states for outward rotation and inward rotation. The product distribution was mainly determined by and parallel to the magnitude of the gauche interactions, which are larger in the methyl group inward transition states.

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Supplementary Material Available: Listing of computed energies and geometries (3 pages). Ordering information is given on any current masthead page.

Theoretical Study on the Insertion of Formaldehyde into the Cobalt-Hydrogen Bond

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Abstract: Theoretical calculations, based on density functional theory, have been carried out on the insertion of formaldehyde into the Co-H bond of $HCo(CO)_3$. The first step of the process was considered to involve the initial formation of a π-complex between $HCo(CO)_3$ and H_2CO. The second step was modeled by a migration of the hydride to either carbon or oxygen on formaldehyde under the formation of a methoxy or hydroxymethyl intermediate. Several structures of the precursor π-complex as well as the methoxy and hydroxymethyl intermediate were fully optimized. The π-complexes were found to have a trigonal bipyramidal structure with H_2CO in either the axial or equatorial position. The equatorial site was favored by 50 kJ/mol. The methoxy and hydroxymethyl groups were found to favor axial coordination with a β-hydrogen in the equatorial position interacting in an agostic manner with cobalt. The corresponding equatorial coordination was calculated to be less stable by 27 (methoxy) and 44 kJ/mol (hydroxymethyl), respectively. The methoxy intermediates were found to be more stable than the corresponding hydroxymethyl intermediates by as much as 40 kJ/mol, primarily as a result of oxygen forming stronger bonds with cobalt than carbon. The reaction profile for the hydride migration was modeled by a linear transit procedure. The formation of methoxy was calculated to have a reaction enthalpy of 6 kJ/mol and an activation barrier of less than 5 kJ/mol. The formation of hydroxymethyl has a reaction enthalpy of 40 kJ/mol and an activation barrier of 15 kJ/mol. It is concluded that the catalytic conversion of aldehydes to alcohols, polyols and esters, by $HCo(CO)_3$, most likely proceeds via the formation of a methoxy intermediate.

I. Introduction

The insertion of an olefin into the cobalt-hydrogen bond, as depicted in eq 1, is one of the key reactions in the hydroformylation process. The insertion process relies on the ability of olefins to

$$HCo(CO)_3 + C_2H_4 \rightarrow HCo(CO)_3\text{-}C_2H_4 \qquad (1a)$$

$$HCo(CO)_3\text{-}C_2H_4 \rightarrow Co(CO)_3\text{-}C_2H_5 \qquad (1b)$$

form π-complexes, eq 1a, as well as their susceptibility to nucleophilic attacks at the olefinic carbon, eq 1b. There have in recent years been a number of studies[1-5] on the insertion of olefins into the metal-hydrogen bond, including a few[4,5] involving the process given in eq 1.

The electronic structure of the C=O linkage in aldehydes bears some resemblance to olefinic double bonds. One might thus anticipate that aldehydes can undergo insertion processes analogous to those of olefins. In fact, the insertion of aldehydes into a cobalt-hydrogen bond, eq 2, has been postulated[6] in connection with the catalytic reduction of aldehydes to alcohols.

$$HCo(CO)_3 + H_2CO \rightarrow HCo(CO)_3\text{-}H_2CO \qquad (2a)$$

$$HCo(CO)_3\text{-}H_2CO \rightarrow Co(CO)_3\text{-}H_2CO(H) \qquad (2b)$$

We shall here investigate the two reactions given in eq 2 using the Hartree-Fock-Slater method[7,8] as our computational model. The emphasis of the investigation lies on the identification of the equilibrium geometries and the relative energies of stable configurations for the π-complex $HCo(CO)_3\text{-}(\eta^2\text{-}H_2CO)$ and the coordinatively unsaturated intermediate $Co(CO)_3\text{-}H_2CO(H)$. However, we shall also attempt to model the energy profile for the formaldehyde insertion into the Co-H bond by an approximate linear transit procedure. We shall further emphasize similarities and differences between the processes in eq 1 and eq 2. The olefin insertion has been investigated in a previous study.[5]

An important aspect of the reactions between metal centers and aldehydes is the fact that the π-complex $HM(CO)_n\text{-}H_2CO$ is believed to be the precursor for the catalytic conversion of aldehydes to alcohols, esters, and polyalcohols.[6b,9] The reaction is, as already mentioned, proposed to proceed via the insertion of the aldehyde group into the metal-hydride bond. The latter process possesses two channels by which the different sets of products can be attained. The first channel, eq 3, proceeds via

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(1) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

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(5) (a) Antolovic, A.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 5828. (b) Antolovic, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 977.

(6) (a) Dombek, B. D. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 176. (b) Dombek, B. D. In *Adv. Catal.* **1983**, *32*, 325.

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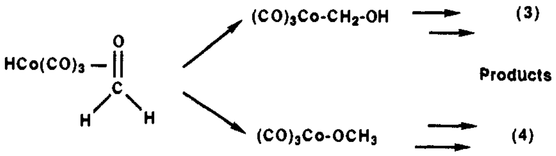
a hydroxymethyl intermediate, whereas the second channel involves an unsaturated alkoxy complex, eq 4. The preferred reaction path has, however, not been clearly established yet.[6b]



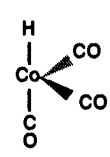
II. Computational Details

The calculations were all based on the Hartree–Fock–Slater (HFS) model as implemented by Baerends et al.,[7,8] where we have used the latest version of the fully vectorized HFS-LCAO-STO program due to Ravenek.[8b] All energy differences were calculated by the generalized transition-state method[10] in conjunction with Becke's[11] non-local exchange correction as well as Stoll's[12] correlation potential for electrons of different spins based on Vosko's[13] parametrization from electron gas data. An uncontracted triple-ζ STO basis set[14] was employed for the 3s, 3p, 3d, 4s, and 4p orbitals of cobalt, whereas 2s and 2p on carbon and oxygen, as well as 1s on hydrogen, were represented by a double-ζ STO basis set.[14] The ligand basis was augmented by a single STO polarization function, 2p on H and 3d on C and O. The other shells of lower energy were considered as core and frozen according to the method of Baerends et al.[8] In order to describe accurately the Coulomb and exchange potentials, extensive fits[15] of the density were carried out with use of a set of fit functions including s-, p-, d-, f-, and g-type functions. All molecular structures were optimized within the C_s symmetry group. The geometry optimizations were carried out according to the algorithm developed by Versluis[16] and Ziegler. The numerical integration scheme employed in this work was formulated by Becke.[17]

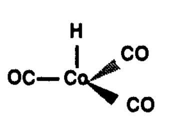
III. Molecular and Electronic Structure of $HCo(CO)_3(\eta^2\text{-}H_2CO)$

The insertion of aldehydes into the metal–hydrogen bond can according to eq 2a proceed via the formation of a π-complex. In this section we shall investigate various π-complexes that can be attained from an interaction of H_2CO with $HCo(CO)_3$. However, our investigation will be restricted to conformations that allow for a migration of the hydrige to the C=O linkage. The frontier orbitals of H_2CO consist of an occupied π_{CO} orbital and an empty antibonding π^*_{CO} orbital, thus the bonding interaction between H_2CO and the metal fragment can be described by the Dewar–Chatt–Duncanson model[18] in a fashion similar to that of olefin complexes.

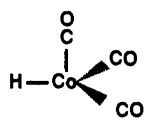
The unsaturated catalytic species $HCo(CO)_3$ is produced[6] from $HCo(CO)_4$ under catalytic conditions by thermal CO dissociation. It is thus reasonable to assume that $HCo(CO)_3$ primarily is present in its singlet state. We[19] have previously established that $HCo(CO)_3$ has three stable conformers, I–III, on the HFS singlet energy surface with the relative order of stable I (0) > II (38 kJ mol^{-1}) > III (69 kJ mol^{-1}).



I



II



III

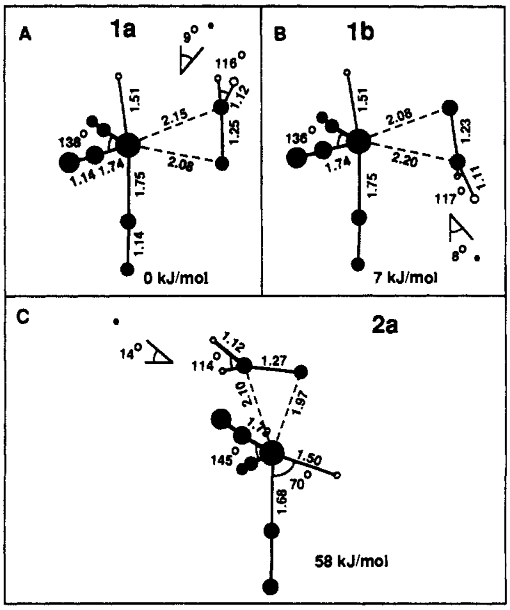
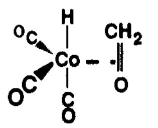
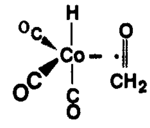


Figure 1. Optimized structures and relative energies of η^2-$HCo(CO)_3$-H_2CO. Bond distances are in Å and angles are in degrees. The energies are relative to structure A, which was set arbitrarily to zero. An asterisk indicates the deviation of the formaldehyde molecule from planarity.

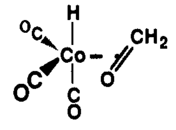
The following configurations for the aldehyde complex will be considered. Structures **1a** and **1b** are derived from the interaction between H_2CO and the most stable conformation, I, of $HCo(CO)_3$.



1a

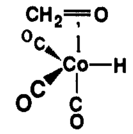


1b

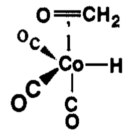


1c

They have the formaldehyde molecule in the equatorial position with the C–O bond of H_2CO parallel to the apical axis of the TBP framework.



2a



2b

The two isomers **2a** and **2b** are the corresponding structures with H_2CO along the apical axis and the C–O bond coplanar with the Co–H bond. They are derived from the interaction between formaldehyde and $HCo(CO)_3$ in the least stable conformation, III.

Structures derived from the interaction between the trigonal shaped conformer, II, and H_2CO are not considered here. The resulting π-complexes would have the hydride and the aldehyde ligands trans to each other, which makes these species unlikely candidates for the subsequent insertion reaction of H_2CO into the Co–H bond. They could, however, by a series of two Berry pseudorotations transform into **1a** or **1b**, both of which are suitable structures for olefin insertion as discussed below.

All selected cases have the formaldehyde molecule ideally positioned for an intramolecular migration of the hydride ligand to the H_2CO group. We should not, however, that these structures do not include the most stable configuration, **1c**, which is expected, as in the ethylene case,[4b] to have the formaldehyde molecule in the basal position with the C–O bond of H_2CO lying in the equatorial plane. It is, however, assumed that prior to the migratory insertion the π-complex rearranges to one of the structures described above. The required energy for this rearrangement was

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(10) (a) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1. (b) Zielger, T. Ph.D. Thesis 1978, University of Calgary, Calgary, Canada.

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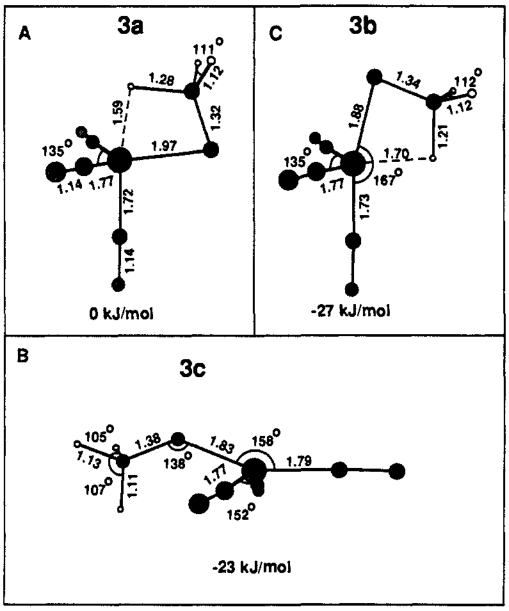


Figure 2. Optimized structures and relative energies of CH_3O–$Co(CO)_3$ (note the methoxy group). Bond distances are in Å and angles are in degrees. The energies are relative to structure A, which was set arbitrarily to zero.

estimated[4b] to be 20 kJ mol^{-1} in the ethylene complexes. We expect it to be even less in the H_2CO complexes where the π-bond to the metal center is weaker (see later).

The full geometry optimization of the four structures revealed that only the π-complexes of configuration **1a**, **1b**, and **2a** were stable on the HFS energy surface (see Figure 1). The optimization of the aldehyde complex of structure **2b** resulted in a migration of the hydride ligand to the carbon atom of H_2CO, thereby forming a methoxy group. This structure (**3c**) will be discussed later along with the other intermediates that can result from a migratory insertion.

Structures **1a** and **1b** are almost equal in energy with **1b** slightly more stable by 7 kJ/mol. The π-complex with H_2CO in the apical site (**2a**) is, on the other hand, 58 kJ/mol less stable than configuration **1a**. The higher energy of **2a** compared to **1a** is primarily a reflection of the fact that the $HCo(CO)_3$ frame work in **2a**, III, is 68 kJ/mol higher in energy than I, which makes up the $HCo(CO)_3$ frame work in **1a**.

Another interesting feature is the distortion of the complexes formaldehyde molecule. The hydrogen atoms on H_2CO are bent away from the metal fragment by 8° in structures **1a** and **1b** and by 14° in **2a** (see Figure 1). This is accompanied by an elongation of the aldehyde C–O bond. The distortions reflect primarily the donation of charge from the metal center to the π^*_{CO} orbital. An additional characteristic of the aldehyde π-complexes is the fact that all three structures have the oxygen atom of the H_2CO group slightly closer to the cobalt center than the carbon atom. This behavior is also observed in the few formaldehyde complexes for which structures have been determined experimentally.[20,21]

We have finally determined the bond energy of the formaldehyde cobalt bond in structure **1a** and found a value of 30 kJ/mol. This is considerably lower than the bond energy for the analogues ethylene complex where $D(C_2H_4$–$Co)$ was found[4b] to be ~70 kJ/mol. The lower bonding energy reflects a more modest metal-to-ligand back-donation. The more moderate metal-to-ligand back-donation is also reflected in the fact that the complexed formaldehyde molecule is less distorted with respect to the free molecule than the corresponding ethylene structures calculated in a previous[4b] study.

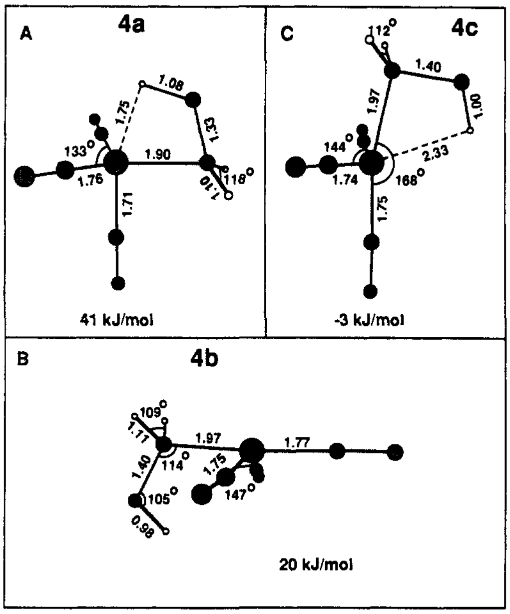
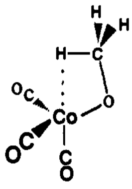


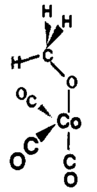
Figure 3. Optimized structures and relative energies of $HOCH_2$–$Co(CO)_3$ (note the hydroxymethyl group). Bond distances are in Å and angles are in degrees. The energies are relative to structure A of Figure 2, which was set arbitrarily to zero.

IV. Molecular and Electronic Structure of $HCo(CO)_3H_2C(H)O$

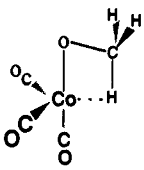
Next, we will focus our attention on the intermediates that can arise from a migratory insertion of the aldehyde group into the cobalt–hydride bond. There are two possible sets of migration products. Structures **3a** to **3c** represent the complexes in which the hydride ligand has shifted to the carbon atom of the aldehyde group forming a methoxy ligand, and structures **4a** to **4c** are the corresponding complexes where the hydride has moved to the oxygen atom creating a hydroxymethyl group.



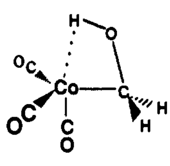
3a



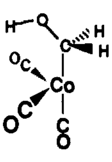
3b



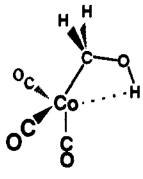
3c



4a



4b



4c

All of the structures were fully optimized and found to be stable on the HFS energy surface. The optimized geometries are shown in Figures 2 and 3. We find that the methoxy intermediates are 25 to 40 kJ/mol more stable than the structurally related hydroxymethyl species. This can be attributed to oxygen forming stronger bonds with cobalt than carbon. Thus, we found in a recent study on metal–ligand bond strengths of early to late transition-metal systems[22] that the Co–OH bond in $LCo(CO)_4$ is 70 kJ/mol stronger than the corresponding Co–CH_3 bond.

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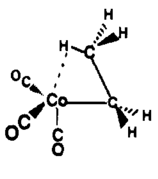
[20] (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019. (c) Floriani, C. *Pure Appl. Chem.* **1983**, *55*, 1.

[21] (a) An exception is $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$, which has the carbon atom closer to the metal center. (b) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Mardesn, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503.

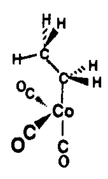
[22] Ziegler, T.; Tschinke, V.; Versluis, L.; Baerends, E. J. *Polyhedron* **1988**, *7*, 1625.

Configuration **3c** was found to have the over-all lowest energy, while **4c** constitutes the most stable hydroxymethyl intermediate. Both structures adopt a butterfly shaped geometry with the shifted hydrogen atom pointing toward the vacant equatorial site. These results parallel the findings of the previously[4b] treated ethylene case where the ethyl intermediate of a similar geometry, **5c**, was found to be lowest in energy. The most striking feature is again the formation of an agostic interaction, which is particularly pronounced in structure **3c** (see Figure 2). The short internuclear distances from the agostic hydrogen to the cobalt metal and the carbon atom of the methoxy ligand show clearly that the H atom is bonded to both centers. A comparison of complex **3c** with the ethyl analogue **5c** reveals that the two molecules are structurally very similar with analogous bonding interactions.

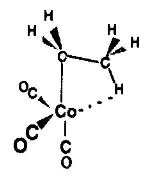
In the ethyl case **5a** was found[4] to be more stable than **5b** by 11 kJ/mol. The order for the relative energies of structures **3a** and **3b** as well as **4a** and **4b** is inverted when compared to the ethyl analogues **5a** and **5b**. That is, **3b** and **4b** are more stable than respectively **3c** and **4c**.



5a



5b



5c

Several factors might contribute to this reversal. The difference in bonding energy between the preferred axial binding site and the less stable equatorial position is, in the ethyl case, outweighed by the formation of an agostic interaction. That is, configuration **5a**, which has the ethyl group in the basal plane and forms an agostic interaction, is more stable than the butterfly shaped configuration **5b** that is unable to create an agostic hydrogen. However, the energy differential between the binding sites can, according to simple perturbation theory, be expected to increase for stronger binding ligands. The order of the relative energies of the methoxy compounds **3a** and **3b** can, therefore, be explained by the latter effect. Thus, the energy differential between the two binding modes is, in the case of the methoxy ligands, larger than the energy stabilization that is gained through the formation of the agostic interaction in structure **3a**.

On the other hand, the bond strengths of the hydroxymethyl groups in **4a** and **4b** should be very similar to the corresponding values of the ethyl intermediates. However, the optimized geometry of **4a**, see Figure 3A, reveals that the agostic interaction is less pronounced than in the ethyl analogue **5a**. An example for this is the 0.13 Å larger internuclear distance between the agostic hydrogen and the cobalt center. Hence, the weaker agostic interaction cannot make up for the higher energy of the equatorial binding site and as a consequence the butterfly shaped hydroxymethyl complex **4b** is lower in energy than **4a**.

In addition, we should also point out that the two intermediates of configurations **3b** and **4b**, which are unable to form an agostic interaction, are stabilized by opening the bond angle between the basal carbonyl coligands. This effect was also observed for the related ethyl compound **5b** and is discussed in ref 4.

V. The Migratory Insertion Process

A compilation of reaction energies for the migratory insertion of the formaldehyde group into the cobalt-hydride bond is given in Table I. We find for the migration of the hydride to the carbon atom in H_2CO of structure **1a** (**1a** → **3a**) an endothermicity of 6 kJ/mol, while the direct insertion of the aldehyde group into the Co–H bond (**1a** → **3b**) shows an exothermicity of −17 kJ/mol.

The corresponding processes where the hydride moves to the oxygen atom (**1b** → **4a** and **1b** → **4b**) are both about 35 kJ/mol more endothermic. This is contrasted by reaction **2a** → **4c** which has an exothermicity ΔE of −55 kJ/mol. However, this process is unlikely to occur, since the formaldehyde complex of configuration **2a** is of much higher energy than either **1a** and **1b** (see Figure 1). The higher energy requirement for the two reactions **1b** → **4a** and **1b** → **4b**, compared to the processes **1b** → **3a** and **1b** → **3b**, can be traced to the difference between the strengths of the cobalt-methoxy and the cobalt-hydroxymethyl bonds. As noted in the previous section, the Co–OR bond is approximately 70 kJ/mol stronger; therefore, the overall energetics favors the formation of a methoxy intermediate.

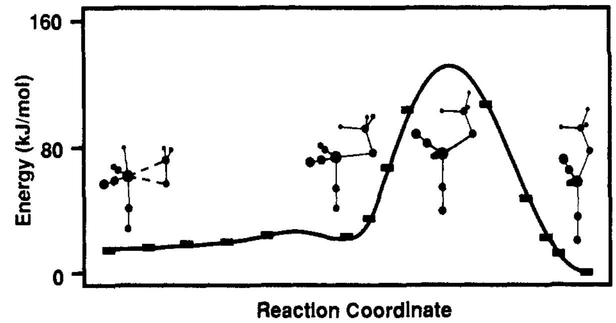
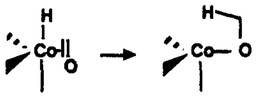
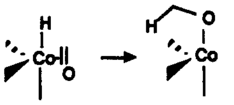
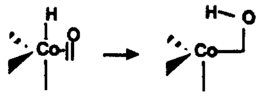
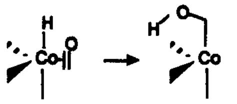
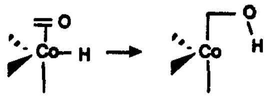


Figure 4. Energy profile of the hydride migration and the rearrangement of the methoxy group for η^2-HCo(CO)$_3$-H$_2$CO. Reaction **1a** → **3a** → **3b**. The energy zero point refers to structure **4b**.

Table I. Calculated Reaction Energies for the Migratory Insertion Process

R → P		ΔE (kJ/mol)
	1a → 3a	6
	1a → 3b	-17
	1b → 4a	40
	1b → 4b	19
	2a → 4c	-55

Whether these reactions have any activation barriers will be assessed in the following where we investigate the various reaction profiles by an approximate linear transit procedure. The internal coordinates of the reactants, $\{\alpha_i^{\mathrm{R}}, i = 1, N\}$, are transformed in the linear transit procedure into the internal coordinates of the products, $\{\alpha_i^{\mathrm{P}}, i = 1, N\}$. The transit takes place in n steps and the internal coordinates are in each step changed by $\{\Delta\alpha_i = (\alpha_i^{\mathrm{P}} - \alpha_i^{\mathrm{R}})/n, i = 1, N\}$. The linear transit affords an upper bound to the actual reaction barrier.

The energy profile for the reaction **1a** → **3a** is represented in Figure 4. This reaction involves the migration of a hydride from the more stable aldehyde π-complex **1a** to the carbon atom of formaldehyde under the formation of the methoxy intermediate, **3a**. We see that the conversion proceeds with an activation barrier that was found to be smaller than 5 kJ/mol. Such a low activation barrier was also calculated[4b] for the related process involving ethylene.

The alternative mechanism, where the hydride ligand migrates to the oxygen atom of the aldehyde group (**1b** → **4a**), is modeled in Figure 5. The activation barrier is somewhat larger with $\Delta E^{\ddagger}$ equal to 15 kJ/mol. However, the energy difference between the transition state and the initial configuration, **1b**, is considerably larger due to the fact that the hydroxymethyl intermediate, **4a**,

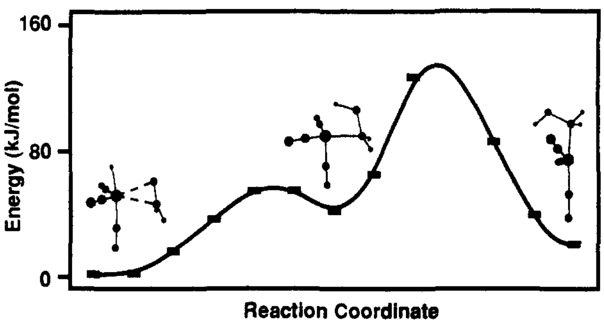
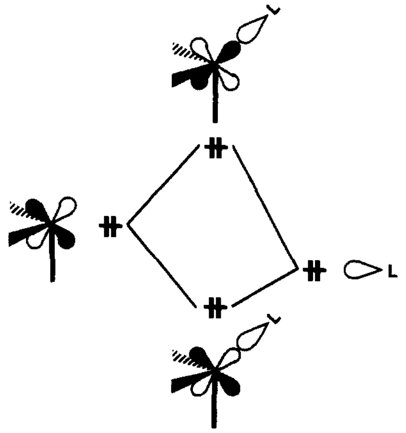


Figure 5. Energy profile of the hydride migration and the rearrangement of the hydroxymethyl group for η^2-HCo(CO)$_3$–H$_2$CO. Reaction **1b** → **4a** → **4b**. The energy zero point refers to structure **1b**.

is calculated to be 34 kJ/mol higher in energy than the methoxy intermediate, **3a**. In fact, we calculate an activation energy of 55 kJ/mol for the process **1b** → **4a**.

We find the insertion of olefin into the Co–H bond to have a very small activation barrier, ΔE^{*}, of less than 20 kJ/mol. This is in sharp contrast to the results by Antolovic and Davidson,[5a] who find 61 kJ/mol at the HF level and 73 kJ/mol at the CI level of theory for the related ethylene insertion into the Co–H bond. The large discrepancy between the HFS and the ab initio results can be attributed to the fact that the latter methods seem not to predict an agostic interaction between the shifted hydride ligand and the metal center in the final structure. As a consequent, the linear transit procedure in the ab initio study yields a transition state that has a large H–Co distance as well as a large H–C$_{\mathrm{Et}}$ distance. In other words, the H–Co bond has to be stretched considerably before the molecular system can be stabilized through the formation of a C–H bond. On the other hand, the Co–H bond of the reactions modeled in Figures 4 and 5 is not broken during the migration process, which results in a low activation energy. It should be noted that the CI study by Antolovic and Davidson employed geometries optimized by HF theory.

Figure 4 reveals also that the rearrangement from **3a** to the more stable butterfly shaped intermediates **3b** has a substantial activation barrier, ΔE^{*}, of 110 kJ/mol. The corresponding rearrangement reaction **4a** → **4b** is shown in Figure 5 to have an activation barrier, ΔE^{*}, equal to 91 kJ/mol. The occurrence of a high activation barrier for the two types of rearrangement processes can be traced back the repulsive two-orbital four-electron interaction illustrated in **6**, where a nonbonding occupied metal d-orbital is engaged in an unfavorable interaction with an occupied ligand σ-orbital that is rotated half-way between the equatorial and axial orientation. The high barriers would indicate that a rearrangement of the methoxy or hydroxymethyl groups from the equatorial position to the more favorable axial site, under catalytic conditions, is superseded by coordination of a CO ligand or a η^2-H$_2$ ligand in the axial position. The saturated intermediates can then rearrange to the more stable TBP configuration, with the methoxy or hydroxymethyl groups in the axial position, by a Berry pseudorotation, for which the activation energy is predicted[23] to be low. The saturated complexes are assumed to participate in the preceding steps of the catalytic aldehyde conversion according to the scheme by Dombek[6] and others[9,25] given in Figure 6.



6

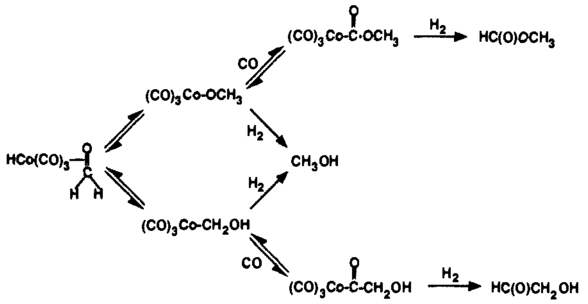


Figure 6. Schematic representation of the cobalt-based catalytic aldehyde conversion (reaction mechanism from ref *xyz*).

As mentioned in the introduction, the aldehyde insertion into the metal–hydride bond is proposed to be a key step for the catalytic conversion of aldehydes to alcohols, polyols, and esters. Experiments with formaldehyde and HCo(CO)$_4$ under H$_2$/CO pressure at catalytic conditions resulted in a conversion of H$_2$CO to methanol, methyl formate, ethylene glycol, and a number of other secondary products.[9,24] A possible reaction mechanism by which these compounds can be attained has been proposed by several authors[6b,9,25] and is presented here in Figure 6.

According to this mechanism the aldehyde π-complex must branch to the hydroxymethyl and the methoxy intermediate in order to produce the observed compounds. The preferred mode of branching has, however, experimentally not been established yet; therefore, conflicting opinions can be found in the literature. Fahey[9] argues that the polarity of the H–Co bond might favor the formation of a hydroxymethyl intermediate; also Rathke and Feder[24] favor the hydroxymethyl species based on the observation that the ratio between methanol and formaldehyde is constant at different H$_2$ pressures.

Dombek,[6b] however, points out that in the cobalt-based catalytic hydroformylation of olefins the alkyl intermediate, which is structurally similar at the cobalt center to the hydroxymethyl complex, converts to an acyl compound rather than producing hydrocarbons from a reductive elimination with a hydride ligand. He implies then that the analogous reaction involving the hydroxymethyl group is under the same conditions unlikely to undergo a reductive elimination in order to form methanol. Dombek[6b] argues further that the observed product distribution is consistent with a mechanism where most of the methanol is produced via the methoxy intermediate and in which the migration of the hydroxymethyl group to a carbonyl ligand is faster than the corresponding migration involving the methoxy group. The latter assumption seems justified in light of the fact that the methoxy ligand forms a stronger bond with the cobalt fragment and therefore requires probably more energy for a migratory motion.

Our results agree with the Dombeck mechanism where the formation of the methoxy intermediate is favored over the hydroxymethyl analogue. Figure 4 illustrates that the hydride ligand can shift to the aldehyde carbon atom practically without an activation energy. The flatness of the energy surface suggests that under catalytic conditions the molecule fluctuates between the π-complex and the methoxy structure. It can then be envisioned that the formation of a methoxy group is accompanied by a concerted coordination of an incoming CO or H$_2$ molecule. The coordinatively saturated methoxy complex will eventually lead to the production of methyl formate or methanol. The alternative path via the hydroxymethyl intermediate constitutes also a viable reaction direction, since the hydride migration possesses a moderate

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(24) Feder, H. M.; Rathke, J. W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45.

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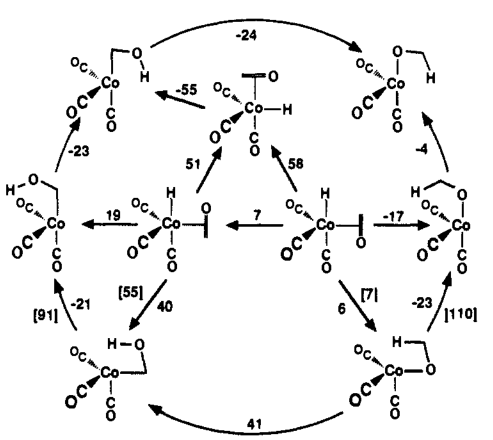

Figure 7. Energy requirements for the insertion of formaldehyde into the Co-H bond of η^2-HCo(CO)$_3$-H$_2$CO. All energies are in kJ/mol. The numbers in brackets represent the activation energies for the reaction in the direction of the arrows. The numbers without brackets stand for the energy difference between two isomers, where a positive value indicates that the resulting complex is higher in energy.

activation energy of only 55 kJ/mol. As indicated above this route might not produce much methanol, since the migratory shift of the hydroxymethyl group to a carbonyl ligand is, in analogy to the alkyl reaction, a very facile process.

VI. Summary and Conclusions

We have investigated here the geometries of the π-complexes that result from an interaction between formaldehyde and the coordinatively unsaturated cobalt complex HCo(CO)$_3$. Furthermore, the insertion of the coordinated formaldehyde group into the Co-H bond was also studied by determining the geometries of some of the insertion products as well as by evaluating the energy profile of the insertion mechanism by a linear transit procedure.

The migratory insertion of formaldehyde into the Co-H bond was shown to produce stable methoxy or hydroxymethyl intermediates. However, the methoxy complexes were 25 to 40 kJ/mol lower in energy. The energy difference was traced to the stronger Co-O bond of the methoxy ligand. Both types of compounds were stabilized by the formation of an agostic interaction between the shifted hydride and the cobalt center. The migration of the hydride ligand to the carbon atom of the complexes aldehyde molecule was found to have a reaction enthalpy, ΔE, of 6 kJ/mol and an activation barrier, ΔE^*, of less than 5 kJ/mol. These values parallel the results of the ethylene insertion and underline the similarity of the two molecular systems. The alternative process where the hydride ligand migrates to the oxygen atom of the H$_2$CO group was somewhat disfavored by an endothermicity of 40 kJ/mol and an activation barrier of 15 kJ/mol. However, the energy requirements of the later process are small enough such that both insertion modes are operative under catalytic conditions where the formation of the methoxy intermediate is favored over the hydroxymethyl analogue. The energetics for the insertion process is summarized in Figure 7.

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Theoretical Evidence for Destabilization of an α-Helix by Water Insertion: Molecular Dynamics of Hydrated Decaalanine

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Abstract: A molecular dynamics (MD) simulation was performed on the hydrated decapeptide Ala$_{10}$·550H$_2$O under periodic boundary conditions. The initial configuration of the peptide was a canonical right-handed α-helix. Over the course of the MD trajectory, the helix is overall intact and dynamically stable, except for one position in which incipient helix destabilization is observed. The helix hydrogen bond at this position was first destabilized transiently for ~10 ps. Some 35 ps later, a persistent destabilization occurred. Analysis reveals that the helix destabilizations are both accompanied by water insertion in a manner consistent with that recently proposed by Sundaralingan and Sekharudu[1] based on a survey of α-helices in protein crystal structures. The geometry of the inserted water was seen to be more favorable for a water bridge in the persistent destabilization than in the transient case. The water-inserted structures may be intermediates in protein-folding processes.

Introduction

Recently, Sundaralingam and Sekharudu[1] surveyed the crystal structures of a number of proteins containing hydrated α-helices. They found a number of instances in which a water molecule is inserted into the N—H···O═C hydrogen bond and correlated this observation with a local destabilization of the helix in the direction of reverse turns and open structures in (ψ,ϕ) space. They further suggested that the observed water-inserted structures may be intermediates in protein-folding processes. Similar observations have been reported in the crystallography of oligopeptide units by Karle and co-workers.[2,3] In view of the current interest in understanding the various mechanisms involved in protein-folding processes,[4] we have carried out a molecular dynamics (MD) simulation on the hydrated decapeptide Ala$_{10}$·550H$_2$O and ex-

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(2) Karle, I. L.; Flippen-Anderson, J L.; Uma, K.; Balaram, P. *Biopolymers* **1989**, *28*, 773.

(3) Karle, I. L.; Flippen-Anderson, J. L.; Uma, K.; Balaram, P. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 299.

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