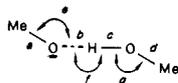
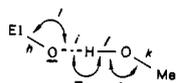


The following calculations on alkoxide-alkanols have been carried out at the 6-31+G level.<sup>52</sup> First, the interconversion of methanol-methoxide ions (eq 8) proceeds through a symmetrical transition state with a barrier of 1.9 kcal mol<sup>-1</sup>; this can be used as a guide for the interconversion of unsymmetrical alkanol-alkoxides. Second, [EtO<sup>-</sup> ···HOME] (eq 9) is a true energy minimum

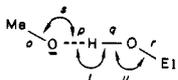
(52) Absolute energies (au) and geometries (Å, deg) for solvated ions as follows:



-229.40171,  $a = 1.39$ ,  $b = 1.54$ ,  $c = 1.01$ ,  $d = 1.41$ ,  $e = 128.0$ ,  $f = 185.2$ ,  $g = 111.3$ .



-268.42849,  $h = 1.39$ ,  $i = 1.55$ ,  $c = 1.01$ ,  $d = 1.41$ ,  $l = 129.1$ ,  $m = 190.5$ ,  $n = 111.4$ .



-268.40054,  $o = 1.43$ ,  $p = 1.54$ ,  $q = 1.01$ ,  $r = 1.44$ ,  $s = 111.4$ ,  $t = 190.5$ ,  $u = 128.3$ .

with formation energy -25.8 kcal mol<sup>-1</sup> (relative to EtO<sup>-</sup> plus HOME). In contrast, [EtOH ···OMe] is a very shallow minimum (formation energy -23.2 kcal mol<sup>-1</sup>). If reaction 9 is an equilibrium, and given thermal energies, [EtO<sup>-</sup> ···HOME] will have a mole ratio >0.95. Even if this ion is vibrationally excited it will be the larger contributor in any reaction. This is in accord with the data listed in Table I and with the mechanistic proposals summarized in Figure 1 and Scheme I.

In conclusion, we propose that exothermic (or thermoneutral) alkoxide displacement reactions of alkanol-alkoxides with boron, carbon, silicon, and titanium ethers are mainly controlled by specific orientation effects as the two reagents approach and not solely by internal barriers as suggested earlier.<sup>8</sup> Reports of such orientation effects are rare in gas-phase ion chemistry,<sup>53</sup> and the present study demonstrates the importance of the application of experiment and theory in concert.

**Acknowledgment.** Part of this work was carried out while J.H.B. was on leave at the University of Amsterdam during the tenure of a visitors grant from the Netherlands Organization for the Advancement of Pure Research (ZWO). J.H.B. and N.M.M.N. acknowledge financial support from the Australian Research Grants Scheme and the Netherlands Organization for Pure Research, respectively.

**Registry No.** Me<sub>3</sub>SiOEt, 1825-62-3; Me<sub>2</sub>Si(OEt)(OC<sub>2</sub>D<sub>5</sub>), 109929-93-3; CH<sub>3</sub>CH<sub>2</sub>C(OEt)<sub>3</sub>, 115-80-0; (EtO)<sub>3</sub>B, 150-46-9; (*i*-PrO)<sub>4</sub>Ti, 546-68-9; Me<sub>3</sub>SiCl, 75-77-4; NH<sub>2</sub><sup>-</sup>, 17655-31-1; F<sup>-</sup>, 16984-48-8; HS<sup>-</sup>, 15035-72-0; N<sub>3</sub><sup>-</sup>, 14343-69-2; NCO<sup>-</sup>, 71000-82-3; MeO<sup>-</sup>, 3315-60-4; H<sub>2</sub>BOMe, 54098-92-9.

(53) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.*, accepted for publication.

## A Theoretical Study of Some Cobalt Carbonyl Complexes Present in the Catalytic Cycle of Hydroformylation

Danko Antolovic and Ernest R. Davidson\*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. Received January 8, 1987

**Abstract:** The molecular geometry and electronic structure of formylcobalt tricarbonyl, ( $\eta$ -ethylene)hydridocobalt tricarbonyl, and ethylcobalt tricarbonyl were investigated by means of ab initio Hartree-Fock and configuration-interaction calculations in a Gaussian basis set. Several stable conformations of each of the complexes were found, and the geometry, frontier orbitals, and the character of chemical bonds of these conformations were examined. Two intramolecular hydrogen migration reactions were investigated, and their energy barriers were found to depend considerably on the choice of the initial and terminal sites of the migrating hydrogen. The effect of electron correlation upon the molecular geometry was examined in some detail in the case of the  $\eta$ -ethylene complex.

The hydroformylation reaction, occurring in the presence of hydridocobalt tetracarbonyl catalyst, has been extensively studied, and a mechanism proposed by Orchin<sup>1</sup> and by Heck and Breslow<sup>2</sup> has been widely accepted. This mechanism involves a cycle of tetra- and pentacoordinated complexes of cobalt, the hydroformylation being carried out as a sequence of complexations and metal-to-ligand migrations. Of the postulated steps of the mechanism, the initial few are of particular interest here: at the beginning of the cycle, the reactive species HCo(CO)<sub>3</sub> forms a  $\pi$  complex with the alkene. The adjacent hydrogen ligand migrates toward the alkene and is inserted into the carbon-carbon double

bond. Thus saturated, the carbon chain migrates toward one of the carbonyls. This last step results in the incorporation of the carbonyl ligand into the original hydrocarbon chain, in the form of an aldehyde group. The entire cycle is discussed in detail in the studies quoted above.

Few experimental facts are known about the postulated intermediate species, of which the tetracoordinated ones can be expected to be particularly unstable. In an earlier article<sup>3</sup> (referred to as paper 1), we described the results of an SCF ab initio theoretical study of the hydridocobalt tetracarbonyl and of the simplest tetracoordinated intermediate, hydridocobalt tricarbonyl. Within a more elaborate theoretical framework, we describe here three further species occurring in the postulated mechanism. We

(1) Orchin, M. *Acc. Chem. Res.* 1981, 14, 259.

(2) Heck, R. F. *Adv. Organomet. Chem.* 1966, 4, 243. Schrauser, G. N., Ed. *Transition Metals in Homogeneous Catalysis*; Marcel Dekker: New York, 1971.

(3) Antolovic, D.; Davidson, E. R. *J. Am. Chem. Soc.* 1987, 109, 977.

have studied the formylcobalt tricarbonyl as a rather approximate model of the more general (and more difficult to describe) acylcobalt carbonyls.

In conjunction with this species, we have investigated the migration of hydrogen from cobalt to the carbonyl ligand. This migration must, of course, proceed toward a ligand adjacent to hydrogen, and we find that the energy profile depends considerably on the choice of initial and terminal sites in the coordination sphere. It can be readily shown that the energetics of this migration agree with the qualitative conclusions concerning the bonding of the ligands, which can be drawn from the analysis of the frontier orbitals. Hydrogen is known experimentally not to undergo this migration while saturated hydrocarbon radicals do. This model reaction, consequently, is expected to show a higher energy barrier than the hydrocarbon migration would have and should provide an explanation as to why hydrogen does not migrate.

Further, we report the results on ( $\eta$ -ethylene)hydridocobalt tricarbonyl, the model of the  $\pi$  complex with alkene, which is postulated to undergo hydrogen migration onto the carbon-carbon double bond. We have studied this migration in some detail, as well as its product, the ethylcobalt tricarbonyl. As in the first reaction, hydrogen migration between different pairs of ligands encounters somewhat different barriers: in this case, we believe that the differences in activation energy also stem from different metal-ligand bond energies.

### Computational Details

As in the study of hydridocobalt carbonyls<sup>3</sup> (paper 1), we have used the DZC basis set for cobalt, as proposed by Tatewaki and Huzinaga,<sup>4</sup> and augmented it with a set of diffuse<sup>5</sup> p functions ( $\alpha = 0.085$ ) to represent the 4p valence orbital. This amounts to a 12s7p4d basis, contracted as (33321/331/4). The standard 3-21 basis was used on the light atoms. We have found this to be an acceptable basis for geometry optimizations, which are too time-consuming to be performed in a more complete basis set. From our previous work on  $\text{HCo}(\text{CO})_4$  we know that the SCF geometries give excessively long bond lengths to the ligands and also underestimate the cobalt-ligand bond strengths.

All of the configuration-interaction calculations are limited to single and double excitations selected by perturbation theory, with the Hartree-Fock configuration as reference and the Hartree-Fock and virtual K orbitals<sup>6</sup> as the basis. The latter are needed in order to provide the CI procedure with a set of localized virtual orbitals, which cannot be obtained by the SCF iterations. All energy values were extrapolated to the full CI limit by means of a variant of the CI extrapolation formula.<sup>7</sup> This extrapolation provides a degree of size consistency, which is necessary for a meaningful comparison of the CI energy of the  $\pi$  complex with that of the products of dissociation,  $\text{HCo}(\text{CO})_3$  and  $\text{CH}_2=\text{CH}_2$ . The extrapolated configuration-interaction energy is also fairly independent of the size of the CI matrix, as we have determined by some exploratory calculations on the hydridocobalt tricarbonyl.

Core orbitals in the CI calculations include 1s, 2s, 2p, 3s, and 3p orbitals on the cobalt atom, 1s orbitals on carbon and oxygen,  $\sigma(\text{CO})$  and  $\sigma^*(\text{CO})$  bond orbitals of the carbonyl, and the  $\sigma(\text{CC})$  and  $\sigma^*(\text{CC})$  bond orbitals of the ethylene. In the complexes for which CI energies were calculated, ( $\eta$ -ethylene)hydridocobalt tricarbonyl and ethylcobalt tricarbonyl, this amounts to 50 electrons in the core and 36 correlated electrons. The entire virtual space of 59 orbitals were used for electron excitations.

Geometry optimizations were performed by means of the software package GAMESS<sup>8</sup> on a Cyber 205, and subsequent single-point CI calculations were done with the program MELD<sup>9</sup> on

a VAX 11/780 and on an FPS 164 vector processor.

### Formylcobalt Tricarbonyls

Compounds with the formula  $\text{CHOCO}(\text{CO})_n$  ( $n = 3, 4$ ) serve as theoretical models for the hypothetical acylcobalt complexes, assumed to be among the intermediate species in the catalytic cycle of the hydroformylation of alkenes.<sup>1</sup> INDO/1 results<sup>10</sup> are available on the formylcobalt tri- and tetracarbonyls, as well as on the related molecules  $\text{CH}_3\text{COCO}(\text{CO})_n$  ( $n = 3, 4$ ). Some ab initio SCF results<sup>11</sup> are known for the molecule  $\text{CH}_3\text{COCO}(\text{CO})_4$ . We are not aware of any experimental data concerning the structure of these model compounds.

We report here the results of a study of  $\text{CHOCO}(\text{CO})_3$ . In an earlier article,<sup>3</sup> we investigated a number of conformations and electronic states of the molecule  $\text{HCo}(\text{CO})_3$ ; there is a similarity of features (and problems) between that molecule and the one considered here. In particular, steric arrangements around the cobalt atom follow the same principles in both cases, giving rise to a plethora of conformations whose relative energies are difficult to resolve at the Hartree-Fock level. However, the formylcobalt tricarbonyl is of interest primarily as the product of the hypothetical migration of hydrogen from the metal to the carbonyl ligand, with hydridocobalt tetracarbonyl as the starting material. All of the Hartree-Fock geometry optimizations of  $\text{HCo}(\text{CO})_3$  and  $\text{HCo}(\text{CO})_4$  indicate that the different conformations, derived from the tetrahedral and trigonal bipyramidal coordinations of cobalt, represent true minima on the SCF potential energy surface. We assume, therefore, that the Berry pseudorotations, which carry the complex from one conformation into another, constitute steps distinct from the hydrogen migration itself and that no significant rearrangement of the remaining carbonyls takes place during the migration. Given the two conformations of  $\text{HCo}(\text{CO})_4$ ,  $C_{3v}$  and  $C_{2v}$  (see paper 1), the hydrogen migration can yield three TBP conformations of the immediate product before any pseudorotations take place. We label the conformations FmC, CC, and CV (labels denoting *formyl*, *carbonyl*, or *vacancy* in the two apical positions) and limit our calculations to these three cases. The results of the geometry optimizations on the single surface justify our assumption that the coordination follows the TBP pattern.

In addition to the geometry around the cobalt atom, we have also considered the rotation of the formyl group about the Co-C bond. Completely unconstrained optimizations of the geometries of  $\text{HCo}(\text{CO})_3$  always produced an arrangement of ligands which had at least  $C_s$  symmetry, and it is also reasonable to assume that the hydrogen migration should follow a path of  $C_s$  symmetry. Therefore, we have constrained all geometry optimizations to  $C_s$ , limiting the calculations to the two symmetry-permitted orientations of the CHO group. These two rotamers are labeled *cis* or *trans*, depending on whether the hydrogen atom and the vacant site from which the hydrogen has migrated are on the same or opposite sides of the Co-C bond.

Previous investigations of hydridocobalt tricarbonyl<sup>3</sup> indicated that the ground state of a tetracoordinate TBP cobalt complex might be a triplet. A definitive answer to the question of multiplicity of the ground state is conditional upon the correct theoretical prediction of the metal-ligand bond lengths, which is not feasible at present. It is reasonable to assume, however, that the hydrogen migration occurs on the singlet energy surface, since the TBP pentacoordinated  $d^8$  complexes undoubtedly have singlet ground states.

With these considerations in mind, we have sought to obtain a tentative description of both the closed-shell states and the low-lying triplets of  $\text{CHOCO}(\text{CO})_3$ , using a procedure similar to that used for the investigation of the hydridocobalt molecule. We performed single-double CI calculations, with the closed-shell Hartree-Fock orbitals as the basis. Orbitals of the triplet con-

(4) Tatewaki, H.; Huzinaga, S. *J. Chem. Phys.* **1979**, *71*, 4339.

(5) Huzinaga, S., Ed. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984; p 24.

(6) Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1981**, *74*, 3877.

(7) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974.

(8) GAMESS was developed by M. Dupuis, D. Spangler, and J. J. Wendoloski at NRCC and has been subsequently modified by M. Schmidt and S. Elbert for the FPS 164.

(9) MELD was written by L. McMurchie, S. Elbert, S. Langhoff, and E. R. Davidson and has been subsequently modified by D. Feller and D. Rawlings.

(10) Iberle, K. A.; Davidson, E. R., unpublished results.

(11) Fønnesbech, N.; Hjortkjær, J.; Johansen, H. *Int. J. Quantum Chem.* **1977**, *12*, (Suppl. 2), 95.

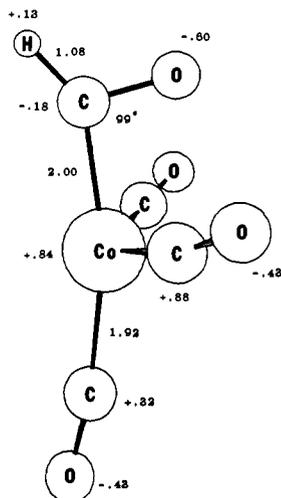


Figure 1. Cis-FmC conformation of  $\text{CHOC}(\text{CO})_3$  showing selected bond lengths (Å), bond angles (degrees), and Mulliken charges. The SCF energy of this structure is  $-1824.5987$  au.

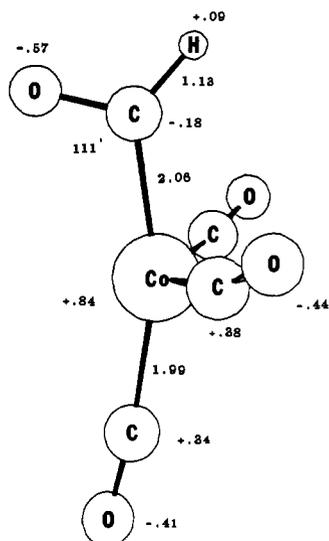


Figure 2. Trans-FmC conformation of  $\text{CHOC}(\text{CO})_3$ . The SCF energy of this structure is  $-1824.5998$  au.

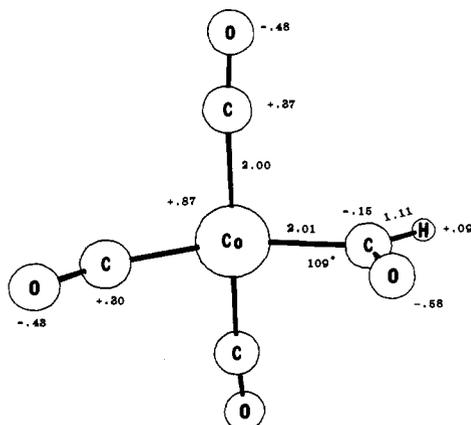


Figure 3. Cis-CC conformation of  $\text{CHOC}(\text{CO})_3$ . The SCF energy of this structure is  $-1824.5963$  au.

figurations obtained in that manner were separately optimized by Hartree-Fock calculations, in order to obtain wave functions of higher quality. Triplet geometries were not optimized; closed-shell geometries were used instead.

**Closed-Shell States of  $\text{CHOC}(\text{CO})_3$ .** Results of the  $C_s$ -constrained geometry optimizations of formylcobalt tricarbonyl are

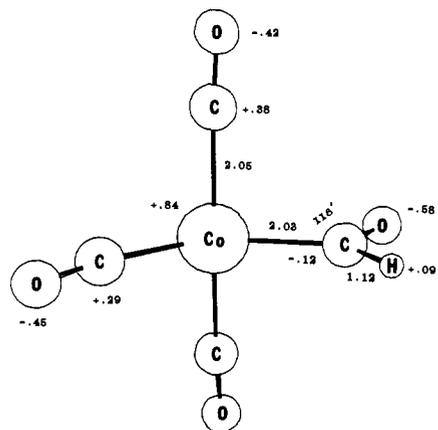


Figure 4. Trans-CC conformation of  $\text{CHOC}(\text{CO})_3$ . The SCF energy of this structure is  $-1824.5927$  au.

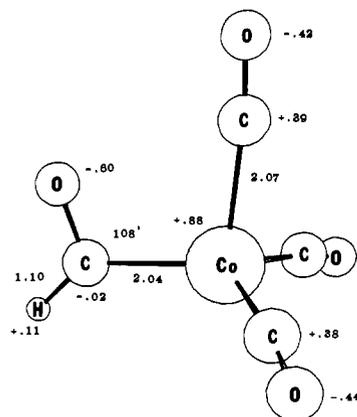


Figure 5. Cis-CV conformation of  $\text{CHOC}(\text{CO})_3$ . The SCF energy of this structure is  $-1824.5978$  au.

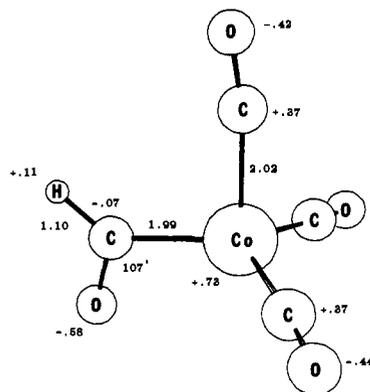


Figure 6. Trans-CV conformation of  $\text{CHOC}(\text{CO})_3$ . The SCF energy of this structure is  $-1824.6011$  au.

listed in Table I of the microfilm supplement. A TBP arrangement of ligands, similar to that of the hydridocobalt carbonyl, is apparent (see Figures 1–6). The formyl-cobalt bond is longer in the FmC case (apical) than in the CC and CV cases (equatorial), although the difference (about 0.01 Å) is not as pronounced as that of the H-Co bond in the hydridocobalt compounds (see paper 1, Tables I and IV). With one exception, the carbonyl-cobalt bonds are distinctly longer in the apical than in the equatorial position.

An interesting structural detail must be pointed out in the FmC case. In the cis rotamer, the angle O-C-Co has the magnitude of  $99^\circ$ , which is rather smaller than the value of  $111^\circ$  in the trans rotamer. There is also a concomitant, smaller increase in the tilt of the equatorial carbonyls toward the formyl group. As a result, the distance between the formyl oxygen and either of the equatorial carbon atoms in the cis form is 2.72 Å. This is smaller than the analogous distance between the formyl hydrogen and the carbons

Table II. Orbital Energies for  $\text{HCo}(\text{CO})_3$ 

cis-FmC	trans-FmC	cis-CC	trans-CC	cis-CV	trans-CV	
-0.30	-0.29	-0.28	-0.27	-0.27	-0.28	HCO "n"
-0.35	-0.36	-0.37	-0.39	-0.49	-0.52	$d_{xy}$
-0.38	-0.38	-0.37	-0.36	-0.36	-0.36	$d_{x^2-y^2}$
-0.42	-0.44	-0.48	-0.50	-0.47	-0.48	$d_{xz}$
-0.44	-0.43	-0.43	-0.43	-0.39	-0.40	HCO " $\pi$ "
-0.49	-0.49	-0.40	-0.45	-0.52	-0.52	$d_{yz}$
-0.51	-0.50	-0.50	-0.51	-0.53	-0.53	Co-C $\sigma$ bond
0.5978 <sup>a</sup>	0.5998	0.5963	0.5927	0.5978	0.6011	

<sup>a</sup>Total SCF energies given as  $-(E + 1824)$ .

in the trans rotamer, which is 3.23 Å. These distances are entirely inexplicable on steric grounds and constitute a good indication that a weak bond is formed between the formyl oxygen and the equatorial carbonyls. The same effect is present in the other two conformations, CC and CV, although to a lesser extent. This brings the oxygen to 2.52 Å from the cobalt in cis-FmC compared to 2.77 Å in trans-FmC.

Table II summarizes the orbital energy and character of the higher energy orbitals. A more detailed table is included in the microfilm supplement. The TBP axis lies along the z axis of the coordinate system, and the symmetry plane coincides with either the xz or the xy plane. Non-carbonyl ligands point in the positive z or x direction, and the vacancy faces the negative directions of the coordinate axes. We follow these conventions throughout the article.

It can be seen from Table II that, despite the substantial deviation from the threefold symmetry axis, the d-orbital splitting pattern, associated with the group  $D_{3h}$ , is still recognizable: there is a low-energy, localized  $e''$ -like pair of orbitals ( $d_{xz}$ ,  $d_{yz}$ ), an  $e'$ -like pair, mixing heavily with the 4p orbitals (equatorial  $d_{xy}$ ,  $d_{x^2-y^2}$ ), and an  $a_1$  (axial  $d_{z^2}$ ), which participates in the axial cobalt-formyl bond.

In comparison with the hydridocobalt carbonyls,<sup>3</sup> we see that the bonding pattern of the equatorial formyl group in the CC and CV conformations is similar to that of the equatorial hydrogen atom in the corresponding  $\text{HCo}(\text{CO})_3$  compound. The equatorial d orbitals mix with doubly occupied  $\sigma$  orbitals on the equatorial carbon atoms to form the equatorial Co-C $\sigma$  bonds. The Co-C antibonding combinations of equatorial d orbitals and ligand  $\sigma$  orbitals are also occupied in the  $d^8$  TBP complexes, but these antibonding combinations are stabilized through hybridization with the metal 4p orbitals.<sup>12</sup> In fact, the metal 4p orbitals are sufficiently diffuse for the d-antibonding combination to acquire bonding character between the 4p and the ligand  $\sigma$  orbital.

Similarly, the FmC conformations follow the pattern of the axial hydrogen in  $\text{HCo}(\text{CO})_3$ . The bonds to the axial ligands involve 4s, 4p<sub>z</sub>, and 3d<sub>z<sup>2</sup></sub> of CO, and the antibonding d<sub>z<sup>2</sup></sub> orbital is empty. The FmC conformation has yet another interesting feature. In the cis rotamer, the Co-C<sub>ax</sub> bond is 0.07 Å shorter than in the trans form, and 0.04 Å shorter than the Co-C<sub>eq</sub> bonds in either. All the other closed-shell TBP geometries featured long bonds to the axial ligands and short bonds to the equatorial ones. This anomaly of the cis-FmC conformation can be related to the bonding to the formyl group.

In analogy with the carbonyl from which it derives, the formyl anion is a  $\sigma$  donor and a  $\pi$  acceptor. Formally, only the  $a''$  part of the original CO  $\pi$  system is available as a  $\pi$  acceptor, the  $a'$  component having been saturated by the bond to hydrogen and the extra charge. However, some of the  $a'$   $\pi$  interaction remains, in the form of unfavorable nonaxial overlap between the filled  $d_{xz}$  orbital on cobalt and the CH and n orbitals of HCO. Orbitals 11a'' and 12a'' constitute the actual metal-formyl bonding  $\pi$  interaction. The difference between cis and trans appears in the way in which the  $a'$   $\pi$  repulsion is relieved. In the trans compound this is accomplished by moving the formyl oxygen (and the n orbital) farther from the cobalt. In the cis compound the n orbital moves closer in such a way that it achieves good overlap with the

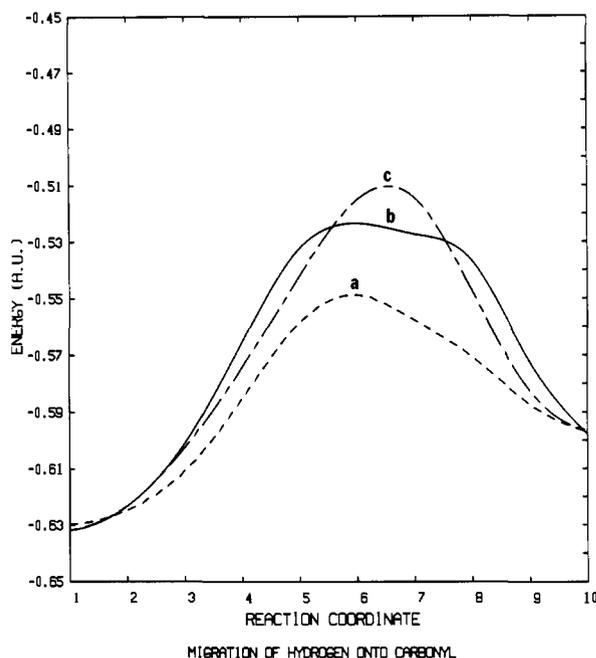


Figure 7. SCF energy profiles of the migration of hydrogen onto carbonyl. Curve a is  $C_{3v} \rightarrow$  cis-CV, curve b is  $C_{2v} \rightarrow$  cis-FmC, and curve c is  $C_{2v} \rightarrow$  cis-CC (see eq 1).

cobalt 3p<sub>x</sub> orbital, which acts as an acceptor, and also some overlap with the axial  $\pi^*$  orbitals. An inspection of the charge distributions shows that, in the transition from the trans to the cis form, formyl oxygen loses 0.03 electron.

Earlier INDO/1 studies of the formylcobalt tri- and tetracarbonyls<sup>10</sup> did not show the FmC effects described above. However, Ziegler et al.<sup>13</sup> describe the so-called  $\eta^2$  structures of the complexes  $\text{CHOMn}(\text{CO})_4$  and  $\text{CH}_3\text{COMn}(\text{CO})_4$ , obtained by partial geometry optimizations in the Hartree-Fock-Slater formalism. The Mn-O distance in these structures was 2.30 Å, comparable to the Mn-C distance of 1.90 Å, and the authors interpret these structures as having Mn-O bonds, establishing the formyl group as a bidentate ( $\eta^2$ ) ligand. This is in agreement with our observation that the diffuse 4p orbital on the cobalt atom contributes to the tilt of the formyl oxygen. However, the geometry of the formyl group cannot be explained entirely in terms of a Co-O bond. The distance between the cobalt atom and the formyl oxygen decreases in the cis rotamer of both FmC and CC, i.e., when the formyl oxygen faces the equatorial carbonyls. The differences are 0.25 and 0.11 Å, respectively. This, again, runs contrary to the steric predictions and leads us to conclude that the proximity of the carbonyl ligands is indispensable for the formation of  $\eta^2$  structures, irrespective of the metal-oxygen interaction.

On the other hand, there is no noticeable tilt of the formyl oxygen in the CV conformation, despite the proximity of a carbonyl ligand. It is plausible to assume that, in this case, the carbonyl is close enough to become a steric hindrance to the

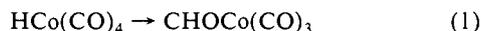
(12) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* 1975, 14, 365.

(13) Ziegler, T.; Versluis, L.; Tschinke, V. *J. Am. Chem. Soc.* 1986, 108, 612.

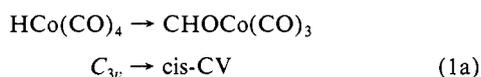
cobalt–oxygen interaction. Thus it appears that only in the FmC conformation is the geometry fully conducive to the formation of the  $\eta^2$  structure.

Unfortunately, the calculations on the complexes of manganese conducted by Ziegler et al.<sup>13</sup> did not allow for a full optimization of the geometry, and it remains uncertain whether the relative position of the formyl/acetyl and carbonyl groups should have any effect upon the Mn–O distance. Also, keeping in mind the well-known problems concerning the theoretical predictions of the metal–ligand bond lengths (see references in the paper 1), it is an open question whether the Hartree–Fock method is capable of providing a sufficiently accurate description of the geometry of such molecular structures.

Finally, we touch upon the subject of hydrogen migration. We consider only the migration between two neighboring sites on the trigonal bipyramid, assuming that no simultaneous pseudorotations around the cobalt atom are taking place. The migration reaction



can occur between three pairs of conformations, provided that the  $C_3$  symmetry is maintained throughout the reaction (see paper 1 for the description of the conformations of  $\text{HCo}(\text{CO})_4$ ):



$$\Delta E_{\text{SCF}} = 20.5 \text{ kcal/mol}$$

$$\Delta E^*_{\text{SCF}} = 50.8 \text{ kcal/mol}$$



$$\Delta E_{\text{SCF}} = 21.3 \text{ kcal/mol}$$

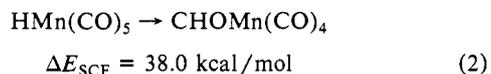
$$\Delta E^*_{\text{SCF}} = 68.0 \text{ kcal/mol}$$



$$\Delta E_{\text{SCF}} = 22.3 \text{ kcal/mol}$$

$$\Delta E^*_{\text{SCF}} = 68.3 \text{ kcal/mol}$$

All three channels are endothermic, although less so than the similar reaction



investigated by Ziegler et al.<sup>13</sup> As the latter authors assume that the product has a square-pyramidal structure, without optimizing the geometry, the calculated energies of the two reactions are somewhat difficult to compare.

A rigorous search for the reaction path of the hydrogen migration is not computationally feasible at the ab initio level, although mappings of certain cross sections of the EHT potential energy surface for reaction 2 have been done by Berke and Hoffmann.<sup>14</sup> Instead, we have approximated the reaction path by interpolating linearly the Cartesian coordinates between the optimized initial and final conformations. Such interpolations are inherent limited to very simple paths, characterized by a concerted linear motion in the degrees of freedom which describe reaction. We did not expect this to present a serious difficulty, since the calculations by Berke and Hoffmann indicate that, in the alkyl migration reaction, the path of the migrating group does not deviate much from a straight line. However, the rotatory motion of the formyl oxygen (by about 60°) cannot be approximated by linear interpolation, which would shorten the C–O bond by 13% at midpoint, yielding an artificially high energy barrier. Instead, we have determined the length of this bond by a separate interpolation of the C–O distance, while retaining the angles provided by the interpolation of Cartesian coordinates. The same procedure was used to describe the rotation of the equatorial carbonyl by about 15°, in the channel (1c). In this manner, we

**Table IV.** Configurations and Energies (au) of the Triplet States of the Formylcobalt Tricarbonyl<sup>a</sup>

	$^3A'$	$^3A''$
cis-FmC	$(d_{x^2-y^2})^1(\text{Co } 4p_x)^1$ -1824.6353	$(d_{xy})^1(\text{Co } 4p_x)^1$ -1824.6298
trans-FmC	$(d_{x^2-y^2})^1(\text{Co } 4p_x)^1$ -1824.6359	$(d_{xy})^1(\text{Co } 4p_x)^1$ -1824.6305
cis-CC	$(d_{y^2} - d_{xy})^1(\text{Co } 4sp_{xy})^1$ -1824.6452	
trans-CC	$(d_{y^2} + d_{xy})^1(\text{Co } 4sp_{xy})^1$ -1824.6337	
cis-CV	$(d_{z^2})^1(d_{x^2-y^2})^1$ -1824.6688	$(d_{x^2-y^2})^1(\text{Co } 4p_y)^1$ -1824.554
trans-CV	$(d_{y^2-z^2})^1(d_{z^2})^1$ -1824.6591	$(d_{x^2-y^2})^1(\text{Co } 4p_y)^1$ -1824.568

<sup>a</sup>Computed at optimum singlet SCF geometries.

have calculated the Hartree–Fock energy for ten geometries along each reaction path (including the reactants and products), and the energy profile was smoothed by spline interpolation.

The energy profiles for the three channels are shown in Figure 7. Although the linear interpolation can be expected to overestimate somewhat the actual energy barrier (e.g., due to the neglect of the anticipatory tilt of the recipient carbon, as described by Berke and Hoffmann<sup>14</sup>) and the heights of the energy barriers must be considered somewhat qualitative, the channel  $C_{3v} \rightarrow$  cis-CV appears to be the most favorable one. This could be explained by the weakness of the axial Co–H bond relative to the equatorial one (see the discussion above concerning the ligand bonding schemes and also paper 1).

On the other hand, orbital rearrangements in the channel  $C_{2v} \rightarrow$  cis-CC differ qualitatively from those in the other two. The hydrogen migration can be analyzed in terms of the symmetry splitting of the metal d orbitals, which retains much of the  $D_{3h}$  pattern, even in tetracoordinated TBP complexes. In the case of the third reaction channel, the hydrogen ligand, held by an interaction with the equatorial ( $e'$ -like) d orbitals, migrates into the overlapping equatorial  $\pi$  system of the carbonyl. This migration does not require mixing of orbitals which belong (formally) to different representations of the  $D_{3h}$  group. In the first channel, on the other hand, hydrogen leaves the  $a_1$  cobalt orbital and forms a bond with the nonoverlapping  $e''$ -like orbitals on cobalt and carbon. Similarly, in the second channel, the transfer is from the  $e'$  into the  $e''$  system. Therefore, symmetry considerations would require that the third channel have a lower barrier than the other two. The actual energy profiles presumably points out the limitations of purely qualitative symmetry- and overlap-based arguments. It must be emphasized, however, that the energy barriers do not differ very much (by about 0.020 au of energy) and that a complete search along the reaction path is required to obtain quantitative energy values.

The lowest of these energy barriers is still much higher than the ligand binding energy of the carbonyls.<sup>27</sup> Apparently the reason hydrogen does not migrate, while hydrocarbons will, is that hydrogen bonds more strongly to cobalt than do hydrocarbon radicals. On the other hand, the structure of the  $\text{RCOCO}(\text{CO})_3$  intermediates is probably adequately modeled by  $\text{HCOCO}(\text{CO})_3$ . If this is so, it is also possible because of microscopic reversibility that the path favored by the calculated hydrogen migration is similar to the path actually followed by hydrocarbon migration.

**Triplet States of  $\text{CHOCO}(\text{CO})_3$ .** A summary of triplet states of the formylcobalt tricarbonyl is given in Table IV. The energy values were obtained by Hartree–Fock calculations at singlet geometries.

We see that the two triplet states of the FmC conformations resemble closely the corresponding  $d^7p^1$  triplets of the HC form of  $\text{HCo}(\text{CO})_3$ . One of the equatorial d electrons is excited into the empty directional receptor of  $a'$  symmetry, left behind after the removal of the equatorial carbonyl from  $\text{HCo}(\text{CO})_4$  (see paper 1 for the full description of these states).

A similar pattern is observed in the conformation CC. In resemblance to its hydridocobalt counterpart, this conformation lacks a low-lying  $^3A''$  state. Since both equatorial d orbitals are

(14) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

of  $a'$  symmetry, such a state would require a high-energy excitation from the set ( $d_{xz}$ ,  $d_{yz}$ ).

The pattern of spin distribution indicates further similarity between the FmC and CC triplets and their counterparts in the molecule  $\text{HCo}(\text{CO})_3$ . In the FmC conformation, about 1.5 unpaired electrons reside on the cobalt atom, and 0.5 on the axial carbonyl. In the CC conformation, spins are similarly distributed between the metal and the equatorial carbonyl.

Geometries of the  $d^7p^1$  triplets of the hydridocobalt tricarbonyl do not differ much from those of the closed-shell,  $d^8$  states. By the same token, we would expect the optimized geometries of the triplet states of the formyl complex to be fairly similar to the geometries of the closed-shell states.

Cis- and trans-CV conformations, on the other hand, give rise to both  $d^8$  and  $d^7p^1$  triplets. In the case of hydridocobalt tricarbonyl, geometry optimization yields tetrahedral  $d^8$  triplet states, considerably different in geometry from the closed-shell form of the CV conformation. The d-orbital set of such triplets is hybridized into orbitals similar to tetrahedral orbitals of symmetry  $t_2$  and e. We expect the formylcobalt molecule to possess similar tetrahedral triplet states. On the other hand, CV triplet states, listed in Table IV, were not found in the molecule  $\text{HCo}(\text{CO})_3$ . There are good reasons for suspecting them of being artifacts, brought about by the imposition of singlet geometry. However, these triplets are not of immediate interest for the hydrogen migration, and we do not explore them further.

**An Account of the EHT Results.** Berke and Hoffmann<sup>14</sup> have studied migration of the methyl group from the transition-metal atom onto the carbonyl ligand. By means of extended Hückel calculations, they obtained the energy profile of the migration reaction, as well as information concerning the electronic structure of the reactants and products. We compare some of these EHT results with the ab initio ones for hydrogen migration.

Extended Hückel calculations carried out on the complex  $\text{CH}_3\text{COMn}(\text{CO})_4$  indicate that both the alkyl group and the metal atom interact with the  $\sigma$  and  $\pi^*$  orbitals of the carbonyl, giving rise to two  $\sigma$ -bonding orbitals of the group  $\text{CH}_3\text{CO}$ . This picture is partially confirmed by the Hartree-Fock calculations on cobalt complexes. The HOMO of the molecule  $\text{CHOC}(\text{CO})_3$  can be related to the carbonyl  $\pi^*$  orbital.

Invoking the results of an earlier EHT analysis of the orbitals of molecular fragments,<sup>15</sup> Berke and Hoffmann predicted the most stable TBP conformation of the complex  $\text{CH}_3\text{COC}(\text{CO})_3$  to be an equivalent of the FmC, without making a distinction between the rotamers. Hartree-Fock calculations on the complex  $\text{CHO-Co}(\text{CO})_3$  favor a different conformation, trans-CV, but the energy differences between conformations are small, <10 kcal/mol in magnitude. Configuration-interaction calculations on related complexes indicate that the energy differences between conformers are rather difficult to resolve. We do not believe that a conclusive differentiation could be achieved at either the semiempirical level or this ab initio level of accuracy.

On the ground of EHT calculations, Berke and Hoffmann further conclude that the lowest TBP conformation of the complex  $\text{CH}_3\text{COC}(\text{CO})_3$  does not represent an absolute energy minimum and could relax into a near-planar structure, with bonds to the pairs of trans ligands forming angles of about  $170^\circ$ . We have not found energy minima of such molecular geometry at the Hartree-Fock optimization level for any of the cobalt complexes studied.

Finally, the EHT studies were limited to the equatorial-to-apical migrations in the TBP complexes, whose symmetry aspects do not differ much from those in the octahedral complexes. Apparently, no EHT results are available on the equatorial migrations.

#### ( $\eta$ -Ethylene)hydridocobalt Tricarbonyl

A crucial step in the hydroformylation reaction consists of the addition of the hydrogen atom to the  $\text{C}=\text{C}$  site of the olefin. The mechanism proposed by Orchin<sup>1</sup> and by Heck and Breslow<sup>2</sup> postulates that the olefin initially forms a  $\pi$  complex with the

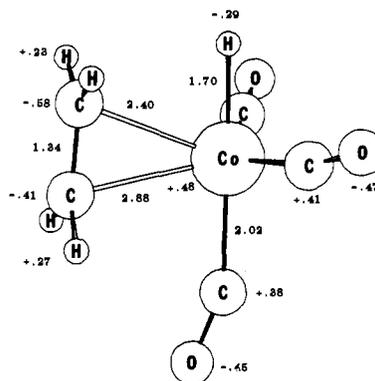


Figure 8. Axial HC conformation of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$ . The SCF energy of this structure is  $-1790.1071$  au and the CI energy with unlinked cluster corrections is  $-1790.712$  au.

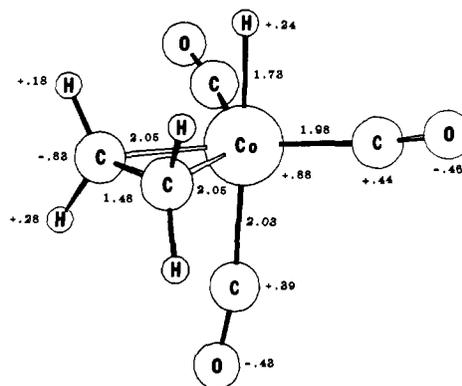


Figure 9. Equatorial HC conformation of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$ . The SCF energy of this structure is  $-1790.1244$  au and the CI energy with unlinked cluster corrections is  $-1790.748$  au.

highly reactive hydridocobalt tricarbonyl. In the subsequent step of the catalytic cycle, the hydride-like hydrogen ligand is transferred from the metal to the olefin molecule, producing a tetra-coordinated alkyl-carbonyl of cobalt.

Of the theoretical results, CNDO/2 geometries and ab initio Hartree-Fock energies and orbital populations are available on certain conformations of the  $\pi$  complexes of hydridocobalt tricarbonyl with ethylene and propylene.<sup>16</sup> Experimental data are available on a number of  $\eta$ -alkene complexes of the transition metals,<sup>17</sup> and a degree of heuristic understanding obtains regarding the factors that determine their structure. However, the authors are not aware of any experimental data relevant to the ( $\eta$ -ethylene)cobalt carbonyl studied here or to similar complexes.

We have investigated  $\pi$  complexes of the hydridocobalt tricarbonyl with ethylene. Our earlier investigations of related compounds<sup>3</sup> produced abundant evidence to the effect that the pentacoordinated  $d^8$  complexes of cobalt have trigonal-bipyramidal geometry; therefore, we assume here that the same is true for this complex and verify the assumption subsequently. There are four possible arrangements of ligands on the vertices of the bipyramid, but one of them, having hydrogen and ethylene in the trans positions, is of no interest in the reaction of hydrogen transfer. We investigate the remaining three conformations, which are labeled HC, CC, and EtC, in accordance with the nomenclature introduced earlier. Of the possible rotational orientations of the ethylene ligand, those which place one carbon atom close to the "hydride" are of most interest. Those are not necessarily the rotamers of lowest energy (possibly not even minima on the potential energy surface), but it is likely that the hydrogen transfer should have such conformations as the starting point. As an illustration of the structural differences between rotamers, we have investigated one alternative conformation, HC with the ethylene

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(16) Grima, J. Ph.; Choplin, F.; Kaufmann, G. *J. Organomet. Chem.* **1977**, *129*, 221.

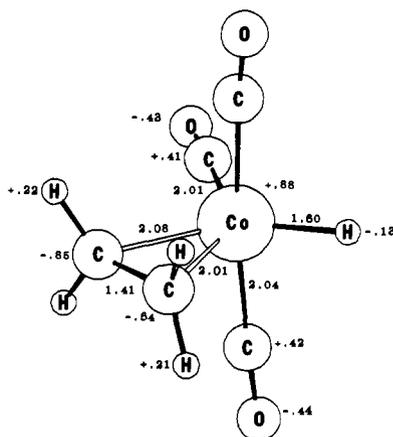


Figure 10. CC conformation of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$ . The SCF energy of this structure is  $-1790.1437$  au and the CI energy with unlinked cluster corrections is  $-1790.757$  au.

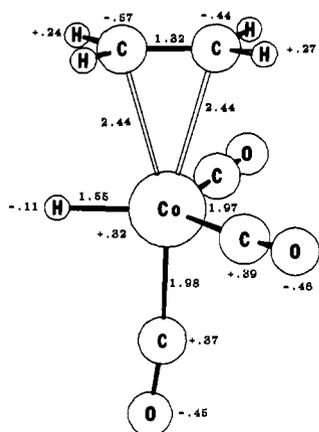


Figure 11. EtC conformation of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$ . The SCF energy of this structure is  $-1970.1262$  au and the CI energy with unlinked cluster corrections is  $-1790.732$  au.

ligand in the equatorial plane. All geometry optimizations were carried out for the closed-shell configurations at the Hartree-Fock level, and the only constraint was the imposition of  $C_3$  symmetry. The geometrical parameters obtained are listed in Table V of the supplement, and the conformations are shown in Figures 8–11.

There are some similarities between the present compound and the hydridocobalt tetracarbonyl (see paper 1). This is mostly due to the fact that, like carbonyl, the ethylene ligand is a  $\sigma$  donor (orbital  $\pi(\text{CC})$ ) and a  $\pi$  acceptor (orbital  $\pi^*(\text{CC})$ ). By way of differences, however, the localized  $\pi$ -bonding orbital in the ethylene ligand is a poorer  $\sigma$  donor than the carbon lone pair in the carbonyl, and the  $\pi^*$  orbital is more distinctly oriented toward the metal atom than the carbonyl  $\pi$  system and is, therefore, a better  $\pi$  acceptor. Unlike that of the carbonyl, the ethylene  $\pi$  system is not axially symmetrical and has only one  $\pi$ -acceptor orbital. Nevertheless, optimized geometries of the sterical conformations follow rather closely the TBP pattern, justifying the treatment of the ethylene as a monodentate ligand.

As in the hydridocobalt tetracarbonyl, the length of the metal-ligand bond depends on the position of the ligand, the equatorial position being generally closer to the metal than the axial one. However, we see that in the HC conformation the equatorial carbonyls are  $0.05$  Å closer to the metal when the ethylene C–C bond is parallel to the TBP axis than when it lies in the equatorial plane. Similarly, the bonds to the equatorial hydrogen and carbonyl(s) are shorter ( $0.05$  and  $0.04$  Å, respectively) in the EtC conformation than in the CC. On the other hand, the bond to the axial carbonyl is  $0.06$  Å longer in the CC than in the EtC conformation.

As for the ethylene ligand, distances from cobalt to the ethylene carbon atoms indicate that this ligand is least tightly bound when

Table VI. Orbital Energies for  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$

HC(axial)	HC(equ)	CC	EtC	
-0.33 (28a')	-0.33 (28a')	-0.41 (27a')	-0.39 (28a')	Co-H
-0.31 (29a')	-0.47 (26a')	-0.29 (29a')	-0.27 (29a')	$d_{x^2-y^2}$
-0.36 (14a'')	-0.34 (15a'')	-0.47 (26a')	-0.41 (14a'')	$d_{xy}$
-0.43 (27a')	-0.54 (25a')	-0.53 (13a'')	-0.49 (26a')	$d_{xz}$
-0.45 (26a')	-0.38 (27a')	-0.37 (28a')	-0.45 (27a')	CC $\pi$
-0.47 (13a'')	-0.54 (13a'')	-0.54 (12a'')	-0.52 (13a'')	$d_{yz}$
-0.53 (12a'')	-0.50 (14a'')	-0.50 (14a'')	-0.53 (12a'')	CH
0.1071 <sup>a</sup>	0.1244	0.1437	0.1262	

<sup>a</sup>Total SCF energies given as  $-(E + 1790)$ .

in the axial position, and most so when residing in the equatorial plane, i.e., in the conformations CC and equatorial HC. Charge distributions show that in these conformations ethylene carbons are more negative, and cobalt is more positive, than in the other two. Bonds to the equatorial hydrogen and carbonyl(s) are also the longest in these cases. This can be explained by a charge transfer from the equatorial d and 4sp orbitals into the ethylene  $\pi^*$ , which weakens the bonds to the other equatorial ligands. The same charge transfer weakens the ethylene C–C bond, and we see that in the above conformations the carbon atoms are rather far apart,  $1.41$  and  $1.46$  Å, respectively. By comparison, the theoretically predicted distance in free ethylene (at the SCF level, in the same basis) is  $1.314$  Å; the experimental value is  $1.337$  Å.

Nonequivalence of the axial and equatorial positions in trigonal-bipyramidal complexes has been corroborated by the X-ray analyses of the crystalline structure of certain complexes of iridium with a bidentate ligand, cycloocta-1,5-diene.<sup>18,19</sup> In each case, the distance between the metal atom and the C=C group was greater in the axial case than in the equatorial one, the largest difference being  $0.08$  Å. The C–C distance in the olefin varies somewhat from case to case, and at least in one complex<sup>18</sup> this bond was found to be  $0.085$  Å longer in the axial position than in the equatorial. No experimental data appear to be available on the cobalt complexes of similar structure.

In comparison with the experimental data quoted above, theory predicts the differences in the olefin bond length fairly well, while exaggerating the differences in the metal-olefin distance. This is not surprising, in the light of the known tendency of the Hartree-Fock method to produce excessively long metal-ligand bonds. Nevertheless, relative trends in the bond lengths are reproduced at this level of theory.

Another known structural detail of the  $\pi$  complexes of alkenes, deviation from the planarity of the carbon-carbon double bond,<sup>17</sup> is present in the geometries calculated here. The hydrogen atoms of the ethylene are tilted away from the metal, since the one-sided bonding interaction of the  $\pi^*$  orbital with metal d favors a tetrahedral, rather than planar, geometry on the carbon atoms. Naturally, this effect should increase as the cobalt-ethylene distance diminishes. The distance of the ethylene carbons from the plane of hydrogen atoms is a measure of the ethylene nonplanarity. The distances of  $0.4$  Å in the CC and equatorial HC conformations correspond to strongly bound ethylene, as can be deduced from the metal-ligand bond lengths and the orbital bonding scheme. The distance of  $0.1$  Å in the conformations EtC and axial HC, on the other hand, corresponds to a weakly complexed ethylene.

In contrast with the equatorial case, axial ethylene gives rise to a weaker trans effect than the carbonyl, as can be seen from the axial metal-carbonyl bond lengths. This is understandable, since the trans carbonyls share both components of the  $\pi$  system, while the ethylene has only the component a'.

High-lying occupied orbitals of the ethylene complexes are listed in Table VI of the text and Table VII of the supplement. As before, we concentrate upon those features that describe the metal valence shell and the bonding between the metal and the ligands

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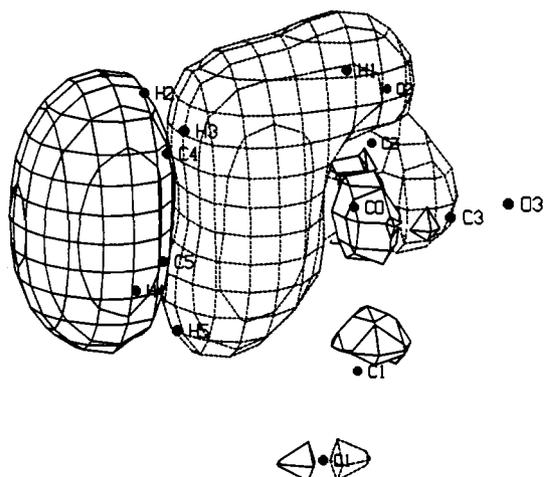


Figure 12. 26a' orbital of the axial HC conformation (contour encloses 90% of the electron density).

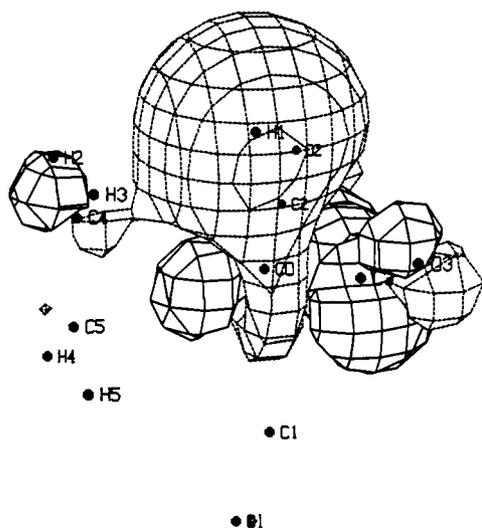


Figure 13. 28a' orbital of the axial HC conformation.

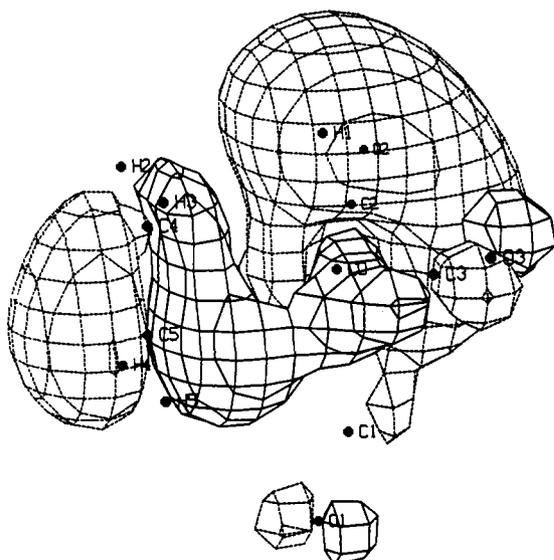


Figure 14. 29a' orbital of the axial HC conformation.

of chemical interest, hydrogen and ethylene. Pictures of the orbitals (Figures 12–23) represent surfaces of constant orbital value, which enclose 90% of the electron density.

A great deal of similarity can be found between the orbitals of the conformation EtC and those of the  $C_{2v}$  form of hydridocobalt

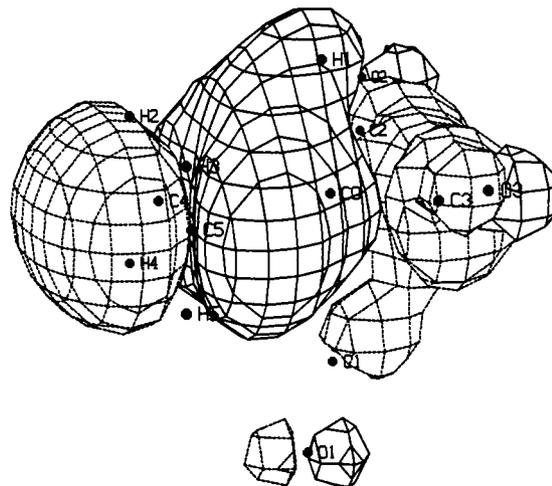


Figure 15. 27a' orbital of the equatorial HC conformation.

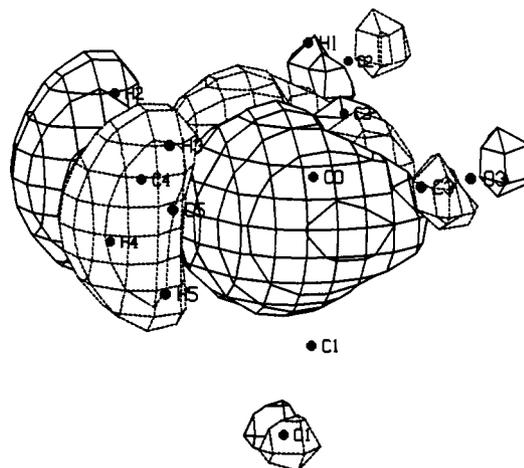


Figure 16. 15a'' orbital of the equatorial HC conformation.

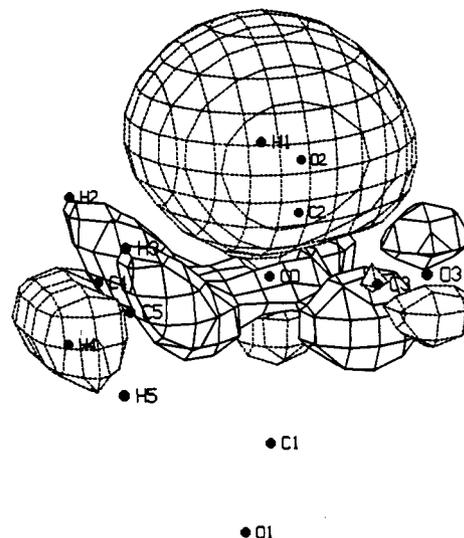


Figure 17. 28a' orbital of the equatorial HC conformation.

tetracarbonyl (see Table III in paper 1). Orbitals 13a'' and 26a' constitute the (almost unperturbed)  $e''$  pair of d orbitals, and the pair  $e'$  is involved in the familiar pattern of the equatorial H–Co bond, featuring hybridization with the 4p atomic orbitals. MOs 28a' and 29a' are bonding to hydrogen in their  $d_{x^2-y^2}$  and  $4p_x$  components, respectively (see Figures 22 and 23).

The cobalt–ethylene bond consists primarily of a  $\sigma$ -type interaction between the ethylene  $\pi$  and  $d_{z^2}$  (orbital 28a', Figure 22). The same  $\pi$  orbital on ethylene interacts in a bonding fashion with

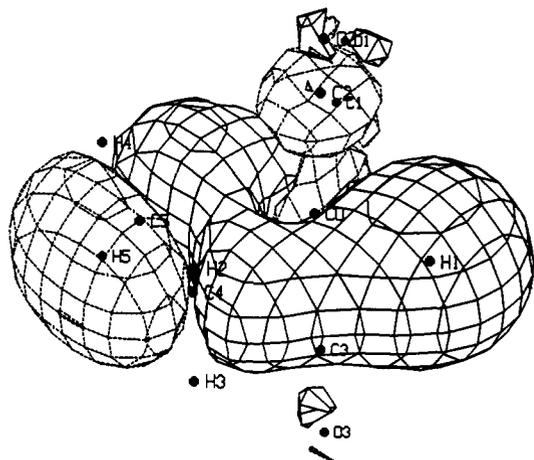


Figure 18. 27a' orbital of the CC conformation.

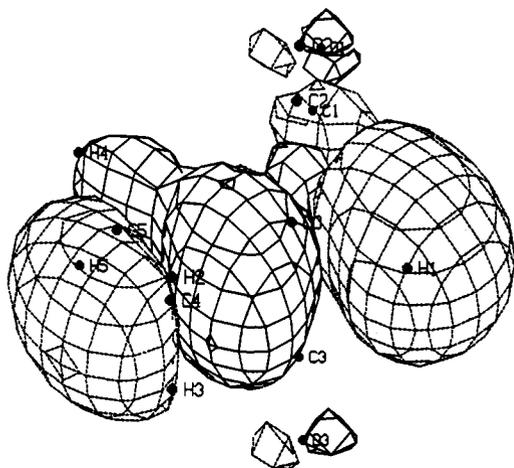


Figure 19. 28a' orbital of the CC conformation.

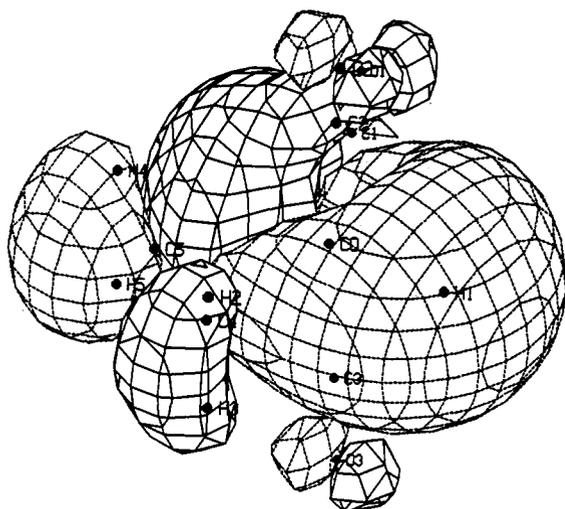


Figure 20. 29a' orbital of the CC conformation.

the  $d_{xz}$  (orbital 27a', Figure 21); this bond is permitted by symmetry but is usually not considered important, due to the small overlap between the atomic orbitals involved.

There is a remarkable absence of any major " $\pi$ -back-bonding" interaction between the ethylene  $\pi^*$  and the metal  $d_{xz}$ . At the same time, ethylene carbons are farthest away from cobalt in this conformation (2.44 Å) and closest to one another (1.32 Å, as compared to the theoretically predicted distance of 1.314 Å in the free ethylene). All of this indicates a weak binding of the ethylene in the axial position and a similarity with the  $C_{2v}$  form of  $\text{HCo}(\text{CO})_4$ .

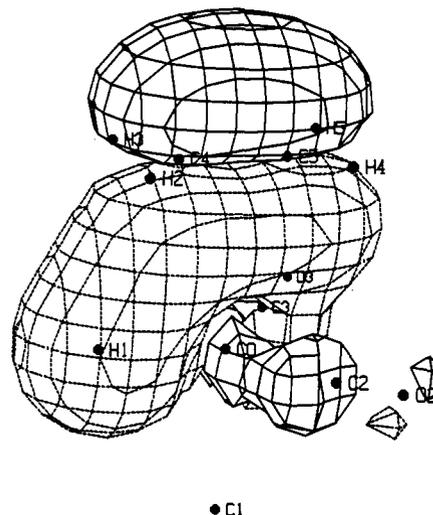


Figure 21. 27a' orbital of the EtC conformation.

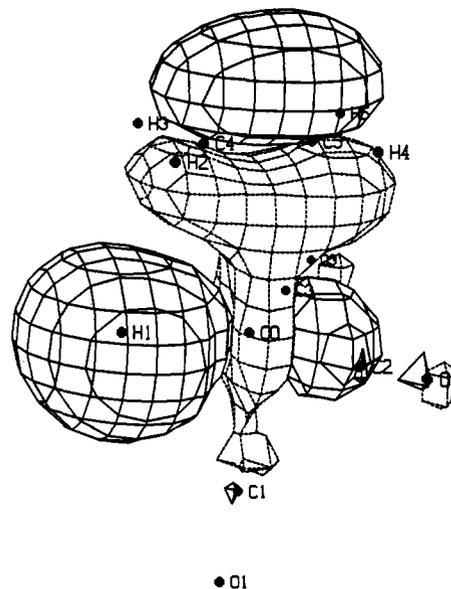


Figure 22. 28a' orbital of the EtC conformation.

Further, we compare the two forms of the HC conformation, having the ethylene molecule aligned axially or equatorially. The geometry of the axial rotamer indicates weak binding of the ethylene, and we indeed see that the most prominent bonding is of  $\sigma$  type, in the MO 26a' (Figure 12; compare with the orbital 28a' in EtC). The  $\pi$ -type bond to ethylene involves both the  $d_{xz}$  (MO 27a') and 4sp (MO 29a', Figure 14), neither interaction being very distinct.

The geometry of the equatorial rotamer, on the other hand, indicates a strongly bound ethylene. The  $\sigma$  bond involves both d and 4sp orbitals, resembling the bonding scheme of the equatorial hydrogen (orbitals 27a', Figure 15, and 28a', Figure 17). A distinct  $\pi$ -bonding interaction with the ethylene  $\pi^*$  orbital is contained in the MO 15a'' (Figure 16).

The equatorial HC conformation has the usual axial H-Co bond, involving the axial  $d_{z^2} + 4p_z$  metal orbital (MO 2a', Figure 17; see also orbital 17a<sub>1</sub> of the  $C_{3v}$  form of  $\text{HCo}(\text{CO})_4$ , paper I, Table III). The same bond in the axial rotamer, however, consists of the sideways interaction with an orbital which is largely  $d_{xz}$  in nature (28a', Figure 13), augmented by overlap with directional 4sp orbitals, which also participate in the  $\pi^*$  bond to ethylene. This difference can be explained in terms of a larger deviation of the axial rotamer from the TBP geometry, and, as we show

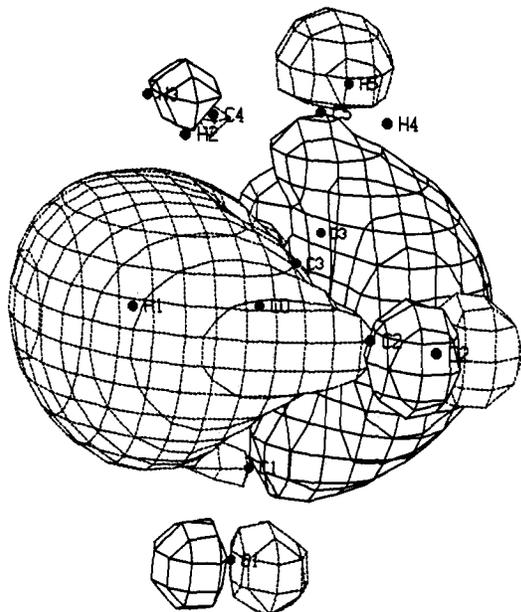


Figure 23.  $29a'$  orbital of the EtC conformation.

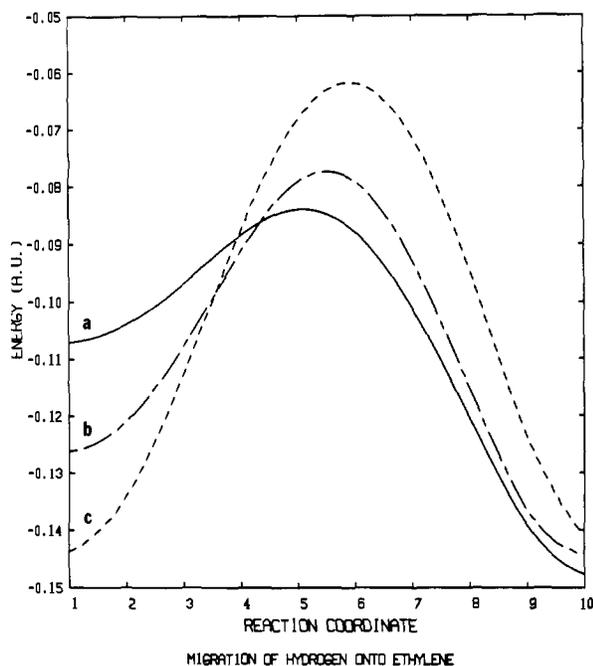


Figure 24. SCF energy profiles of the migration of hydrogen onto ethylene. Curve a is HC, ax  $\rightarrow$  CV, curve b is EtC  $\rightarrow$  RC, and curve c is CC  $\rightarrow$  CC (see eq 3).

below, the axial HC conformation undergoes the hydrogen migration more readily than CC or EtC.

Equatorial bonds to the ethylene and hydrogen ligands in the CC case exemplify what has been said above, and we do not find it necessary to elaborate upon the orbitals of this conformation (see Figures 18–20 for the three-dimensional contours of the frontier orbitals).

Although the conformations of the  $\eta$ -ethylene complex have rather well-defined TBP geometries, it is also possible to interpret the tight complexation of ethylene in the CC and equatorial HC forms as belonging to a distorted octahedron, the higher positive charge on cobalt indicating a  $\text{Co}^{\text{III}}$  state rather than  $\text{Co}^{\text{I}}$ . A vaguely octahedral pattern can be discerned in the orbitals of the form HC:  $13a''$ ,  $25a'$  and  $26a'$  belong to the symmetry  $T_{2g}$ , while  $15a''$  and  $28a'$  belong to  $E_g$ . The assignments are more difficult to make in the CC case.

Several qualitative conclusions can be drawn from the shapes of the orbitals, as shown in Figures 12–23. First, the 4sp orbitals

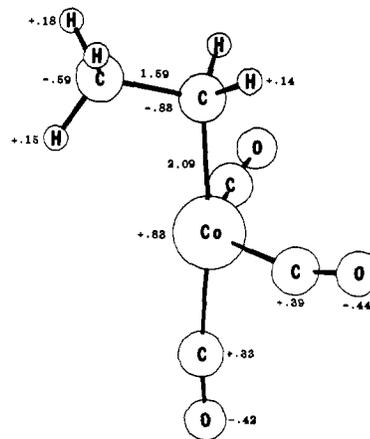


Figure 25. RC conformation of  $\text{CH}_3\text{CH}_2\text{Co}(\text{CO})_3$ . The SCF energy of this structure is  $-1790.1439$  au and the CI energy with unlinked cluster corrections is  $-1790.734$  au. The reacting H is  $2.86$  Å from the Co.

of the metal atom participate substantially in the formation of bonds toward both the axial and equatorial ligands. Further, the appearance of the SCF orbitals shows less overlap between the ligand  $\pi$  and metal d orbitals than one would expect in accordance with the Dewar–Chatt–Duncanson model.<sup>20</sup> Such  $\pi$  overlap as there is occurs in the equatorial plane and involves the metal 4p orbitals heavily (Figures 16 and 20). It should be kept in mind that, although these 90% density contours are dominated by the Co 4p orbital, most of the electron density is actually in a cobalt d orbital.

Axial  $\sigma$  bonds, however, are quite prominent (see Figures 13, 17, and 22), and their d contributions are more readily apparent. Presumably, this absence of the axial back-bonding in the SCF picture is partially related to the excessively long metal–ligand bonds, a defect of the SCF methodology that affects the axial bonds in TBP complexes more than the equatorial ones (see also paper 1).

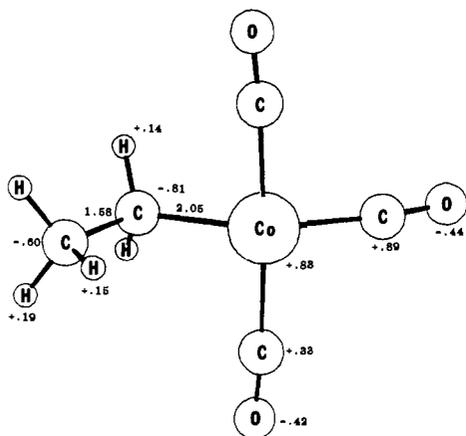
A summary of the results on ethylene, in the 3-21G basis, is given in Table X of the supplement. Configuration-interaction calculations on the hydridocobalt tricarbonyl<sup>21</sup> in the basis used here yield the CV conformation as the lowest singlet, at the energy of  $-1712.984$  au. Therefore, on the singlet surface, the conformations of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$  considered here are stable with respect to the departure of ethylene by at least 43 kcal/mol (axial HC). However, the lowest triplet state of  $\text{HCo}(\text{CO})_3$  is an almost tetrahedral  $^3A_2$ , at the energy of  $-1713.061$  au. With respect to this state, the lowest energy (CC) conformation of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$  is unstable by 15 kcal/mol even after extensive CI.

If the postulated mechanism of hydroformylation is correct,  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$  should be stable enough to undergo a hydrogen migration. Apart from the possibility that the  $\pi$  complex indeed dissociates spontaneously into ethylene and the triplet  $\text{HCo}(\text{CO})_3$ , there are some ways in which this instability could be explained as being due to theoretical difficulties. First, the conformation EtH or some nonsymmetrical orientation of ethylene, which were not considered here, could provide the overall stability of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$ . Further, it is possible that the triplet states of  $\text{HCo}(\text{CO})_3$  have artificially low calculated energies<sup>21</sup> (see also paper 1). Finally, it is possible that the true tetracoordinated complexes, which could give rise to low-energy triplet states, do not occur in the mechanism of hydroformylation. In that case, the migration steps, which are postulated to produce tetracoordinated species, would have to be followed by rapid or concurrent complexations, without allowing for a transition onto the triplet energy surface.

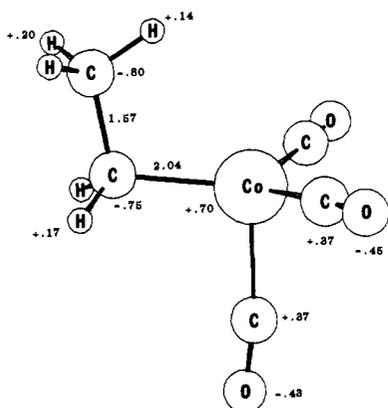
The ethylcobalt tricarbonyl complex, which is produced by the migration of the hydrogen ligand onto ethylene, was also studied

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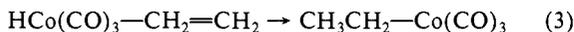
**Figure 26.** CC conformation of  $\text{CH}_3\text{CH}_2\text{Co}(\text{CO})_3$ . The SCF energy of this structure is  $-1790.1409$  au and the CI energy with unlinked cluster corrections is  $-1790.734$  au. The reacting H is  $2.92$  Å from Co.



**Figure 27.** CV conformation of  $\text{CH}_3\text{CH}_2\text{Co}(\text{CO})_3$ . The SCF energy of this structure is  $-1790.1477$  au and the CI energy with unlinked cluster corrections is  $-1790.742$  au. The reacting H is  $2.76$  Å from Co.

in some detail. The results are presented in Tables VIII–X of the supplement and the optimized geometries are shown in Figures 25–27. This tetracoordinated complex resembles the hydrido-cobalt tricarbonyl, with the additional conformations brought about by the motions in the internal degrees of freedom of the ethyl group. It is reasonable to expect the cobalt coordination to follow a pattern analogous to that in the hydridocobalt complex, featuring several singlet and triplet states, but we have investigated only those conformations on the singlet surface that are produced by the migration of hydrogen onto ethylene. Geometry optimizations, constrained to the  $C_s$  symmetry, yield three such conformations, of the TBP type. The geometries of these conformations do not differ substantially from those of the analogous states of  $\text{HCo}(\text{CO})_3$  (see paper 1), except for a larger Mulliken charge attributed to the cobalt atom in the ethyl complex. The  $\text{Co}-C_\alpha$  bond is somewhat shorter in the equatorial position than in the axial one, and the bonding orbitals are similar to those of the  $\text{H}-\text{Co}$  bond.

We assume that the migration of the hydrogen from the cobalt atom onto the ethylene double bond



occurs between the neighboring sites on the trigonal bipyramid, without simultaneous pseudorotations taking place. We have examined the three possible channels which preserve  $C_s$  symmetry



$$\begin{aligned} \Delta E_{\text{SCF}} &= -25.5 \text{ kcal/mol} \\ \Delta E^*_{\text{SCF}} &= 14.5 \text{ kcal/mol} \\ \Delta E_{\text{CI}} &= -18.8 \text{ kcal/mol} \\ \Delta E^*_{\text{CI}} &= 17.4 \text{ kcal/mol} \end{aligned}$$



$$\begin{aligned} \Delta E_{\text{SCF}} &= -11.1 \text{ kcal/mol} \\ \Delta E^*_{\text{SCF}} &= 29.6 \text{ kcal/mol} \\ \Delta E_{\text{CI}} &= -1.0 \text{ kcal/mol} \\ \Delta E^*_{\text{CI}} &= 22.8 \text{ kcal/mol} \end{aligned}$$



$$\begin{aligned} \Delta E_{\text{SCF}} &= +1.7 \text{ kcal/mol} \\ \Delta E^*_{\text{SCF}} &= 51.1 \text{ kcal/mol} \\ \Delta E_{\text{CI}} &= +14.7 \text{ kcal/mol} \\ \Delta E^*_{\text{CI}} &= 54.8 \text{ kcal/mol} \end{aligned}$$

by means of the linear search on the SCF energy surface. The SCF energy profiles are shown in Figure 24, and the heights of the respective energy barriers can be readily correlated with the nature of the bonds to hydrogen and ethylene, as discussed above. The slightly higher barrier of the second channel over the first relates to the stronger equatorial  $\text{H}-\text{Co}$  bond, since the geometrical parameters of the cobalt–ethylene bond indicate that the complexation of ethylene is of comparable strength in the EtC and axial HC conformations. The fact that the third channel displays the highest energy barrier corresponds to the earlier observations to the effect that the equatorial bonds are shorter, and presumably stronger, than the apical ones, for both hydrogen and ethylene. As in the case of the migration to carbonyl, the symmetry of the interaction orbitals would favor the third reaction channel.

Figure 24 shows that the most stable of the considered conformations of the  $\pi$  complex, CC, leads to the path with the highest barrier, while the high-energy HC conformation, on the other hand, is the starting point of the most favorable migration path. Berry pseudorotations of  $C_s$  symmetry connect the CC conformation with both EtC and HC; it can be assumed that such rearrangements have a low energy barrier, since they involve neither a significant change in the bond lengths nor a rotation of the ethylene ligand with respect to the rest of the molecule. Therefore, the pseudorotation is unlikely to offset the energetic advantages of the first reaction channel and probably constitutes the initial step in the hydrogen migration reaction.

**Electron Correlation and the Problem of Bond Lengths.** The fact that the Hartree–Fock calculations consistently predict metal–ligand distances that are substantially larger than the ones found experimentally is a matter of considerable concern in the case of unstable species, for which the molecular geometry cannot be determined by other than theoretical methods. Most obviously, this phenomenon makes it difficult to obtain reliable energy differences between states of different multiplicity, which are sensitive to the extent of splitting of the metal d orbitals.

Studies on ferrocene<sup>22–24</sup> show that the size of the basis set does not play a crucial role in determining the metal–ligand bond lengths. The problem appears to lie with the Hartree–Fock method, and hypotheses were proposed about the nature of the correction introduced by electron correlation.<sup>24</sup> A study of iron pentacarbonyl by Lüthi et al.,<sup>25</sup> shows that both the bond lengths and force constants are sensitive to electron correlations, and the authors have investigated the change in electron density engendered by the inclusion of the correlation effects.

We have investigated the difference in electron density distribution between the CI and SCF wave functions for the four conformations of  $\text{HCo}(\text{CO})_3-\text{C}_2\text{H}_4$ . One example is shown in Figures 28 and 29. In general, we find the CI wave function to have a somewhat more spherical density distribution than the SCF, with a buildup in the region of hydrogen and carbon atoms. The difference in the electric field, due to this redistribution of charge

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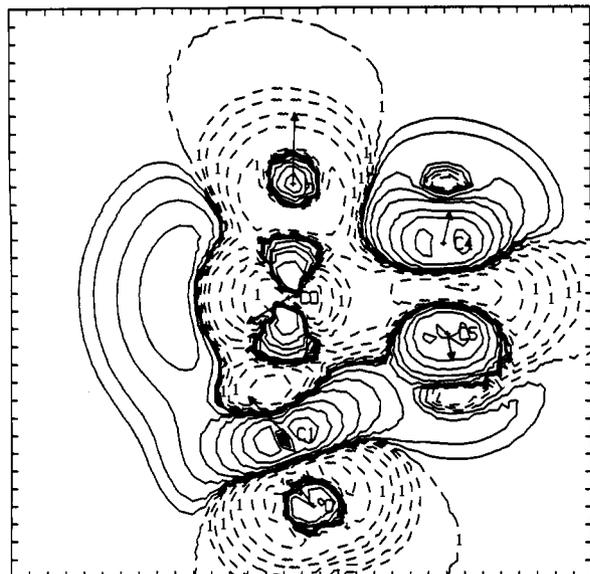


Figure 28. Density difference between the correlated (CI) and uncorrelated (SCF) wave function of the axial HC conformation of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$  in the symmetry plane. Full lines indicate higher density of the CI wave function, and the contours are drawn at 0.00001, 0.00002, 0.00005, 0.0001, 0.0002, 0.0005, 0.001, 0.002, and 0.005  $e/a_0^3$ . Arrows show the direction of the differential electric field at nuclear positions.

Table XI. Magnitude of the Differential Electric Field<sup>a</sup> ( $10^{-3}$  au<sup>2</sup>) at Atomic Centers of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$

atom	HC(axial)	HC(equ)
H	1.901	1.447
Co	1.262	0.886
C <sub>ax</sub>	1.358	1.724
O <sub>ax</sub>	0.714	0.633
C <sub>eq</sub>	0.894	1.478
O <sub>eq</sub>	0.516	0.824
C <sub>cis</sub>	0.810	0.746
C <sub>trans</sub>	0.651	

atom	CC	EtC
H	3.313	4.073
Co	0.764	0.899
C <sub>ax</sub>	1.572	1.324
O <sub>ax</sub>	0.398	0.503
C <sub>eq</sub>	1.736	1.044
O <sub>eq</sub>	0.547	0.532
C <sub>cis</sub>	0.398	0.641
C <sub>trans</sub>	0.751	0.528

<sup>a</sup>  $\int (\tau_A/r_A^3) \Delta\rho \, d\tau$ , where  $\Delta\rho = \rho_{\text{CI}} - \rho_{\text{SCF}}$ . <sup>b</sup> 1 au =  $5.1429 \times 10^{11}$  V/m.

and calculated at the positions of the nuclei, provides a measure of the differences in geometry which are due to correlation. Evidently, the carbonyl ligands are being pulled inward in all cases. The somewhat smaller forces on the oxygen atom corresponds to the usual elongation of the SCF-optimized bonds between the light atoms, due to the  $\sigma\text{-}\sigma^*$  and  $\pi\text{-}\pi^*$  correlations (see Table I in paper I for a comparison between the SCF and experimental C–O distances in  $\text{HCo}(\text{CO})_4$ ).

Further, the ethylene carbons are being drawn inward, at least in the equatorial HC and CC conformations, which we associate with strong  $\pi$  complexation (see above). In the other two cases, nothing very definite could be said about the influence of these electrostatic effects upon the cobalt–ethylene distance. The carbon atoms are also being drawn apart in all four cases, a phenomenon analogous to the increase in C–O distance, due to the ethylene  $\sigma\text{-}\sigma^*$  and  $\pi\text{-}\pi^*$  correlation and apparently unrelated to complexation. The regions of diminished density between the ethylene carbons, as well as between the carbonyl atoms, correspond to these bond elongations.

The outward pull on hydrogen, stronger in the equatorial cases (CC and EtC), runs contrary to the expected effect. Although

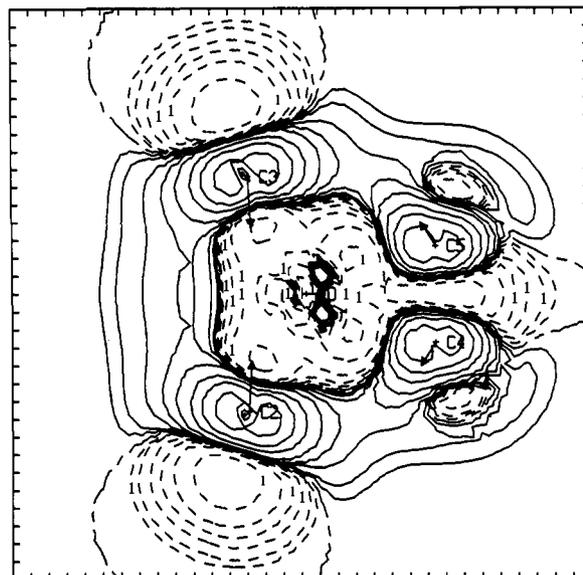


Figure 29. Density difference of the equatorial HC conformation of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$  in a plane perpendicular to the TBP axis.

there are no reliable estimates of the H–Co bond lengths in the complexes considered here, at least in the case of hydridocobalt tetracarbonyl, it is clear that the Hartree–Fock method overestimates the length of that bond (paper I, Table I).

**An Account of the CNDO/2 Results.** Grima et al.<sup>16</sup> report the results of CNDO/2 and ab initio optimizations of the geometries of ( $\eta$ -ethylene)- and ( $\eta$ -propylene)hydridocobalt tricarbonyls. They considered the HC conformations, with the axially and equatorially aligned alkene, as well as the trans conformation (EtH and PrH in our notation), which they found to have the lowest energy in both complexes.

The chief discrepancy between our findings and those of Grima et al. lies in the geometries of the complexes, which were only partially optimized in the above study. The authors have assumed that the olefin acquisition does not introduce substantial change into the geometry either of the olefin or of the hydridocobalt carbonyl and have apparently limited the optimization to the relative position of the two and to the metal–ligand bond angles within  $\text{HCo}(\text{CO})_3$ . Our calculations indicate that the addition of the olefin engenders two kinds of readjustments in the geometry of the cobalt carbonyl; changes in the metal–hydrogen and metal–carbonyl bond lengths, due to the transfer of charge onto the ethylene, and probably best described as a trans effect, were discussed above. Changes in the bond angles of the free  $\text{HCo}(\text{CO})_3$ , on the other hand, are readily explained as sterically dictated rearrangements, providing space for the extra ligand.

Similarly, elongation of the carbon–carbon bond in the olefin, inversely proportional to the metal–olefin distance and attributable to the  $\pi$ -back-bonding, has been detected experimentally in the complexes of iridium.<sup>19</sup> The nonplanarity of the olefin, a structural detail observed in many  $\pi$  complexes and which can be similarly explained as a consequence of  $\pi$ -back-bonding,<sup>17</sup> was also omitted from the above CNDO/2 study. Our calculations confirm the (not quite unexpected) strong interdependence of the geometrical parameters throughout the complex and lead us to the conclusion that the fragmentation of the geometry optimizations is probably not justifiable in the case of transition-metal complexes in general, and certainly not in the  $\pi$  complexes considered here.

The qualitative features of the ethylene complexation, described by Grima et al., agree with our results: there is a significant transfer of charge onto the ethylene carbons, accompanied by a  $\pi$ -back-bonding. The above authors do not provide ab initio energies of the  $\pi$  complexes of ethylene and propylene, and the CNDO/2 method favors the axial alignment of the propylene C=C bond over the equatorial one, by 0.017 au of energy. The cobalt–alkyl distance is larger in the latter rotamer, by 0.02 Å. These results run contrary to our findings as well as to the heuristic

argument that in TBP complexes the  $\pi$ -back-bonding with  $e'$  d orbitals is stronger than that with  $e''$  d orbitals, due to the favorable mixing of equatorial 4p orbitals of the metal.<sup>12</sup> We believe that this discrepancy is a consequence of incomplete geometry optimizations: since the geometry of the free olefin corresponds more closely to that of the weakly complexed one, it precludes an adequate description of the forward- and back-bonding of the  $\pi$  orbitals. This omission has a potential for reversing the already close energy levels of the two conformations.

By the same token, comparison with Zeise's anion,  $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ , made by Grima et al.<sup>16,26</sup> to the effect that the geometry of the olefin should not change much because of complexation is not entirely justified. In this anion, the platinum atom has an approximate  $D_{4h}$  coordination, in which the p orbitals belong to symmetry types  $a_{2u}$  and  $e_u$ , different from the symmetry types of d orbitals ( $a_{1g}$ ,  $b_{1g}$ ,  $b_{2g}$ , and  $e_g$ ). This hinders the 4p-orbital

enhancement of the  $\pi$ -back-bonding,<sup>12</sup> which is symmetry-allowed in the  $D_{3h}$  coordination and which our calculations confirm.

**Acknowledgment.** This paper is based upon work supported by the National Science Foundation under Grants No. CHE-83-09446, CHE-84-05851, and CHE-85-03415. We also wish to acknowledge the NSF support for the calculations done on the Cyber 205 supercomputer at Purdue University in West Lafayette, IN.

**Supplementary Material Available:** Bond lengths and bond angles (Table I) and frontier orbitals (Table III) of the closed-shell configurations of  $\text{CHO-Co}(\text{CO})_3$ , bond lengths and bond angles (Table V) and frontier orbitals (Table VII) of the closed-shell configurations of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$ , bond lengths, bond angles, and SCF energies of the conformations of  $\text{CH}_3\text{CH}_2\text{Co}(\text{CO})_3$  (Table VIII), CI energies of the closed-shell configurations of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$  and  $\text{CH}_3\text{CH}_2\text{Co}(\text{CO})_3$  (Table IX), summary of the results on ethylene  $^1A_g$  (3-21G basis) (Table 10), and density difference of the CC (Figure 30) and EtC (Figure 31) conformations of  $\text{HCo}(\text{CO})_3\text{-C}_2\text{H}_4$  in the symmetry plane (25 pages). Ordering information is given on any current masthead page.

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## Communications to the Editor

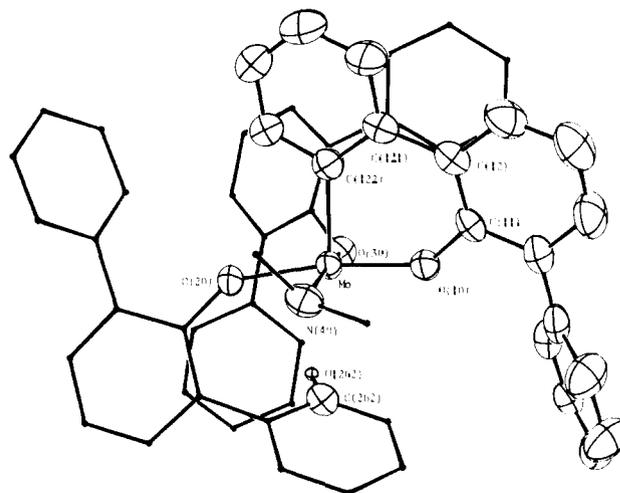
### Molybdenum and Tungsten Derivatives of 2,6-Diphenylphenoxide: Chelation via Metal-Carbon $\sigma$ -Bonds or Metal- $\pi$ -Arene Interactions

Judith L. Kerschner, Phillip E. Fanwick, and Ian P. Rothwell\*<sup>1</sup>

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

Received April 23, 1987

The early transition-metal chemistry associated with 2,6-dialkylphenoxide and 2,6-dialkylthiophenoxide ligation has recently received considerable research interest.<sup>2-6</sup> Following our studies



**Figure 1.** ORTEP view of **1** emphasizing the central coordination sphere and metallacycle ring. Selected bond distances (Å) and angles (°) are as follows: Mo-O(10), 1.919 (2); Mo-O(20), 1.976 (2); Mo-O(30), 1.962 (3); Mo-N(40), 2.288 (4); Mo-C(122), 2.075 (4); Mo-C(262), 2.814 (5); Mo-H(262), 2.67 (5); O(10)-Mo-O(20), 165.8 (1); -O(30), 97.9 (1); -N(40), 87.3 (1); -C(122), 86.4 (1); C(122)-Mo-C(262), 174.5 (1); -H(262), 164 (1).

of the sometimes mild intramolecular activation of the aliphatic carbon-hydrogen bonds in 2,6-di-*tert*-butylphenoxide ligands,<sup>7</sup> we have turned our attention to the organometallic chemistry associated with 2,6-diphenylphenoxide groups.<sup>8</sup> This ligand also

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