually long C═C bond length in silacyclopropene, in contrast to earlier semiempirical results.[2]

The total energies for the molecules considered here are listed in Table III, while the ΔE's for the strain energy reactions 1–3 are given in Table IV. For comparison, note that experimentally

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(12) H. Oberhammer and J. E. Boggs, *J. Mol. Struct.*, 57, 175 (1979).

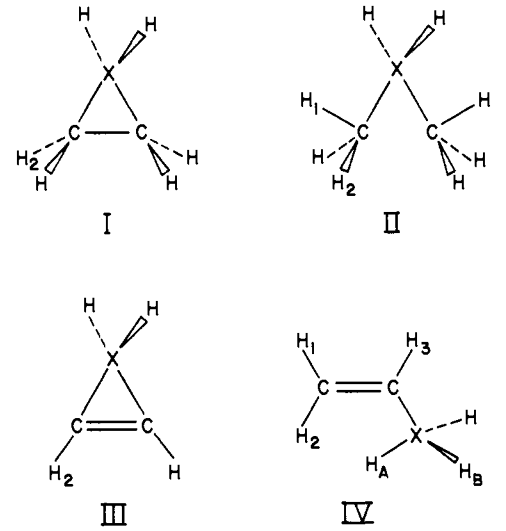


Figure 1. Numbering system for molecular structures.

Table V. Frequencies for Ring Motions

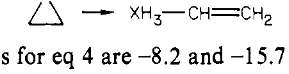
molecule	approximate description[a]	freq, cm^{-1} [b]
cyclopropane	ring deformation[c] (e")	903 (866)
	ring stretch (a_1')	1356 (1188)
silacyclopropane	ring deformation (a_1)	669
	antisym stretch (b_2)	729
	sym stretch (a_1)	1028
cyclopropene	ring deformation (a_1)	1197 (1105)
	antisym stretch (b_2)	807 (769)
	sym stretch (a_1)	1818 (1653)
silacyclopropene	ring deformation (a_1)	795
	antisym stretch (b_2)	732
	sym stretch (a_1)	1621

[a] Since these frequencies correspond to normal modes, there is considerable mixing of internal motions. Thus, only approximate descriptions can be given for each frequency. The irreducible representations are given in parentheses. [b] Experimental values given in parentheses for cyclopropane (see ref 16) and cyclopropene (see ref 17). [c] The ring deformation motion in cyclopropane (D_{3h}) is doubly degenerate and correlates with the ring deformation and antisymmetric stretching motions in C_{2v}.

the heat for reaction 1 with X = C is −27.4 kcal/mol.[1] As has been noted previously,[9] the addition of polarization functions lowers the predicted strain energies, although the effect appears to be somewhat smaller for silicon. Note, however, that the *relative* strain energies are unaffected by polarization functions. Thus, the qualitative results contained in Table IV need not rely on d orbital arguments for an explanation.

The 6-31G* strain energy in cyclopropane is found to be more than 10 kcal/mol smaller than that in its silicon analogue. This may be at least partially understood by comparing the structures reported in Tables I and II. Because of the longer Si–C bond length, the apex C–Si–C angle in silacyclopropane must close down considerably (relative to the 60° angle in cyclopropane) in order to reduce the base C–C bond length to a reasonable value. Even though the ring deformation motions have smaller frequencies in silacyclopropane (see the values listed in Table V), the reduction of the apex angle to less than 50° must introduce considerable strain into the system. Despite the small apex angle, the base C–C bond length is still nearly 0.05 Å longer in silacyclopropane than in cyclopropane. That this results in further destabilization of the system is reflected in a smaller ring-stretching frequency (Table V) in the silicon-containing ring.

A greater strain energy in silacyclopropane is also supported by the relative isomerization energies for the two rings, relative to their most stable acyclic analogues:[13]



(4)

The 6-31G* ΔE's for eq 4 are −8.2 and −15.7 kcal/mol for X = C and Si, respectively. The latter value is similar to that obtained by Barthelat and co-workers.[5]

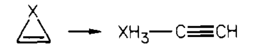
Table VI. Vibrational Frequencies in Saturated Rings

approximate description	freq, cm^{-1} [a]	
	X = C[b]	X = Si
CH_2 rock	840 (e", 739)	487 (a_2),[c] 822 (b_1)
XH_2 rock	935 (a_2", 854)	515 (b_1)
CH_2 wag	1211 (e", 1029)	1133 (a_1), 1193 (b_2)
XH_2 wag	906 (a_2', 1070)	676 (b_2)
XH_2 twist	1269 (a_1", 1126)	882 (a_2)[d]
CH_2 twist	1327 (e", 1188)	1019 (b_1), 1315 (a_2)
CH_2 scis	1627 (e', 1438)	1577 (b_2), 1592 (a_1)
XH_2 scis	2006 (a_1', 1479)	942 (a_1)
CH_2 sym str	3292 (e', 3025)	3284 (b_2), 3290 (a_1)
XH_2 sym str	2816 (a_1', 3038)	2345 (a_1)
CH_2 antisym str	3369 (e", 3082)	3359 (a_2), 3378 (b_1)
XH_2 antisym str	3394 (a_2", 3103)	2357 (b_1)

[a] Irreducible representations given in parentheses. [b] Experimental values given in parentheses, ref 16. [c] SiH_2 twist motion is strongly mixed into this mode. [d] CH_2 twist motion is strongly mixed into this mode.

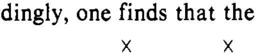
Based on qualitative considerations one would expect cyclopropene to be more strained than its saturated analogue. In analogy with the discussion of silacyclopropane, the difference in C—C and C═C bond lengths will lead to a decrease in the apex angle, an unusually long C═C, or both. Reference to Tables I and II indicates that the apex angle is similar to that in silacyclopropane, and this is likely to increase the strain. In addition, one expects greater strain in this system since the base carbons will prefer 120° angles, while those in cyclopropane prefer 109.5° angles for an unstrained system. These qualitative speculations are supported by the calculated strain energies. Reactions 2 and 3 predict essentially the same strain energies for cyclopropene—nearly 30 kcal/mol greater than that in cyclopropane.

Both reactions 2 and 3 predict silacyclopropene to be less strained than cyclopropene. The fact that these two reactions are in such close agreement is an indication of the lack of coupling between ring strain and unsaturation effects. Two other energy differences, based on 6-31G* energies, are in agreement with the relative strain energies for the unsaturated rings. The isomerization energy for the reaction[13]



(5)

for X = C has been predicted to be −25.4 kcal/mol by Hariharan and Pople,[9] in good agreement with the experimental value of −22.3 kcal/mol. The corresponding value for X = Si has been found in the present work to be −14.8 kcal/mol. This is a dramatic reversal relative to the results for reaction 4. One might also consider the hydrogenation energies by uisng the values listed in Table III. Accordingly, one finds that the ΔE for the reaction



(6)

is −68.7 or −43.5 kcal/mol, depending on whether X = C or Si, respectively. Experimentally, it has been noted by Conlin and Gaspar[6] that silacyclopropenes have been found to be unusually stable.

One might speculate that the strain in the base of silacyclopropene is less severe than that of the carbon analogue since the XCC angles are each more than four degrees larger in the former molecule. Furthermore, it is likely that the more diffuse orbitals on Si are better able to form "bent" bonds with the base carbons. This latter notion is supported by the delocalization effect pointed out earlier with regard to the Si–C bond length in silacyclopropene and by the fact that the antisymmetric stretching frequency is nearly the same in the two molecules (Table V), despite the fact that one normally expects Si–C to be weaker than C–C bonds. In addition, of the four rings, only in silacyclopropene is there a

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[13] Note that these isomerization reactions include other effects in addition to ring strain since they are not isodesmic.

Table VII. Vibrational Frequencies in Unsaturated Rings[a]

approximate description	freq, cm^{-1} X = C	freq, cm^{-1} X = Si	symmetry
HCCH out-of-plane	782 (569)	823	b_1
HCC scis	1012 (905)	1093	a_1
HCCH twist	1035 (815)	1107	a_2
XH_2 twist	1125 (996)	623	a_2
XH_2 wag	1186 (1011)	707	b_2
XH_2 rock	1191 (1088)	652	b_1
HCCH wag	1216 (1043)	1268	b_2
XH_2 scis	1664 (1483)	1038	a_1
XH_2 sym str	3255 (2909)	2323	a_1
XH_2 antisym str	3332 (2995)	2314	b_1
=CH antisym str	3455 (3116)	3390	b_2
=CH sym str	3513 (3152)	3423	a_1

[a] Experimental frequencies given in parentheses for cyclopropane (see ref 17).

positive X–C pπ–pπ overlap population.[14] In contrast, the ring deformation frequency is much "looser" in silacyclopropene, indicating that the effect of a small apex angle is less in this molecule.

Finally, both reactions 2 and 3 predict the strain in the two silicon rings to be very similar. This is particularly true for the 6-31G* calculations. Thus, introduciton of a C=C bond into cyclopropane has a much greater destabilizing effect than in silacyclopropane.

The vibrational frequencies (determined by using 3-21G) for the normal modes not involving ring motions are listed in Tables VI and VII for the saturated and unsaturated rings, respectively.[15] The experimental[16] frequencies for cyclopropane and cyclopropene are also given. Most of the trends are correctly reproduced, and the magnitudes are typically in error by about 10% for cyclopropane and 15–20% for cyclopropene. The one cyclopropane frequency seriously in error is the nondegenerate CH_2 scissor motion. Interestingly, the corresponding frequency in cyclopropene is closer to the experimental value. Not surprisingly, the frequencies for motions involving silicon are typically considerably smaller than the corresponding carbon frequencies. This is particularly apparent for the XH stretching motions which are predicted to differ by as much as 1000 cm^{-1}. This appears to be a reasonable estimate in view of typical experimental[16] SiH stretching frequencies.

Acknowledgment. This work was supported in part by Grant CHE77-16362 from the National Science Foundation. The computer time made available by the North Dakota State University Computer Center is gratefully acknowledged.

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[14] Note, however, that the "aromatic character" predicted by semiempirical calculations (ref 2) for silacyclopropene is not supported by the present calculations. A similar comment has been made by Barthelat et al., ref 5.

[15] In the interest of brevity, the normal coordinates are not included here. They will, however, be made available upon request.

[16] (a) J. L. Duncan and D. C. McKean, *J. Mol. Spectrosc.*, **27**, 117 (1968); (b) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", Consolidated Vol. I, NSRDS-NBS-39, National Bureau of Standards, 1972.

[17] T. Y. Yum and D. F. Eggers, Jr., *J. Phys. Chem.*, **83**, 502 (1979).

Electronic Structure and Photoelectron Spectra of $S_2Fe_2(CO)_6$

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Abstract: The valence photoelectron spectrum of $S_2Fe_2(CO)_6$ has been measured in the gas phase with Ne(I) and He(I) radiation. The observed bands are assigned on the basis of intensity changes with photon energy, relative band areas, past experience with related molecules, and molecular orbital calculations of the Extended Hückel (EH), Fenske–Hall (FH), and Self-Consistent-Field-Xα-Scattered-Wave (SCF-Xα-SW) types. While none of the theoretical approaches provides a direct quantitative interpretation of the spectrum, the overall agreement for the Xα calculations is sufficient to allow a meaningful discussion of the salient features of the binding in the series CO, $Fe(CO)_3$, $Fe_2(CO)_6$, S_2, and $S_2Fe_2(CO)_6$. The Xα results indicate *two* important Fe–Fe bonding orbitals, the HOMO of a_1 symmetry which is a slightly bent σ bonding orbital and a lower-lying b_1 orbital which has a significant direct Fe–Fe π component *induced* by interaction with the bridge. The former has previously been discussed on the basis of FH calculations but the latter has not. In addition there is a large effect of the S_2 bridge on the Fe–CO binding which shows up as a stabilization of the CO $5\tilde{\sigma}$ levels by nearly an electron volt compared with their position in $Fe_2(CO)_6$.

In the study of bridged binuclear transition-metal complexes a central question concerns the influence of the bridging ligands on metal–metal bonding and also on the bonding between the metal atoms and the other (terminal) ligands.[2] The question may be posed whether it is fruitful to consider $M_2T_xB_y$ (M = metal, T = terminal ligand, B = bridging ligand) as M_2T_x perturbed by the presence of the bridging ligands or as an M_2B_y fragment to which the terminal ligands are attached or, indeed, whether either of these decompositions of the molecule are of use in gaining insight into the structure, bonding, reactivity, catalytic activity, and other properties of this type of complex. Progress in several fields has allowed some first steps to be made toward answering this type of question. Two of these fields that are of direct interest to us in this paper are (i) the photoelectron spectroscopy (PES) of transition-metal complexes and (ii) molecular-orbital (MO) theory. Both PES and MO theory are currently well developed and tested tools for organic chemistry.[3] Inorganic applications,

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[2] (a) Teo, B. K; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103. (b) Anderson, A. B. *Ibid.* **1976**, *15*, 2598. (c) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240. (d) Burdett, J. K. *J. Chem. Soc. Dalton Trans.* **1977**, 423. (e) Thorn, D. L.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 126.

[3] Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1977.

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