

# Ground- and Excited-State Iron Atom Interactions with Methane and Ethylene. Molecular Orbital Theory for Coordination and CH Activation

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An ASED-MO study shows the oxidative addition of CH bonds in methane and ethylene in ground-state ( $3d^64s^2$ ) Fe atoms is hindered by a closed-shell repulsion between the CH  $\sigma$  bond pair and the 4s electrons of the Fe atoms. Excitation of the Fe atom to the  $3d^64s^14p^1$  configuration greatly reduces the barrier to oxidative addition because the 4p electron donates into the CH  $\sigma^*$  orbital as the bond is stretched. This provides an explanation for the experimental observations of the Margrave and Ozin groups. Ethylene is found to  $\pi$  coordinate to  $d^6s^2p^0$  Fe more weakly than it  $\sigma$  coordinates. This weakness is caused by the closed-shell repulsion of the ethylene  $\pi$  and Fe s orbitals and explains the observations of Margrave. Structure effects on CH activation are discussed, and the structures of methyliron and ethynyliron hydride products are calculated and analyzed.

## Introduction

It has recently been established in the laboratories of Margrave<sup>1</sup> and Ozin<sup>2</sup> that methane oxidatively adds to a number of transition-metal atoms in low-temperature matrices when exposed to light of a frequency which promotes metal valence s to p excitations:



The Margrave group has found a small softening of CH vibrational modes due to Fe-CH<sub>4</sub> interactions in an Ar host matrix. Both groups observed higher quantum yields in a neat methane matrix. The question naturally arises about the nature of the bonding interactions and photoactivation process.

From vibrational analyses the Margrave group has determined that acetylene<sup>3</sup> and ethylene<sup>4</sup> bind to iron atoms through one and two hydrogen atoms, respectively, when complexed in inert-gas argon matrices. There is experimental<sup>5</sup> and theoretical<sup>6-7</sup> evidence that acetylene and ethylene form strong  $\pi$ -complex bonds to iron surfaces and, of course,  $\pi$  coordination in complexes is understood in the Dewar-Chatto-Duncanson bonding description.<sup>8</sup> Why it is that an iron atom does not  $\pi$  bond acetylene and ethylene is an interesting question. Further, these complexes can be photoactivated like methane:



The purpose of the present study is to calculate structures and stabilities for CH<sub>4</sub>...Fe and H<sub>2</sub>CCH<sub>2</sub>...Fe complexes and transition-state structures and relative activation energies for H atom abstraction from methane and

ethylene by ground- and excited-( $s^2p^0 \rightarrow s^1p^1$ ) state iron atoms. Various reaction pathways are assumed. The ASED-MO procedure is used, which was also used to carry out the above-mentioned<sup>5-7</sup> surface studies. The questions raised above will be addressed and explanations given through the use of molecular orbital theory. Key results are (a) Fe...C<sub>2</sub>H<sub>4</sub>  $\pi$  coordination is destabilized relative to  $\sigma$  coordination by the closed-shell Fe  $s^2$ -C<sub>2</sub>H<sub>4</sub>  $\pi^2$  repulsion, (b)  $4s^14p^1$  excited-state Fe atoms activate CH bonds through the formation of a stabilized CH  $\sigma^* + Fe 4p \sigma$  orbital which contains the promoted electron, and (c) the iron hydride products are bent.

## Theoretical Method

The ASED-MO theory partitions the electronic charge density function of a molecule into rigid free-atom densities which follow the nuclear centers and a flexible nonperfectly following density redistribution function that is due to chemical bond formation.<sup>9</sup> The atom superposition energy is calculated by using the atomic densities and integrating the electrostatic force on the nucleus of the less electronegative atom of each pair of atoms.<sup>9</sup> The energy due to electron delocalization can in principle be calculated from integration of the force due to the charge density redistribution.<sup>9</sup> This density is not available, but the energy is well approximated by a molecular orbital delocalization energy in the ASED-MO theory.<sup>10</sup> The hamiltonian used shares some features with the extended Hückel hamiltonian and is semiempirical, employing valence-state ionization potentials as parameters and single- $\zeta$  s and p and single- or double- $\zeta$  d orbitals. In this paper the C and H VSIP are decreased by 1 eV and the Fe VSIP are increased by 1 eV to approximate the results of self-consistency as in the above-mentioned surface studies.<sup>5,6</sup> One change has been made: the carbon 2s ionization potential is now, for reasons given in a recent study,<sup>11</sup> based on the experimental value, as are the other ionization potentials, rather than the extended Hückel value. This change is important to the orientation of CO on platinum surfaces<sup>11</sup> but does little to the description of CH bonds. For example, the new VSIP changes the CH bond length in methane by less than 0.01 Å and increases the calculated CH bond strength by 0.1 eV. ASED-MO calculations overestimate the dia-

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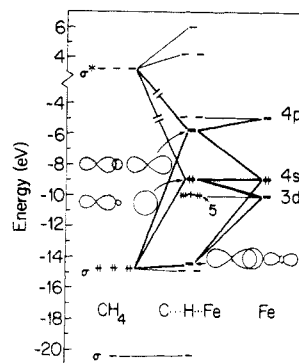
	$s^2p^0$	BE (kJ/mol)	$s^2p^0$	EA (kJ/mol)	$s^1p^1$	EA (kJ/mol)
1-fold		10		10	—	0
2-fold		3		221		50
3-fold		11		252		73

**Figure 1.** Calculated structures and energies for  $\text{CH}_4/\text{Fe}$  complexes and CH activation by ground-state  $s^2p^0$  and  $s^1p^1$  Fe. BE and EA refer to binding and activation energies. Bond lengths and angles are optimized in 0.01-Å and 1-deg increments. Transition-state CH and CFe distances are optimized in 0.1-Å increments. As discussed in the text, EA for the 1-fold orientation should be larger than the calculated value.

tomic CH bond length by 0.04 Å and overestimate the methane, acetylene, and ethylene CH bond lengths by 0.12, 0.08, and 0.08 Å, respectively.<sup>5</sup> The calculated CH dissociation energy ( $D_0$ ) of methane is 5.4 eV, overestimating the experimental value of 4.5 eV by 20%. Experimentally observed chemisorption structures and decomposition reactions of acetylene<sup>5,6</sup> and ethylene<sup>5</sup> on several iron surfaces have been calculated and explained by using the ASED-MO theory. Structures of iron complexes have been calculated and compare well with experiment. For example, calculations with a very similar parameter set on (cyclobutadiene) iron tricarbonyl<sup>12</sup> produce Fe-CO and Fe-C(ring) lengths within 3% of experiment and OC-Fe-CO angles identical with experiment. We have also calculated the structure and spin density for the iron pentacarbonyl anion,<sup>13</sup> finding agreement with experiment. On the basis of these and other studies, we expect to be able to obtain numerically reasonable results for the bonding and reaction of methane and ethylene with iron atoms in the present work. The most significant conclusions to be gained from this type of study are the development of molecular orbital explanations for structures and reactivities, and such explanations are the main focus. In this study carbon bond lengths are optimized in 0.01-Å steps and angles in 1-deg steps. Because of the softness of the potential, transition-state Fe-C and Fe-H distances are optimized to the nearest 0.1 Å. Note that these calculations systematically overestimate equilibrium CH internuclear distances by  $\sim 0.1$  Å and C=C bond lengths by  $\sim 0.15$  Å. For simplicity, no attempt is made to model the inert-gas or methane matrix.

**Methane CH Activation by  $s^1p^1$  Fe and the Properties of  $\text{HFeCH}_3$ .** The three symmetric ways of coordinating methane to a ground-state ( $s^2p^0$ ) iron atom, 1-fold, 2-fold, and 3-fold, were studied. The 3-fold one was calculated to be slightly favored—see Figure 1. These energies are about  $1/3$  of the value calculated for methane absorption on an iron surface as discussed in ref. 5.

The 1-, 2-, and 3-fold coordinations of Figure 1 were used as starting points for the CH activation studies. Of the three, the linear C-H-Fe 1-fold coordination yielded the lowest barrier for hydrogen abstraction by  $s^2p^0$  iron. This barrier is clearly underestimated because for H abstraction the activation energy should be the reaction energy, which is around 268 kJ/mol. The actual mechanism should be an oxidative addition as in our recent study of methane



**Figure 2.** Orbital correlation diagram for the 1-fold transition state of Figure 1 for methane CH bond scission by a ground-state Fe atom. Important interactions discussed in the text are heavy to stand out. Occupations of highest occupied orbitals are shown explicitly.

activation on metal surfaces.<sup>14</sup> Nevertheless the electronic structure for the abstraction transition-state series provide the framework for discussing the results of photoactivation of the iron atoms. As shown in Figure 2 the interaction between the CH  $\sigma$  bond and the doubly occupied Fe 4s orbital is closed-shell, and this interaction is essentially responsible for the activation barrier.

A few comparisons with other theoretical work are possible. Saillard and Hoffmann<sup>15</sup> reported an interesting extended Hückel study of some of the descriptive aspects of the orbital interactions accompanying CH activation by metal complexes. Ground and excited metal atoms were not considered, and activation energies and transition-state orbitals were not calculated by them. Nonlinear C...H...M transition states have been examined in CI calculations for Ni<sup>16</sup> and GVBCI calculations for Pd.<sup>17</sup> Transition-state energies are 100–200 kJ/mol in those insertion studies which lead directly to methyl metal hydrides.

From Figure 2, which shows the electronic structure at the transition state for ground-state  $s^2p^0$  iron, it is clear that if there is an  $s \rightarrow p$  excitation prior to the onset of reaction, the p electron will enter the stabilized CH  $\sigma^* + \text{Fe } p$  orbital as the reaction proceeds. In our calculations, for the 1-fold orientation this is a downhill reaction with no activation energy, as shown in Figure 1. For the 2- and 3-fold orientations the calculated activation energies are reduced by  $\sim 75\%$ . For them as well, the CH  $\sigma^* + \text{Fe } p$  bonding orbital is occupied by 1 electron as the transition state is reached. It is this partial occupation of the CH  $\sigma^*$  orbital which reduces the barrier and causes it to occur with a smaller CH stretch, as shown in Figure 1. The actual mechanism is likely to be Fe insertion into the CH bond (oxidative addition) as for the non-activated case and ultimately the excitation energy must be liberated as heat as both the Fe 4s and 4p electrons end up in Fe-H and Fe-C bonds of methyliron hydride. This finding explains the photoactivation of methane by iron and the various other transition-metal atoms as observed by the Margrave and Ozin groups. It is noted that the possibility of p electron donation to the CH  $\sigma^*$  orbital was discussed by Ozin and co-workers<sup>2</sup> for the case of excited Cu  $d^{10}s^0p^1$ , and our results confirm their belief.

In our calculations the methyl radical orbital energy lies 1.39 eV below the Fe 4s level, which means the methyl species which is formed during dehydrogenation bonds to

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Table I. Atomic Parameters Taken from Ref 5 But with the New Carbon 2s Ionization Potential, IP (eV)

atom	s			p			d					
	n	IP	$\zeta$	n	IP	$\zeta$	n	IP	$c_1$	$\zeta_1$	$c_2$	$\zeta_2$
Fe	4	8.87	1.7	4	4.87	1.4	3	10.0	0.5366	5.35	0.6678	1.8
C	2	15.59	1.658	2	10.26	1.618						
H	1	12.6	1.2									

<sup>a</sup> See text. Slater orbital parameters are principal quantum number  $n$ , orbital exponents  $\zeta$  (au), and linear coefficients for double- $\zeta$  d orbitals,  $c$ .

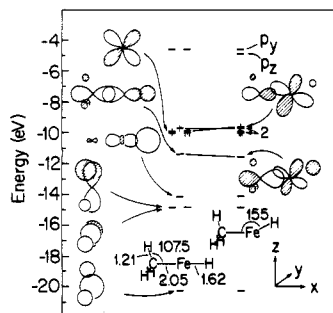


Figure 3. Calculated structure for methyliron hydride and orbital correlation diagram illustrating various methyl orbitals and the orbital stabilization responsible for the C-Fe-H bend from linearity.

the iron atom as an anion. We calculate a stability for methyl iron hydride formation of 311 kJ/mol. As shown in Figure 3, the C-Fe  $\sigma$  orbital energy level lies above the Fe-H  $\sigma$  level. The C and H charges are calculated to be  $-0.36$  and  $-0.44$ , respectively, and the Fe charge is 1.03. There is some Fe 4s contribution to these orbitals with a net 4s occupation of 0.65 electron, but from the electronic structure, the net result of methyl iron hydride formation is the transfer of the Fe 4s electrons to H<sup>+</sup> and <sup>•</sup>CH<sub>3</sub>, forming anions which bond with covalent stabilization and back-donation to the Fe 3d orbitals. The iron atom effectively changes from 3d<sup>6</sup>4s<sup>2</sup> to 3d<sup>8</sup> in the transaction. Since the ASED-MO method cannot handle energies for such state changes in an explicit way, the effects can be estimated empirically. If we suppose a two-step process, the destabilization energy to go from 3d<sup>6</sup>4s<sup>2</sup> to 3d<sup>7</sup>4s<sup>1</sup> is 83 kJ/mol,<sup>18</sup> and once this d electron transfers to form an anion, the destabilization energy for Fe<sup>+</sup> to go from 3d<sup>6</sup>4s<sup>1</sup> to 3d<sup>7</sup>s<sup>0</sup> is 22 kJ/mol.<sup>18</sup> This Fe<sup>+</sup> would then form the second anion by electron transfer, resulting in d<sup>6</sup>s<sup>0</sup> Fe<sup>2+</sup> which corresponds to the electronic structure of methyliron hydride in figure 3. From these figures and the 3d-4s energy difference in Table I, the reaction energy to form the methyliron hydride product becomes 311 + 105 - 218 = 198 kJ/mol, which should lie closer to the experimental value.

Figure 3 also explains why methyliron hydride is bent; we predict the CFeH angle to be 25 deg. Bending stabilizes the Fe-C bonding orbital by allowing the nonbonding Fe d<sub>zz</sub> orbital to mix in. The antibonding counterpart lies in the high-spin d set and is half-filled, so there is a net increase in bond order on bending. The calculated barrier to rotating the methyl group is very small, with the eclipsed conformation favored by less than 1 kJ/mol. The calculated stability gain due to bending is only 3 kJ/mol. It is noted that HMOH, where M is Sc, Ti, V, Cr, Mn, Fe, Co, or Cu, is also bent,<sup>19</sup> and the correlation diagram in Figure 4 should apply to and explain these departures from linearity too. Finally, the vibrational analysis of Ozin and

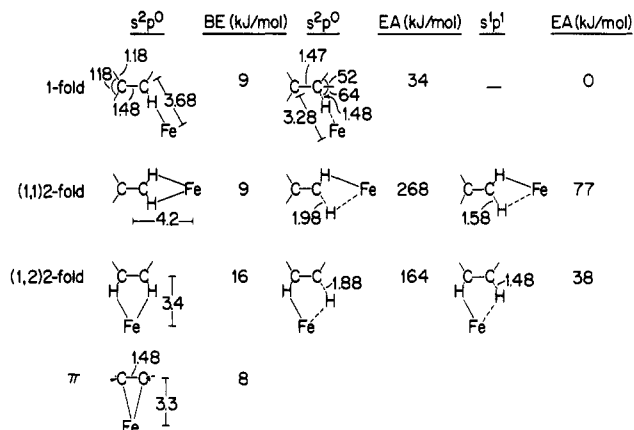


Figure 4. As in Figure 1, but for C<sub>2</sub>H<sub>4</sub>/Fe complexes and activation.

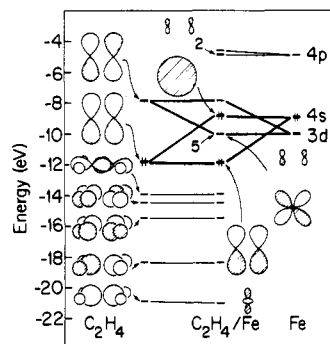


Figure 5. Orbital correlation diagram for the C<sub>2</sub>H<sub>4</sub>/Fe  $\pi$  complex for Fe in the s<sup>2</sup>p<sup>0</sup> ground state. Important interactions discussed in the text are heavy to stand out.

McCaffrey<sup>20</sup> led them to conclude HFeCH<sub>3</sub> is bent.

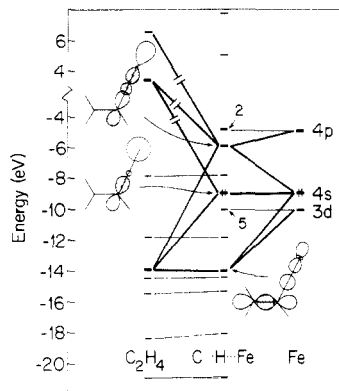
**Bonding of H<sub>2</sub>CCH<sub>2</sub> to an Fe Atom.** Shown in Figure 4 are the calculated structure parameters and energies for iron-ethylene complexes. Let us begin by discussing the  $\pi$  complex structure, which is less stable than any of those involving Fe-H bonding, in agreement with the observations of the Margrave group for ethylene-iron in argon and krypton matrices.<sup>1</sup> The  $\pi$ -coordination structure has low stability because of the state of the Fe atom, d<sup>6</sup>s<sup>2</sup>. When in this (ground) state, the closed-shell  $\pi^2$ -s<sup>2</sup> repulsion prevents both a close approach of the ethylene to Fe and the formation of strong bonds to Fe. Figure 5 shows the bonding in this fragile complex. The  $\pi$ -donation stabilization is cancelled by the occupied antibonding counterpart, and the long Fe-ethylene distance is responsible for the very weak back-bonding from Fe to the ethylene  $\pi^*$  orbital. Because of the weakness of the bonding, ethylene remains planar.

Earlier theoretical work elucidated the importance of closed-shell s<sup>2</sup> metal configurations to  $\pi$  bonding of ethylene to metal centers. At the single determinant SCF level d<sup>5</sup>s<sup>2</sup> Mn forms no bond to ethylene,<sup>21</sup> and in other

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**Figure 6.** Orbital correlation diagram for the 1-fold transition state of Figure 5 ethylene CH bond scission by a ground-state Fe atom. Important interactions discussed in the text are heavy to stand out.

studies ethylene is predicted to bond with 17 kJ/mol<sup>22</sup> stability to  $d^9s^1$  Ni and  $\sim 50$  kJ/mol<sup>23</sup> to  $d^8s^0$  Pd. The relationship of these strengths is as expected from bond order arguments based on Figure 5; for general consideration of the importance of variations of other atom parameters such as orbital sizes and ionization potentials, our recent study may be consulted.<sup>24,25</sup>

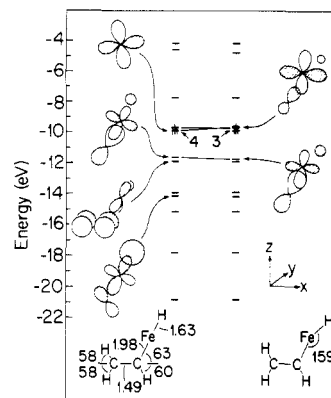
According to our calculations, the (1,2) 2-fold ethylene-iron coordination is most stable (Figure 4). The participation of two carbon atoms in the bonding appears to be responsible for (1,2) 2-fold structure preference.

**Ethylene CH Activation by  $s^1p^1$  Fe and the Properties of HFeCHCH<sub>2</sub>.** As for methane, the barrier for hydrogen abstraction by a ground-state iron atom is lowest for the 1-fold coordination, but as for methane, as discussed above, this barrier is underestimated in our calculations and the correct mechanism should be one of oxidative addition of Fe to the CH bond. Again, a CH  $\sigma$  + Fe  $\zeta$  closed-shell repulsion is evident as shown in Figure 6.

We know of no other theoretical studies of CH activation in ethylene by metal atoms. However, an ASED-MO study of dehydrogenation and rearrangement reactions of ethylene on the Pt(111) surface predicts CH activation barriers in the 100 kJ-range.<sup>25</sup> In this case ethylene twists easily as a result of back-donation to the  $\pi^*$  orbital, and this motion helps activate a CH for oxidative addition bond by directing it toward the surface.

Our results and their interpretation for ethylene CH activation by  $s^1p^1$  Fe are the same as for methane. Referring to Figure 6, promotion of an Fe 4s electron to a 4p orbital results in its donation to the CH  $\sigma^*$  orbital as the reaction progresses, and, for the case of 1-fold coordination, the resulting activation barrier is zero. The barrier for (1,2) 2-fold coordination is smaller than that for (1,1) 2-fold coordination because the structure allows better  $\sigma$  overlap in the (1,2) case—see Figure 4. As discussed above for methane, the actual mechanism is probably Fe insertion into the CH bond.

Calculated properties of ethynyliron hydride parallel those for methyliron hydride. The calculated reaction energy is 317 kJ/mol which is reduced to the more reasonable value of 204 kJ/mol when the iron atom state



**Figure 7.** Calculated structure for ethynyliron hydride and orbital correlation diagram illustrating various ethynyl orbitals and the orbital stabilization responsible for the C-Fe-H bend from linearity.

change is taken into account as discussed earlier for methyl iron hydride. The CFeH angle changes 21 deg from linear due to a stabilization of the CFe bonding orbital as shown in Figure 7. Bending is favored by 3 kJ/mol. The ethynyl  $\pi$  orbital is stabilized by mixing of the higher lying  $d_{yz}$  orbital on iron, with the result that the calculated CFe internuclear distance is 0.07 Å shorter than in methyliron hydride. This delocalization causes the CC bond to stretch 0.01 Å, which is responsible for the experimentally observed decrease in vibrational frequency which was seen in ref 4.

## Discussion

Activation of CH bonds in methane and ethylene by Fe atoms with an electron promoted to a 4p orbital is evidently the result of donation of this electron into the CH  $\sigma^*$  orbital as the bond stretches. Ground-state  $s^2p^0$  Fe atoms yield higher barriers to oxidative addition of CH bonds because of the initially closed-shell repulsion with the CH bond electron pair.

We have shown that it is the closed-shell repulsion of the filled ethylene  $\pi$  orbital and the doubly occupied Fe 4s orbital that makes  $\pi$  coordination less stable than  $\sigma$  coordination. The activation of CH bonds by ground  $s^2$  and excited  $s^1p^1$  Fe atoms has the same description as for methane.

Acetylene<sup>3</sup> has the same experimental behavior in the presence of ground- and excited-state Fe atoms as ethylene,<sup>4</sup> and it is clear that its theoretical treatment would be identical with the one given here for ethylene.

The Margrave group found  $\pi$ -complexed  $\text{Fe}(\text{C}_2\text{H}_4)_2$  stable to 75 K, where it totally dissociated. We expect two ethylene ligands can cause a change in Fe atom configuration to  $d^7s^1$  or  $d^8s^0$ , allowing a nonzero bond order with the ligands. The excitation to  $d^7s^1$  costs less than 1 eV and is probably overcome by the  $\pi$  coordination of two ethylene ligands. Ultraviolet photolysis led to decomposition to methane and ethane. This is expected because the structure is inappropriate for CH activation initially, and, as shown in Figure 5, the  $s^1p^1$  Fe will donate an electron to the ethylene  $\pi^*$  orbital, leading to low barrier to dissociation, just as on an iron surface where there is back-donation to the  $\pi^*$  orbital.<sup>5,7</sup> To characterize the subsequent steps would be a worthwhile study.

As shown by the Margrave group,<sup>4</sup>  $\text{Fe}_2$  molecules react with ethylene to form  $\text{Fe}_2(\text{C}_2\text{H}_4)$  and  $\text{Fe}_2(\text{C}_2\text{H}_4)_2$   $\pi$  complexes. This is expected because when the  $\text{Fe}_2$  molecule forms, the  $\sigma_g$  orbital is doubly occupied and the  $\sigma_g^*$  orbital becomes very antibonding so that it donates its electrons to the d set. For a discussion of this in the case of  $\text{Ni}_2$ , the

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literature may be consulted.<sup>26</sup> The delocalization of the two remaining s-like electrons, now in the  $\sigma_s$  orbital, should reduce the closed-shell repulsion with the ethylene  $\pi$  orbital, if the ethylene molecule binds to one end of  $\text{Fe}_2$ . Another possible orientation is di- $\sigma$ , as occurs on the Pt(111) surface.<sup>27</sup> Two isomers of the ethylene monomer and dimer have been observed.<sup>4</sup>

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The methyliron and ethynyliron hydrides can be photolytically converted back to methane and ethylene plus iron atoms, suggesting an interesting topic for future theoretical analysis.

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## Cobalt Carbonyl and Phase Transfer Catalyzed Carbonylation of Thiiranes

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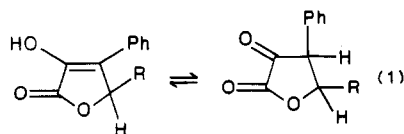
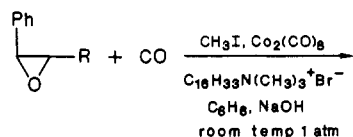
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Cobalt carbonyl catalyzes the carbonylation of thiiranes to  $\beta$ -mercapto acids using methyl iodide or a benzylic bromide, 3 N potassium hydroxide, benzene as the organic phase, and polyethylene glycol (PEG-400) as the phase-transfer agent. An acylcobalt carbonyl and a thietan-2-one are possible intermediates in this reaction.

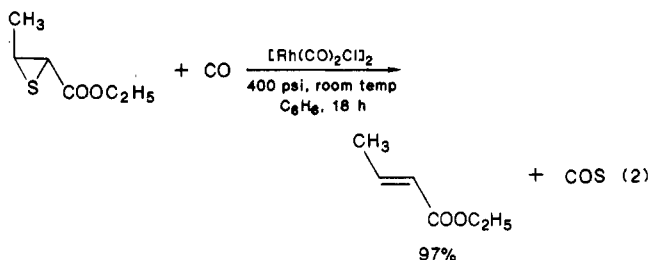
Phase-transfer catalysis is a useful method for effecting a variety of carbonylation reactions under remarkably mild conditions.<sup>2</sup> Of particular note are reactions involving halides and epoxides as substrates. For example, cyanonickel(II) complexes are active catalysts for the phase-transfer-catalyzed carbonylation of allyl halides to acids,<sup>3</sup> and cobalt carbonyl can catalyze the conversion of benzylic halides, and methyl iodide, to acids in the fine yields.<sup>4,5</sup> The key intermediate in the latter reaction is believed to be an acylcobalt tetracarbonyl complex. Such a complex can be intercepted by effecting the phase-transfer process in the presence of suitable unsaturated substrates [e.g. alkynes, dienes]<sup>2</sup> or haloarenes.<sup>6</sup>

A fascinating double carbonylation is observed when a styrene oxide is employed as the reactant, together with methyl iodide, carbon monoxide, benzene as the organic phase, aqueous sodium hydroxide, and cetyltrimethylammonium bromide as the phase-transfer agent (eq 1).<sup>7</sup>



In contrast to the reaction involving haloarene or unsaturated reactants, the methyl group of the iodide is not incorporated in the product, although the  $\alpha$ -keto lactone is not formed in the absence of methyl iodide.

Little is known concerning metal-catalyzed reactions of thiiranes, which are sulfur analogues of epoxides. Recently, it was shown that chlorodicarbonylrhodium(I) dimer can catalyze the homogeneous desulfurization of thiiranes to olefins.<sup>8</sup> This stereospecific reaction proceeds for thiiranes bearing aliphatic, aromatic, ether, and ester substituent groups (eq 2). We now wish to report that one can achieve the carbonylation of thiiranes to  $\beta$ -mercapto acids by cobalt carbonyl and phase-transfer catalysis.



### Results and Discussion

When 2-phenylthiirane (styrene sulfide), 1, was treated with carbon monoxide, methyl iodide, potassium hydroxide (3 N), benzene as the organic phase, a catalytic amount of cobalt carbonyl, and tetrabutylammonium bromide as the phase-transfer agent, at room temperature and one atmosphere, the  $\beta$ -mercapto acid 2 was isolated in 17% yield (no reaction occurs in the absence of the phase-

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