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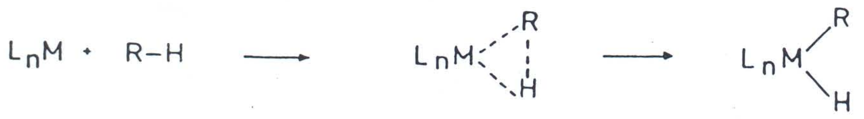
2.2: Inevitability of agostic interactions. β-CH bond activation.

2.2.1: Abstract

Oxidative addition of a coordinatively unsaturated pentacoordinate ethyl complex to the octahedral ethylene-hydride complex involves an intermediate agostic complex. The geometric factors that are unique to β-CH bond addition are discussed. Extended Hückel Molecular Orbital calculations of the reaction profile $L_4MC_2H_5$ to $L_4M(C_2H_4)H$, (M = Co with six d electrons) shows an intermediate structure with agostic interactions to be more stable than the octahedral ethylene-hydride complex. The transformation from the agostic structure to the pentacoordinate species involves a barrier.

2.2.2: Introduction

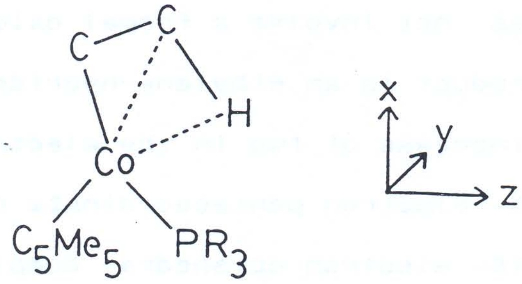
The C-H bonds are one of the strongest bonds commonly encountered in chemistry.[1] It is not easy to form derivatives of hydrocarbons that can be obtained in plenty from various industrial sources.[2,3] Several methods have been sought to activate the usually inert C-H bonds of alkanes and other hydrocarbons.[4] The term activation is used to describe the process of increasing the reactivity of C-H bonds so that it can be broken to make derivatives. Unsaturated transition metal centres are found to be ideal in helping this process. The reaction begins by the donation of the C-H bonding electrons to the transition metal centre to completely fill its valence orbitals. This weakens the C-H bond and the process of breaking the C-H bond continues ultimately leading to M-C and M-H bonds. This process also increases the oxidation state of the metal by two. Hence, the reaction is known as oxidative addition.[5] One of the first instances of C-H bond activation was found in the cyclometalation reaction.[6] Crabtree et al have shown that the activation of a number of alkanes by iridium complexes proceed through oxidative addition.[7] Graham,[8] Bergman,[9] Whitesides[10] and others[11] have also studied the activation of C-H bond by transition metals. The mechanism of oxidative addition involves a coordinatively unsaturated metal center which reacts with the alkane C-H in a three center transition state forming the hydrido alkyl metal complex (eq. 2.2.1). Brookhart and Green have coined the name agostic for such a transition state.[12] The hydrido alkyl



(eq. 2.2.1)

complex on subsequent loss of the alkane regenerates the reactive metal complex. Even though the majority of C-H bond activation reactions appear to be oxidative addition type, some undergo radical processes in which a hydrogen atom is abstracted from the alkane[13] and some others undergo a four center mechanism as seen in the activation of C-H bonds by lanthanides and actinides.[14]

The activation of C-H bonds are of two types: intra and inter molecular. In the intra molecular activation the activated C-H bond is already attached to the metal through other atoms or groups and in the inter molecular variety it comes from an independent alkane. Intramolecular C-H bond activation involves α, β, γ, δ etc C-H bonds. Of these the activation and addition of the β-CH bond is unique because the addition does not involve a formal oxidation at the metal, since the product is an ethylene-hydride complex and there is simply an increase of two in the electron count around the metal. A 16- electron pentacoordinate complex with d^6 metal becomes an 18- electron octahedral complex with ethylene and hydride as cis ligands. $C_6H_6M(PR_3)_2(C_2H_4)H^+$, M = Ru, Os,[15] $C_5H_5Rh(PR_3)(C_2H_4)H^+$ [16] and $(CO)ClOs(PR_3)_2(C_2H_4)H$[17] have been prepared in solution. Nuclear magnetic resonance data have been used to show the existence of distinct ethylene and hydride ligands in these complexes. Well characterized structures with agostic interactions are available for isoelectronic Co compounds $(C_5Me_4R)Co(Et)(C_2H_4)^+$ and $(C_5Me_5)Co(PR_3)Et^+$.[12, 18, 19] Experimental evidence abounds for the intermediacy of agostic interactions of C-H-M with other coordination numbers.[12, 20, 21] Several single crystal structural studies of complexes involving agostic interactions are available.[12, 20, 22] $(C_5Me_5)Co(PR_3)(C_2H_5)^+$ (1) represents an example of an intermediate caught between the C-H bond addition. The product of additon, were it to take place, corresponds to an octahedral ethylene-hydride complex. However, no well documented structure from diffraction studies is available for the octahedral ethylene-hydride complex with Co as the metal. In this section, the geometrical and electronic factors that favour the agostic interactions of β-CH bonds are analyzed. Extended Hückel method[23] is used to obtain wave



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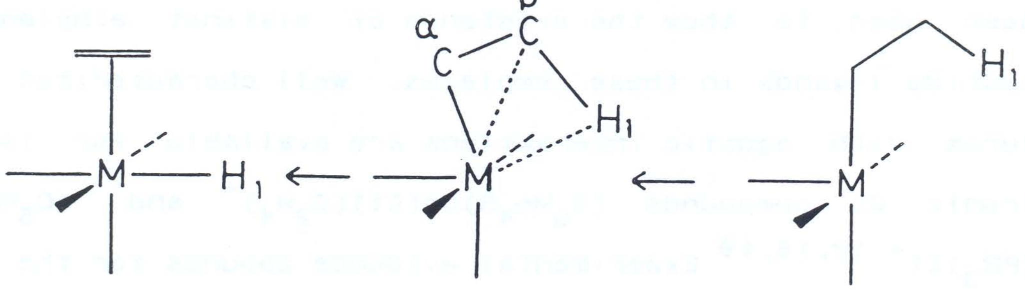

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functions along a reaction coordinate[20] that connects an agostic structure (2) to an octahedral ethylene-hydride complex (3) and to a pentacoordinate ethyl complex (4). The ligands used, in addition to ethylene and hydride were C_5H_5 and PH_3 or four hydrides with appropriate charges to retain the d-electron count of Co as d^6. There has been previous theoretical studies on C-H bond activation[24] but none to delineate the electronic factors of β-CH bond metal interactions.

2.2.3: Results and Discussion

The complex $(C_5Me_5)Co(PR_3)C_2H_5^+$ (1) was selected as the reference structure with agostic interactions. This was modelled by $(C_5H_5)Co(PH_3)Et^+$ (2) with geometry adapted from the X-ray structure.[19] The transformation of 2 to the octahedral ethylene-hydride complex (3) and to the pentacoordinate ethyl complex (4) was studied using extended Hückel calculations (4 --> 2 --> 3). The geometry of $(C_5H_5)Co(PH_3)$ was kept constant during this process. The Co, C_α, C_β and the shifting hydrogen were kept in the same plane throughout. The exact geometries and the parameters are given in appendix 1.2.

Fig. 2.2.1 shows the variation of total energy with C_α - C_β distance (4 --> 2 --> 3). There is a minimum corresponding to 2 (the agostic structure) with energy increasing in either directions. Interestingly, the energy increases continuously in the direction of the octahedral complex (3) from

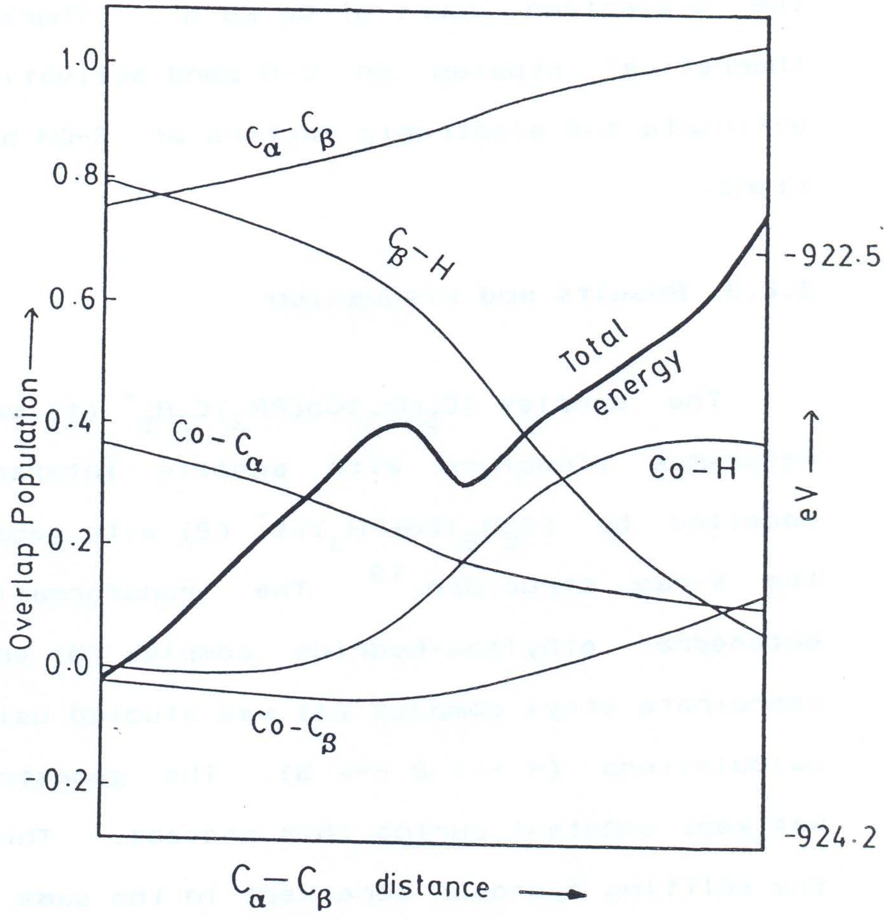
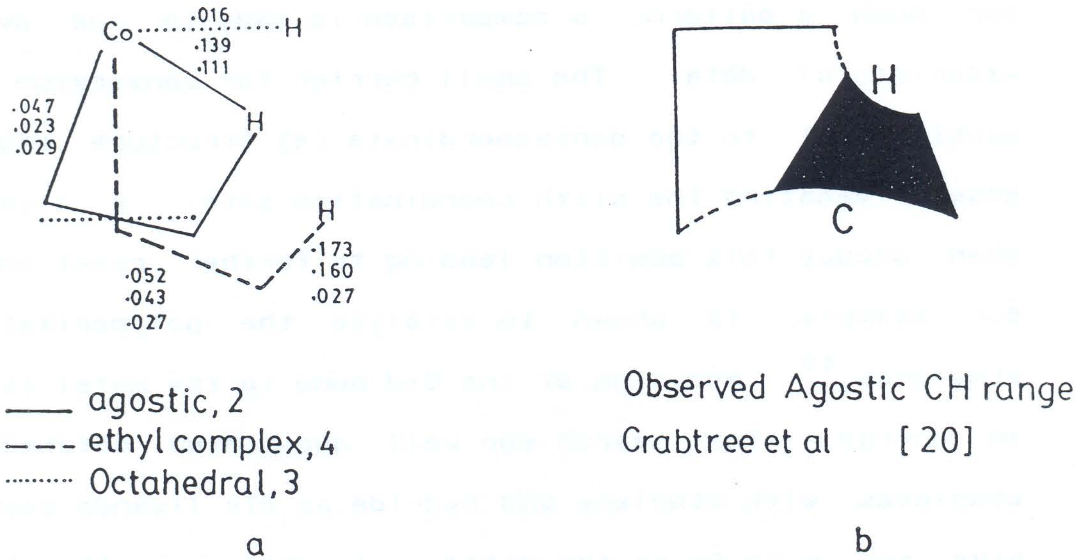


Fig. 2.2.1 The variation of total energy (thick line) and the Mulliken overlap population for the process (1 -->2 -->3) starting from $[(C_5H_5)Co(PH_3)(C_2H_5)]^+$.

2. While along the path towards 4, the energy goes up initially and comes down again. Before analyzing the reasons for such a pattern, a comparison is made to the available experimental data. The small barrier for conversion of the agostic (2) to the pentacoordinate (4) structure shows the ease of vacating the sixth coordination site. π ligands may then occupy this position leading to further reactions. 1, for example, is known to catalyze the polymerization of ethylenes.[19] Addition of the C-H bond to the metal is uphill in energy. The search for well documented octahedral d^6 complexes with ethylene and hydride as cis ligands could not give any with Co as the metal. It appears as though β-CH bond addition in these complexes proceeds to the agostic stage only. The initial calculations involved ligands very close to that found in 1. The general trend in energy is not different when ligands were changed into simpler ones. Thus replacement of Cp^- and PH_3 by H_4^{-4} did not change the reaction profile. Hence, $(H_4)Co(H)(C_2H_4)^{-2}$ is considered further in the discussion.

The easiest point to understand along the reaction coordinate is the final one with the octahedral geometry (3). The variation in geometry in relating 3 to 2 and 4 gives the key for the ease of formation of structures with agostic interactions. Crabtree et al have constructed a reaction coordinate for C-H bond addition from single crystal structural data.[20] A comparison of the ethylene-hydride complex geometry (3) to this scheme (Fig. 2.2.2) shows that the carbon



ig. 2.2.2 A comparison of the reaction profile for β-CH bond addition. (a) this study (b) that given by Crabtree et al (ref. 20). The geometry of the agostic point (solid line) in Fig. 2.2.2a falls approximately in the region of agostic interaction. The dotted lines refer to the octahedral complex and the broken lines to the ethyl complex. The Mulliken overlap population corresponding to the MO that makes the dominant contribution to the C-H-M interaction is also given in Fig. 2.2.2a. The middle value corresponds to the agostic point, the lower one to the octahedral complex and the upper one to the ethyl complex.

is already close to the strucutre with agostic interactions. Fig. 2.2.2a gives the point corresponding to 2, 3 and 1. Thus the deviation from the octahedral geometry needed to reach the agostic point is not large. As seen below, 2 retains much of the M-C and M-H bonding present in the complex although the C-H interaction is substantially increased.

A Walsh diagram that connects 3, 2 and 1 for the process shown in Fig. 2.2.2 is given in Fig. 2.2.3. The details of the variation of the energy levels may be understood starting from the MOs of the octahedral ethylene-hydride complex (3). The HOMO 9a' orbital corresponds to the bonding combination of ethylene π bond and the $d_{x^2-z^2}$ (obtained as a linear combination of $d_{x^2-y^2}$ and d_{z^2}) at 3. This also has considerable M-H bonding. However, it is C_β -H antibonding. At the agostic point (2) this antibonding interaction is at a maximum. The M-C_α and C_β -H bonding interactions predominate at the pentacoordinate point (1). Instead of going through the details of all the orbitals, we concentrate on 3a'. This ligand based orbital follows the general trend in total energy. It is mainly an M-H bonding orbital at 3, retains much of this at the agostic point (2), but in addition gains substantial C-H bonding. The contribution of this MO to Mulliken overlap population for various atom pairs is given in Fig. 2.2.2a. The upper number corresponds to 1, the middle one to 2 and the lower one to 3. A cross section of this MO in the xz plane is shown in Fig. 2.2.1. The balance of C-H, M-H and M-C interactions in stabilizing agostic structures are

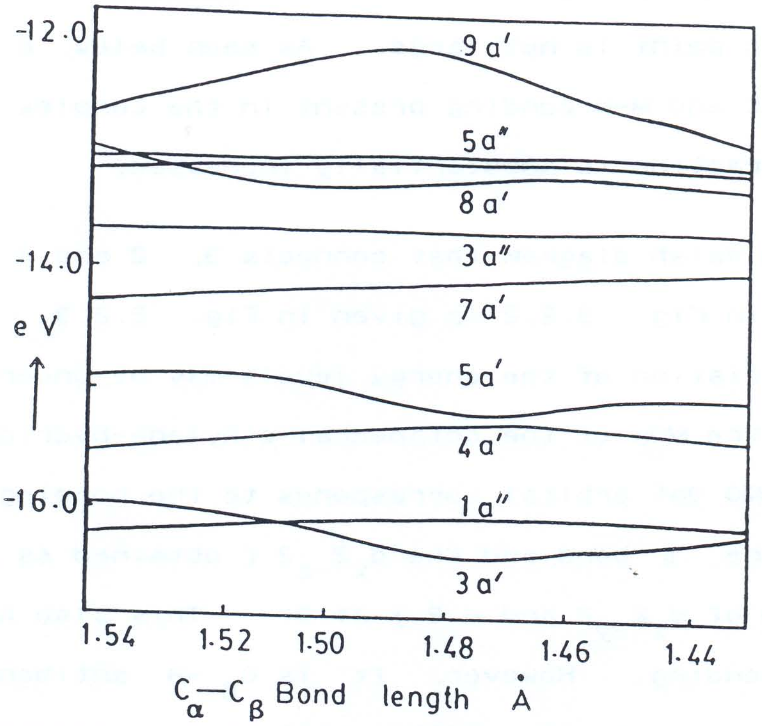


Fig. 2.2.3 Walsh diagram for the process 4 --->2 --->3 starting from $H_5CoC_2H_4^{-2}$.

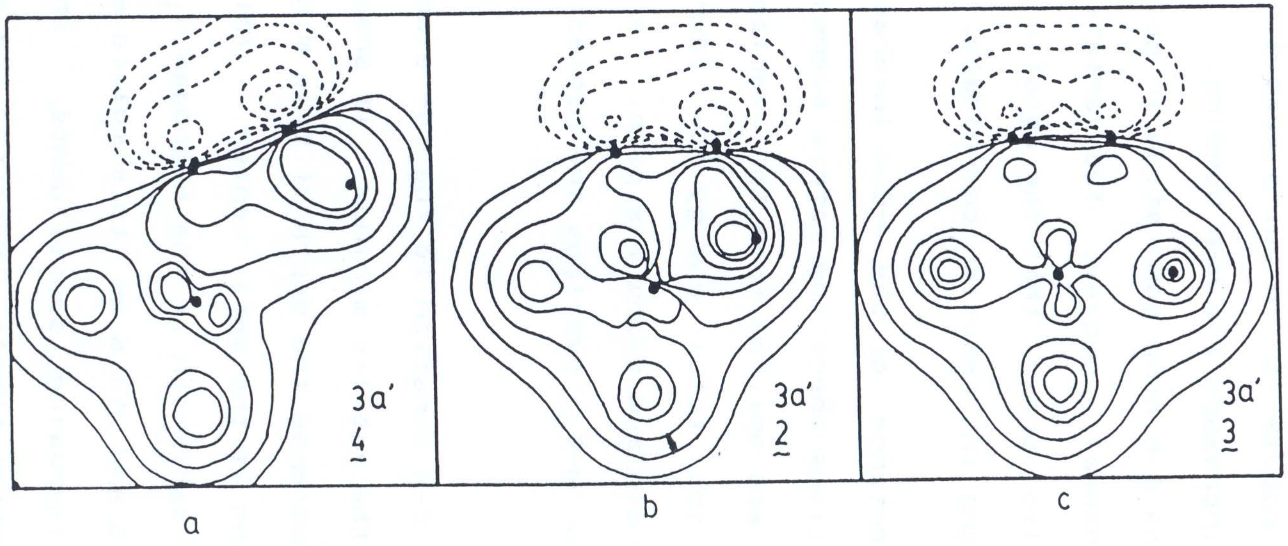


Fig. 2.2.4 Cross section of the 3a' MO along the MCCH plane of $H_5CoC_2H_4^{-2}$, (a) 4 (b) 2 (c) 3. The contours used for plotting were ± 0.550, 0.275, 0.200, 0.180, 0.150, 0.138, 0.100, 0.069, 0.034, 0.017, 0.009.

also seen in the variation of the Mulliken overlap populations summed over all occupied orbitals (Fig. 2.2.1). The decrease in the C-H population in going from 1 to 2 is negligible, while this increases the M-H bonding. There is a drastic decrease in the C-H bond population in going from the agostic to the octahedral complex. The variation in the overlap population also shows that the agostic point is the best compromise along the reaction coordinate.

The importance of the M-C-H interactions is also seen from calculations where the matrix elements corresponding to M-H overlaps are omitted from the overlap matrix. Unlike in Fig. 2.2.1, the total energy now increases continuously. There is no minimum along the path. A similar result is obtained when M-C_β overlaps are neglected in the calculations.

If the C-H donation to the 16- electron system is the reason for the agostic minimum, it should be possible to increase or decrease the depth of this minimum by changing the electron demand at the metal center. This indeed is found to be the case. Variation of the hydrogen H_{ii} from the standard -13.6 to -12.6 and -14.6 eV to simulate electron donating and electron withdrawing substituents, showed that electron withdrawing substituents increased the depth of the well, stabilizing the agostic structure. Since bond distances involving hydrogen and heavier atoms are overestimated by 10% by X-ray studies, the calculations are repeated by decreasing the M-H and C-H distances at the agostic point by 10%. Total energy and other parameters did not change from the earlier values considerably here. In particular the agostic point appeared as a minimum.

The above results point to the conclusion that complexes involving agostic interactions are preferred to octahedral ethylene-hydride complexes in the process (1 --> 2 --> 3). A recent experimemtal study by Brookhart on this problem also came to the same conclusion that no alkyl-alkene complexes are directly observed during the migratory reaction of a pentacoordinate complex $CpCo(L)C_2H_5^+$ (L = $P(OMe)_3$), which supports the above theoretical analysis.[25]

2.2.4: Summary

The geometric factors that favour agostic interactions involving β-CH bonds have been analyzed using model compounds, $(C_5H_5)Co(PH_3)H(C_2H_4)^+$ and $(H_4)Co(H)C_2H_4^{-2}$. Extended Hückel calculations along the reaction coordinate that connects pentacoordinate ethyl complex to the octahedral ethylene-hydride complex via the structure involving agostic interactions showed that there is a minimum corresponding to this structure.[26] Mulliken overlap population analysis of the pentacoordinate, agostic and octahedral complexes shows that the agostic point retains most of the C-H bonding character while also gaining M-H bonding. A comparison of this reaction profile to that formulated by Crabtree and coworkers[20] indicates how small a change in geometry is required to convert the octahedral ethylene-hydride complex to the agostic complex with β-C-H-M interaction. The stability of the structure with agostic interaction can be increased or decreased by increasing or decreasing the electron withdrawing nature of the remaining ligands.

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