calculations over less time-consuming molecular mechanics and semiempirical methods. The ab initio heats of formation could be of use in helping to reparametrize lower level computational methods such as molecular mechanics, which might yield accurate results with sufficient numbers of specialized parameters.

Since we have established that the IS methine group equivalent furnishes more accurate heats of formation for $(CH)_{2n}$ hydrocarbons than the W1 value, our previous ΔH_f of dodecahedrane should be revised slightly upward from 6.4 kcal/mol[8] (from W1) to 12.8 kcal/mol (from IS), although this value may be 1 to 2 kcal/mol too high.

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Appendix

The symmetry species of the vibrational modes of the D_{nh} prismanes are as follows. For odd n, there are 10 nondegenerate modes and $6n - 8$ degenerate pairs: $4A'_1 + A'_2 + 2A''_1 + 3A''_2 + 5E'_1 + 5E''_1 +$ (for $n > 3$) $6E'_2 + ... + 6E'_{(n-1)/2} + 6E''_2 + ... + 6E''_{(n-1)/2}$. For even n ($n > 4$), there are 22 nondegenerate modes and $6n - 14$ degenerate pairs: $4A_{1g} + A_{2g} + 2B_{1g} + 4B_{2g} + 2A_{1u} + 3A_{2u} + 4B_{1u} + 2B_{2u} + 5E_{1g} + 5E_{1u} + 6E_{2g} + ... + 6E_{(n/2-1)g} + 6E_{2u} + ... + 6E_{(n/2-1)u}$. Thus, all these prismanes have three nondegenerate and five twofold degenerate infrared active fundamentals. For $n = 4$ (cubane), octahedral symmetry leads to three threefold degenerate active fundamentals.

A Comparison of the Energies of Double Bonds of Second-Row Elements with Carbon and Silicon

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Abstract: Theoretical π-bond energies (E_π) are evaluated for the double bond systems $H_2Y{=}XH_n$ (Y = C, Si; X = B, C, N, O, Al, Si, P, S) employing the MP4SDTQ/6-31G*//6-31G* + ZPE level of theory. The difference in energy between two single bonds, X–Y, and a double bond, X=Y, is calculated by means of isodesmic equations. E_π is given by subtraction of this difference from the dissociation energies of the single bond system, $D_0°$. Si=X bonds are found to have significantly lower E_π energies than the corresponding C=X bonds; for each series, C=X and Si=X, the π-bond energies for both first- and second-row substituents correlate with the electronegativities of X. When electronegativity differences between carbon and silicon and among the X groups is taken into account, second- and first-row π-bond energies are similar. Families of linear correlations are also observed for E_π and Y=X bond lengths. Alternative procedures for estimating π bond energies (rotation barriers and diradical components) are criticized.

Until relatively recently, molecules with double bonds involving second-row elements were comparatively rare.[2] This was commonly attributed to the weakness of second-row π bonds due to poor p-orbital overlap.[3] This situation has changed drastically by the experimental realizations of one second-row double bond system after another.[2,4,5] Such molecules are persistent when isolated in a matrix or can be stabilized by bulky substituents. While it now seems clear that the earlier inability to observe such multiple bond systems was due primarily to their high reactivity, thermochemical factors also may contribute. The present state of affairs emphasizes the desirability of ascertaining the energies of double bonds involving second-row elements, particularly in comparison with their first-row counterparts. A survey of conventional double bond systems involving carbon ($H_2C{=}XH_n$, where XH_n = BH, CH_2, NH, O, AlH, SiH_2, PH, and S) as well as the silicon counterparts, $H_2Si{=}XH_n$, with the same XH_n groups is the subject of this paper.[5,6] Our results reveal unrecognized aspects of this problem.

Methods

Since experimental measurements on these molecules are difficult, ab initio molecular orbital theory affords an excellent source of data.[7] The level chosen for the thermochemical comparisons was MP4SDTQ/6-31G*//6-31G* + ZPE. All of the double bond systems and the single bond reference molecules were optimized by using the GAUSSIAN 82 program[7] with the 6-31G* basis set, which contains a set of d-functions on all non-hydrogen atoms. Electron correlation corrections, which have significant effects from about 5–12 kcal/mol on the relative energies, were estimated at the MP4SDTQ (complete fourth-order Møller–Plesset) level by using the frozen core approximation and the 6-31G* geometries. The latter also were used for frequency analyses to establish that all double bond structures were minima. Zero-point vibrational energies (ZPE) were estimated from our calculations or from the literature (Table I). Some of the data were taken from the CMU archive.[8] For those

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(1) Presented, in part, at the *8th International Conference on Physical Organic Chemistry*, Tokyo, August 1986: *Pure Appl. Chem.* **1987**, *59*, 1647.

(2) For reviews with leading references, see: (a) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386. (b) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (c) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (d) Müller, G. *Nachr. Chem. Tech. Lab.* **1986**, *34*, 778. (e) Guselnikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (f) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 2. Also, see: ref 5 and 9i.

(3) See, for instance: ref 2c and ref 10–18 therein.

(4) (a) Issleib, K.; Schmidt, H.; Wirkner, Ch. *Z. Anorg. Allg. Chem.* **1981**, *473*, 85. (b) Xie, Z.-M.; Wisian-Neilson, P.; Neilson, R. H. *Organometallics* **1985**, *4*, 339. (c) Sommer, L. H.; Parker, D. R. *J. Organomet. Chem.* **1976**, *110*, C1.

(5) Luke, E. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Carny, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270 and references cited. This paper compared double bond energies involving silicon and first-row elements.

(6) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 260. This paper deals with single bonds involving silicon.

(7) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: *New* York, 1986.

(8) Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon University: 1983. This source lists a complete set of MP4/6-31G*//3-21G(*) data for the single bond systems. We refined these to MP4/6-31G*//6-31G*; the changes are significant in some instances.

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Table I. Zero-Point Energies (kcal/mol)

H_3CXN_{n+1} Molecules[a]								
XH_{n+1}	BH_2	CH_3	NH_2	OH	AlH_2	SiH_3	PH_2	SH
ZPE	33.1	44.7	38.0	30.4	28.6	36.0	32.2	27.2
$H_2C{=}XH_n$:								
XH_n	BH	CH_2	NH	O	AlH	SiH_2	PH	S
ZPE	20.1[b]	30.9[c]	23.9[d]	16.1[c]	16.8[b]	24.1[b]	17.8[e]	15.0[b]
H_3SiXH_{n+1}[a]								
XH_{n+1}	BH_2	CH_3	NH_2	OH	AlH_2	SiH_3	PH_2	SH
ZPE	25.4	36.0	29.6	22.4	21.4	28.4	24.5	19.6
$H_2Si{=}XH_n$:								
XH_n	BH	CH_2	NH	O	AlH	SiH_2	PH	S
ZPE	15.0[d]	24.1[b]	17.8[b]	10.9[d]	12.0[d]	18.1[d]	14.9[b]	10.3[b]
XH_{n+1} Radicals:								
XH_{n+1}	BH_2	CH_3	NH_2	OH	AlH_2	SiH_3	PH_2	SH
ZPE	8.6[b]	18.2[b]	11.5[b,f]	5.1[b,f]	6.1[b,f]	12.8[b]	8.2[b]	3.7[b]

[a] Data from ref 6, calculated at the 3-21G level and scaled by 0.89 [b] Data at 6-31G* basis, scaled by 0.89. [c] Experimental data from Shimanouchi (Shimanouchi, T. *Table of Molecular Vibration Frequencies*; NSRDS-ABS 6, 11, and 17, National Bureau of Standards, Washington, D.C., 1967 and 1968). [d] Data at 3-21G from ref 5, scaled by 0.89. [e] Data at 3-21G from Pietro et al. (Pietro, W. J.; Francl, N. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039) scaled by 0.89. [f] Calculated from data in Pople et al. (Pople, J. A.; Luke, B. T.; Frisch, M. J.; Binkely, J. S. *J. Phys. Chem.* **1985**, *89*, 2198).

molecules calculated here, full data are provided in the Supplementary Material in the form of archive entries. There have been a number of recent theoretical studies on some of these systems[9] but no comprehensive treatment at uniform levels for all these species.

Discussion

The energies of double bonds often are divided into σ and π contributions, but these are not observable quantities. A common approach is to equate the π-bond energy with the rotational barrier.[9a,h,i] However, this assumes that the rotational transition structure (state) has no π-bond character, whereas some residual π interactions (e.g., hyperconjugation and with lone pairs on N and P) are present. Moreover, linear groupings, such as X = BH, AlH, O, and S, cannot be "rotated", and some species, e.g. $HP{=}CH_2$[10] and $HP{=}SiH_2$, rearrange to ylid forms on attempted optimization of perpendicular geometries. (However, see ref 9i.)

Another, more general, procedure is to compare the bond dissociation energies of double, $D°(X{=}Y)$, and single, $D°(X\text{-}Y)$, bonds, eq 1 and 2, respectively.[11] However, the energy differences

$$H_2Y{=}XH_n \rightarrow H_2Y{:} + {:}XH_n \qquad D°(X{=}Y) \qquad (1)$$

$$H_3Y\text{-}XH_{n+1} \rightarrow H_3Y\cdot + \cdot XH_{n+1} \qquad D°(X\text{-}Y) \qquad (2)$$

between eq 1 and 2 do not correspond to the rotational barriers of X=Y systems. For example, experimental data (0 K) for X, Y=C give 173.3 kcal/mol for eq 1 and 86.1 kcal/mol for eq 2.[12] The difference, 87.2 kcal/mol, is far greater than the rotational barrier for ethylene (65 kcal/mol). On this basis, the π bond in ethylene is deduced to be stronger (87.2 kcal/mol) than the σ bond (86.1 kcal/mol) which is not what is commonly believed.

The procedure we have adopted here first compares the energy of an X=Y double bond with those of two X-Y single bonds by means of isodesmic reactions (eq 3).[13] These have been evaluated

$$H_2Y{=}XH_n + YH_4 + XH_{n+2} \rightarrow 2H_3Y\text{-}XH_{n+1} \qquad (3)$$

$$Y = \text{C or Si} \qquad \Delta E(3)$$

with apparently reasonable accuracy (ca. ±5 kcal/mol, see Table II) at the MP4/6-31G*//6-31G* + ZPE level. The energies of eq 3, when subtracted from $2D°(X\text{-}Y)$, provide an estimate of the total double bond energy, $E_{\sigma+\pi}$. If $D°(X\text{-}Y)$ is assumed to approximate E_σ, E_π can readily be obtained. Thus, for X, Y = C, the energy of eq 3 is −18.8 kcal/mol at MP4/6-31G* + ZPE. E_π(ethylene) = 67.8 kcal/mol on this basis, much closer to the rotational barrier and not far from the 0 K experimental value of 70.6 kcal/mol, deduced by the same procedure.

The determination of $D°(X\text{-}Y)$ values (eq 2) remains a problem, since the experimental data are incomplete and sometimes only crudely estimated. Equation 2 is not isodesmic, and high levels of theory are believed to be needed to calculate bond dissociation energies accurately.[7] Nevertheless, MP4/6-31G*//6-31G* + ZPE data give reasonably good results (see the comparisons in Table I), and we have employed them for uniformity to obtain the estimates for $D°(X\text{-}Y)$, (which represents E_σ). These data, along with the resulting $E_{\sigma+\pi}$ and E values, are listed in Table II. (We recognize the inconsistencies in the definition of bond energies implied by this model and also the implied assumption of constant X-H and Y-H bond energies.)

Large differences in single and double bond energies and large variations are revealed by Table II. Consider first the $\Delta E(3)$ data. As is well known, the C=O double bond in formaldehyde is *stronger* than two isolated C-O bonds,[11] but all other C=X and Si=X double bonds are weaker than two of the corresponding single linkages. The energy differences, $\Delta E(3)$, for $CH_2{=}XH_n$ compounds correlate roughly with the electronegativity of X; larger $\Delta E(3)$ values are found with electronegative elements, and smaller differences with electropositive ones. For Si=X double bonds, $\Delta E(3)$ values tend to be larger than those for C=X double bonds and depend much less regularly on electronegativity. However, the difference between the $\Delta E(3)$ values for C=X and for Si=X ($\Delta\Delta E(3)$, Table II, last column) show a remarkably linear relationship when plotted against element electronegativities (Figure

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(9) Recent papers pertinent to the present study include references 4 and 5 (as well as citations therein) and the following: (a) Truong, T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1775. (b) Lee, J.-G.; Boggs, J. E.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 773. (c) Lahr, L. C.; Schlegel, H. B.; Morkuma, K. *J. Phys. Chem.* **1984**, *88*, 1981. Lohr, L. L.; Panos, S. H. *Ibid.* **1984**, *88*, 2992. (d) Kudo, T.; Nagase, S. *Organometallics* **1986**, *5*, 1207. (e) Cook, C. M.; Allen, L. C. *Ibid.* **1982**, *1*, 246. (f) Schleyer, P. v. R.; Stout, P. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1373. (g) Bestmann, H. J.; Kos, A. J.; Witzgall, K.; Schleyer, P. v. R. *Chem. Ber.* **1986**, *119*, 1331. (h) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *5*, 2057. (i) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217. This paper reviews the literature comprehensively. Unfortunately, many of the π bond strengths derived in this paper do not agree with our estimates. These discrepancies are due to the use of different (and in our view, inappropriate) sets of reference species.

(10) Goubeau, D.; Pfister-Guillanzo, G.; Barrans, J. *Can. J. Chem.* **1983**, *61*, 1371.

(11) The following publication gives an extensive list of bond energies: Huheey, J. H. *Inorganic Chemistry*, 3rd. ed.; Harper and Row: New York, 1983; Appendix E, p A28f. (a) Another procedure for estimating π bond energies has been suggested by Benson (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976).

(12) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Heron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, supplement 1.

(13) Note that eq 3 is the difference between the heats of hydrogenation of related double ($H_nX{=}YH_m$ to $H_{n+1}X\text{-}YH_{m+1}$) and single bond ($H_{n+1}X\text{-}YH_{m+1}$ to XH_{n+2} + YH_{m+2}) systems; this also can be employed to evaluate relative bond energies.

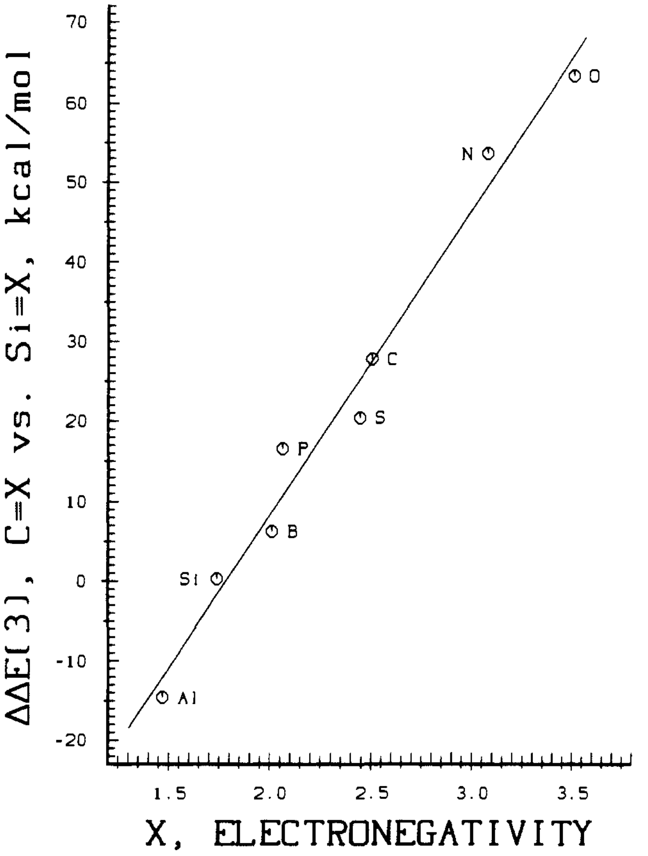

Figure 1. Plot of the difference in $\Delta E(3)$ for C=X and Si=X against X electronegativity. (Allred, A. L.; Rochow, E. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.)

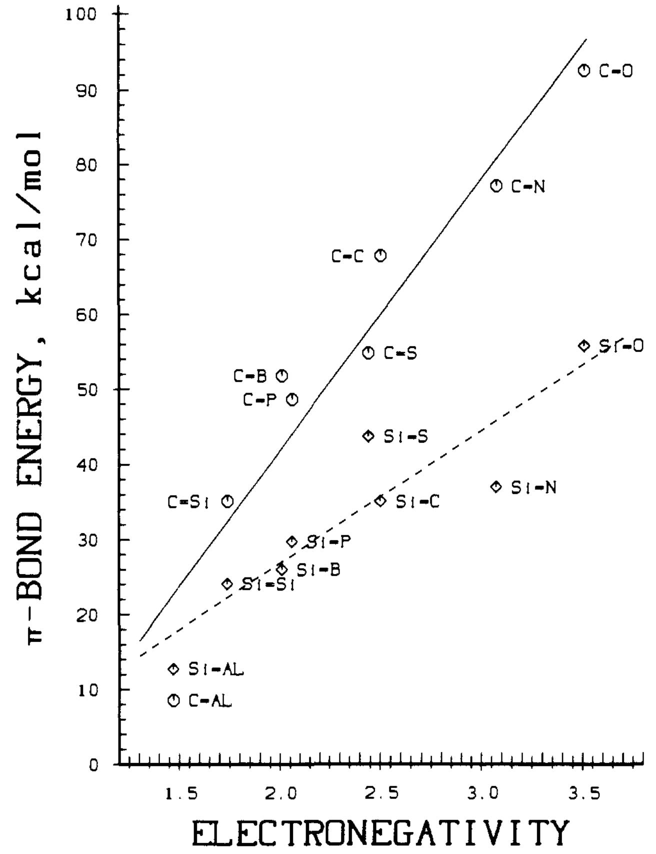

Figure 2. π-Bond energies (E_π) for $H_2C{=}X_n$ (solid line) and for $H_2Si{=}XH_n$ (dashed line) plotted against X electronegativity.

1). When such *differences* in single and double bond energies are compared, first- and second-row elements do not show divergent behavior. The factors which influence double bond energies act in a parallel manner.

As we have pointed out earlier,[5] the $D°$(Si-X) values in Table II (but not $D°$(C-X) values) correlate quite linearly with electronegativity. The same is true for E_π C=X and Si=X energies (Figure 2). However, the other quantities, $\Delta E(3)$ (at least for Si compounds) and $E_{\sigma+\pi}$, do not show any simple behavior in this regard. Even energy differences between carbon and silicon values seldom give the regular trends shown in Figure 1. This is only true for $D°$(C-X)-$D°$(Si-X) (with separate lines for first- and second-row X's) but not for the other quantities. Hence the linearity of Figure 1 must be due to the balancing of the other factors which contribute to single and double bond energies.

Since the C=X bond lengths (Table III) also parallel the electronegativity of X within each row (see below), the falloff in π overlap is a major factor responsible for the trends in Figure 2. This is shown more directly by the Wiberg bond indexes and by the natural localized molecular orbital population bond orders[15] in Table III. The larger radial extension of 3p-orbitals[14] compensates in part for the increase in C=X distances.

The linear relationship between the π-bond energies and the X=Y bond lengths is brought out by Figure 3. The bond lengths depend on the number of first- and second-row atoms involved. The two lines describing first- and second-row C=X bonds are roughly parallel, and so are the corresponding correlations for Si=X bonds. However, the slopes for the Si=X lines are different from those for the C=X lines, indicating a greater sensitivity of C=X bond energies for variation in Y=X bond lengths than that shown by Si=X bonds. This greater sensitivity is retained even when E_π is plotted against the *relative* change in bond length in each series. Note that the chemically very different Si=O and C=S bonds have nearly the same length and nearly the same E_π values. The two correlation lines in Figure 2 may be somewhat misleading, as the E_π(Si=C) values for the same compound (H_2SiCH_2) are plotted against X_{Si} = 1.74 and X_C = 2.50 in the

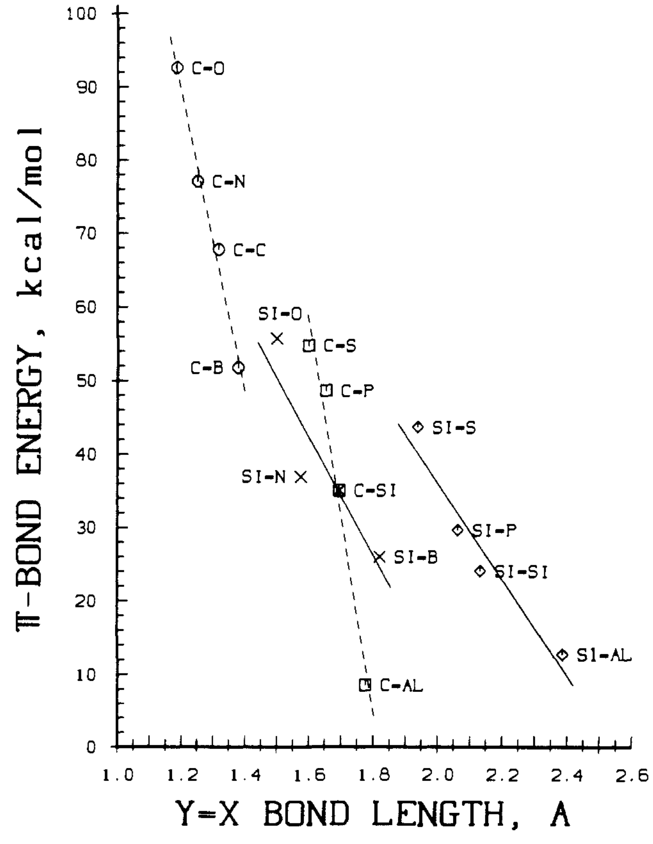

Figure 3. π-Bond energies (E_π) for C=X (dashed lines) and Si=X (solid lines) bonds plotted against 6-31G* X=Y bond lengths.

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(14) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262.

Table II. Single and Double Bond Energies[a]

system	$\Delta E(3)$	D_0(X–Y), ($\equiv E_\sigma$)	$E_{\pi+\sigma}$[b]	E_π[c]	calcd rotatnl barrier	$\Delta\Delta E(3)$, C vs Si
$H_2C=BH$	-48.0	101.7	155.3	53.7		6.3
$H_2C=CH_2$	-18.8 (-15.6)[d]	88.4 (86.1)[d]	157.9 (156.6)	69.6 (70.6)	66.0,[e] 65.0,[f] 65.4[u]	27.7
$H_2C=NH$	+1.4	79.4 (78.8)[g]	160.2	80.8	*h*, 63.3[u]	56.4
$H_2C=O$	+8.0 (9.4)[d]	85.5 (89.4)[d]	178.9 (188.2)	93.4 (98.8)		63.4
$H_2C=AlH$	-66.7	76.1	85.5	9.4		-16.2
$H_2C=SiH_2$	-46.5 (-45 ± 5)[i]	82.6 (88.2)[i]	118.6 (131 ± 5)[j]	36.1 (43 ± 5)[j]	37.0,[k] 35.6[u]	-0.3
$H_2C=PH$	-16.7	66.1	115.4	49.4	*l*, 45[u]	16.3
$H_2C=S$	-13.5[m]	69.2 (68.7)[n]	124.9	55.7		20.5
$H_2Si=BH$	-54.3	81.4	108.4	27.0		
$H_2Si=CH_2$	-46.5 (-45 ± 5)[i]	82.6 (88.2)[i]	118.6 (131 ± 5)[j]	36.1 (43 ± 5)[j]	37.0,[k] 35.6[u]	
$H_2Si=NH$	-55.0	92.0 (100)[i,o]	129.0	37.0	37.9,[p] 36.4[u]	
$H_2Si=O$	-55.4	111.2 (128)[i,o]	167.0	55.8[q]		
$H_2Si=AlH$	-50.5	64.6	78.7	14.1		
$H_2Si=SiH_2$	-46.3	70.5 (74)[i]	94.7	24.2[r]	22.0,[s] 22.7[u]	
$H_2Si=PH$	-33.0	62.7	92.4	29.7	*t*, 35[u]	
$H_2Si=S$	-34.0	77.7 (90)[i]	121.3	43.6		

[a] Values in parentheses were evaluated from experimental data by using the appropriate equations for $\Delta E(3)$, D_0(X–Y), E_σ and $E_{\pi+\sigma}$. [b] Calculated by adding the energies in column 2 with twice the energies in column 3. [c] Calculated by adding together the energies in columns 2 and 3. [d] Data from ref 12. [e] Data at MP4SDTQ/6-31G*//6-31G* (RHF for the planar and UHF for the nonplanar structures) from ref 8. [f] Experimental measurement by Douglas et al. (Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315). [g] Experimental data from Gibson et al. (Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4319). [h] Both rotation and planr inversion are possible mechansism for the topomerization of imine and its derivatives. Experimental evidence indicates that the mechanism is largely inversion and hence irrelevant to the problem of hand: Kalinowski, H.-O.; Kessler, H. *Topics Stereochem.* **1973**, *7*, 295. [i] Data from Walsh (Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246). [j] Si=C—experimental estimates, as discussed by Walsh (Footnote *i*), have ranged from −28 to −46 kcal/mol. [k] Schmidt, M. W.; Gordon, M. S.; Dupuis, M. *J. Am. Chem. Soc.* **1985**, *107*, 2585. See this paper and ref 2c,f for discussions of other experimental and theoretical estimates of the bond energy which range from 34 to 46 kcal/mol (Ahlrichs, R.; Heinzmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7452). [l] Attempts to calculate a rotation barrier were unsuccessful due to rearrangement of the C_s torsional transition structure to the C_{3v} H_3CP geometry: ref 10. [m] The most recent experimental determinations of ΔH_f° ($H_2C=S$) are 21.5 ± 2 kcal/mol (Roy, M.; McMahon, T. B. *Org. Mass. Spectrom.* **1982**, *17*, 392) and 33.1 ± 1.5 kcal/mol (Kutina, R. E.; Edwards, A. K.; Goodman, G. L.; Berkowitz, J. *J. Chem. Phys.* **1982**, *77*, 5508). These numbers give −18.6 and −7.0 kcal/mol, respectively, for $E(3)$. [n] From Traeger, J. C. *Org. Mass. Spectrom.* **1984**, *19*, 514. [o] On the basis of data for substituted molecules: [p] Truong, T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1775. [q] There are no experimental data for the evaluation of $E(3)$ and the derived quantities. Experimental estimates of the Si=O bond strength range from 38 kcal/mol (Murdoch, J. R. *J. Phys. Chem.* **1983**, *87*, 1571. *J. Am. Chem. Soc.* **1983**, *105*, 2667) to 63 kcal/mol (Hughes, E. D.; Ingold, C. K.; Shapiro, U. G. *J. Am. Chem. Soc.* **1936**, 225). [r] Experimental data for evaluation of *E* (experimental) are not available. The π-bond strength has been estimated to be between 22 and 30 kcal/mol by Raabe and Michl (ref 2c) based on rotational barrier measurements. [s] Olbrich, G.; Potzinger, P.; Reimann, B.; Walsh, R. *Organometallics* **1984**, *3*, 1267. [t] Our attempt to optimize a C_s torsional transition structure at the 6-31G* level resulted in a similar rearrangement to that found for the carbon analogue (footnote *l*). However, see ref 9i. [u] Data from ref 9i. Also see ref 9h.

Table III. Point Groups, Y=X Bond Lengths, and Bond Order Indices[a]

molecule	point group	X=Y, Å	X=Y "Wiberg" bond index[b]	X=Y net linear NLMO/NPA bond order[c]
$H_2C=BH$	C_{2v}	1.377	1.848	1.411
$H_2C=CH_2$	D_{2h}	1.317	2.035	2.026
$H_2C=NH$	C_s	1.251	2.011	1.686
$H_2C=O$	C_{2v}	1.184	1.882	1.371
$H_2C=AlH$	C_{2v}	1.776	1.518	1.038
$H_2C=SiH_2$	C_{2v}	1.694	1.770	1.342
$H_2C=PH$	C_s	1.652	1.928	1.676
$H_2C=S$	C_{2v}	1.597	2.014	1.718
$H_2Si=BH$	C_{2v}	1.819	1.966	1.765
$H_2Si=CH_2$	C_{2v}	1.694	1.770	1.342
$H_2Si=NH$	C_s	1.573	1.558	1.006
$H_2Si=O$	C_{2v}	1.498	1.325	0.787
$H_2Si=AlH$	C_s[d]	2.385	1.405	1.378
$H_2Si=SiH_2$	C_{2h}[d]	2.131	1.982	2.011
$H_2Si=PH$	C_s	2.060	1.927	1.611
$H_2Si=S$	C_{2v}	1.936	1.798	1.265

[a] At 6-31G* optimized geometries (all structures had zero imaginary frequencies and represent minima on the potential energy hypersurfaces). [b] On the basis of "natural atomic orbitals", see: ref 15. [c] As defined by Reed and Schleyer (Reed, A. E.; Schleyer, P. v. R., to be published). [d] Trans bent geometry.

separate treatments. If the *sum* of the electronegatives for the constituent atoms, X and Y, were employed instead, the Si=X and C=X correlation lines would intersect.[16] Bonds having similar X and Y electronegativity sums will also have rather similar π bond energies.

Conclusions

In terms of *absolute* E_π values, Si=X double bonds are weaker and often much weaker than their first-row counterparts. (The Si=Al π bond, which is slightly stronger than π (C=Al), is an exception, but both bonds are very weak.) However, the strengths of π bonds depend on the electronegativity of the constituent elements. When this is taken into consideration a rather different picture emerges.

For example, it is more appropriate to compare E_π(C=P) = 48.6 kcal/mol not with E_π(C=N) = 77.1 but with E_π(C=B) = 51.8 kcal/mol since P (χ = 2.06) and B (χ = 2.01) have nearly the same electronegativity. The π-bond energy in $H_2C=CH_2$ (67.8 kcal/mol; χ_C = 2.50) is only a little larger than that in $H_2C=S$ (54.8, χ_S = 2.44). In the corresponding silicon examples, the π-bond energies involving second-row elements actually are larger than those to first-row elements with similar electronegativity: E_π(Si=P) = 29.7 kcal/mol > E_π(Si=B) = 26.0 kcal/mol and E_π(Si=S) = 43.7 kcal/mol > E_π(Si=C) = 35.1 kcal/mol. In analyzing series of C=X (or Si=X) bonds, different behavior is not observed for first- and second-row elements. Their π-bond energies fit the same linear correlation with electronegativity.

This study is being extended to all combinations of first- and second-row elements. The results will be reported subsequently.

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(16) The connection between the sum of the electronegativities and double bond strength was discussed by Goubeau (Goubeau, J. *Angew. Chem.* **1966**, *78*, 565; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 567; *Angew. Chem.* **1957**, *69*, 77; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1038).

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Registry No. $H_2C{=}BH$, 56125-75-8; $H_2C{=}NH$, 2053-29-4; $H_2C{=}AlH$, 79435-76-0; $H_2C{=}SiH_2$, 51067-84-6; $H_2C{=}PH$, 61183-53-7; $H_2C{=}S$, 865-36-1; $H_2Si{=}BH$, 98976-97-7; $H_2Si{=}NH$, 32520-13-1; $H_2Si{=}O$, 22755-01-7; $H_2Si{=}AlH$, 111771-61-0; $H_2Si{=}SiH_2$, 15435-77-5; $H_2Si{=}PH$, 98360-04-4; $H_2Si{=}S$, 69639-29-8; BH_2, 14452-64-3; CH_3, 2229-07-4; NH_2, 13770-40-6; OH, 3352-57-6; AlH_2, 14457-65-9; SiH_3, 13765-44-1; PH_2, 13765-43-0; SH, 13940-21-1; C, 7440-44-0; Si, 7440-21-3.

Supplementary Material Available: Absolute energies and geometries of all species calculated here in GAUSSIAN 82 archive format (3 pages). Ordering information is given on any current masthead page.

An Electrochemical Study of the Substitution and Decomposition Reactions of (Arene)tricarbonylchromium Radical Cations

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Abstract: Voltammetry with conventional electrodes and microelectrodes establishes that (arene)$Cr(CO)_3$ (arene = benzene, mesitylene) is oxidized by a chemically and electrochemically reversible one-electron step when the solvent is dichloromethane or benzene and the supporting electrolyte is tetrabutylammonium hexafluorophosphate or tetrahexylammonium hexafluorophosphate, respectively. With a more nucleophilic solvent (e.g., acetone or acetonitrile) or electrolyte (e.g., tetrabutylammonium perchlorate or tetrahexylammonium perchlorate), a two-electron oxidation obtains for $(C_6H_6)Cr(CO)_3$, corresponding to an $\bar{E}C\bar{E}$ process where the chemical step is associative attack by the nucleophile on the radical cation to produce free benzene and a Cr(I) species which is rapidly oxidized. The rate constant for the reaction of $(C_6H_6)Cr(CO)_3^+$ in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate was found to be 30 ± 10 s^{-1} at 20 °C. In the presence of tertiary phosphine and phosphite nucleophiles, (arene)$Cr(CO)_3^+$ undergoes rapid CO substitution in competition with decomposition. $P(OBu)_3$ substitution for CO in (mesitylene)$Cr(CO)_3^+$ is quantitative in propylene carbonate. While only monosubstitution occurs with $P(OBu)_3$ and PBu_3, the caged phosphite $P(OCH_2)_3CMe$ gives disubstitution at slow scan rates and monosubstitution at fast scan rates. Voltammetry with (mesitylene)$W(CO)_3$ shows that it is oxidized via a two-electron process in acetonitrile and dichloromethane, most likely to give an 18-electron W(II) species. The data are in conflict with recently published work on $(C_6Me_6)W(CO)_3$.

Over the past few years there has been an increasing appreciation of the importance of 17-electron organometallic radicals in stoichiometric and catalytic transformations. One of the primary reasons for this interest is the large increase in reactivity that frequently accompanies the oxidation or reduction of 18-electron complexes.[1] Truly amazing electrocatalytic syntheses and rate accelerations are known. The first organometallic example of ligand substitution initiated and catalyzed by electron addition was reported in 1981.[2] It was then demonstrated that electron-transfer-catalyzed nucleophilic substitution in polynuclear metal carbonyls is a rather general reaction and can lead to striking results.[3] Ligand substitution can also be initiated by oxidation, and examples of very rapid and efficient reactions are known.[4] Whether the reaction is initiated by oxidation or reduction, it is likely that the electroactivated substitutions proceed via 17-electron radical intermediates and that the mechanism is associative.[1] Carbon monoxide insertion reactions are also known to be subject to electroactivation. For example,[5] CO insertion into the Fe–Me bond in $CpFe(CO)(PPh_3)Me$ does not progress detectably after 5 days at 0 °C and 1 atm of CO; the addition of a few mole percent of Ag^+ causes complete conversion to $CpFe(CO)(PPh_3)COMe$ within 2 min. Interestingly, catalytic CO insertion may also be induced by reduction.[6] The application of electrochemistry to the synthesis of organometallics and the study of organometallic reaction mechanisms is an extremely promising field that has yet to be exploited in depth. Reactions like those listed above illustrate the chemistry waiting to be discovered and guarantee that organometallic electrochemistry will enjoy increasing popularity (and importance) in the years ahead.[7]

The recent development[8] of platinum and graphite disk microelectrodes with diameters ≤10 μm should prove to be particularly useful in organometallic chemistry. Microelectrodes offer several advantages over conventional electrodes in linear sweep voltammetric experiments. Of special interest in this paper is the steady-state response that is shown by microelectrodes at low sweep rates due to the predominance of spherical diffusion under these conditions. While the theory of steady-state response at microelectrodes is yet to be fully developed, it is already known[9] that

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