a conceptual framework that accounts for the intriguing substituent orientation trends observed in the fluorinated oxiranes and cyclopropanes.

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Registry No. *cis,trans*-**1**, 80397-38-2.

Supplementary Material Available: Tables of the Pierce double substitution result for equivalent hydrogens and parameters obtained from specialized forms of Kraitchman's equations (2 pages). Ordering information is given on any current masthead page.

Electronic Structure Factors of Carbon-Hydrogen Bond Activation. The Photoelectron Spectroscopy of (Cyclohexenyl)manganese Tricarbonyl[1]

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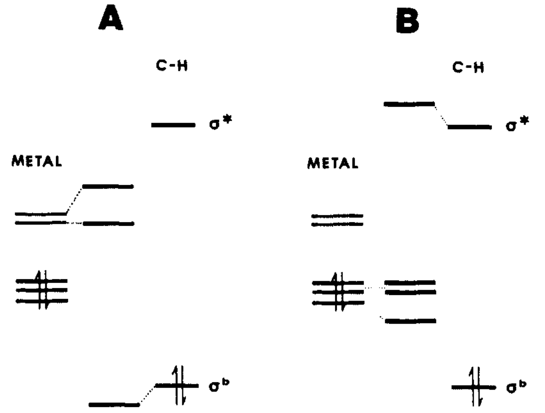
Abstract: The He I and He II ionizations for (cyclohexenyl)manganese tricarbonyl, a molecule which exhibits an activated C-H bond, are reported. Comparisons are made to the electronic structures of (methylcyclopentadienyl)manganese tricarbonyl, (cyclohexadienyl)manganese tricarbonyl, and (cyclohexadiene)iron tricarbonyl. Electronic structure factors contributing to the initial activation of the C-H bond are discussed in terms of two limiting descriptions that have been presented in the literature. These descriptions are labeled σ activation, involving the donation of C-H σ bonding orbital electron density into the empty metal orbitals, and σ* activation, involving electron density flow in the opposite direction, i.e., from filled metal levels into the empty C-H σ* antibonding level. Both processes are shown to be possible based only on geomertry, symmetry, and overlap considerations. The experimental data demonstrate that the principal electronic structure mechanism for the early stages of C-H bond lengthening and interaction with the metal exhibited in (cyclohexenyl)manganese tricarbonyl is σ activation. The data are also related to variable-temperature NMR studies of this complex which show that fluxionality proceeding through a 16 e^- intermediate is more favorable than that through an 18 e^- intermediate with a full metal-hydrogen bond. Both bond strength and ionization energy data show that the C-H activation of (cyclohexenyl)manganese tricarbonyl stops at the agostic stage because there is no net gain in carbon-carbon or metal-carbon bonding to compensate the loss of the C-H bond.

The study of small molecules activated by transition metals is an important aspect of the continuing investigations of metal-assisted chemistry and catalysis. One of the most important classes of small molecule-metal interactions involves the specific activation of the C-H bond.[2,3] Aliphatic hydrocarbons are abundant industrial materials but are generally unreactive in the absence of a catalyst because the C-H bond is relatively strong and difficult to attack both sterically and electronically. Both surface[4-6] and homogeneous systems capable of activating hydrocarbons have been reported. In fact the discrete molecules which activate C-H bonds include metals representing both ends of the transition series and the lanthanides and actinides.[7-18] The relationship between the electron count or availability at the metal (i.e., electron rich or poor) and the metal's ability to insert into the C-H bond has not been fully developed.

Scheme I. (A) σ and (B) σ* Activation Modes



There are two limiting case electronic descriptions for initiation of carbon-hydrogen bond activation.[19] We will refer to these by the names σ activation and σ* activation. The first occurs when the C-H σ (bonding) orbital donates electron density into an empty metal level. This model is depicted in Scheme IA.

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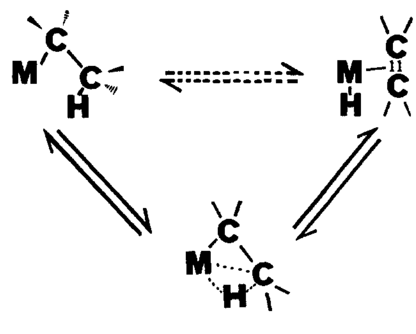
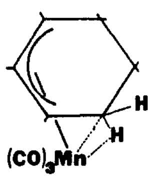
Scheme II. β-Hydride Abstraction



Hoffmann[20] and others have advocated this model for the initial activation of H_2 and CH_4 by transition-metal fragments. Anderson[21] also proposes this model for α-hydrogen abstraction at Pt and Fe surfaces. Obara[22] attributes the methyl group distortion in $Ti(CH_3)(PH_3)Cl_3$ to this type of activation. Eisenstein[23] supports this mechanism for $Ti(H)_5(CH_3)$ distortions. The other type of activation, σ*, occurs when filled metal levels donate into the empty C–H σ* antibonding orbital (Scheme IB). Shustorovich,[24] Sevin and Chaquin,[25] and Lebrilla and Maier[26] propose that this model is applicable in a variety of cases. Hoffmann[20] uses this model to explain the activation of H_2 and CH_4 by surfaces.

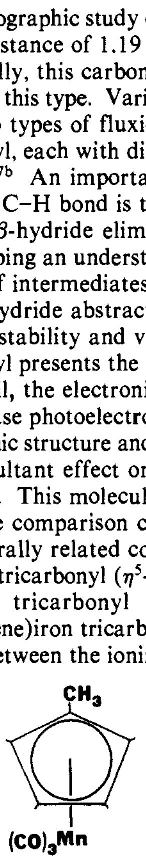
Molecules which represent intermediates for C–H bond activation by having distorted C–H bond geometries in close proximity to a metal have been characterized in recent years.[27-33] These molecules are of particular interest in understanding the transition-metal activation of carbon–hydrogen bonds. Brookhart and Green[34] have systemized much of this chemistry and have proposed the term "agostic" to describe hydrogens (of C–H bonds) that are interacting with the metal as well as with the carbon. This interaction is typically referred to as a 3-center/2-electron bond involving the metal, carbon, and hydrogen. Physical measurements such as ^1H or ^{13}C NMR and X-ray and neutron diffraction crystallography can be used to confirm the presence of an agostic C–H bond.[34]

A particularly interesing example is provided by (cyclohexenyl)manganese tricarbonyl (η^3-$C_6H_9Mn(CO)_3$),[27] I, which has been prepared and characterized by Brookhart. This complex conforms to the "EAN of 18" rule only if a 3-center/2-electron bond description is invoked for the carbon–hydrogen–manganese interaction. (Cyclohexenyl)manganese tricarbonyl contains an agostic C–H bond as evidenced by a recent neutron diffraction crystallographic study of the methylated species[35] showing a C–H bond distance of 1.19 Å and a Mn–H approach of 1.84 Å. Incidentally, this carbon–hydrogen distance is the longest known bond of this type. Variable-temperature NMR showed that there are two types of fluxionality for (cyclohexenyl)manganese tricarbonyl, each with distinct, electronically significant transition states.[27b] An important aspect of complexes with this type of agostic C–H bond is that they can be considered intermediates of the β-hydride elimination reaction as shown in Scheme II. Developing an understanding of the electronic structure of these types of intermediates will reveal important information about the β-hydride abstraction process.

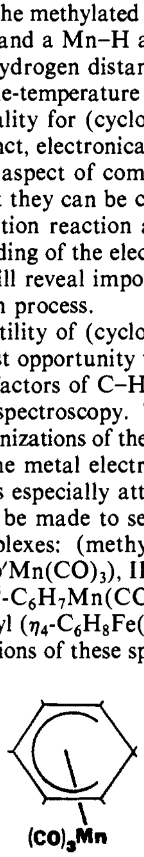


I

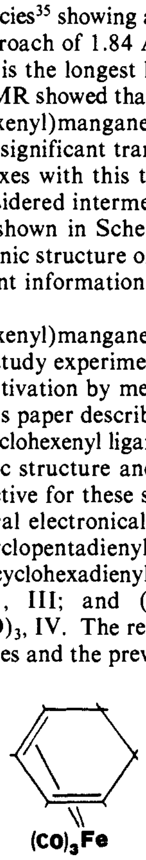
The stability and volatility of (cyclohexenyl)manganese tricarbonyl presents the first opportunity to study experimentally, in detail, the electronic factors of C–H activation by means of gas-phase photoelectron spectroscopy. This paper describes the electronic structure and ionizations of the cyclohexenyl ligand and the resultant effect on the metal electronic structure and ionizations. This molecule is especially attractive for these studies because comparison can be made to several electronically and structurally related complexes: (methylcyclopentadienyl)manganese tricarbonyl (η^5-$Cp'Mn(CO)_3$), II; (cyclohexadienyl)manganese tricarbonyl (η^5-$C_6H_7Mn(CO)_3$), III; and (cyclohexadiene)iron tricarbonyl (η_4-$C_6H_8Fe(CO)_3$, IV. The relationships between the ionizations of these species and the previously unreported ionizations of I enable a clearer understanding of the unique stability of the "activated"species I. In this paper, the electronic factors that contribute to the agostic C–H bond in (cyclohexenyl)manganese tricarbonyl will be described, and experimental evidence for a dominant σ electronic mode in the early stages of C–H bond activation will be presented.



II



III



IV

Experimental Section

Preparation of Complexes. (Cyclohexadienyl)manganese tricarbonyl[36] and (cyclohexadiene)iron tricarbonyl[37] were prepared by published techniques.

Photoelectron Spectra. All He I and He II spectra were recorded with use of techniques described earlier.[38,39] All spectra were run at room temperature with the exception of the He II

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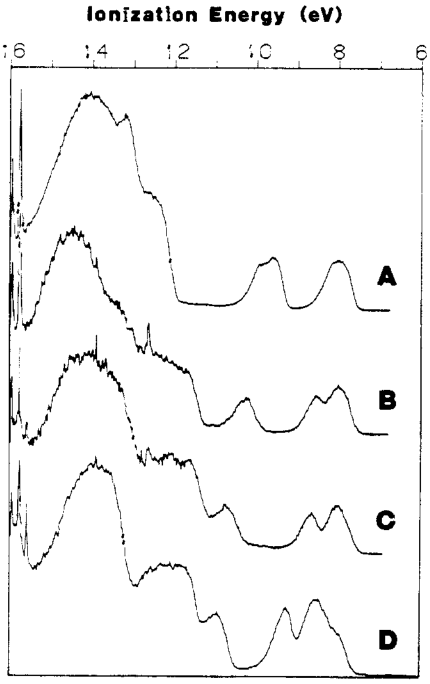

Figure 1. He I full spectra (16–6 eV) for (A) (methylcyclopentadienyl)manganese tricarbonyl, (B) (cyclohexadienyl)manganese tricarbonyl, (C) (cyclohexenyl)manganese tricarbonyl, and (D) (cyclohexadiene)iron tricarbonyl. Callibrant gas (Ar) ionizations are shown at 15.94 and 15.76 eV. Contaminant ionizations are present in some spectra: N_2 (15.58 eV) and H_2O (12.7 eV).

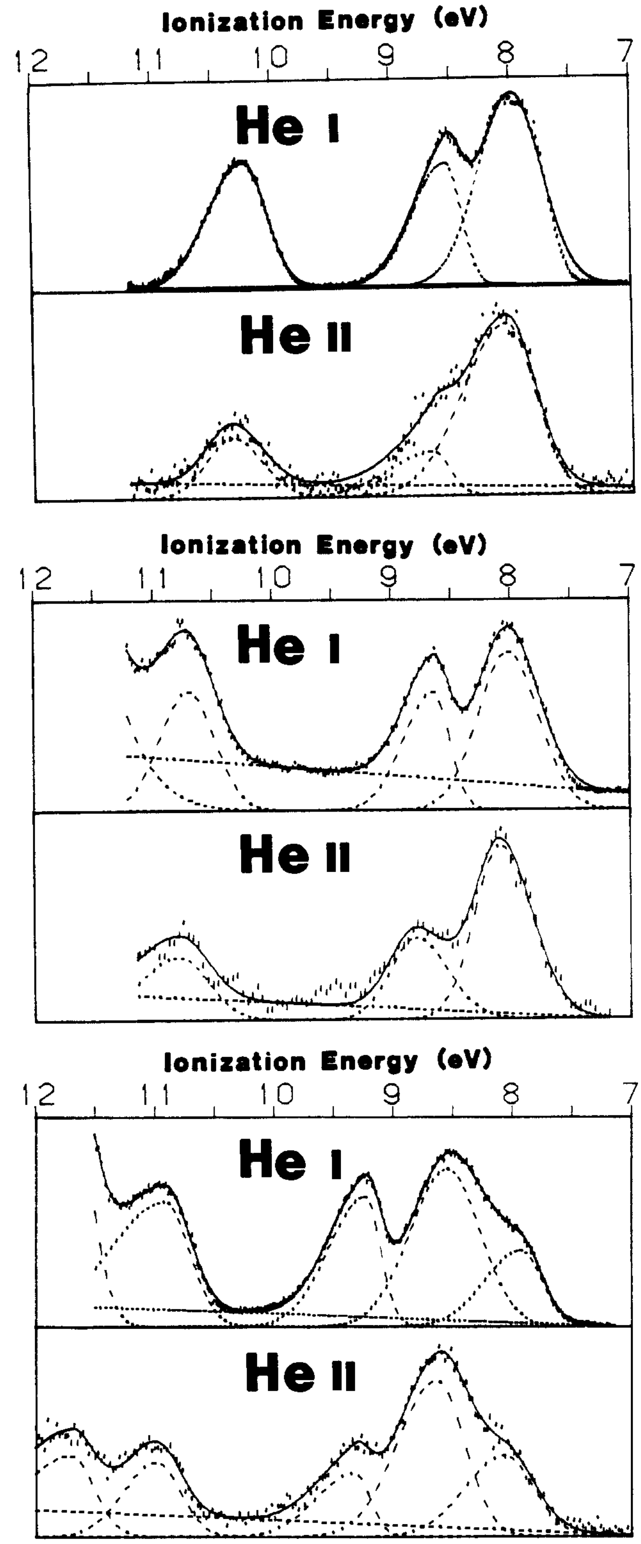

Figure 2. He I/He II comparisons (12–6) eV) for (A) (cyclohexadienyl)manganese tricarbonyl, (B) (cyclohexenyl)manganese tricarbonyl, and (C) (cyclohexadiene)iron tricarbonyl.

spectra of (cyclohexenyl)manganese tricarbonyl and (cyclohexadienyl)manganese tricarbonyl which were run at a slightly elevated temperature (40 °C).

Calculations. Orbital eigenvalues and distributions were calculated by the Fenske–Hall[40] method. The atomic orbital basis functions and geometry of the $Mn(CO)_3^+$ fragment are unchanged from previous work.[41,42] The bond distances of the cyclohexenyl ligand were taken from the neutron diffraction results.[35] Two-dimensional electron-density plots were calculated by MOPLOT.[43]

Results and Ionization Band Assignments

The He I full spectra of (methylcyclopentadienyl)manganese tricarbonyl (II),[38,41] (cyclohexadienyl)manganese tricarbonyl (III),[42] (cyclohexenyl)manganese tricarbonyl (I), and (cyclohexadiene)iron tricarbonyl (IV),[44] are displayed in Figure 1, A–D, respectively. The He I/He II comparison for (cyclohexadienyl)manganese tricarbonyl (II), (cyclohexenyl)manganese tricarbonyl (I), and (cyclohexadiene)iron tricarbonyl (IV) are presented in Figure 2, A–C. In addition, the ionization energies, half-widths, and relative intensities for all bands of interest are in Table I.

(Methylcyclopentadienyl)manganese Tricarbonyl. The starting point for all assignments is (methylcyclopentadienyl)manganese tricarbony (Figure 1A). These ionizations have been discussed extensively previously[38,41] and will be briefly summarized here. The broad band of overlapping ionizations from about 13–16 eV binding energy are predominantly due to the carbonyl 5σ and 1π as well as other C–C and C–H σ orbitals of the organic ring. The shoulder on the leading edge (around 12–13 eV) is primarily the C–H bond ionizations from the methyl on the ring. Below 11 eV there are two distinct bands. The band at around 8.0 eV is predominantly metal in character and can be attributed to the approximately t_{2g} set of metal electrons in this pseudooctahedral system. This ionization feature is deconvoluted with two bands (e + a) because of reduction from octahedral symmetry, but it could be approximately represented by a single ionization band. The second band (9.8 eV) is predominantly associated with ligand π character. It correlates with ionization from the filled e_1'' set of π bonds of the Cp^- ring. This band is slightly split due to the reduction in symmetry upon coordination to the metal.[38] The a_1'' totally symmetric orbital of the Cp^- π system is much deeper than the e_1'' set and ionization from this orbital is under the large

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Table I. Valence Band Positions, Half-Widths, and Relative He I/He II Intensities for C-H Bond Activated and Related Complexes[a]

			half-width[b] (eV)		relative area	
complex	ionization	position (eV)	high	low	He I	He II
$Cp'Mn(CO)_3$	M1(e)	7.89	0.65	0.38	1.00	1.00
	M2(a)	8.23	0.65	0.38		
	L1	9.57	0.57	0.36	0.58	0.39
	L2	10.00	0.57	0.36	0.35	0.23
$C_6H_7Mn(CO)_3$	M1	7.98	0.66	0.57	1.00	1.00
	L1	8.54	0.66	0.30	0.50	0.22
	L2	10.23	0.69	0.44	0.60	0.27
$C_6H_9Mn(CO)_3$	M1	8.01	0.60	0.59	1.00	1.00
	L1	8.64	0.59	0.31	0.56	0.47
	L2	10.70	0.56	0.52	0.68	0.44
$C_6H_8Fe(CO)_3$	M1	7.92	0.72	0.41	1.00	1.00
	M2	8.55	0.72	0.65	2.50	1.85
	L1	9.23	0.72	0.30	1.53	0.61
	L2	10.91	1.11	0.49	2.30	0.74

[a] Bands are labeled as metal (M1 or M2) and π ligand (L1 or L2). [b] Bands are deconvulated with asymmetric Gaussians. The half-widths are the values used in the Gaussian functional form on the high and low binding energy sides of the peak position.[45] The full half-width is the average of the high and low half-widths.

envelope of ionizations at 13–16 eV.

(Cyclohexadienyl)manganese Tricarbonyl. Cyclohexadienyl is related to cyclopentadienyl by insertion of a methylene into the ring. Because of the changes in carbon pπ orbital interactions, the ionization associated with the e_1'' π levels of Cp^- split into the bands at 8.5 and 10.2 eV in the case of cyclohexadienyl (Figure 1B).[42] As is always the case with first-row organo-transition-metal complexes,[46] the He I/He II comparison (Figure 2A) can be used to clearly show that these two bands are higher in ligand character than the predominantely metal ionization band at 8.0 eV. Note that this metal ionization feature show that the 3d orbitals remain essentially degenerate and do not significantly shift between the methylcyclopentadienyl and cyclohexadienyl complexes (II and III). This emphasizes that the pseudo-t_{2g} set of orbitals is largely nonbonding with respect to these rings. As above for (methylcyclopentadienyl)manganese tricarbonyl, the a_1''-type totally symmetric π band is under the envelope from 13 to 16 eV that also includes the carbonyl 5σ and 1π orbital ionizations.

(Cyclohexenyl)manganese Tricarbonyl. Comparison of the spectra of (cyclohexadienyl)manganese tricarbonyl (Figure 1B) and (cyclohexenyl)manganese tricarbonyl (Figure 1C) indicates an immediate tentative assignment of the observed ionizations of Figure 1C. With reference to the He I/He II comparison in Figure 2B it is clear that in the region from 7 to 11 eV the three observed bands can be assigned as a predominantly metal band at 8.0 eV and a pair of ligand π bands (10.7 and 8.6 eV). The implications of these ionizations in the context of the models for C–H bond activation will be presented in the following section. The region from about 11–13 eV shows many bands due to the large number of C–H bonds of different electronic environments. This region will be discussed in more detail in the following sections. It should be emphasized here that this experiment is clearly measuring the photoelectron spectrum of the molecule with the lengthened C–H bond and not some other isomer or decomposition product. There is no evidence for broadening of any of the ionizations which would indicate decomposition or thermal population of other conformations. These spectra were measured near room temperature where kT is about 0.6 kcal/mol. The solution NMR studies of this complex have shown the lowest barrier to rearrangement to be 8.3 kcal/mol and did not detect other conformations at temperatures up to 119 °C.[27b] Thus the Boltzmann population for excited levels is very small.

(Cyclohexadiene)iron Tricarbonyl. The photoelectron spectrum of the d^8 (cyclohexadiene)iron tricarbonyl complex (IV) (Figure 1D) is strikingly similar to that of the d^6 (cyclohexenyl)manganese tricarbonyl (Figure 1C). The major difference occurs in the metal region (7.5–9.0 eV) where ionization of the fourth pair of d electrons is visible as a shoulder (at about 7.9 eV) on the low binding energy side of the metal band. The He I/He II comparison (Figure 2C) shows the bands at 9.2 and 10.9 eV to be high in ligand π character and they are assigned to the diene ionizations.[44] Interesting observations that will be referred to again later are the ionization stabilization energies of the two cyclohexadiene π orbitals (relative to the free ligand) due to bonding to the metal fragment. The more stable, totally symmetric, π orbital is ionized at only 0.17 eV higher energy whereas the other, one-node, π orbital is ionized at 0.92 eV greater potential.[44b] Supporting this information is the He I/He II comparison for these ionizations. The a_1-type ionization collapses more with He II than does the other, indicating more carbon character and less mixing with the metal for the a_1.

Discussion

The electronic and structural requirements for activating and breaking a C–H bond are important aspects of metal-assisted organic chemistry and catalysis. The series of molecules studied in this paper provide a simple route to ionization band assignments and interpretation for a molecule that contains a strong C–H bond interaction with a metal, (cyclohexenyl)manganese tricarbonyl. This is, in fact, an unusual opportunity to *experimentally* determine the electronic mechanism for an initial stage of C–H activation. In this section we present a detailed examination of the σ and σ^* C–H activation modes and their relationship to this interesting species.

General Bonding Picture of (Cyclohexenyl)manganese Tricarbonyl. The ionizations described in the Results section can be summarized in terms of the simple molecular orbital diagram based on the Fenske–Hall calculational method shown in Figure 3. The chosen coordinate system is the one where the z axis is coincident with the threefold of the $Mn(CO)_3^+$ fragment. The manganese tricarbonyl cation fragment levels retain pseudooctahedral symmetry, splitting into e and a levels separated by only 0.35 eV (left side of Figure 3). This "t_{2g}" set is basically nonbonding with respect to the cyclopentadienyl ring and these levels are not significantly altered in going from the $Mn(CO)_3^+$ fragment to the (methylcyclopentadienyl)manganese tricarbonyl complex, II. The filled Cp e_1'' orbitals are donating into the empty metal orbitals that are predominantly d_{xz} and d_{yz} in this coordinate system. This is a four-electron donation and forms the primary metal–ring bond. The e_1'' set is split slightly because of ring distortion.[38] Note that the a_1'' level of the Cp ring does not overlap significantly with the metal orbitals[41] and is only a poor two-electron donor.

The cyclohexadienyl ligand is related to the Cp^- ligand by insertion of a CH_2 group into the five-carbon ring. This ring expansion further splits the e_1'' orbitals of Cp^- because of the reduction in local symmetry. These orbitals are labeled e_1^+ and e_1^- because of their correlation with the e_1'' orbitals and their symmetry with respect to the vertical mirror plane.[47] The e_1^+

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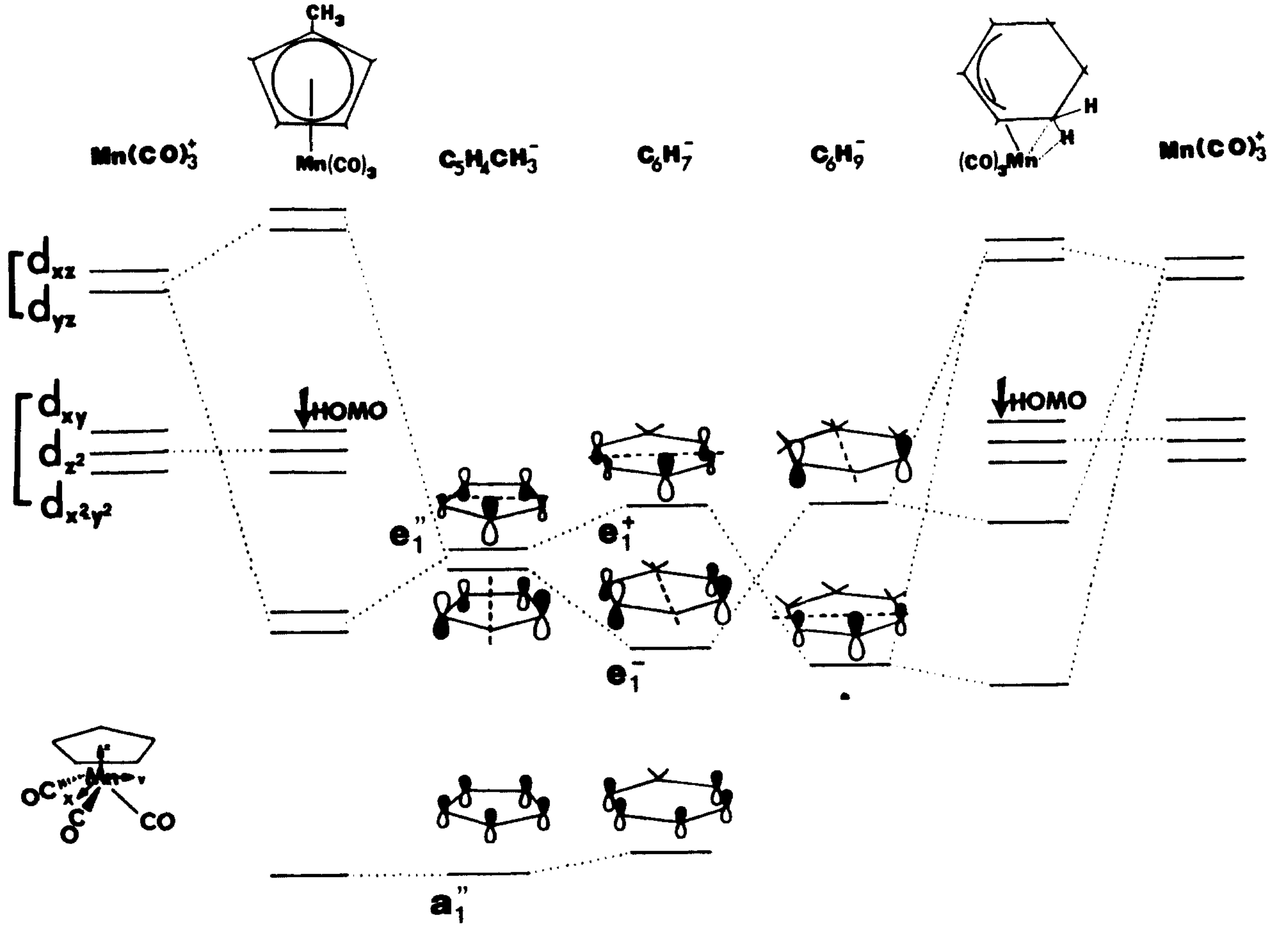


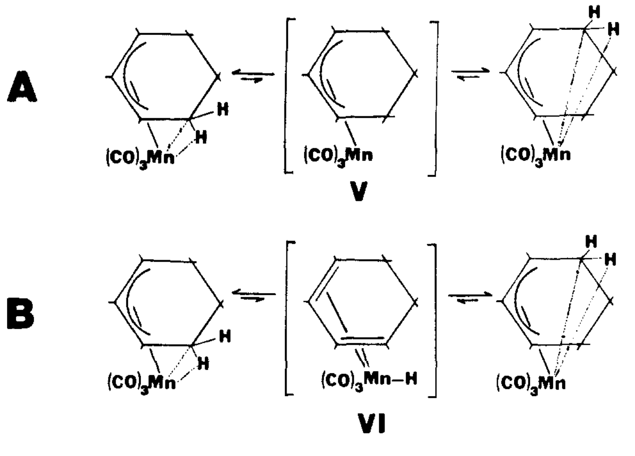
Figure 3. Orbital correlation diagram for interactions between the $Mn(CO)_3^+$ fragment and the methylcyclopentadienyl, cyclohexadienyl, and cyclohexenyl ligands.

orbital is destabilized relative to e_1'' by loss of π bonding character between the two ring carbons that have been separated by insertion of the sixth carbon. The e_1^- is stabilized relative to e_1'' by loss of antibonding character between these two carbons. The total bonding interactions of the cyclohexadienyl ligand to the metal are still very similar to those of the Cp^- ligand and the nonbonding metal levels of III are not split or significantly shifted from $Cp'Mn(CO)_3$ by the reduced symmetry.

When changing from the η^5-cyclohexadienyl to the η^3-allyl of the cyclohexenyl ligand, the π levels cross as shown in Figure 3 because the lower lying symmetric allyl level is derived from the higher lying cyclohexadienyl π level. The symmetry, however, has the same essential features with one exception. There is no level in cyclohexenyl analogous to the five-carbon a_1'' π orbital in the cyclopentadienyl and cyclohexadienyl ligands. But, as was mentioned above, this orbital is not a major factor in bonding. The π levels of the cyclohexenyl fragment are the correct symmetry for donation into the empty metal levels much as those of Cp^- in II and cyclohexadienyl in III.

Electron Counting and Stability of (Cyclohexenyl)manganese Tricarbonyl. It is helpful at this point to clarify the qualitative description of (cyclohexenyl)manganese tricarbonyl. The simplest level of electron structure consideration is electron counting and the "EAN of 18" rule. (Cyclohexenyl)manganese tricarbonyl can be considered an 18-electron molecule only if the agostic C–H bond is considered as a two-electron donor to a vacant coordination site at the metal. This interaction would be interpreted as the σ mode of C–H activation. However, there are numerous known violations of the 18-electron rule, and it is important to understand the individual factors that actually contribute to the overall stability of a complex. As pointed out above, the symmetric a_1'' orbital of cyclopentadienyl has a very weak interaction with the metal center. The a_1'' orbital is required for considering the Cp^- a 6-electron donor in an 18-electron complex, but this orbital is actually a very ineffective donor. Interestingly, this understanding is supported by the NMR fluxionality studies of Brookhart[27b] on (cyclohexenyl)manganese tricarbonyl (I). Two different dynamic ligand exchange processes were observed. The first process (Scheme IIIA) has a 16-electron intermediate, V, best described as (cyclohexenyl)manganese tricarbonyl *without* the activated C–Hh bond. This process has a barrier of 8.3 kcal/mol (0.36 eV). The second dynamic ligand exchange process (Scheme IIIB) is consistent with an 18-electron intermediate, VI, which can be described as (hydridocyclohexadiene)manganese tricarbonyl and has an activation barrier of 15.4 kcal/mol (0.67 eV). Note that the more stable of the two intermediates is the 16-electron one. As Figure 3 shows, the bonding of cyclohexenyl to $Mn(CO)_3^+$

Scheme III. Two Types of Fluxionality for the (Cyclohexenyl)manganese Tricarbonyl Molecule



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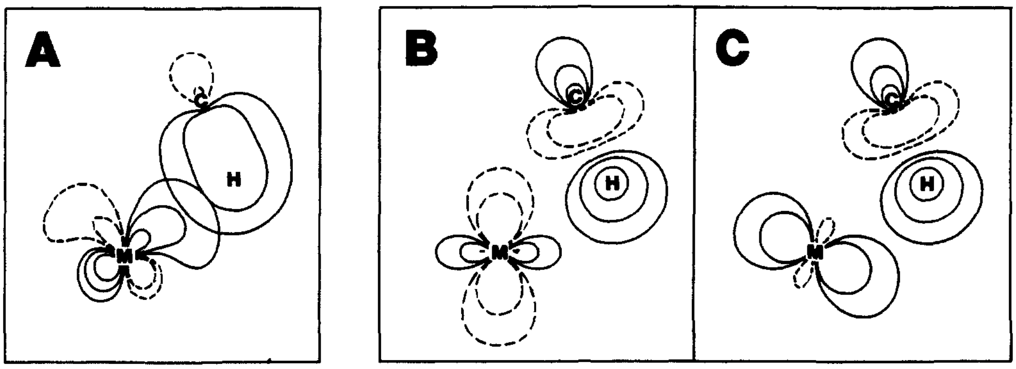
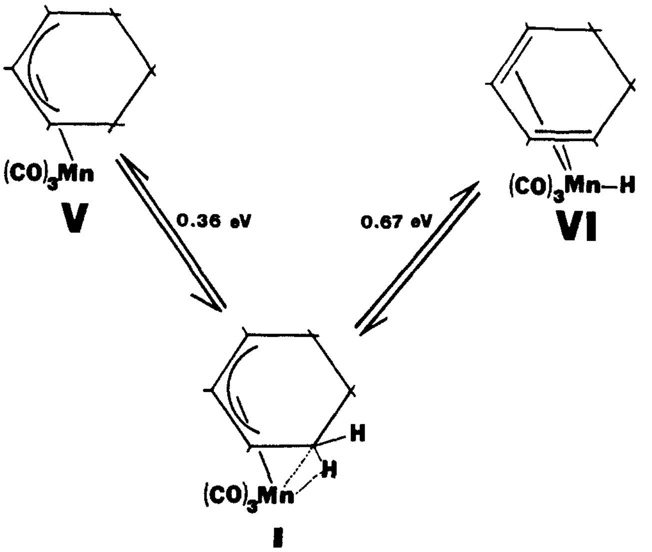
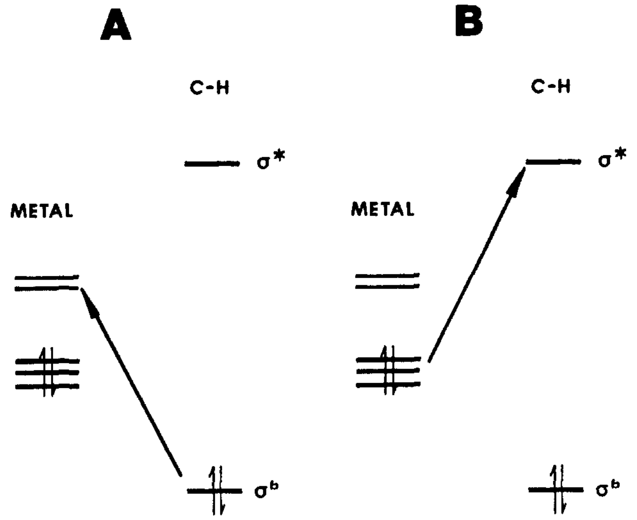


Figure 4. MOPLOT orbital contours for the interactions of the C–H orbitals with $Mn(CO)_3^+$ orbitals. (A) C–H σ bonding orbital and the predominantly d_{xz} acceptor, (B) C–H σ^* antibonding orbital and the predominantly d_{z^2} metal donor, and (C) C–H σ^* antibonding orbital and the predominantly $d_{x^2-y^2}$ metal donor. Displayed contour is for the xz plane which contains one CO (trans to the C–H) and bisects the other two carbonyls. The value of the outermost contour level is 0.10 $e^-/(au)^3$ and the value of each inner level is doubled from the previous one.

Scheme IV. β-Hydride Abstraction Cycle Including (Cyclohexenyl)manganese Tricarbonyl



Scheme V. Molecular Orbital Correlation for (A) σ Activation Mode and (B) σ^* Activation Mode



is similar to the bonding of cyclopentadienyl to $Mn(CO)_3^+$ and the single bonding interaction lost by the cyclohexenyl complex is that between the five-carbon symmetric π orbital and the metal. As was pointed out above this is not a major factor for the electronic stability of this class of complex. As an additional example, the totally symmetric diene orbital of the iron complex (IV) was seen in the previous section to interact only weakly with the metal.

The two transition-state complexes V and VI, implicated in the dynamic NMR studies, can be arranged as in Scheme IV to mimic the β-hydride abstraction process that was shown generically in Scheme II. It will be shown below that there are important electronic factors that demonstrate the greater stability of I than V or VI. Extended-Hückel calculations[48] on these three isomers show that the parent agostic complex, I, is the most stable isomer. These results are similar to those of Ittel[49] for (butenyl)CoL_3 that showed the geometry to vary with electron count at the metal center. When the complex was electron poor (Co^{II} or Co^{III}) there was an agostic CH–M interaction, but for Co^{I} there was no distortion of the methyl C–H bonds.

C–H Orbital Interactions. Consideration of the geometry and basic orbital occupations shows that both the σ and σ^* modes of C–H activation are possible in (cyclohexenyl)manganese tricarbonyl on the basis of the geometry and overlap between the C–H and metal orbitals. The agostic C–H bond in the (cyclohexenyl)manganese tricarbonyl complex is nearly trans to one of the carbonyls and on an octahedral coordination site. Two-dimensional orbital interaction contours are presented in Figure 4 that demonstrate the geometry and overlap between the σ and σ^* C–H orbitals and the $Mn(CO)_3^+$ fragment orbitals. This C_{3v} metal fragment has directed d orbitals as donors and acceptors. The most important aspect of the $Mn(CO)_3^+$ fragment is that trans to each carbonyl there are both potential donor (for σ^* of C–H) and acceptor (for σ of C–H) metal orbitals. In Figure 4A the C–H σ orbital interacts with an empty metal orbital from the $Mn(CO)_3^+$ fragment. This acceptor orbital is predominantly d_{xz} in character and the overlap between it and the C–H σ level is 0.24. Figure 4B shows the interaction of a filled $Mn(CO)_3^+$ orbital (predominantly d_{z^2}) with the empty C–H σ^* antibonding orbital with an overlap of 0.07, and Figure 4C shows the overlap between a second metal orbital (largely $d_{x^2-y^2}$) and the C–H σ^* ($S = 0.05$).

Both modes of C–H activation have precedence and can occur on the basis of orbital symmetries. The calculations support the σ mode of C–H activation over the σ^* mode because of larger overlap and smaller energy separation between the C–H donor and metal-acceptor orbitals. Another important observation in the calculations is that the C–H σ^* level is reasonably localized in one molecular orbital but the C–H σ level is extremely delocalized throughout the ring. The certainty in the placement for the orbital eigenvalue of the virtual C–H σ^* level is poor, so that this mode may be more probable than indicated by the calculations.

The (cyclohexenyl)manganese tricarbonyl complex provides a unique opportunity to experimentally evaluate these factors of C–H bond activation with a metal. The two proposed modes of C–H activation, σ and σ^*, would each produce characteristic features

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in the ionization spectra. σ activation, as described in Scheme IIA, is indicated by the transfer of electron density from the C–H σ bonding level to the empty e set of metal levels. As indicated in Scheme VA the net result would be a *stabilization* in the ionization potential of the "activated" C–H bond. This is similar to many common ligand bonding arrangements where the metal acts as an acceptor from the ligand lone pair orbital. Ionization energy increases of 1–2 eV have been observed for typical lone pair orbitals bonding to metals.[50,51] The degeneracy of the t_{2g} set of filled metal levels would not be largely affected. Within the simple overlap model of Scheme VA, there also would be no shift or loss of degeneracy of the t_{2g} levels. This does not preclude, however, significant collective shifts in the metal ionizations due to the change in charge potential at the metal with ligand replacement (vida infra).[52] The physical characteristics of a C–H σ activated complex would indicate a protic hydrogen rather than a hydridic hydrogen due to the net flow of electron density away from the C–H bond toward the empty metal levels. σ activation would thus appear to be prevalent in systems where there is an electron deficiency.

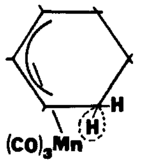
σ^* activation has the C–H σ^* antibonding orbital acting as an electron density acceptor from the filled t_{2g} set of metal levels. As shown in Scheme VB, the MO level stabilized by this interaction would be one of the t_{2g} set, thereby lifting the degeneracy of these levels. Since the flow of electron density in σ^* activation is from the metal to the C–H bond, the physical properties of the activated C–H bond would indicate a hydride hydrogen. The end result of C–H bond breaking through bonding to the metal is commonly referred to as oxidative addition and has been implicated in many catalytic reaction schemes.[53] Many theoretical treatments[24-26] have invoked σ^* activation. The driving force (Scheme VB) is the gained stability of the metal d t_{2g} set of electrons by interaction with the C–H σ^* level. An ionization energy shift to higher binding energy of several tenths of an electron volt for the interacting metal orbital would be expected for this case. This magnitude of shift is commonly observed for metal-donor orbitals able to interact with acceptors such as the carbonyl π^* orbital.

The magnitude of the expected ionization shifts due to the agostic CH–Mn interaction is conveniently provided by the NMR experiments. These experiments showed that the barrier for the fluxional process proceeding through structure V, which does not have the agostic CH–Mn interaction, is 0.36 eV. This thermodynamic energy difference between structures I and V largely represents the stability the molecule gains from the CH–Mn interaction. This energy should also be seen as either an increase in the C–H bond ionization energy (in the case of σ activation) or as an increase in one of the t_{2g} ionization energies (in the case of σ^* activation). Actually, this 0.36 eV represents a lower limit to the "agostic" stabilization energy because the NMR barrier also involves reoptimization of bonding and structure within the ring and with the metal after loss of the CH–Mn interaction. For example, one of the important reoptimizations is the shortening of the C–H bond to its normal length. A simple potential well calculation shows that the energy released in changing the C–H bond length from 1.19 Å to 1.09 Å is about 0.16 eV. Estimates for the energy released from other bonding changes within the ring and with the metal are unavailable, but obviously the specific interaction of the C–H bond with the metal in this system is associated with a stabilization of at least 0.5 eV.

Ionization Information and the Electronic Mode of C–H Activation. With this understanding of the basic orbital interactions and expected energy effects, the implications of the valence ionizations of (cyclohexenyl)manganese tricarbonyl (I) are now clear. Most importantly, there is no evidence for loss of degeneracy in the predominantly metal "t_{2g}" ionizations. In fact, this ionization band is even slightly narrower for the cyclohexenyl complex than for the methylcyclopentadienyl or cyclohexadienyl complexes. Thus the σ^* activation mode is shown not to be a major factor in the CH–Mn interaction in this complex. On the basis of the limits of resolution of these ionization band envelopes, the *maximum* contribution of the σ^* mode to the CH–Mn interaction is (charitably) estimated to be 20%. The predominant effect of the σ C–H bond interaction with the metal occurs in the ionization energy region from 11 to 14 eV. The overlapping ionizations from the other CH_2 bonds in this region make it difficult to identify a specific ionization feature associated with the CH–Mn interaction. In the methylcyclopentadienyl complex (II) the ionization shoulder at approximately 12.5 eV is known to represent the e symmetry combination of the methyl C–H bonds.[38] In the cyclohexadienyl complex (III) the ionization intensity from 11.5 to 13 eV is predominantly from the CH_2 bonds. The cyclohexenyl complex (I) has increased intensity in this region because of the greater number of CH_2 functionalities, but more interesting is the increased intensity in the 13–13.5-eV region that may be due to the CH–Mn interaction. Coincident with the loss of the agostic C–H stabilization between (cyclohexenyl)manganese tricarbonyl and (cyclohexadiene)iron tricarbonyl is the loss of intensity in the 13–13.5-eV region in the spectrum of (cyclohexadiene)iron tricarbonyl (IV). Other studies on acyclic (alkenyl)manganese tricarbonyls may isolate and clarify the agostic CH–Mn bond ionizations by reducing the number of interfering C–H ionizations.[54]

Another significant point is that the predominantly metal "t_{2g}" ionization does not shift (7.95 ± 0.06 eV) between the manganese complexes. Normally an additional two-electron donation to a metal center will shift the metal ionizations to lower energy because of the increase in negative charge potential in the vicinity of the metal. This is commonly observed for electron donations from lone pairs and π bonds.[52] However, in this case the negative charge potential donated from the C–H bond is compensated by the positive proton charge of hydrogen in the electron cloud. Thus the electron density on manganese is not destabilized and the bonding capabilities of the metal to the carbonyls and the ring are not significantly altered.

The unique stability of the activated species, I, represents a compromise struck in the β-hydride abstraction process between the 16-electron allyl complex, V, nad the 18-electron diene hydride complex, VI. It is also interesting, and equally important, to determine why the C–H activation of (cyclohexenyl)manganese tricarbonyl stops at the agostic stage. At the electronic level all three representations of $(C_6H_9)Mn(CO)_3$ differ for the most part in the position of one pair of electrons and the proton of the "activated" C–H bond. Progress from the 16 e^- complex to the 18 e^- metal hydride complexes was also accompanied by conversion of the 4 e^- allyl to a 4 e^- diene. The iron complex IV can be considered a continuation of this process in the sense that the d^8 Fe^0 center can be thought of as a hydride (2 electrons, 1 proton) added to a Mn^1 center, and the organic ligand is a complete 4 e^- donor diene.



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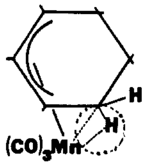

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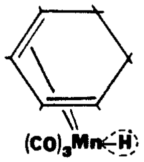
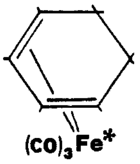


VI



IV

The photoelectron spectrum of the (cyclohexadiene)iron tricarbonyl complex in comparison to the spectrum of the (cyclo-

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(54) We are currently studying (butenyl- and methylbutenyl)manganese tricarbonyl[55] and tetracarbonyl complexes. These molecules will show the extent of perturbation on the ligand due to the CH–Mn interaction and have fewer interfering C–H bonds.

(55) Timmers, F.; Brookhart, M. *Organometallics* **1985**, *4*, 1365–1371.

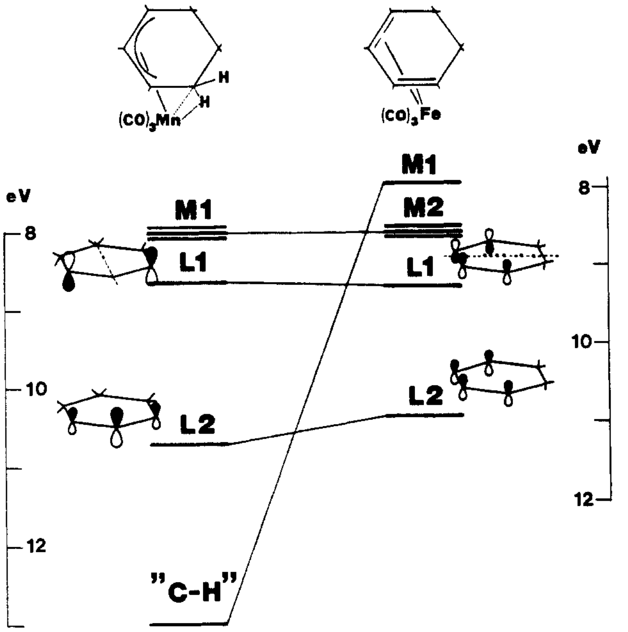

Figure 5. Valance ionization correlation between (cyclohexenyl)manganese tricarbonyl and (cyclohexadiene)iron tricarbonyl. The ionization energy scales are shifted 0.54 eV to visually align the metal t_{2g} ionizations.

Table II. Comparison of Thermodynamic Bond Strengths and Ionization Potentials

bond	ionization energy, eV	bond strength, kcal/mol
C—H	12-14	99
Mn—C	9.5[a]	37[b]
Mn—H	10.6[c]	51[d]
C=C (π only)	10.5[e]	63[f]

[a] For $CH_3Mn(CO)_5$ (ref 57). [b] For $CH_3Mn(CO)_5$ (ref 58). [c] For $HMn(CO)_5$ (ref 56). [d] For $HMn(CO)_5$ (ref 58). [e] For C_2H_4 (ref 59 and 60). [f] Average bond strength of C—C subtracted from average bond strength of C=C.

hexenyl)manganese tricarbonyl complex gives an indication of those factors that must be balanced in the addition of the C-H bond to the metal center. This is illustrated in the ionization correlation diagram in Figure 5. The "t_{2g}" ionizations of the Fe complex are stabilized relative to those of the Mn complex because of increased nuclear charge at the metal center. This is not a factor in the formation of the manganese hydride and therefore the ionizations of the iron complex are shifted relative to those of the manganese complex in Figure 5 for purposes of the comparison. It is noted first that there are relatively small changes in the ionizations localized largely on the ligands. Both ligands have four pπ electrons and changes in carbon pπ-pπ bonding are accompanied by changes in metal-ring bonding in the opposite direction. The most significant observation is that the electrons associated with the hydride transfer of 2 e^- and a proton give rise to a band at the very low ionization energy of 7.92 eV. In (cyclohexenyl)manganese tricarbonyl these electrons were in the C-H bond and ionized in the region of 11-14 eV. Note that the ionization from the Mn-H bond of $Mn(CO)_5H$ occurs at 10.6 eV,[56] which is intermediate between these values. The limit of complete breaking of the C-H bond may be viewed as the point at which the σ and σ^* levels have collapsed together. The large destabilization of the electron pair from the C-H bond to the formation of the metal-hydride bond cannot be compensated in this case by the other electronic interactions in the complex.

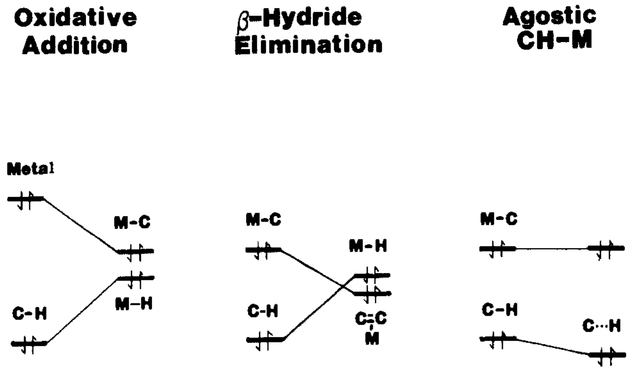

Figure 6. Orbital correlations for oxidative addition, β-hydride elimination, and agostic CH-M Activation.

Bond Strength/Ionization Energy Correlations. The concepts presented in the preceding paragraph can be further developed by examining some known bond strengths and ionization energies of related manganese complexes. Table II contains representative bond energies and ionizations for manganese alkyls and hydrides in comparison to C—H and C=C bonds. The C-H bond is the strongest on the list and has the largest ionization potential. Both the Mn-H and Mn-C bonds are considerably weaker and their ionization potentials are lower. The orbital correlations shown in Figure 6 are based on the experimental ionization energies of Table II. Correlations for oxidative addition, β-hydride elimination, and agostic C-H activation are displayed. In oxidative addition, a pair of metal electrons combines with the C-H bond to form a M-H and a M-C bond, with a fairly small change in overall orbital energetics. The β-hydride elimination also has a small total energy change as the loss of a C-H bond is offset by the gain of a π-bonded olefin. There is a balance of electronic and thermodynamic factors that dictates whether a given metal will break a C-H bond by oxidative addition or β-hydride elimination. Obviously the direction of the balance is largely a function of the metal and its electronic (ligand) environment, but the Mn bond strength data in Table II crudely estimate β-hydride elimination to be endothermic by 22 kcal/mol. The reverse process, olefin insertion, has been shown to be exothermic by 9-16 kcal/mol.[61] This is good agreement considering that the five carbonyl π acids of the $Mn(CO)_5$ fragment may have a substantial effect on the perceived strength of the Mn-C and Mn-H bonds. Why the C-H activation of (cyclohexenyl)manganese tricarbonyl stops at the agostic complex is simple in the context of the correlations of Figure 6. Both isomer V, the 16-electron allyl, and VI, the 18-electron diene hydride, have four π electrons in the organic ring and similar bonding with the metal. There is not a sufficient gain in these or other bonding interactions from V to VI to offset the stability loss between a C-H and a Mn-H bond. Thus the β-hydride elimination reaction proceeds only part way and gains the agostic C-H stabilization without completely sacrificing the C-H bond.

Acknowledgment. We gratefully acknowledge the Department of Energy (Contract DE-AC02, 80ER10746) and the University of Arizona for partial support of this research. Professor Maurice Brookhart and his research group contributed a sample of (cyclohexenyl)manganese tricarbonyl, for which we are extremely grateful.

Registry No. I, 76830-97-2; II, 12108-14-4; III, 12108-13-3; IV, 12152-72-6.

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