6

heteroatoms are stabilized in those positions where topology produces an accumulation of negative charge in the homoatomic system. Since positions 2 and 3 are the most negative in **6**, they would be preferred locations for the pair of carbon atoms for the most stable isomer of $C_2B_9H_{11}$. For other isomers, consider the charges Q_m and Q_n on sites m and n in **6**. Assume that the sum $Q_m + Q_n$ is a measure of the energy of the isomer m,n-$C_2B_9H_{11}$. For example, the energy of the 2,3-isomer must be related to $Q_2 + Q_3 = 2 \times (-0.090) = -0.180$. Higher in energy would be the 2,10-isomer with $Q_2 + Q_{10} = -0.090 - 0.055 = -0.145$ and so on for the 20 positional isomers of $C_2B_9H_{11}$. In several cases two or more isomers turn out to have the same energy. These charge sums or energies can be divided into six groups, and this has been done in the middle course of Table IV. The rule of topological charge stabilization has been quite successful in correctly ordering the isomer energies of other series of *closo*-carboranes.[29,30,40] We have used similar estimates of relative isomer energies in conjunction with reaction graphs to study the stabilities of heteroatomic and substituted species related to the fluxional ion P_7^{3-}.[41] With so many isomers, $C_2B_9H_{11}$ offers the most challenging test.

The three models agree that the most stable isomer is the 2,3. The empirical valence rules and ab initio calculations both distribute the same three isomers to group II. Beyond these there is little detailed similarity among the compositions of the six groups for the three models. In general one can say that isomers with a carbon at position 2 (four-coordinate; most negative in **6**) are among those at the high-stability, low-energy end of the sequence, and those with a carbon at position 1 (six-coordinate; most positive in **6**) are at the high-energy, low-stability range. But as we can see from reaction graphs, the relationship between energy and stability is not direct. Only the qualitative aspects of energy ordering are useful in predicting stability, and for these the three models agree. In our earlier discussion of the reaction graph we predicted the stability of the unknown isomers 2,8 and 2,9. These fall in groups II or III by the three models. Acting as barriers to the rearrangement of these isomers to the most stable 2,3-isomer are 1,4 and 1,10, which are classified by the three models as members of groups V and VI. Because qualitative, semiquantitative, and quantitative models lead to similar qualitative predictions, we have more confidence in these results.

For this paper we obtained geometry-optimized total energies and bond distances from ab inito SCF-MO (STO-3G) calculations for 17 positional isomers of $C_2B_9H_{11}$. These results, along with those for the other three $C_2B_9H_{11}$ isomers plus structures and energies of the carborane isomers of other classes previously published elsewhere,[5,29,30] constitute a complete set of geometry-optimized calculations at the same level of approximation for $C_2B_{n-2}H_n$, $n = 5$–12, or a total of 52 isomers in 8 polyhedral classes. We plan to submit these data to the Quantum Chemistry Archive of Carnegie-Mellon University.

Conclusions

From reaction graphs based on a proposed rearrangement mechanism and relative energies from ab initio SCF-MO calculations, we predict that 2,9- and 2,8-$C_2B_9H_{11}$ positional isomers should be metastable, blocked from rearranging to more stable structures by higher energy isomers that intervene along the reaction path. So far, only the 2,3-isomer has been prepared. We note that the degree of the vertex in the reaction graph is related to the symmetry of the corresponding isomer: the greater the symmetry, the lower the degree of the vertex. We report geometry-optimized total energies for 17 positional isomers of $C_2B_9H_{11}$, completing a set of calculations at the same level of approximation for a total of 52 polyhedral structures for the $C_2B_{n-2}H_n$.

Ab Initio Study of the Interaction of Fe, Fe⁺, and HFe with H, CH, CH₂, CH₃, and C₅H₅

Michael L. McKee

Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36849-5312. Received August 24, 1989

Abstract: Ab initio calculations using a single configuration and employing an effective core potential on iron have been used to study the interaction of Fe, Fe⁺, and HFe with H, CH, CH₂, CH₃, and C₅H₅. By comparing bond dissociation energies calculated with large basis sets and experiment it was found that trends are well reproduced. For example, the Fe–CH₃ bond is weaker than the Fe–H bond in the neutral complex but stronger in the ionized complex. Also, the Fe—C, Fe=C, and Fe≡C bond dissociation energies are predicted to increase in reasonable agreement with experiment. All H–Fe–X complexes (X = H, CH₃, C₅H₅) are predicted to have quintet ground states with a H–Fe–ligand bond angle of 180°.

In recent years, the unqualified success of theoretical calculations in the area of organic chemistry has been taken largely for granted. In contrast, calculations on unsaturated transition-metal complexes, which are just recently becoming commonplace,[1]

Table I. Computed Relative Energies (kcal/mol) of Several Electronic States of the Fe and Fe$^+$ Atom

configuration	state	HF	PMP2	PMP3	exptl[a,b]
Fe					
$3d^6 4s^2$	^5D	0	0	0	0
$3d^7 4s^1$	^5F	33.4	11.5	19.9	19.8
$3d^7 4s^1$	^3F	48.0	25.6	33.0	34.2
$3d^6 4s^2$	$^3P^c$	57.5	54.1	52.8	52.5
Fe$^+$					
$3d^6 4s^1$	^6D	0	0	0	0
$3d^7$	^4F	23.6	-5.7	-1.8	5.3

[a] Reference 20. [b] The given separations are weighed over J values of each term. [c] Not a pure state.

yield near-quantitative accuracy only if very large basis sets are used in conjunction with extensive electron correlation. However, the cost of such calculations has often limited the study to a metal atom plus a small ligand. The purpose of the present work is to show that calculations based on a single configuration and corrected for electron correlation via perturbative expansion (i.e. Møller–Plesset expansion) can provide qualitative accuracy for the interpretation of simple unsaturated organometallic complexes of iron. In unsaturated complexes the small splitting between occupied and unoccupied orbitals often leads to a number of low-lying electronic states. To predict the ordering of these states and the properties of a particular state some care must be taken since different electronic states may be affected differently by increasing the size of the basis set or the amount of electron correlation. In contrast, a number of methods have been shown to be successful in predicting properties of saturated organometallics complexes including "semi-ab initio" methods such as Fenske–Hall[2a] and PRDDO.[2b] These complexes usually have a low-spin ground state and no low-lying excited states (<10 kcal/mol) due to the interaction of the ligands with the d orbitals which leads to a significant splitting between the occupied and unoccupied orbitals.

Understanding the interaction of Fe, Fe$^+$, and HFe with simple organic ligands to form coordinatively unsaturated organoiron complexes (i.e. less than 18 electrons around iron) is relevant to work in a variety of diverse fields including catalysis, matrix isolation, and mass spectrometry. For example, the activation of a C–H bond by iron is a well-known step[3,4] in many catalytic cycles. Recent work in an inert Ar matrix has shown that iron atoms can insert into H–H or C–H bonds as indicated by the formation of such complexes as HFeH, HFeCH$_3$, and HFeC$_5$-H$_5$.[5–11] Isolated metal ion–ligand interactions are particularly suitable for study by mass spectrometry, and new techniques have led to rapid development of this field.[3,12–19]
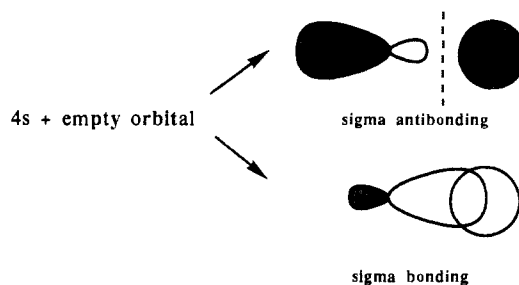

4s + empty orbital   sigma antibonding

sigma bonding

Figure 1. Illustration of the mode of bonding in the $4s^2 3d^6$ configuration of Fe, which rehybridizes the 4s orbital with an empty orbital to give two orbitals that are singly occupied and point in opposite directions. One orbital can form a σ bond while the second orbital is somewhat antibonding.

An important requirement for a theoretical treatment of transition metals is that the splitting between atomic electronic states be reproduced. A comparison of theoretical and experimental state separations is given in Table I for Fe and Fe$^+$. The agreement is exceptionally good, in fact much better than should be expected at this level of theory and no doubt due to the use of an effective core potential on iron. The symmetry of all states included in Table I can be obtained by a single configuration except the ^3P state. The D symmetry states of Fe and Fe$^+$ are described by four singly occupied d orbitals and one doubly occupied d orbital while the F states are described by two doubly occupied d orbitals and the d_{xy}, d_{xy}, and d_{yz} orbitals singly occupied. The wave function of the ^3P state was obtained by locating the lowest energy triplet solution with the 4s orbital doubly occupied. For the Fe$^+$ cation, the ^{4}Fe state is predicted to be 23.6 kcal/mol above the ^6D state at the HF level, while experimentally it is only 5.3 kcal/mol above the ^6D state.[20] Since this is the promotion energy necessary for bonding through a d orbital, it may be assumed that bonding through 4s orbitals will be somewhat overestimated in Fe$^+$ at the HF level. A similar conclusion can be reached for the first two states of Fe whose configurations are $3d^6 4s^2$ and $3d^7 4s^1$ (^5D and ^5F, respectively) where the energy to promote an electron to the 3d sublevel is overestimated by 13.6 kcal/mol ($^5D - ^5F$, 33.4 kcal/mol, HF; 19.8 kcal/mol, exptl[20]).

A detailed analysis of bonding in metal hydrides has been made by several groups.[21–24] The analysis is usually based on (i) the energy required to prepare the metal atom or ion, (ii) the loss of exchange energy caused by forming a covalent bond with an unpaired electron on the metal, (iii) the energy released by formation of a covalent bond. If we consider the neutral complexes first, the ground-state configuration of Fe is $3d^6 4s^2$; promotion to a $3d^7 4s^1$ configuration costs 19.9 kcal/mol of energy (Table I). Bonding of hydrogen to the metal can occur in one of two ways. The first mode, which requires no promotion energy but suffers from an antibonding component to the Fe–H bond, hybridizes the 4s orbital with an empty orbital giving two orbitals of s, p, and d character that can each be occupied by one electron and that point in opposite directions (Figure 1).[21] One orbital is used to form a σ bond to hydrogen and the other, singly occupied, is antibonding in character. This gives an electron configuration of $3d^6 \sigma^2 \sigma^{*1}$. Alternatively, promotion of an electron into the d subshell can occur followed by covalent bonding to the

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Table II. Total Energies (hartrees) at the DZ/ECP Level for Various Species

	state	Fe–H/Fe–C	$\langle S^2 \rangle$	HF	PMP2	PMP3
H	^2S		0.75	−0.497 64	−0.497 64	−0.497 64
H_2	$^1\Sigma_g^+$			−1.126 66	−1.143 87	−1.149 02
CH	$^4\Pi$		3.75	−38.278 20	−38.308 08	−38.315 23
CH_2	$^3B_1$		2.02	−38.917 97	−38.969 39	−38.979 35
CH_3	$^2A_2''$		0.76	−39.552 55	−39.625 27	−39.637 69
CH_4	$^1A_1$			−40.185 43	−40.277 45	−40.291 74
C_5H_5	$^2A''$		0.93	−192.139 35	−192.525 37	−192.554 30
C_5H_6	$^1A_1$			−192.736 17	−193.146 28	−193.178 07
Fe⁺	^6D		8.75	−21.261 30	−21.282 62	−21.283 57
Fe	^5D		6.00	−21.506 04	−21.547 89ᵃ	−21.555 69ᵃ
FeH⁺	$^3\Phi$	2.229	2.98ᵇ	−21.727 15	−21.798 94	−21.793 63
FeH⁺	$^3\Delta$	1.663	3.05ᵇ	−21.697 22	−21.745 76	−21.753 77
FeH⁺	$^5\Pi$	1.667	6.12	−21.792 57	−21.832 59	−21.838 05
FeH⁺	$^5\Delta$	1.693	6.10	−21.792 36	−21.832 39ᵃ	−21.838 01ᵃ
FeH	$^4\Delta$	1.790	4.77ᵇ	−22.031 72	−22.078 05	−22.084 75
FeH	$^6\Delta$	1.788	8.75	−22.047 51	−22.088 33ᵃ	−22.093 93ᵃ
$FeCH_3^+$	$^3A_1$	2.550	2.99ᵇ	−60.795 99	−60.943 80	−60.951 38
$FeCH_3^+$	^3E	2.168	3.32ᵇ	−60.753 44	−60.883 18	−60.898 93
$FeCH_3^+$	^5E	2.237	6.46	−60.851 60	−60.968 04	−60.982 03
$FeCH_3^+$	^5E	2.244	6.49	−60.850 41	−60.966 33	−60.980 38
$FeCH_3$	^4E	2.189	4.77ᵇ	−61.069 83	−61.201 88ᵃ	−61.217 06ᵃ
$FeCH_3$	^6E	2.176	8.75	−61.083 81	−61.214 94	−61.228 27
HFeH	$^3\Delta$	1.737	3.00ᵇ	−22.529 90	−22.596 38	−22.607 08
HFeH	$^3\Pi$	1.747	3.02ᵇ	−22.522 30	−22.583 99ᵃ	−22.595 50ᵃ
HFeH	$^5\Delta$	1.764	6.04	−22.617 63	−22.671 85ᵃ	−22.680 55ᵃ
FeCH⁺	$^3\Delta$	1.960	3.98ᵇ	−59.603 05	−59.696 54	−59.707 54
FeCH⁺	$^7\Delta$	2.038	12.05	−59.580 90	−59.667 38	−59.678 80
HFeCH	$^3\Delta$	1.749/2.050	3.98ᵇ	−60.428 53	−60.537 47	−60.552 37
HFeCH	$^7\Delta$	1.748/2.120	12.05	−60.415 71	−60.514 31	−60.529 32
$FeCH_2^+$	$^4B_1$	2.070	4.96ᵇ	−60.222 71	−60.328 62	−60.341 29
$FeCH_2^+$	$^6A_1$	2.031	8.79	−60.208 38	−60.319 40	−60.331 84
$FeCH_2^+$	$^6B_1$	2.063	8.78	−60.208 22	−60.318 13ᵃ	−60.330 69ᵃ
$HFeCH_3$	^3E	1.736/2.130	3.00ᵇ	−61.566 72	−61.719 92ᵃ	−61.738 47ᵃ
$HFeCH_3$	^5E	1.768/2.155	6.04	−61.654 36	−61.797 90	−61.814 53
η^5-C_5H_5FeH	$^3E_2$	1.729	3.01ᵇ	−214.164 47	−214.647 51	−214.677 16
η^5-C_5H_5FeH	$^5E_2$	1.740	6.04	−214.256 07	−214.727 79ᵃ	−214.755 65ᵃ
$FeC_5H_5^+$	$^5E_2$		6.02	−213.440 27	−213.900 77	−213.925 05
$\overline{CH(CH)_4}FeH$	$^3A_1$	1.775	3.01ᵇ	−214.052 49	−214.517 70	−214.553 46
$\overline{CH(CH)_4}FeH$	$^5A_1$	1.778	6.03	−214.143 97	−214.594 51	−214.628 22

ᵃThe unprojected correlation energy is used because the projected $\langle S^2 \rangle$ deviates more from the expected $\langle S^2 \rangle$ value. ᵇThe wave function is characterized by a significant deviation from the expected value of $\langle S^2 \rangle$.

1s orbital of hydrogen which yields a $3d^7\sigma^2$ configuration. The high promotion energy required and loss of exchange energy for a $4s^03d^7\sigma^2$ configuration compared to a $4s^13d^6\sigma^2$ configuraton should favor the $4s^13d^6\sigma^2$ mode of bonding with hydrogen and methyl.

Method

The GAUSSIAN 86 program was used throughout.[25] The valence double-ζ basis of Dunning and Huzinaga was used for carbon and hydrogen.[26] The core electrons of Fe were fit to an effective core potential while the valence electrons were described with a double-ζ basis (3s2p5d → 2s2p2d) as described by Hay and Wadt.[27] The resulting basis set will be referred to as ECPDZ (effective core potential; double-ζ).

Large basis set calculations with extensive electron correlation have shown that molecular properties of transition-metal complex converge very slowly with respect to the level of theory.[28-37] It is clear that large basis sets that have been used in calculations of metal hydrides and simple metal complexes cannot be used in the study of larger complexes.[38] The purpose of this paper is to explore the use of a level of theory that is able to correctly predict relative trends in bond dissociation energies and geometries but yet to be simple enough to be applied to larger organometallic complexes. After some testing it was decided to study complexes of Fe, Fe⁺, and HFe with simple ligand employing the following: (1) a single configuration with HF/ECPDZ (closed shell) or UHF/ECPDZ (open shell); (2) an effective core potential (ECP) for iron from Hay and Wadt;[27] (3) a full double-ζ basis on the valence shell of iron (4s, 3d, and 4p orbitals); (4) a Dunning basis set (double-ζ) on carbon and hydrogen; and (5) full optimization (within the appropriate point group) and single calculation including electron correlation through MP3/ECPDZ with spin projection[39,40] (PMP3/ECPDZ).

The most difficult aspect of this study was to ensure that the dominant configuration was correctly chosen. In order to ensure that the best choice was made, several optimizations were made with alternate occupation of the starting molecular orbitals. The best choice for a particular electronic state was determined by the lowest PMP3/ECPDZ energy.

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Table III. Calculated Mulliken Populations for Fe or Fe^+ in Various Complexes

	state	s	p	d σ	d π	d δ	d total	total
FeH^+	$^3\Phi$	0.04	0.04	1.02	3.36	2.64	7.02	7.10
FeH^+	$^3\Delta$	0.67	0.14	1.18	2.00	2.96	6.14	6.95
FeH^+	$^5\Pi$	0.75	0.12	1.10	3.00	2.00	6.10	6.97
FeH^+	$^5\Delta$	0.71	0.13	1.12	2.00	3.00	6.12	6.96
FeH	$^4\Delta$	1.26	0.48	1.08	2.00	3.00	6.08	7.82
FeH	$^6\Delta$	1.08	0.62	1.08	2.00	3.00	6.08	7.78
$FeCH_3^+$	$^3A_1$	0.06	0.03	1.02	3.34	2.67	7.03	7.12
$FeCH_3^+$	^3E	0.76	0.06	1.14	2.03	2.95	6.12	6.94
$FeCH_3^+$	^5E	0.83	0.06	1.07	2.03	2.99	6.09	6.98
$FeCH_3^+$	^5E	0.85	0.06	1.06	3.02	2.01	6.09	7.00
$FeCH_3$	^4E	1.21	0.32	1.07	2.02	3.00	6.09	7.62
$FeCH_3$	^6E	0.96	0.45	1.07	2.01	3.00	6.08	7.49
HFeH	^3A	0.82	0.64	1.23	2.00	2.93	6.16	7.62
HFeH	^3A	0.78	0.66	0.74	3.00	2.38	6.12	7.56
HFeH	^5A	0.83	0.65	1.13	2.00	3.00	6.13	7.61
$FeCH^+$	$^3\Delta$	0.40	0.12	1.07	2.14	3.00	6.21	6.73
$FeCH^+$	$^7\Delta$	0.34	0.75	1.12	2.02	3.00	6.14	7.23
HFeCH	$^3\Delta$	0.66	0.44	1.12	2.07	3.00	6.19	7.29
HFeCH	$^7\Delta$	0.66	0.45	1.14	2.02	3.00	6.16	7.27
$FeCH_2^+$	$^4B_1$	0.61	0.07	1.08	2.06	3.00	6.14	6.82
$FeCH_2^+$	$^6A_1$	0.49	0.12	1.10	3.02	2.00	6.12	6.73
$FeCH_2^+$	$^6B_1$	0.46	0.11	1.12	2.02	3.00	6.14	6.71
$HFeCH_3$	^3E	0.70	0.45	1.22	2.02	2.94	6.18	7.33
$HFeCH_3$	^5E	0.71	0.46	1.13	2.02	3.00	6.15	7.32
$\eta^5\text{-}C_5H_5FeH$	$^3E_2$	0.56	0.53	1.20	2.11	2.97	6.28	7.37
$\eta^5\text{-}C_5H_5FeH$	$^5E_2$	0.60	0.53	1.10	2.15	3.00	6.25	7.38
$FeC_5H_5^+$	$^5E_2$	0.27	0.39	1.03	2.28	3.01	6.32	6.98
$\overline{CH(CH)_4}FeH$	$^3A_1$	0.67	0.52	1.23	2.12	2.84	6.19	7.38
$\overline{CH(CH)_4}FeH$	$^5A_1$	0.68	0.53	1.26	2.09	2.81	6.16	7.37

Table IV. Calculated Bond Dissociation Energies $(kcal/mol)^{a,b}$

	HF	PMP2	PMP3
$^5FeH^+ \rightarrow {}^6Fe^+ + H$	21.0	32.7	35.6
$^6FeH \rightarrow {}^5Fe + H$	27.5	26.8	25.5
$^5FeCH_3^+ \rightarrow {}^6Fe^+ + CH_3$	23.7	37.7	38.1
$^6FeCH_3 \rightarrow {}^5Fe + CH_3$	15.8	26.2	21.9
$^5HFeH \rightarrow {}^6HFe + H$	45.5	53.9	55.8
$^3FeCH^+ \rightarrow {}^6Fe^+ + {}^4CH$	39.9	66.4	68.2
$^7FeCH^+ \rightarrow {}^6Fe^+ + {}^4CH$	26.0	48.1	50.2
$^3HFeCH \rightarrow {}^6HFe + {}^4CH$	64.5	88.5	89.9
$^7HFeCH \rightarrow {}^6HFe + {}^4CH$	56.5	74.0	75.4
$^4FeCH_2^+ \rightarrow {}^4Fe^+ + {}^3CH_2$	50.8	42.4	47.4
$^6FeCH_2^+ \rightarrow {}^6Fe^+ + {}^3CH_2$	18.3	42.3	43.2
$^3HFeCH_3 \rightarrow {}^4HFe + CH_3$	-11.0	10.4	10.0
$^3HFeCH_3 \rightarrow H + {}^4FeCH_3$	-0.5	12.8	14.9
$^5HFeCH_3 \rightarrow {}^6HFe + CH_3$	34.1	52.9	52.0
$^5HFeCH_3 \rightarrow H + {}^6FeCH_3$	45.8	53.5	55.6
$^3FeH^+ \rightarrow {}^4Fe^+ + H$	3.6	6.0	6.0
$^4FeH \rightarrow {}^3Fe + H$	65.6	46.0	52.7
$^3FeCH_3^+ \rightarrow {}^4Fe^+ + CH_3$	12.4	16.8	17.1
$^4FeCH_3 \rightarrow {}^3Fe + CH_3$	55.0	43.6	47.8
$^5FeC_5H_5^+ \rightarrow {}^6Fe^+ + C_5H_5$	24.9	58.2	54.7
$^3HFeC_5H_5 \rightarrow {}^4HFe + C_5H_5$	-4.1	27.7	23.9
$^5HFeC_5H_5 \rightarrow {}^6HFe + C_5H_5$	43.4	71.6	67.4

^{a} Zero-point correction is not included. ^{b} For a given multiplicity the lowest electronic state is used to calculate the bond dissociation energy.

Vibrational frequencies have not been calculated and therefore zero-point corrections have not been made.

Electronic symmetries, Fe–H and/or Fe–C bond distances, spin-squared values, and total energies at the UHF, PMP2, and PMP3 levels are collected into Table II. Mulliken populations[41] for the complexes calculated in Table II are given in Table III, and the bond dissociation energies (without zero-point corrections) are given in Table IV.

Results and Discussion

In an analysis of $CrH/CrCH_3$ and $MnH^+/MnCH_3^+$, Ziegler et al.[42] found that the methyl group is destabilizing in $CrCH_3$ due
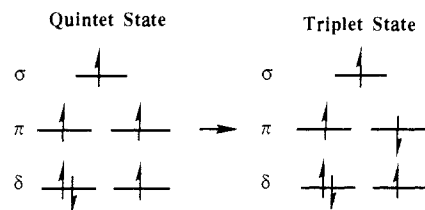

Quintet State   Triplet State

Figure 2. The configuration of the lowest energy triplet (except for FeH^+ and $FeCH_3^+$ where it is the second lowest triplet) can be obtained from the ground-state quintet configuration by a spin flip of an electron in a nonbonding d orbital.

to an unfavorable 2-center 4-electron interaction while the methyl group in $MnCH_3^+$ is stabilizing due to a methyl-to-metal charge transfer (the methyl group is more polarizable).[43] The result is a $M\text{-}CH_3$ bond that is weaker than a M–H bond in the neutral complex but stronger in the ionized complex. While the spread in experimental values is large, the same trend appears in experimental bond energies of iron.[19] The $Fe\text{-}CH_3^+$ bond is about 8 kcal/mol stronger than $Fe\text{-}H^+$ while $Fe\text{-}CH_3$ is about 9 kcal/mol weaker than Fe–H. In the present calculations the trend is reproduced; in the ionized complex $Fe\text{-}CH_3$ is 2.5 kcal/mol stronger and in the neutral complex it is 3.6 kcal/mol weaker than the corresponding metal hydride (Table V).

The absolute bond dissociation energies calculated here are 14 to 20 kcal/mol smaller than the experimental values and from 12 to 17 kcal/mol smaller than very high level ab initio values by Bauschlicher and co-workers[30] (Table V). If one compares the bond dissociation energies (BDE) calculated by Bauschlicher and the PMP3 bond dissociation energies, it is apparent that the BDE at the PMP3 level is consistently 12 kcal/mol too low for the neutral complexes and 16 kcal/mol too low for the ionized complexes. Although further comparisons are necessary, it may be possible to obtain a reasonable estimation of the BDE for an organic ligand bonded to either Fe or Fe^+ in a similar electronic environment by calculating the PMP3 value and adding 12 or 16 kcal/mol, respectively.

While the experimental ground state of Fe^+ is ^6D $(3d^64s^1)$,[20] the present calculations predict the ^4F state $(3d^7)$ to be 1.8 kcal/mol lower in energy (PMP3/ECPDZ). Bonding in FeH^+ can occur either through the 4s orbital or, after promotion, through a 3d orbital. Goddard and co-workers[24,44,45] have made a detailed analysis of metal hydride bonding with the first-row transition metals. When promotion energy and exchange energy loss on bonding are taken into account, they find that the intrinsic strength of a $Fe\text{-}H^+$ bond through the 4s orbital is 31 kcal/mol stronger than bonding through the 3d orbital. The bonding in the quintet state of FeH^+ is in accordance with this analysis. However, if one considers the triplet state of $Fe\text{-}H^+$, bonding through the 4s orbital in the $3d^64s^1$ configuration will require that two unpaired electrons in d orbitals couple as a singlet, which will reduce exchange stabilization by $3K_{dd}$ (about 60 kcal/mol).[24] On the other hand, bonding through a 3d orbital in the promoted $3d^7$ configuration will yield a triplet without significant additional exchange loss. Therefore, bonding in the triplet will occur after promotion of a 4s electron to the 3d subshell because exchange energy loss resulting from bonding to the 4s orbital is more unfavorable than the smaller bond strengths in bonding to a 3d orbital compared to a 4s orbital. The $^3\Phi$ state of FeH^+ is 27.8 kcal/mol higher in energy than the $^5\Delta$ state and the Mulliken populations of the 4s and 4p orbitals are very small $(0.04e^-$ and $0.03e^-$, respectively; Table III). The analogous state of $FeCH_3^+$ $(^3A_1)$ is 19.2 kcal/mol higher than the ^5E state and the 4s and 4p populations are $0.06e^-$ and $0.03e^-$, respectively.

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

(42) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351.

(43) Mandlich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403.

(44) Schilling, J. B.; Goddard, W. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 582.

(45) Schilling, J. B.; Goddard, W. A.; Beauchamp, J. L. *J. Phys. Chem.* **1987**, *91*, 5616.

Table V. Comparison of Bond Dissociation Energies (kcal/mol) for FeH⁺, FeH, FeCH₃⁺, and FeCH₃

	HF	PMP2	PMP3	exptl[a]	exptl − PMP3	theory[b]	theory − PMP3
FeH⁺	21.0	32.7	35.6	49.8 ± 1.4	14.2	52.3	16.7
FeH	27.5	26.8	25.5	46 ± 3	20.5	37.8	12.3
FeCH₃⁺	23.7	37.7	38.1	57.9 ± 2.4	19.8	53.1	15.0
FeCH₃	15.8	26.2	21.9	37 ± 7	15.1	33.4	11.5

[a] See ref 19. [b] Reference 30.

Table VI. Multiplicity Separation (kcal/mol) for Electronic States Differing Only in the Spin Coupling of Two Nonbonding d-Orbital Electrons

	HF	PMP2	PMP3
³FeH⁺[a] − ⁵FeH⁺	59.8	54.5	52.9
³FeCH₃⁺[a] − ⁵FeCH₃⁺	61.6	53.2	52.1
³HFeH − ⁵HFeH	55.0	47.4	46.1
³HFeCH₃ − ⁵HFeCH₃	55.0	48.9	47.7
³HFeC₅H₅ − ⁵HFeC₅H₅	57.5	50.4	49.2

[a] Not lowest triplet state.

Table VII. Comparison of Calculated Mulliken Populations for FeH

	⁴Δ			⁶Δ		
	s	p	d	s	p	d
HF[a]	1.26	0.48	6.08	1.08	0.62	6.08
MCPF[b]	1.15	0.20	6.48	1.05	0.59	6.09

[a] This work. HF/ECPDZ. [b] Modified coupled pair functional: ref 28.

Table VIII. Calculated Separation (kcal/mol) of the ⁴Δ and ⁶Δ States of FeH

	⁴Δ	⁶Δ		⁴Δ	⁶Δ
HF[a]	0	−9.9	MRCI (0.05)[b,c]	0	−5.5 (0.7)[d]
PMP2[a]	0	−6.4	MRCI (0.01)[b,c]	0	−2.1 (1.8)[d]
PMP3[a]	0	−5.8	MCPF[b]	0	2.3
CASSCF[b]	0	−14.3	exptl[e]	0	5.8

[a] This work. [b] Reference 28; Fe and H contracted to 7s6p4d3f2g and 4s3p2d, respectively. [c] Threshold for configuration selection. [d] Davidson correction. [e] Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *J. Chem. Phys.* **1983**, *78*, 5420.

In the HFeX complexes where X = H, CH₃, and C₅H₅ the lowest triplet state is from 46.1 to 49.2 kcal/mol higher than the quintet state (Table VI). The excitation energy is due almost entirely to loss of exchange energy since the triplet configuration only differs by a spin flip of an electron in a nonbonding d orbital (Figure 2). While the complexes FeH⁺ and FeCH₃⁺ also have analogous triplet states, which are 52.9 and 52.1 kcal/mol higher than the quintet state, respectively, a lower energy triplet state is obtained through bonding to a 3d orbital (see above).

A comparison of Mulliken populations is made in Table VII for FeH calculated at the HF/ECPDZ level and the modified coupled-pair functional (MCPF) treatment[46] using a very large basis set.[28] While the populations are nearly identical for the ⁶Δ state of FeH, for the ⁴D state, the HF/ECPDZ level indicates too little 3d orbital population and too much 4s and 4p population compared to the MCPF results. As pointed out above, the HF method overestimates the energy required to promote an electron to the 3d subshell. Hence, the underestimation of the d-orbital population may reflect the overestimation of the promotion energy.

A comparison of the level of theory employed here with very high level theory[28] is presented for the splitting of the ⁴Δ and the ⁶Δ states of FeH in Table VIII. At the PMP3 level the ⁶Δ state is predicted to be 5.8 kcal/mol more stable than the ⁴Δ state while experiment predicts the ⁴Δ state to be lower by the same amount. Bauschlicher and Langhoff[28] used a basis on Fe and H contracted to 7s6p4d3f2g and 4s3p2d, respectively, and at the CASSCF level they predict the ⁶Δ state to be lower by 14.3 kcal/mol. Only after

(46) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606. Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J. Chem. Phys.* **1985**, *82*, 890.

Table IX. Calculated Energy Difference (kcal/mol) between States with Different Spin Multiplicity[a]

	HF	PMP2	PMP3
⁴FeH − ⁶FeH	9.9	6.4	5.8
⁴FeCH₃ − ⁶FeCH₃	8.8	8.2	7.0
³FeCH⁺ − ⁷FeCH⁺	−13.9	−18.3	−18.0
³HFeCH − ⁷HFeCH	−8.0	−14.5	−14.5
⁴FeCH₂⁺ − ⁶FeCH₂⁺	−9.0	−5.8	−5.9

[a] The lowest electronic state of a given multiplicity is used to calculate the energy difference.

Table X. Calculated Sequential Bond Dissociation Energies (kcal/mol) at the PMP3/ECPDZ Level

	1st bond broken		2nd bond broken	
HFeCH₃	H–Fe	(55.6)	Fe–CH₃	(21.9)
HFeCH₃	Fe–CH₃	(52.0)	H–Fe	(25.5)
HFeH	H–Fe	(55.8)	Fe–H	(25.5)

Table XI. Comparison of Bond Dissociation Energies (kcal/mol) for Multiply Bonded Metal Complexes

	HF	PMP2	PMP3	APUMP4	exptl[a]	Δ
⁵Fe—CH₃⁺	23.7	37.7	38.1		57.9 ± 2.4	19.8
⁴Fe=CH₂⁺	50.8	42.4	47.4		83.0 ± 4[b]	35.6
³Fe≡CH⁺	39.9	66.4	68.2		118 ± 5[c]	51.6
Cr=CH₂⁺[d]				32.0	54 ± 7	22.0
Mn=CH₂⁺[d]				57.9	94 ± 4	36.1

	MCSCF	+ CI	POLCI	exptl[a]	Δ
Cr—CH₃⁺[e]	12.0	17.0	19.5	30 ± 5	10.5
Cr=CH₂⁺[e]	26.3	38.7	43.2	54 ± 4	10.8
Cr≡CH⁺[e]	53.8	70.8	78.2	92 ± 7[c]	13.8

[a] Reference 19. [b] Armentrout, P. B.; Sunderlin, L. S.; Fisher, E. R. *Inorg. Chem.* **1989**, *28*, 4437. [c] Thermochemical value plus ⁴Σ⁻ − ²Π splitting of CH (17 kcal/mol). [d] Reference 47. [e] Reference 34.

applying the Davidson correction to a large multireference CI is the correct order obtained. The most accurate splitting is obtained by using the large basis set and the MCPF treatment.

Calculated splitting between states of different multiplicity is given in Table IX. Since the bonding in FeH and FeCH₃ is similar, it is reasonable to predict that improvement in theory will affect the two systems similarly. If one assumes that ⁴FeCH₃ will be stabilized by 11.2 kcal/mol with respect to ⁶FeCH₃, which is the value obtained by comparing PMP3 and experiment for FeH, one might predict that the quartet state is in reality about 4 kcal/mol lower than the sextet state. Another observation from Table IX is that at the PMP3 level, the high-spin state is preferred when iron forms a single bond while the low-spin state is preferred when iron forms a multiple bond.

The strength of a metal–ligand bond is dependent on the order in which it is broken. In the complex HFeCH₃, the FeH BDE is 55.6 kcal/mol if it is the first bond to be broken but only 25.5 kcal/mol if it is the second bond to be broken (Table X). Likewise, the Fe–CH₃ bond is worth 52.0 or 21.9 kcal/mol if it is the first or second bond to be broken, respectively. In the complex HFeH, the two FeH BDE are 55.8 and 25.5 kcal/mol, respectively. The sizable difference in BDE is understandable if one realizes that the electronic preparation (reorganization) that Fe must undergo in order to bind the first ligand is not necessary to bind the second ligand. Therefore, in reverse order, the first bond is stronger as the metal fragment is not stabilized by electronic relaxation while the second bond is weaker since the iron

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Table XII. Calculated C–H Bond Dissociation Energies (kcal/mol)

|	HF	PMP2	PMP3	exptl[a]	exptl – PMP3
CH_4	84.9	97.0	98.1	105.1	7.0
C_5H_6	62.2	77.4	79.1	86.7[b]	7.6
$FeCH_3^+$	82.4	89.0	89.8	97[c]	
$FeCH_2^+$	76.6	84.4	85.4	92[c]	

[a] Reference 48. [b] The BDE of the C–H bond in C_5H_6 is assumed to be the same as the C–H bond BDE in propene (propene → allyl radical). [c] The estimated value is obtained by adding 7 kcal/mol to the calculated value.
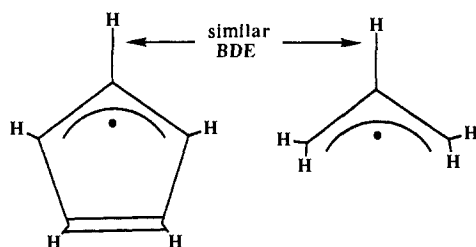
Figure 3. Delocalization in the cyclopentadienyl radical showing the resemblance to an allyl radical.

atom undergoes relaxation. The major cost of preparation is the rehybridization of the 4s orbital on iron to form two orbitals each of which is singly occupied and capable of σ bonding. In a sense, the cost of rehybridization must be paid whether one or two σ bonds are formed.

Bond dissociation energies for iron–carbon multiple bonds are underestimated by an even larger amount than found for iron–carbon single bonds (Table XI). The BDE of the double bond in $Fe=CH_2^+$ is predicted to be too small by 35.6 kcal/mol and the BDE of the triple bond in $Fe\equiv CH^+$ is predicted to be too small by 51.6 kcal/mol. The dissocation limit of the $Fe\equiv CH^+$ complex is computed with respect to the quartet state of CH which is known to be 17 kcal/mol above the doublet state. The experimental thermodynamic BDE of 101 ± 5 kcal/mol[19] (which is with respect to the doublet state) has been adjusted by 17 kcal/mol in Table XI to reflect the quartet state of CH as the reference. It appears that the magnitude of deviation between theory and experiment depends upon the bond order of the iron–carbon bond and is probably due to the small basis set and limited electron correlation. Larger basis set calculations[34] with POLCI on the $Cr–CH_3^+$, $Cr=CH_2^+$, and $Cr\equiv CH^+$ series reveal a 10–14 kcal/mol underestimation of the bond dissociation energy (Table XI). Very recent BDE's were reported[47] for $Cr=CH_2^+$ and $Mn=CH_2^+$ with use of a triple-ζ basis with electron correlation accounted for at the APUMP4 level (approximate projected unrestricted Møller-Plesset to 4th order). The degree of underestimation (22.0 and 36.1 kcal/mol, Table XI) is similar to that found for $Fe=CH_2^+$ (35.6 kcal/mol).

The effect of Fe^+ on the C–H BDE was also calculated from eq 1 and 2 (Table XII). In addition, the BDE was calculated

$$^5FeCH_3^+ \rightarrow {}^4FeCH_2^+ + H \qquad (1)$$

$$^4FeCH_2^+ \rightarrow {}^3FeCH^+ + H \qquad (2)$$
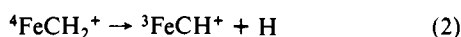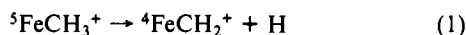
for CH_4 and C_5H_6 and compared with experiment.[48] At the PMP3 level the C–H BDE of CH_4 is underestimated by 7.0 kcal/mol (Table XII). The C–H BDE of cyclopentadiene is calculated to be 7.6 kcal/mol lower than the BDE for propene going to the allyl radical which should be close to that of C_5H_6 since delocalization in the C_5H_5 radical closely resembles that of the allyl radical (Figure 3). The C_5H_5 radical has C_s symmetry rather than C_5 symmetry due to a Jahn–Teller energy lowering.[49]

(47) Takahara, Y.; Yamaguchi, K.; Fueno, T. *Chem. Phys. Lett.* **1989**, *158*, 95.

(48) Colussi, A. J. *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC: Boca Raton, FL, 1988; p 25.

(49) Engelman, R. *The Jahn-Teller Effect in Molecules and Crystals*; Wiley-Interscience: New York, 1972.

Table XIII. Comparison of Bond Dissociation Energies (kcal/mol) at the PMP3/ECPDZ Level for Fe^+–X and HFe–X

|	X = H	X = CH	X = CH_3	X = C_5H_5
Fe^+–X	35.6	68.2	38.1	54.7
HFe–X	55.8	89.9	52.0	67.4

Table XIV. Calculated Reaction Energies (kcal/mol) for Insertion of Fe into a H–H or C–H Bond

	product	HF	PMP2	PMP3	CASSCF +CI	PMP3 – CASSCF+CI
			^5Fe + Substrate			
H_2	^5HFeH	9.4	12.5	15.2	0.6[a]	15.8
$^3CH_2$	^7HFeCH	5.2	1.9	3.6		
$^3CH_2$	^3HFeCH	-2.8	-12.7	-10.9		
CH_4	$^5HFeCH_3$	23.3	17.2	20.6		
C_5H_6	$^5HFeC_5H_5$	-8.7	-21.1	-13.7[b]		
			^3Fe + Substrate			
H_2	^3HFeH	16.5	34.2	28.3	16.0[a]	12.3
CH_4	$^3HFeCH_3$	30.3	40.6	35.4		
C_5H_6	$^3HFeC_5H_5$	0.8	3.7	2.5		

[a] Reference 29. [b] Margraves[11] has estimated the reaction energy to be between -40 and -60 kcal/mol. An underestimation by 30–50 kcal/mol, which is the known underestimation of the bond dissociation energy for iron to carbon multiple bonds, would put the calculated value into this range (-44 to -64 kcal/mol).

Replacing H with Fe^+ in CH_4 causes the C–H BDE to decrease by 8.3 kcal/mol, which indicates that the metal cation has a stabilizing effect on the methyl radical. Removing a second hydrogen atom from $FeCH_3^+$ requires slighlty less energy (4.4 kcal/mol) than the first. If 7 kcal/mol is used as an approximate correction factor (difference between experiment and theory for CH_4), the predicted first and second C–H BDEs in $Fe–CH_3^+$ are 97 and 92 kcal/mol, respectively.

It is interesting to compare the bond dissociation energy of Fe^+-X and HFe–X (Table XIII), since the fragments Fe^+ and HFe are isoelectronic if one considers the latter fragment to be H^-–Fe^+. On average the Fe^+-X BDE is about 15 to 20 kcal/mol less than HFe–X. Since the ^6D state of Fe^+ is predicted to be

$$^5Fe^+-X \rightarrow {}^6Fe^+ + X \qquad (3)$$

$$^5HFe-X \rightarrow {}^6HFe + X \qquad (4)$$
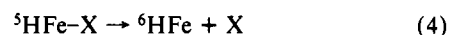
7.1 kcal/mol too *unstable* with respect to the ^4F state (Table I) while the $^6\Delta$ state of HFe is predicted to be 11.6 kcal/mol too *stable* with respect to the $^4\Delta$ state (Table VIII), the difference between the Fe^+-X BDE and the HFe–X BDE could be overestimated.

Heats of reaction have been calculated for the insertion of ^5Fe or ^3Fe into H–H or C–H bonds in Table XIV. For insertion into a H–H bond the exothermicity is underestimated by 12–16 kcal/mol when comparing with high-level CASSCF+CI results. It would be anticipated that the underestimation would be of the same magnitude for the insertion into the C–H bond of CH_4 from which one could conclude that formation of $^5HFeCH_3$ from ^5Fe + CH_4 could be nearly thermoneutral (or slightly endothermic). A theoretical semiempirical study of the insertion of Fe into the C–H bond of methane has estimated the reaction to be 47 kcal/mol endothermic.[50] Insertion into a C–H bond of $^3CH_2$ may be underestimated by an even greater amount since the method used here considerably underestimates the bond stength of iron–carbon triple bonds. It is certain that the reaction to form ^3HFeCH from ^5Fe + $^3CH_2$ should be exothermic and perhaps by as much as 40 to 60 kcal/mol.

Margrave has shown[11] that iron atoms insert in the C–H bond of cyclopentadiene and that the IR spectra of the complex at 14 K in an argon matrix is consistent with C_{5v} symmetry. Although the barrier to addition has not been calculated, the calculated exothermicity is consistent with the formation of a stable complex

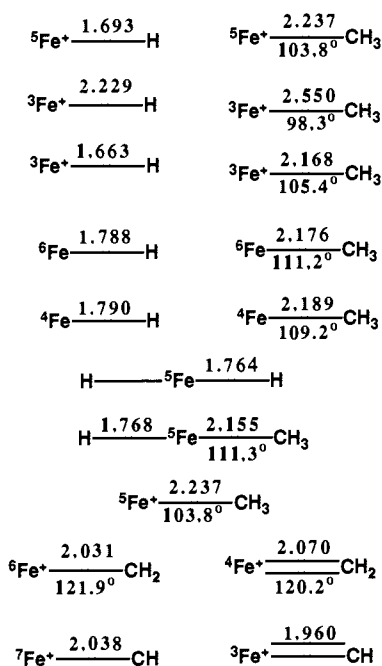(50) Anderson, A. B.; Baldwin, S. *Organometallics* **1987**, *6*, 1621.

^{5}Fe⁺——1.693——H ^{5}Fe⁺——$\dfrac{2.237}{103.8°}$——CH₃

^{3}Fe⁺——2.229——H ^{3}Fe⁺——$\dfrac{2.550}{98.3°}$——CH₃

^{3}Fe⁺——1.663——H ^{3}Fe⁺——$\dfrac{2.168}{105.4°}$——CH₃

^{6}Fe——1.788——H ^{6}Fe——$\dfrac{2.176}{111.2°}$——CH₃

^{4}Fe——1.790——H ^{4}Fe——$\dfrac{2.189}{109.2°}$——CH₃

H————^{5}Fe——1.764——H

H——1.768——^{5}Fe——$\dfrac{2.155}{111.3°}$——CH₃

^{5}Fe⁺——$\dfrac{2.237}{103.8°}$——CH₃

^{6}Fe⁺——$\dfrac{2.031}{121.9°}$——CH₂ ^{4}Fe⁺——$\dfrac{2.070}{120.2°}$——CH₂

^{7}Fe⁺——$\dfrac{2.038}{}$——CH ^{3}Fe⁺$\equiv\dfrac{1.960}{}$CH

Figure 4. Selected geometric parameters for Fe complexes optimized at the HF/ECPDZ level. The Fe–H or Fe–CH₃ bond distance is given above the line in ångstroms and the Fe–C–H bond angle is given below the line in degrees.
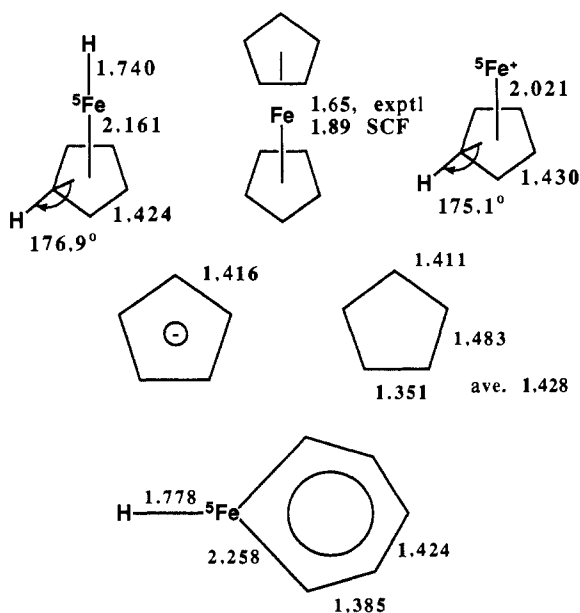

Figure 5. Selected geometric parameters for HFeC₅H₅ isomers and related complexes optimized at the HF/ECPDZ level.

of C_{5v} symmetry (Figure 5). If the underestimation of the exothermicity is assumed to be in the range of 30–50 kcal/mol, which is the range of error in the BDE of Fe=CH₂⁺ and Fe≡CH⁺ (Table XI), the exothermicity is predicted to be between 44 and 64 kcal/mol, which is also in agreement with an estimate made by Margrave.[11]

Geometries of Iron Complexes

The geometries of simple iron complexes optimized at the UHF/ECPDZ level are generally in good agreement with previous calculations. For example, the Fe–H distances for the $^5\pi$ and $^5\Delta$ states of FeH⁺ are predicted to be 1.667 and 1.693 Å compared to a GVB value[45] of 1.641 and 1.653 Å and large basis set ROHF values[32] of 1.657 and 1.678 Å, respectively. When large basis

sets including electron correlation are used,[32] the iron–hydrogen distance significantly decreases. The distances in the $^5\pi$ and $^5\Delta$ states of FeH⁺ decrease to 1.578 and 1.611 Å, respectively. At a similar level, the Fe–H bond distances in the $^4\Delta$ and $^6\Delta$ states of Fe are also predicted to be shorter than found here (1.790, 1.788 Å, UHF/ECPDZ: 1.578, 1.678 Å, MRCI[28]). The $^3\Delta$, $^3\Pi$, and $^5\Delta$ states of HFeH are calculated to have FeH distances of 1.737, 1.747, and 1.764 Å compared to CASSCF values[29] of 1.70, 1.69, and 1.74 Å, respectively.

It is probably more productive and certainly more reliable to compare trends at a single computational level. The geometries of the triplet/quintet state and quartet/sextet states are very similar when the corresponding configurations differ only in the spin coupling of the nonbonding d-orbital electrons. For the lowest triplet state of FeH⁺ and FeCH₃⁺ the configuration is different from the quintet state and corresponds to bonding through the 3d orbital rather than the 4s orbital. The corresponding FeH and FeC distances in the triplet are 0.54 and 0.31 Å longer than those in the quintet state (Figure 4).

The iron complexes HFeH and HFeCH₃ are predicted to have shorter Fe–H and Fe–CH₃ bond distances than the isolated FeH or FeCH₃ fragment. A reasonable explanation is that adding the second ligand reduces the antibonding component of the rehybridized orbital not involved in σ bonding to the first ligand.

The complexes H–Fe–X, X = CH₃ and C₅H₅, have a degenerate electronic state in C_{3v} and C_{5v} symmetry (E and E₂, respectively), and should be subject to a Jahn–Teller distortion.[49] In order to determine the magnitude of stabilization, the ^{5}E state of HFeCH₃ was reoptimized within the C_s point group. Very little geometric reorganization was observed; the largest change in geometry for the ^{5}A″ state was the HFeC bond angle, which decreased 0.2 deg to 179.8°. The PMP3 energy in C_s symmetry was 0.7 kcal/mol lower than the PMP3 energy in C_{5v} symmetry. The extent of stabilization in the HFeC₅H₅ complex, which was not calculated, is expected to be similar.

Another comparison that can be made is the reduction of the Fe–C bond distance as the bond order increases. In the series Fe⁺—CH₃, Fe⁺=CH₂, and Fe⁺≡CH, the bond distances decrease in the order 2.237, 2.070, and 1.960 Å. However, bond distance is not a good indicator of bond order as indicated by the ^{6}A₁ state of FeCH₂⁺, which has a single Fe–C bond shorter than the ^{4}B₁ state (2.031, 2.070 Å). Similarly the $^7\Delta$ state of FeCH⁺ is only slightly longer than the $^3\Delta$ state (2.038, 1.960 Å).

The cyclopentadienyliron hydride complex (^{5}E₂ state) is characterized by a short FeH bond (1.740 Å) and a long Fe–C₅H₅ distance (2.161 Å, Figure 5). The metal–ring distance is much longer than the metal–ring distance in ferrocene (1.65 Å).[33] However, the HFe–ring distance may be overestimated since it is known that HF calculations considerably overestimate the metal–ring distance in ferrocene (1.89 Å calculated).[33] The calculated C–C distances in the complexed ring are intermediate to the C–C distances in C₅H₅ anion and the average C₅H₅ distances in the radical, which is in keeping with a predicted charge transfer of 0.43e⁻ to the ring. In the complex of Fe⁺ with C₅H₅, the metal-to-ring distance has decreased (2.021 Å) and the C–C distances have increased (1.430 Å). The latter distances are much closer to the average C–C distance in the radical which reflects the smaller charge transferred to the ring (0.03e⁻).

An alternative complex was studied with FeH included in a six-membered ring (Figure 5). The assumed-planar complex was found to be 80.0 kcal/mol higher in energy than the cyclopentadienyliron hydride at the PMP3/ECPDZ level, which indicates that the complex is an unlikely candidate for the species observed by Margrave[11] in an inert matrix.