Journal of Organometallic Chemistry, 315 (1986) 361–367
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

AGOSTIC INTERACTIONS AS AN ALTERNATIVE TO OCTAHEDRAL ETHYLENE-HYDRIDE COMPLEXES. β-CH BOND ACTIVATION

P.N.V. PAVANKUMAR, B. ASHOK and ELUVATHINGAL D. JEMMIS *

School of Chemistry, University of Hyderabad, Central University P.O., Hyderabad 500 134 (India)

(Received May 23rd, 1986)

Summary

The geometric factors unique to β-CH bond addition are discussed. Extended Hückel Molecular Orbital calculations of the reaction profile for the conversion of $[\eta^5\text{-}C_5H_5Co(PH_3)C_2H_5]^+$ into $[\eta^5\text{-}C_5H_5Co(PH_3)(C_2H_4)H]^+$ shows that an intermediate structure with an agostic interaction is more stable than the octahedral ethylene-hydride complex. The transformation from the agostic structure to the pentacoordinate species involves a barrier.

Introduction

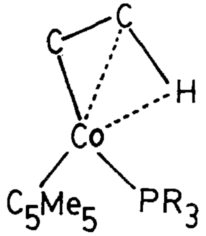
Activation of the C–H bond is considered to be the first step in the oxidative addition of a C–H bond to metals [1]. The C–H bond may be a part of the alkyl group already attached to the metal (intramolecular activation) or of an independent alkane (intermolecular activation). Intramolecular C–H bond 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 2 in the electron count around the metal. A 16-electron pentacoordinate complex with a d^6 metal becomes an 18-electron octahedral complex with ethylene and hydride as *cis* ligands. $C_6H_6M(PR_3)(C_2H_4)H^+$ (M = Ru, Os) [2], $C_5H_5Rh(PR_3)(C_2H_4)H^+$ [3], and $Os(PR_3)_2(CO)Cl(C_2H_4)H$ [4] have been prepared in solution, and NMR data have been used to show the presence of distinct ethylene and hydride ligands in these complexes. However, isoelectronic Co compounds $Co(C_5Me_4R)Et(C_2H_4)^+$ [5] and $Co(C_5Me_5)PR_3Et^+$ [6] have been assigned structures involving agostic β-CH–metal interactions. There is much experimental evidence for agostic interactions in reactions of β-CH bonds with metals having other coordination numbers [7,8]. Crystal structures of several complexes involving agostic interactions of β-CH bonds are available [7–9]. The complex $C_5Me_5Co(C_2H_5)(PR_3)^+$ (**1**) [6] can be regarded as an example of an intermediate

0022-328X/86/$03.50

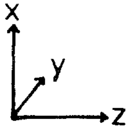
on the pathway of a C–H bond addition; the product of addition, were it to take place, would correspond to an octahedral ethylene-hydride complex. However, no crystal structure is available for the octahedral ethylene-hydride complex. We analyze here the geometrical and electronic factors that favour agostic interactions of β-CH bonds. The Extended Hückel (EH) [10] method is used to obtain wave functions along a reaction coordinate [7] connecting 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 one hydride are either C_5H_5 and PH_3 or four hydrides with appropriate charges to retain the *d* electron count at Co as d^6. There have been previous theoretical studies of CH bond activation [1b,11], but none set out to delineate the geometrical features of β-CH bond metal interactions.

Results and discussion

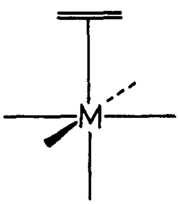
The complex, $Co(C_5Me_5)(PR_3)C_2H_5^+$ (**1**) was selected as the reference structure



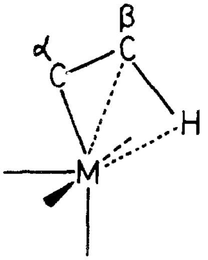
1



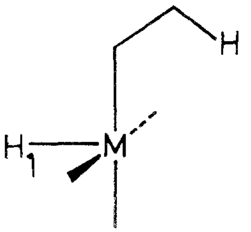
with agostic interactions, but $Co(C_5H_5)Et(PH_3)^+$ (**2**) was used as a model with geometry adapted from the X-ray structure [6]. The transformation of **2** to the octahedral ethylene-hydride complex **3** and to the pentacoordinate ethyl complex **4**



3



2



4

was examined through EH calculations (**4** → **2** → **3**), the $C_5H_5MPH_3$ geometry being kept constant during this process. The Co, C_α, C_β and the migrating hydrogen were kept in the same plane throughout. The exact geometries and the parameters used in these and other calculations are given in the appendix.

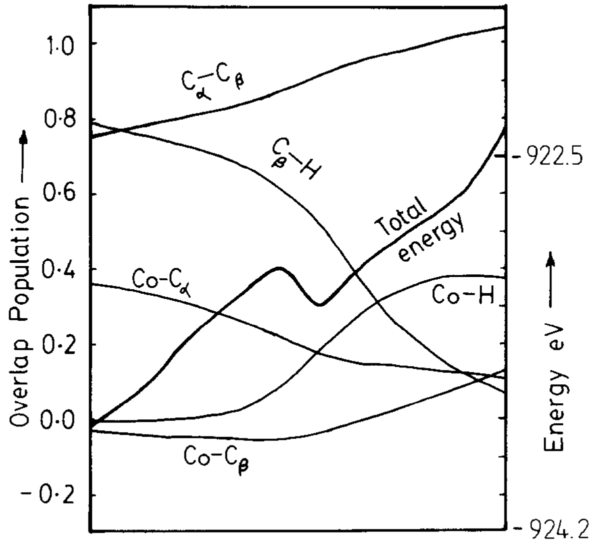


Fig. 1. The variation of total energy (thick line) and the Mulliken overlap population for the process (4 → 2 → 3) starting from $[(\eta^5\text{-}C_5H_5)Co(PH_3)(C_2H_5)]^+$.

Figure 1 shows the variation of the total energy (the sum of the one electron MO energies) with C_α–C_β distance (**4** → **2** → **3**). There is a minimum corresponding to **2**, with the energy increasing in either direction. Interestingly the energy increases continuously in the direction of the octahedral complex **3** from **2**, whereas along the route towards **4**, the energy initially rises and then falls.

The small barrier for the conversion of the agostic into the pentacoordinate structure shows the ease of vacating the sixth coordination site; π ligands may then occupy this position leading to further reactions. Complex **1**, for example, is known to catalyze the polymerization of ethylenes [6]. Addition of the C–H bond to the metal is uphill in energy. We carried out a search for well documented octahedral d^6 complexes with ethylene and hydride as *cis* ligands but could not find any with Co as the metal. It appears that the β-CH bond addition in these complexes proceeds to the agostic stage only with the C–H bond persisting. Our initial calculations involved ligands very close to that in **1**. The general trend in energy is not different when ligands are changed to simpler ones; thus, replacement of $C_5H_5^{-1}$ and PH_3 by H_4^{4-} did not change the reaction profile. Hence, $H_4CoH(C_2H_4)^{-2}$ is considered in the subsequent discussion.

The easiest point to understand along the reaction coordinate is the final one, with the octahedral geometry **3**. The variation in the geometry between **3** and **2** or **4** provides 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 X-ray structural data [7]. A comparison of the ethylene-hydride geometry **3** with their scheme (Fig. 2) shows that the carbon is already close to the structures with agostic interactions. Fig. 2a shows the point corresponding to the agostic interaction **2**, **3** and **4**. Thus, the deviation from the octahedral geometry needed to reach the agostic point is not large. As seen below, this retains much of the M–C and M–H

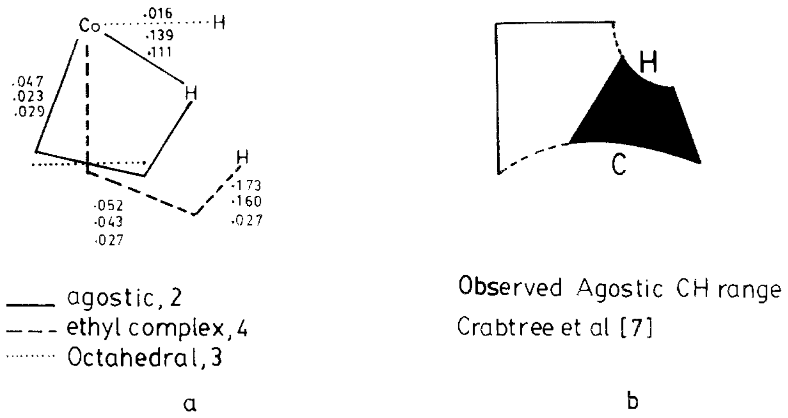


Fig. 2. A comparison of the reaction profile for β-CH bond addition (a) with that given by Crabtree et al. (b) [7]. The geometry of the agostic point [solid line] in (a) falls approximately in the region of agostic interaction. The dotted lines refer to the octahedral complex and the broken lines to 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 (a). The middle value corresponds to the agostic point, and the lower one to the octahedral complex.

bonding present in the complex although the C–H interaction is substantially increased.

A Walsh diagram connecting **4**, **2** and **3** for the process depicted in Fig. 2 is given in Fig. 3. The details of the variation of the energy levels may be accounted for by condensation of the MOs of the octahedral ethylene-hydride complex **3**. The HOMO, $9a'$, orbital corresponds to the bonding combination of ethylene π-bond and the x^2-z^2 (obtained as a linear combination of x^2-y^2 and z^2) at **3** *. This also has considerable M–H bonding, but is C_β–H antibonding. At the agostic point, **2**, this antibonding interaction is at a maximum. The M–C_α bonding and C_β–H bonding interactions predominate at the pentacoordinate point **4**. Rather than going through the details of all the orbitals, we concentrate on $3a'$. This ligand-based orbital follows the general trend in energy; it is mainly an M–H bonding orbital in **3**, and retains much of this character 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. 2a. The upper number corresponds to **4**, 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. 4. The balance of C–H, M–H and M–C interactions in stabilizing agostic structures are also seen in the variation of the Mulliken overlap population summed over all occupied orbitals (Fig. 1). The decrease in the C–H population in going from **4** to **2** is negligible while this increases the M–H bonding. There is a drastic decrease in the C–H bond population on going from the agostic to the octahedral complex. The variations in the overlap populations also show that the agostic point is the best compromise along the reaction coordinate.

---

[*] Throughout this paper the orbitals are designated by subscripts only; for example $d_{x^2-y^2}$ is represented as x^2-y^2, p_y as y etc.

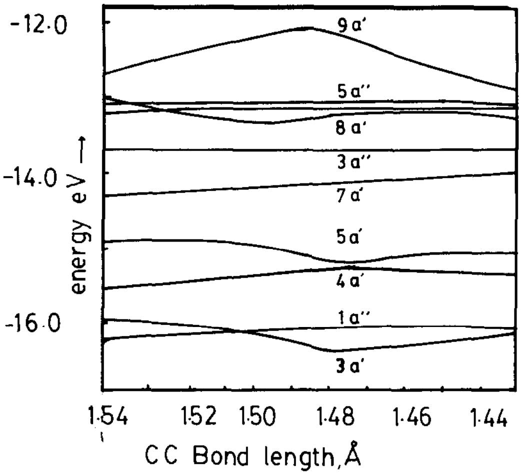


Fig. 3. The Walsh diagram for the process **4** → **2** → **3** starting from $H_5CoC_2H_4{}^{2-}$.

The importance of the M–C–H interactions is also seen from calculations in which the matrix elements corresponding to M–H overlaps are omitted from the overlap matrix. In contrast to the pattern in Fig. 1, the total energy now increases continuously. There is no minimum along the path. A similar result is obtained when the M–C_β overlaps are neglected in the calculations.

If the CH donation to the 16-electron system is responsible 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 is found to be the case; variation of the hydrogen H_{ii} 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 about 10% by X-ray studies, we repeated the calculations by increasing the M–H and C–H distances at the agostic point by 10%; the total energy and other parameters did not

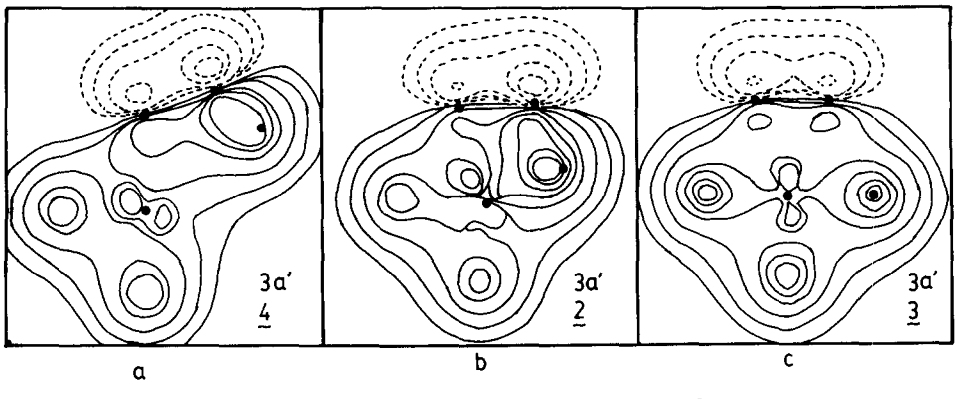


Fig. 4. Cross section of the 3*a*′ MO along the MCCH plane of $H_5CoC_2H_4{}^{2-}$ **4** (a), **2** (b) and **3** (c). The contours used for plotting were ±0.550, 0.275, 0.200, 0.180, 0.150, 0.138, 0.100, 0.069, 0.034, 0.017, 0.009.

change appreciably from the earlier values and, in particular, the agostic point still appeared as a minimum.

Conclusions

The geometric factors favouring agostic interactions involving β-CH bonds have been analyzed using the model compounds, $C_5H_5Co(PH_3)H(C_2H_4)^+$ and $CoH_5C_2H_4^{2-}$. Extended Hückel calculations along the reaction coordinate connecting the 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. 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 with that formulated by Crabtree and coworkers [7] reveals how small a change in geometry is required to convert the octahedral ethylene-hydride complex into the agostic complex with β-CH–M interaction. The stability of the structure with agostic interaction can be increased or decreased by increasing or decreasing the electron-withdrawing ability of the remaining ligands.

Appendix

The exponents and H_{ii} for cobalt, phosphor, carbon and hydrogen used in the Extended Hückel calculations are indicated in Table 1. The geometric changes in six equal increments for the process **4** → **2** are as follows. On going from **4** to **2** the $Co–C_\alpha$ distance is kept constant at 1.97 Å and the $C_\alpha–C_\beta$ and $C_\beta–H$ distances are varied from 1.54 to 1.48 Å and 1.08 to 1.31 Å, respectively. The angles $Co–C_\alpha–C_\beta$ (of $CoH_4C_2H_5^{-2}$, **4**) $H^1–Co–C_\alpha$ and $C_\alpha–C_\beta–H$ are varied from 109.5, 90 and 109.5° to 74.6, 74.6 and 105.8°, respectively. In the second process, **2** to **3**, the $Co–C_\alpha$, $C_\alpha–C_\beta$ and $C_\beta–H$ distances are varied from 1.97, 1.48 and 1.31 Å to 2.41, 1.43 and 2.15 Å, respectively, and the angles $C_\alpha–C_\beta–H$, $H^1–Co–C_\alpha$ and $Co–C_\alpha–C_\beta$ from 105.8, 74.6 and 74.6° to 116.9, 69.5 and 69.5°, respectively, in six equal increments. C_5Me_5 replaces three hydrides and PH_3 replaces the other hydride in $H_4Co(C_2H_5)^{-2}$ to give $(C_5Me_5)Co(PH_3)(C_2H_5)^+$ (**1**). The Co–P, P–H and $Co–C(C_5Me_5)$ distances are kept constant at 2.18, 1.44 and 2.09 Å, respectively.

TABLE 1

PARAMETERS USED IN EXTENDED HÜCKEL CALCULATIONS

Orbital		H_{ii} (eV)	ζ_1	ζ_2	C_1 [a]	C_2 [a]
Co	3*d*	−13.18	5.55	2.10	0.5679	0.6059
	4*s*	−9.21	2.00			
	4*p*	−5.29	2.00			
C	2*s*	−21.40	1.625			
	2*p*	−11.40	1.625			
P	3*s*	−18.60	1.60			
	3*p*	−14.00	1.60			
H	1*s*	−13.60	1.30			

[a] Contraction coefficients used in the double-ζ expansion.

throughout the reaction profile (**4** → **2** → **3**) and other geometric changes are similar to those defined above.

Acknowledgements

The Council of Scientific and Industrial Research, New Delhi is thanked for financial assistance. Computations were carried out at the University of Hyderabad Computer Centre. Support under a UGC Special Assistance Program in Organic Chemistry is also acknowledged.

References

1 (a) J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1980; (b) J. Saillard and R. Hoffmann, J. Am. Chem. Soc., 106 (1984) 2006; (c) E.L. Muetterties, Chem. Soc. Rev., 12 (1983) 283; (d) R.G. Bergman, P.F. Seidler and T.T. Wenzel, J. Am. Chem. Soc., 107 (1985) 4358; (e) A.H. Janowicz and R.G. Bergman, ibid., 104 (1982) 352; 105 (1983) 3929; (f) J.K.H. Hoyano and W.A.G. Graham, ibid., 104 (1982) 3723; (g) R.G. Bergman, Science (Washington, D.C.), 223 (1984) 902; (h) W.D. Jones and F.J. Feher, Organometallics, 2 (1983) 562; J. Am. Chem. Soc., 106 (1984) 1650; (i) R.A. Periana and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 7272.

2 R. Werner and H. Werner, Chem. Ber., 116 (1983) 2074.

3 R. Werner and R. Feser, J. Organomet. Chem., 232 (1982) 351.

4 M.A. Esteruelas and H. Werner, J. Organomet. Chem., 303 (1986) 221.

5 M. Brookhart, M.L.H. Green and R.B.A. Pardy, J. Chem. Soc., Chem. Commun., (1983) 691.

6 R.B. Cracknell, A.G. Orpen and J.L. Spencer, J. Chem. Soc., Chem. Commun., (1984) 326.

7 R.H. Crabtree, E.M. Holt, M. Lavin and S.M. Morehouse, Inorg. Chem., 24 (1985) 1986.

8 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.

9 (a) Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1982) 802 and 1410; (b) E. Carmona, L. Sanchez, J.M. Marin, M.L. Poveda, J.L. Atwood, R.D. Priester and R.D. Rogers, J. Am. Chem. Soc., 106 (1984) 3214; (c) R.K. Brown, J.M. Williams, A.J. Schultz, G.D. Stucky, S.D. Ittel and R.L. Harlow, ibid., 102 (1980) 981; (d) G.M. Dawkins, M. Green, A.G. Orpen and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1982) 41; (e) M. Green, N.C. Norman, A.G. Orpen, J. Am. Chem. Soc., 103 (1981) 1269; (f) G. Erker, W. Fromberg, K. Angermund, R. Schlund and C. Kruger, J. Chem. Soc., Chem. Commun., (1986) 372.

10 R. Hoffmann, J. Chem. Phys., 39 (1963) 1397; R. Hoffmann and W.N. Lipscomb, ibid., 36 (1962) 3179, 3489. Despite the approximate nature of the method its success in transition metal organometallic chemistry has been demonstrated (e.g. see R. Hoffmann, Science, 211 (1981) 995). Although the absolute energies and even the position of the minimum we obtained by this method may not be correct, the conclusions we draw from the overlap populations for the retention of the C–H bond along the addition pathway are unlikely to be proved invalid by more sophisticated calculations.

11 (a) O. Eisenstein and Y. Jean, J. Am. Chem. Soc., 107 (1985) 1177; (b) R.L. Harlow, R.J. McKinney and S.D. Ittel, ibid., 101 (1979) 7496; (c) N. Koga, S. Obara and K. Morokuma, ibid., 106 (1984) 4625; (d) R.J. Goddard, R. Hoffmann, and E.D. Jemmis, ibid., 102 (1980) 7667; H. Rabaa, J.-Y. Saillard and R. Hoffmann, J. Am. Chem. Soc., 108 (1986) 4327.