Theoretical Study on Acetaldehyde and Ethanol Elimination from the Hydrogenation of CH$_3$(O)CCo(CO)$_3$

Miquel Solà$^+$ and Tom Ziegler$^*$

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received November 13, 1995

A theoretical study based on density functional theory (DFT) has been carried out on the reaction pathways leading to acetaldehyde and ethanol formation from the hydrogenation of the coordinatively unsaturated CH$_3$(O)CCo(CO)$_3$ complex (1). Hydrogenation of 1 represents the last step of the catalytic hydroformylation process. We have found that, in the H$_2$-induced acetaldehyde elimination reaction, the energy barrier for the oxidative addition/reductive elimination process is only 36.3 kJ mol$^{-1}$. This process is kinetically favored over a $\sigma$-bond metathesis pathway involving a four-center transition state with a barrier of 70.4 kJ mol$^{-1}$. The possible formation of a hydroxycarbene complex which easily will add hydrogen yielding ethanol and regenerating the HCo(CO)$_3$ catalyst has also been discussed. This hydroxycarbene complex is thermodynamically accessible, although the energy barriers for the reaction pathways leading to its formation are larger than 95.5 kJ mol$^{-1}$. On the other hand, the production of ethanol from hydrogenation of acetaldehyde through a hydroxymethyl intermediate has an energy barrier of 42.3 kJ mol$^{-1}$. It is concluded that the catalytic generation of alcohols does not proceed via the formation of a hydroxycarbene intermediate but rather through further hydrogenation of the aldehyde molecules.

Introduction

The hydroformylation process converts olefins and synthesis gas to predominantly aldehydes with alcohols and alkanes as minor products. It involves low-valent cobalt$^+$ and rhodium complexes$^{2a,3}$ as catalysts, and it is carried out on a massive industrial scale. The amount of alcohols produced can be increased by raising the temperature or adding water.$^{2a,b,4,5}$

The overall equation for the formation of propanol from ethylene and CO can be written as:

\[ 2\text{HCo(CO)}_4 + \text{CH}_2\text{CH}_2\text{CH}_2 + \text{CO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{Co}_2(\text{CO})_8 \]  (1)

The most widely accepted mechanism for the hydroformylation reaction of eq 1 is due to Heck and Breslow$^6$ and involves five steps;\textsuperscript{7-15} see Scheme 1.

The active catalyst in Scheme 1 is HCo(CO)$_3$, which is generated from HCo(CO)$_4$ by loss of a CO ligand, step a of Scheme 1. Evidence for the presence of HCo(CO)$_3$

\begin{center}
\textbf{Scheme 1}
\end{center}

The theoretical study based on density functional theory (DFT) has been carried out on the reaction pathways leading to acetaldehyde and ethanol formation from the hydrogenation of the coordinatively unsaturated CH$_3$(O)CCo(CO)$_3$ complex (1). Hydrogenation of 1 represents the last step of the catalytic hydroformylation process. We have found that, in the H$_2$-induced acetaldehyde elimination reaction, the energy barrier for the oxidative addition/reductive elimination process is only 36.3 kJ mol$^{-1}$. This process is kinetically favored over a $\sigma$-bond metathesis pathway involving a four-center transition state with a barrier of 70.4 kJ mol$^{-1}$. The possible formation of a hydroxycarbene complex which easily will add hydrogen yielding ethanol and regenerating the HCo(CO)$_3$ catalyst has also been discussed. This hydroxycarbene complex is thermodynamically accessible, although the energy barriers for the reaction pathways leading to its formation are larger than 95.5 kJ mol$^{-1}$. On the other hand, the production of ethanol from hydrogenation of acetaldehyde through a hydroxymethyl intermediate has an energy barrier of 42.3 kJ mol$^{-1}$. It is concluded that the catalytic generation of alcohols does not proceed via the formation of a hydroxycarbene intermediate but rather through further hydrogenation of the aldehyde molecules.

---

$^*$ Permanent address: Institut de Química Computacional and Departamento de Química, Universitat de Girona, 17071 Girona, Catalonia, Spain.

$^+$ Abstract published in Advance ACS Abstracts, May 1, 1996.


---

\[ \text{Heck and Breslow, 1962} \]
has been provided by matrix isolation techniques. A kinetic study by Ungváry and Markó indicated further that HCo(CO)₄ is about 0.3% dissociated to HCo(CO)₃ at room temperature.

The focus of the present study is on the final elimination of aldehyde, step e of Scheme 1. In this step, H₂ is assumed to add oxidatively to the unsaturated acyl complex yielding a dihydro acyl species

$$\text{R(O)CCo(CO)₃} + \text{H₂} \rightarrow \text{R(O)CCo(CO)₃(H)₂} \quad (2)$$

followed by an irreversible reductive elimination of the aldehyde molecule:

$$\text{R(O)CCo(CO)₃(H)₂} \rightarrow \text{RCHO} + \text{HCo(CO)₃} \quad (3)$$

Oxidative addition (eq 2) and reductive elimination (eq 3) are common elementary reaction steps among late transition metals such as cobalt. However, aldehyde elimination could alternatively proceed directly through the formation of a four-center transition state in a σ-bond metathesis process. The activation of H–H and C–H linkages by σ-bond metathesis is a well-established process among electron-poor early transition metals and it has been invoked for late transition metals as well. The first objective of our study will be to examine aldehyde elimination by H₂ for both pathways. A previous theoretical investigation on this subject was inconclusive since it made use of limited geometry optimization.

The other point we want to address is also connected to step e of Scheme 1. It is concerned with possible pathways leading to alcohol formation as a side reaction in the hydroformylation process. Alcohol formation is normally assumed to result from further reaction of the aldehyde formed in step e with the catalyst HCo(CO)₃ to form a hydroxyalkyl complex:

$$\text{HCo(CO)₃} + \text{RC(O)H} \rightarrow \text{R(OH)(H)CCo(CO)₃} \quad (4)$$

which can react with H₂ to eliminate the alcohol and regenerate the catalyst HCo(CO)₃:

$$\text{R(OH)(H)CCo(CO)₃} + \text{H₂} \rightarrow \text{RCH₂OH} + \text{HCo(CO)₃} \quad (5)$$

Some authors have suggested an alternative mechanism. This mechanism involves hydroxycarbene as an intermediate. It is suggested that hydroxycarbene is formed in step e of Scheme 1 by a hydride transfer to the acyl oxygen rather than the acyl carbon:

\text{(18) Nicholas, K. M. Organometallics 1982, 1, 1713.)}
Further isomerization of the hydroxycarbene complex will produce the hydroxalkyl complex

\begin{equation}
R(OH)CCl(CO)_{3}H \rightarrow R(OH)(H)CCl(CO)_{3}
\end{equation}

which again can react with \(H_2\) to eliminate \(HCo(CO)_3\) and an alcohol according to eq 5.

We shall here investigate the processes in eqs 4 and 5 as well as the alternative mechanism of eqs 6, 7, and 5. The alternative route toward alcohol formation has not been studied previously in any detail, probably because there are little experimental data on hydroxycarbene complexes. On the other hand, several methoxy carbene complexes have been characterized.

Our theoretical investigation will be based on density functional theory (DFT). The application of approximate density functional theory to organometallic chemistry has been reviewed recently.

### Computational Details

The reported calculations were carried out by using the Amsterdam density functional (ADF) program system, developed by Baerends et al. and vectorized by Ravenek. The numerical integration scheme employed was that of te Velde and Baerends. An uncontracted triple-ζ basis set was used for describing the 3s, 3p, 3d, 4s, and 4p orbitals of cobalt. For carbon (2s,2p), oxygen (2s,2p), and hydrogen (1s), double-ζ basis sets were employed and augmented by an extra polarization function. Electrons in lower shells were treated by numerical integration scheme employed was that of te Velde et al.

### Results and Discussion

The starting point for our discussion is the acyl intermediate \(\text{CH}_3(\text{O})\text{CCl(CO)}_3\). It is shown as 1 in Scheme 2. The reaction of 1 with \(H_2\) can lead to formation of aldehyde and regeneration of the catalyst \(\text{HCo(CO)}_3\), 2 → 5 of Scheme 2. Alternatively, 1 can react with two molecules of \(H_2\) to form alcohol and \(\text{HCo(CO)}_3\), 2 → 10 of Scheme 2. We turn first to the process in which acetaldehyde is formed from the interaction of \(\text{CH}_3(\text{O})\text{CCl(CO)}_3\) (1) with molecular hydrogen.

\[ \text{H}_2\text{-Induced Acetaldehyde Elimination from CH}_3(\text{O})\text{CCl(CO)}_3 \]

Optimized key structures for the aldehyde forming process are depicted in Figure 1. Table 1 gathers the relative energies of minima and approximate transition states (TS) obtained from the linear transit procedures. The most stable structure for the reactant \(\text{CH}_3(\text{O})\text{CCl(CO)}_3\), (1), was found to have the acyl group in the axial position, Figure 1. In this structure, there is a marked \(\eta^2\) interaction between a lone pair on the acyl oxygen and the coordinatively unsaturated metal center.

The reaction of 1 with \(H_2\) results in the dihydrogen complex \(\text{CH}_3(\text{O})\text{CCl(CO)}_3\)(η²-\(\text{H}_2\)). Complex 2 with \(H_2\) in an equatorial site and the hydrogen–hydrogen vector perpendicular to the Co–\(\text{C}_{\text{acyl}}\) bond was found to be the conformation of lowest energy. In this conformation, the empty \(\sigma^*_{\text{H-H}}\) orbital has the correct orientation to interact with the HOMO of complex 1 and the occupied \(\alpha_{\text{H-H}}\) orbital can interact with the LUMO of complex 1. Electron donation to the \(\sigma^*_{\text{H-H}}\) orbital leads to the activation of molecular hydrogen which has a larger H–H bond distance in the \(\eta^2\) adduct (0.826 Å) than in the free \(\text{H}_2\) molecule (0.755 Å). The dihydrogen complex 2 is more stable than 1 + \(\text{H}_2\) by 10.5 kJ·mol⁻¹. Interestingly, the Co–\(\text{C}_{\text{acyl}}\) bond distance is increased by 0.2 Å in 2 compared to 1. The weaker bond in 2 will facilitate aldehyde elimination in a subsequent step. It is generally assumed that the aldehyde elimination step proceeds from 2 by oxidative addition of the \(\eta^2\)-\(\text{H}_2\) ligand to form the dihydride complex, 3. We find the addition process 2 → 3 to be endothermic by 25.8 kJ·mol⁻¹. This is in agreement with the experimental fact that, in a similar complex, the predominant intermediate observed is 2 rather than 3. It is worth noting that the nature of the ancillary ligands may change the relative energy of the dihydrogen complex.
compared to its dihydride isomer. Thus, substitution of CO by PR$_3$ leads to a stabilization of complex 3 compared to 2. The position of the transition metal center within a triad may also affect the relative stability of the dihydrogen and dihydrides species. Calculations have shown$^{15c}$ that the stability of the dihydride isomer increases in comparison to the dihydrogen adduct going from the 3d (Co) and 4d (Rh) congeners to the 5d (Ir) homologue. This trend is caused by relativistic effects$^{15c}$ which become important for 5d transition elements.

Figure 2 depicts the energy profiles for the paths connecting complexes 2 to 7. The activation barrier for $2 \rightarrow 3$ is only 30.5 kJ · mol$^{-1}$. Such a low energy barrier is in agreement with previous kinetic studies in related complexes.$^{15a}$ At the highest point along the transit the H–H bond length is 1.298 Å, the transition state being product-like; see TS($2 \rightarrow 3$) of Figure 3. This low energy barrier can be attributed to the aforementioned favorable interactions along the transit of the $\sigma_{12}$ and $\sigma^*_{12}$ orbitals with the LUMO 1b and HOMO 1a of complex 1, respectively.

The elimination of CH$_3$C(O)H from 1 by H$_2$ gives rise to the adduct 4, where acetaldehyde is complexed to the HCo(CO)$_3$ fragment through the hydrogen of the carbonyl carbon in an agostic$^{20}$ interaction. The Co–H distance of 1.827 Å is only 0.3 Å longer than a normal

---

Table 1. Relative Energies$^a$ for Species Involved in the H$_2$-Induced Aldehyde Elimination Process

<table>
<thead>
<tr>
<th>species</th>
<th>rel energy$^a$</th>
<th>species</th>
<th>rel energy$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 + H$_2$</td>
<td>10.5</td>
<td>TS(3 $\rightarrow$ 4)$^b$</td>
<td>36.3</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>TS(2 $\rightarrow$ 4)$^b$</td>
<td>70.4</td>
</tr>
<tr>
<td>3</td>
<td>25.8</td>
<td>TS(2 $\rightarrow$ 6)$^b$</td>
<td>95.5</td>
</tr>
<tr>
<td>4</td>
<td>14.0</td>
<td>TS(4 $\rightarrow$ 6)$^b$</td>
<td>185.0</td>
</tr>
<tr>
<td>5</td>
<td>6.1</td>
<td>TS(5 $\rightarrow$ 7)$^b$</td>
<td>48.4</td>
</tr>
<tr>
<td>6</td>
<td>33.2</td>
<td>TS(6 $\rightarrow$ 7)$^b$</td>
<td>39.8</td>
</tr>
<tr>
<td>7</td>
<td>-5.0</td>
<td>CH$_3$CHO + HCo(CO)$_3$</td>
<td>41.1</td>
</tr>
<tr>
<td>TS(2 $\rightarrow$ 3)$^b$</td>
<td>30.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All energies in kJ · mol$^{-1}$ are relative to 2. $^b$ The energy of the approximate transition state TS(a $\rightarrow$ b) is taken from the highest energy point on the linear transit a $\rightarrow$ b.

---

Figure 1. Optimized structures for complexes 1–5. Bond distances are in Å, and angles are in deg.

Figure 2. Energy profile for the paths connecting complexes 2–7. The energy zero point refers to structure 2. The H–H bond distance represents the reaction coordinate.
Co–H bond, and the C–H distance is stretched to 1.167 Å. Complex 4 is 14.0 kJ mol\(^{-1}\) less stable than complex 2, and 27.1 kJ mol\(^{-1}\) more stable than acetaldehyde and HCo(CO)\(_3\). However, it must be noted that the final elimination of acetaldehyde will be facilitated by the formation of HCo(CO)\(_4\) as CO adds to the HCo(CO)\(_3\) species. This process was found to be highly exothermic by 169 kJ mol\(^{-1}\).

As mentioned in the Introduction, complex 4 could conceivably be formed through an oxidative addition/reductive elimination path (2 \(\rightarrow\) 3 \(\rightarrow\) 4) or alternatively in a process involving a four-center transition state which avoids direct oxidative addition of H\(_2\) to the metal center (2 \(\rightarrow\) 4). The total activation energy found for the 2 \(\rightarrow\) 3 \(\rightarrow\) 4 path is 36.3 kJ mol\(^{-1}\) with the barrier for the oxidative addition step 2 \(\rightarrow\) 3, Figure 2, given by 30.5 kJ mol\(^{-1}\) and that of the reductive elimination step 3 \(\rightarrow\) 4 given by 10.5 kJ mol\(^{-1}\). Thus, for the path 2 \(\rightarrow\) 3 \(\rightarrow\) 4 the oxidative addition is the crucial step. The approximate transition state for the reductive elimination path, TS(2 \(\rightarrow\) 4) of Figure 3, has a stretched H–H bond of 0.985 Å, indicating that H\(_2\) activation as for the alternative path 2 \(\rightarrow\) 3 \(\rightarrow\) 4 is the crucial part of the reaction. However, in TS(2 \(\rightarrow\) 4) the H–H bond has to be perpendicular to the HOMO 1a of the fragment 1 in order to produce a C–H bond. Thus, the \(\sigma^*\)H\(_2\) orbital cannot be stabilized by 1a. Instead \(\sigma^*\)H\(_2\) interacts with the Co–C(O)CH\(_3\) \(\sigma\)-bonding orbital, 1c. Unfortunately, the Co–C(O)CH\(_3\) \(\sigma\)-bonding orbital is of lower energy than 1a and forms in addition a smaller overlap with \(\sigma^*\)H\(_2\). For this reason the stabilization of \(\sigma^*\)H\(_2\) is much poorer in TS(2 \(\rightarrow\) 4) than in TS(2 \(\rightarrow\) 3) and the activation energy accordingly higher for breaking the H–H bond.

It is worth to note that the CO ligands of the distorted octahedral complexes 2 and 3 rearrange along the transit to 4, so as to place the hydride in an axial position. In this way the HCo(CO)\(_3\) framework regains its most stable conformation. Adduct 4 can be viewed as a trigonal bipyramid (TBP) species with the aldehyde attached via a C–H \(\sigma\)-bond to the metal center. In the \(\sigma\)-complex, 4, the aldehyde ligand is in an equatorial position.
position and density is donated from the σCH orbital to the LUMO 1b. In some ways 4 is similar to an η1 conformation of the dihydrogen complex 2 in which H2 is bound end-on.

The σ-complex 4 can rearrange by a simple rotation of the acetaldehyde fragment to the π-complex 5, which is more stable than 4 by only 7.9 kJ/mol. There are a number of possible conformations for the aldehyde π-complex, of which structures with CH3CHO in the axial position were found to be less stable than those with the aldehyde coordinated at an equatorial site.4d Here, we have considered only the equatorial coordination with the CO bond of CH3CHO parallel to the H–Co–CO axis of the TBP framework and with the oxygen atom of the CH3CHO fragment close to the hydride coordinated to cobalt. In complex 5 there is an η2 interaction in which the πCO and π*CO of acetaldehyde interact with the metal center in a way similar to σH2 and η2H2, respectively, of the η2-H2 complex 2.31 The C–O bond of the aldehyde is seen to be elongated as a result of the donation of charge from the cobalt center to the π*CO orbital. Finally, it is worth noting that the Co–O bond length is shorter than the Co–C bond length as experimentally found in similar complexes.32

It has been suggested10b,c that the hydrogen used in aldehyde elimination comes from the strong acidic HCO(CO)4 species which is present as a precataylist in significant quantities10b,c rather than from H2 as assumed in step e of Scheme 1. According to this mechanism, HCO(CO)4 interacts with the unsaturated R(O)CCo(CO)3 complex and transfers its hydrogen to form the aldehyde and Co2(CO)8:

R(O)CCo(CO)3 + HCo(CO)4 → RCHO + Co2(CO)8  (8)

The latter unsaturated species adds subsequently a CO molecule:

Co2(CO)8 + CO → Co2(CO)9  (9)

The Co2(CO)9 dimer finally reacts with H2 to regenerate HCo(CO)4.12b,12c Similar steps have been invoked in the homolysis of alcohols13 and in the reduction of aldehydes.10c

An elegant experiment14 based on IR spectroscopy has been designed in order to determine the source of hydrogen in the aldehyde elimination step. The experiment was carried out under normal hydroformylation conditions with hydrogen gas replaced by a mixture of H2 and D2. It was established in this study that H2 is the main source of hydrogen in the aldehyde elimination step, even in the presence of large amounts of HCo(CO)4. The hydride HCo(CO)4 was found to be responsible for only 5% of the hydrogen present in the synthesized aldehydes. We have as a result not considered the elimination path given in eqs 8 and 9.

H2-Induced Ethanol Elimination from CH3(O)-CCo(CO)3 via Hydroxycarbene Complex Formation and via Further Hydrogenation of Acetaldehyde. We have in the previous section studied the transfer of hydrogen from complexes 2 and 3 to the coordinated carbon atom of the acyl group. One might wonder whether an alternative transfer to the oxygen atom of the acyl group would not be feasible as well. Such a transfer will result in the hydroxycarbene complex 6 of Scheme 2. This species is interesting since it could isomerize further to the hydroxymethyl complex 7 by hydride transfer from the metal center to the carbene carbon. The hydroxymethyl complex 7 can lead to generation of alcohol2a,10c,17 in the sequence of steps 7 → 8 → 9 → 10 or 7 → 8 → 10, as illustrated in Scheme 2.

Alcohol formation is one of the important side reactions observed in connection with hydroformylation. It is normally attributed2a,10c,17 to a further reaction of the aldehyde eliminated in step e of Scheme 1 with the catalyst HCo(CO)4 and H2. More specifically, aldehyde can complex to HCo(CO)4, 5 of Scheme 2, followed by hydride transfer to form a hydroxymethyl complex, 7. After formation of 7, alcohol is formed in the sequence of steps mentioned above.

This section is concerned with alcohol formation as a side reaction in the hydroformylation process. It is clear from Scheme 2 that the hydroxymethyl complex 7 must be a key intermediate in this process and that 7 might be formed from the aldehyde adduct 5 as well as the dihydrogen complex 2 via the hydroxycarbene 6. We shall examine both pathways toward 7 as well as the further conversion of this species to alcohol.

This kinetic investigation was prompted by the fact that we find aldehyde formation

CH3(O)CCo(CO)3 + H2 → CH3CHO + HCo(CO)3  (10)

to be a slightly endothermic reaction with a reaction enthalpy of 30.6 kJ·mol−1 whereas alcohol formation

CH3(O)CCo(CO)3 + 2H2 → CH3CH2OH + HCo(CO)3  (11)

is exothermic by −39.3 kJ·mol−1. Yet, only aldehyde is formed in large quantities under normal hydroformylation conditions.

We begin by discussing the formation of 7 from 2 via the hydroxycarbene 6. Table 1 gathers the energies of complexes 6 and 7 relative to 2. Also given are the activation energies for the pathways leading to 6 and 7. The molecular structures of complexes 6 and 7 are depicted in Figure 4.

It follows from Table 1 that the hydroxycarbene 6 is only 33.2 kJ·mol−1 above 2 in energy, and so it is accessible from a thermodynamic point of view. We have analyzed its possible formation from complexes 2–4.

The reaction path corresponding to the 2 → 6 interconversion has an energy barrier of 95.5 kJ·mol−1. Thus, this process is not likely to take place at room temperature. The transition state for the 2 → 6 interconversion is shown in Figure 3 as TS(2 → 6). It exhibits as for TS(2 → 4) a stretched H–H bond perpendicular to the plane holding the HOMO 1a. Therefore the stabilization of the σ*H2 orbital is of the
inefficient type, 1c, already encountered in TS(2 \rightarrow 4). However, the barrier for the 2 \rightarrow 6 paths is higher than for the 2 \rightarrow 4 step. This is so, since the H2 molecule in order for one of the hydrogens to reach the acyl oxygen is further away from the metal center.

We have also traced the energy profile for the 3 \rightarrow 6 transit starting from complex 3 and using the O\-H bond formed as the reaction coordinate, although in this case the hydrogen is not directly transferred to the oxygen atom but rather goes first to the carbon atom yielding complex 4, 3 \rightarrow 4 of Figure 3, followed by a migration of hydrogen from carbon to oxygen on the acyl group, 4 \rightarrow 6 of Figure 3. In a direct transfer of hydrogen the Co-H bond would presumably have to be nearly broken before a O-H bond could be formed.

The exothermic 3 \rightarrow 4 transit has already been discussed. It has a low barrier of 10 kJ \cdot mol^{-1} and is quite feasible. The energy profile corresponding to the 4 \rightarrow 6 process has an energy barrier as high as 172.0 kJ \cdot mol^{-1}, and therefore this interconversion is not possible at room temperature. The high barrier for 4 \rightarrow 6 is associated with the strain in the three-center transition state TS(4 \rightarrow 6) of Figure 3. In orbital terms this translates into poor bonding overlaps between \( t_{1u} \) and the \( \sigma \)-orbitals on oxygen and carbon of the acyl groups since these orbitals are unable to direct themselves straight toward the hydrogen atom.

To sum up, the hydroxycarbene complex 6 is kinetically only accessible at high temperatures, and it is unlikely that significant concentrations of this intermediate are present under normal hydroformylation conditions. Nevertheless, if obtained, complex 6 would be easily transformed to complex 7, since the 6 \rightarrow 7 conversion has a calculated energy barrier of only 6.6 kJ \cdot mol^{-1}. The pseudotetrahedral complex 7 is the most stable among the 2 \rightarrow 7 systems. It has a marked agostic interaction in which the Co-H bond distance is 1.812 Å and the C-H bond length is 1.177 Å; see Figure 4.

The alternative pathway to the hydroxymethyl complex 7, starting from the aldehyde \( \pi \)-adduct 5, has been discussed in details elsewhere.7d The energy barrier for this process is a modest 42.7 kJ \cdot mol^{-1}. Thus it is clear that the migratory insertion step 5 \rightarrow 7 represents a more facile path to the hydroxymethyl complex 7 than any of the processes involving the hydroxycarbene intermediate 6.

We shall finally briefly discuss the conversion of 7 to alcohol and the HCo(CO)3 catalyst. The relative energies for the species involved are compiled in Table 2. Complex 7 can easily add H2 to yield complex 8 in a process which is exothermic by 28.5 kJ \cdot mol^{-1}, despite the fact that the Co-H agostic interaction is lost in complex 8. It is expected that during the initial interaction between H2 and complex 7 a rearrangement of the CO ligands will occur to leave complex 8 in its most stable conformation.7e We note that the process 7 + H2 \rightarrow 8 is more exothermic than the analogous reaction 1 + H2 \rightarrow 2. This can be rationalized by observing that the hydroxymethyl group, CH3(H)C(OH), in 8 is less electron withdrawing than the acyl fragment CH3CO in 2. Thus the back-donation to \( \sigma^*_{\text{H2}} \) in 8 is more pronounced and stabilizing. It is in line with this argument that the H-H distance is larger in 8 than in 2, 0.851 Å in complex 8 vs 0.826 Å in 2. Also the H2 fragment charge is 0.130 e- in complex 8 vs 0.164 e- in complex 2. The molecular structure of 8 and those of complexes 9 and 10 are drawn in Figure 5.

Table 2. Relative Energies\(^a\) for the Species Involved in H2-Induced Ethanol Elimination

<table>
<thead>
<tr>
<th>species</th>
<th>rel energy</th>
<th>species</th>
<th>rel energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 + H2</td>
<td>28.5</td>
<td>TS(8 \rightarrow 9)(^b)</td>
<td>24.8</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>TS(8 \rightarrow 10)(^b)</td>
<td>49.8</td>
</tr>
<tr>
<td>9</td>
<td>24.8</td>
<td>TS(9 \rightarrow 10)(^b)</td>
<td>44.5</td>
</tr>
<tr>
<td>10</td>
<td>-30.1</td>
<td>CH3H2O + HCo(CO)3</td>
<td>4.8</td>
</tr>
</tbody>
</table>

\(^a\) All energies in kJ \cdot mol^{-1} are relative to 8. \(^b\) The energy of the approximate transition state TS(a \rightarrow b) is taken from the highest energy point on the linear transit a \rightarrow b.
The energy barrier is 49.8 kJ \textperiodcentered mol\textsuperscript{−1}. The oxidative addition/reductive elimination reaction route (8 → 9 → 10) is again more favorable than the four-center transition state pathway (8 → 10), although the energy difference between these two pathways is now smaller, and therefore both mechanisms can be operative in this case.

The energy barrier for the four-center transition state pathway 8 → 10 is lower than for the corresponding 2 → 4 process on account of the fact that back-donation to σ\textsubscript{H\textsubscript{2}} is more facile with the hydroxymethyl group, CH\textsubscript{3}(H)C(OH), than the acyl fragment, CH\textsubscript{3}CO, as argued above. For the same reason, in the oxidative addition/reductive elimination reaction pathway (8 → 9 → 10) the activation energy for the addition step 8 → 9 of 24.8 kJ \textperiodcentered mol\textsuperscript{−1} is lower than the barrier of 30.5 kJ \textperiodcentered mol\textsuperscript{−1} calculated for the corresponding step 2 → 3 in the addition/reductive elimination reaction pathway (2 → 3 → 4). For the reductive elimination part, 9 → 10 has a barrier of 19.7 kJ \textperiodcentered mol\textsuperscript{−1}, 9.2 kJ \textperiodcentered mol\textsuperscript{−1} higher than 3 → 4 with 10.5 kJ \textperiodcentered mol\textsuperscript{−1}. Now the superior electron-withdrawing ability of CH\textsubscript{3}CO is better able to redistribute the electron density left on the metal from the reduction.

The geometrical changes undergone by complexes 8–10 during these transits are similar to those experienced by complexes 2–4. Thus, from 8 to 9 there is a significant closing of the CO\textsubscript{3}aH\textsubscript{2} and CO\textsubscript{3}aH\textsubscript{2} angles, and also in the linear transit from 8 or 9 to 10 there is a rearrangement of the coordinated CO ligands to leave the hydride in an axial position of the TBP.

Finally, elimination of ethanol from complex 10 it is found to be an endothermic process by 34.9 kJ \textperiodcentered mol\textsuperscript{−1}, but as in the release of acetaldehyde, this elimination will be facilitated by the formation of the HCo(CO)\textsubscript{4} species.

**Concluding Remarks**

In this work, we have shown that the hydrogenation of the 16-electron coordinatively unsaturated CH\textsubscript{3}(O)-CCo(CO)\textsubscript{3} species to produce acetaldehyde proceeds through the oxidative addition/reductive elimination pathway (2 → 3 → 4) with an energy barrier of only 36.3 kJ \textperiodcentered mol\textsuperscript{−1}. The hydrogenation via a four-center transition state (2 → 4) is less likely, since it has a larger energy barrier of 70.4 kJ \textperiodcentered mol\textsuperscript{−1}.

The generation of alcohol as a side product in the hydroformylation process was also considered. It was found that alcohol production is most likely to take place after aldehyde has been generated as an adduct in the π-complex HCo(CO)\textsubscript{3}(η\textsuperscript{2}-CH\textsubscript{3}C(O)H), 5. The first step is an isomerization of 5 to the hydroxymethyl species 7, which after further hydrogenation can produce alcohol, Scheme 2.

We have also considered an alternative route to the key intermediate 7 and alcohol production without prior aldehyde generation. In this mechanism hydrogenation of the 16-electron coordinately unsaturated CH\textsubscript{3}(O)-CCo(CO)\textsubscript{3}, 1, species leads to the hydroxycarbene intermediate 6 rather than aldehyde and HCo(CO)\textsubscript{3}. Subsequently 6 could isomerize to the key intermediate 7. It was found that 6 is thermodynamically accessible from 1 and H\textsubscript{2}. However, the kinetic barrier associated with the process 1 + H\textsubscript{2} → 6 was estimated to be 96 kJ \textperiodcentered mol\textsuperscript{−1} or more. This makes it unlikely that 6 is formed in significant quantities under normal hydroformylation conditions.

**Acknowledgment.** This investigation was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). We also acknowledge access to the IBM-RISC/6000 installations at the University of Calgary. M.S. acknowledges financial support provided by the Spanish Ministerio de Educación y Ciencia through DGICYT Contract No. PR95-110.