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THEORETICAL STUDY OF THE HYDROFORMYLATION REACTION MECHANISM

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Summary

CNDO/2 and ab initio MO-SCF calculations have been carried out to study the cobalt complex-catalyzed alkylation of propylene. The geometries of the initial complex $HCo(CO)_4$ and of the intermediates $HCo(CO)_3$ and $HCo(CO)_3$-C_3H_6 have been optimized and the electronic structures analyzed. The $HCo(CO)_3$ complex is obtained from $HCo(CO)_4$ with a calculated activation energy of 45 kcal/mol, and would be highly reactive on geometric and electronic grounds. The study of the reaction path from the π-complex $HCo(CO)_3C_3H_6$ to the σ-complex $Co(CO)_3C_3H_7$ clearly shows the influence of the electronic factors on the linearity of the final products.

Introduction

Despite the fact that the oxo synthesis is the oldest and one of the most important industrial prosesses using coordination complexes, the mechanism of the hydroformylation reaction is still imperfectly understood. Moreover the experimental conditions of the reaction (pressure: 200—300 atm, temperature >100°C) are not conveniently amenable to structural or spectroscopic studies of the intermediate complexes involved in this synthesis.

It therefore appeared of interest to study this problem from a different point of view, by using quantum mechanical methods giving access to the electronic structure of the transition states, and to the reaction and activation energies, since no complete theoretical study of this particular problem appears to have been previously reported.

In our calculations we could not consider environmental effects, which are very important. Further, in view of the lack of structural data and the considera-

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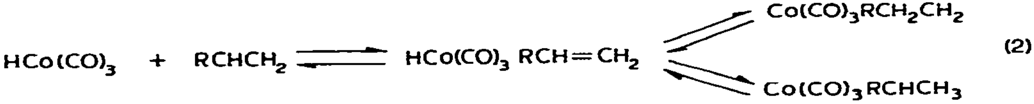
ble number of possible pathways, we have restricted our investigation to the following key steps of the reaction:

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \qquad (1)$$



$$HCo(CO)_3 + RCHCH_2 \rightleftharpoons HCo(CO)_3\,RCH{=}CH_2 \rightleftharpoons \begin{cases} Co(CO)_3RCH_2CH_2 \\ Co(CO)_3RCHCH_3 \end{cases} \qquad (2)$$

It is currently considered that the active catalyst is $HCo(CO)_3$ [1,2] (reaction 1), but its existence has never been proved and dependence on other possible complexes cannot be excluded. Moreover, a very important problem is the stereospecificity of the reaction. According to many authors, the isomerisation of the olefin mostly occurs in the π-complex of the alkylation reaction (reaction 2).

To provide information on the mechanism and on the main factors which affect the result of the reaction, this paper describes the results obtained by both ab initio and CNDO techniques for the hydroformylation of ethylene and propylene.

Computational details

Ab initio calculations are more reliable than CNDO ones, and have been performed in order to obtain energetical results. However, computing time limitations have led us to use CNDO/2 for the geometry optimizations. This method, extended to transition elements [3], has already been tested on many metallic complexes [4,5,6]. The results given in this paper are obtained with an orthogonal basis set of single ζ STO's (Slater-type orbitals).

Ab initio calculations in the Roothan formalism have been performed using a modified version of the POLYATOM program. The basis set of gaussian orbitals of the form (9*s*, 5*p*, 3*d*) [7] for the transition elements, was contracted in (4*s*, 3*p*, 1*d*) and increased with one 3*d* function ($\alpha = 0.2$) and a 4*p* function ($\alpha = 0.25$). For the first row elements, we used a (7*s*, 3*p*) basis set [8], contracted in (2*s*, 1*p*), and for the hydrogen, the (3*s*) basis was reduced to (1*s*) [9].

In order to reduce computing time, the ab initio calculations were performed on the complex with ethylene. The isomerization process for propylene was studied by CNDO.

Results

Reaction 1

The first complex studied, $HCo(CO)_4$, is the only one for which experimental data are available, and its structure has been the subject of much work and controversy [10,11].

The results of the geometries optimizations are summarized in Table 1, and the most probable types of structure are represented by IA and IC (Fig. 1). Structure IB (not shown) is derived from IA by taking a (C_i—Co—C_j) angle of 109°28′. It can be seen that structure IA is the most stable one, and that the agreement between ab initio and CNDO results is satisfactory.

TABLE 1

HCo(CO)$_4$ EXPERIMENTAL AND CALCULATED GEOMETRIES

Interatomic distance (Å)	Experimental ref. 12–16	CNDO			Ab initio (C_{3v})
		IA (C_{3v})	IB (C_{3v})	IC (C_{4v})	
Co—C_{eq}	1.83	1.76	1.76	1.75	1.83 [a]
Co—C_{ax}	1.75	1.75	1.76		1.83
Co—H	1.57	1.60	1.60	1.58	1.55
C—O	1.16	1.23	1.23	1.23	1.16 [a]
Angle H—Co—CO_{eq}	~87°	83.5°	109.5°	106°	~90°
Total energy (a.u.)		−124.769	−124.714	−124.711	−1825.841

[a] Not optimised.

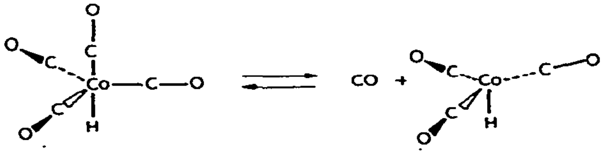


Fig. 1. Possible geometries for HCo(CO)$_4$ (I).

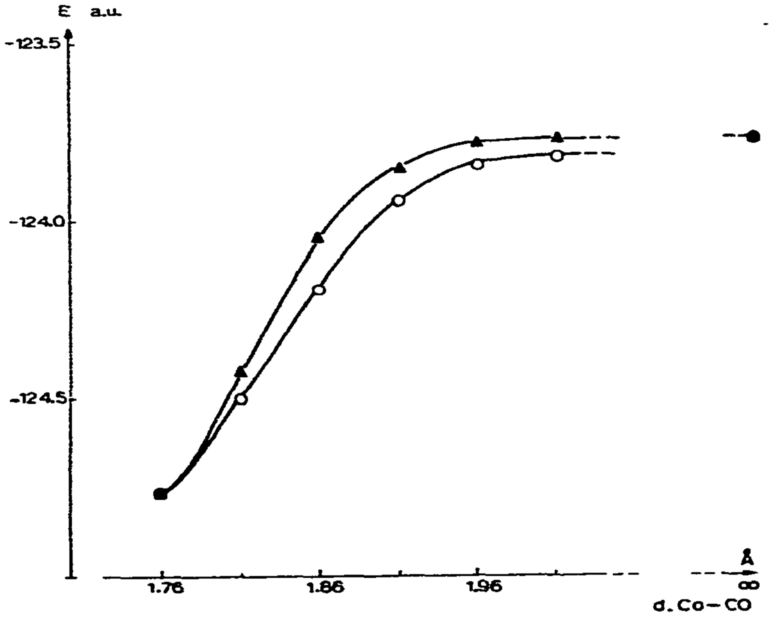


Fig. 2. Variation of the CNDO total energy of HCo(CO)$_4$ vs. the cobalt—carbonyl distance during the reaction HCo(CO)$_4$ → HCo(CO)$_3$ + CO. ▲, apical departure; ○, equatorial departure.

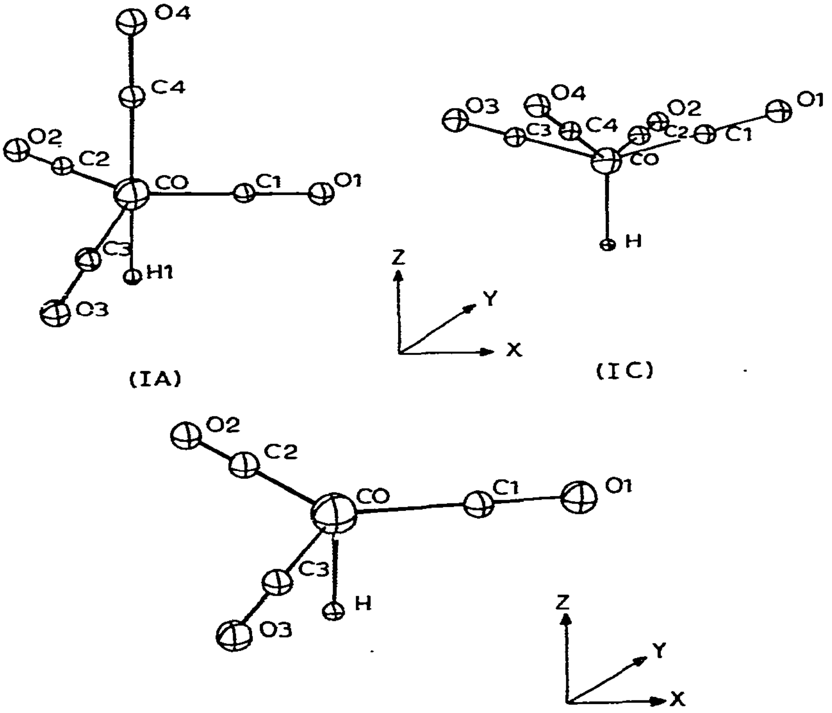


Fig. 3. Optimized geometry for $HCo(CO)_3$.

The $HCo(CO)_3$ complex can be obtained from $HCo(CO)_4$ by stretching either an equatorial or an apical carbonyl group. CNDO results (Fig. 2) show that an equatorial departure is favoured, but the final structure (Fig. 3) is the same in both cases, and has been optimized by CNDO and ab initio (Table 2). Once the site occupied initially by the apical ligand is vacant, the complex is highly reactive and the approach of an olefin is greatly facilitated. The distances are unchanged with respect to $HCo(CO)_4$, except for the Co—H bond which is slightly shorter.

From ab initio results, the activation energy required to obtain $HCo(CO)_3$ is equal to ca. 45 kcal/mol, since the total energy of $HCo(CO)_3$ is equal to

TABLE 2

$HCo(CO)_3$ CALCULATED GEOMETRIES

Interatomic distances (Å)	CNDO	Ab initio
Co—C	1.76	1.83 [a]
C—O	1.23	1.16 [a]
Co—H	1.56	1.55 [a]
Angle H—Co—CO	90°	90°

[a] Not optimised.

—1713.424 a.u. These results will be discussed in the last section.

The electronic structure of $HCo(CO)_4$ corresponds to the following geometry: $Co—C_{ap} = 1.80$ Å, $Co—C_{eq.} = 1.83$ Å, $Co—H = 1.60$ Å, $C = O = 1.16$ Å. The angle $C_{ap}—Co—C_{eq}$ is equal to 90°.

The MO descriptions obtained by CNDO and ab initio are similar, but with a striking difference for the Co—H bond. The occupied MO's sequence found by ab initio is closely analogous to that obtained by CNDO, except for the Co—H bond: $(1a_1)^2(2a_1)^2(3a_1)^2(1e)^4(4a_1)^2(5a_1)^2(2e)^4(6a_1)^2(7a_1)^2(3e)^4(8a_1)^2$-$(9a_1)^2(4e)^4(10a_1)^2 < (5e)^4 < (11a_1)^2 \ll (12a_1)^2 < (13a_1)^2 \sim (6e)^4 < (14a_1)^2 \sim (7e)^4 < (8e)^4 \sim (15a_1)^2 \sim (9e)^4 < (1a_2)^2 < (10e)^4 \sim (16a_1)^2 < (11e)^4 < (12e)^4 < (17a_1)^2$.

The highest occupied MO's are mainly located on the cobalt atom and describe the metal—ligand bonds. Considerable contribution of the $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals in the 12*e* level and of the $3d_{xz}$ and $3d_{yz}$ orbitals in the 11*e* level is observed while in the $16a_1$ level, the main contribution comes from the $3d_{z^2}$ orbital.

The next 8 inner MO's describe the carbon—oxygen bond. The orbitals $12a_1$, 6*e* and $13a_1$ are not well defined and include participation from the central atom and all the ligands, except the hydrogen. These results agree with those obtained for $Ni(CO)_4$ [17].

The general description of the ground state configuration is similar in CNDO and ab initio, except for the frontier orbitals. If in CNDO the 12*e* level is the HOMO, in ab initio there is a higher occupied MO of a_1 symmetry. This $17a_1$ orbital is the only one which describes the Co—H bond in ab initio. The CNDO counterparts of this orbital are the lower $17a_1$ and $14a_1$ levels.

The higher MO's in $HCo(CO)_3$ are unaffected with respect to $HCo(CO)_4$. The Co—H bond is still stronger in CNDO, but the HOMO symmetry is the same for both calculations.

The electron distribution for $HCo(CO)_4$ and $HCo(CO)_3$ (obtained by a Mulliken population analyses) is summarized in Table 3. For $HCo(CO)_4$, ab initio results show that the charge transfer from the cobalt is 0.09*e* to each equatorial carbonyl group and 0.03*e* to the apical carbonyl. The CNDO results describe the equatorial carbonyls as acceptors (3 × 0.02*e*), but the apical group is found to be a donor (0.05 *e*). A closer study indicates that, in ab initio, the charge transfers occur mainly between the cobalt and the carbon atoms. The population of the $p\pi$ orbitals increases by 0.23*e* in the apical carbon atom and 0.20*e* in the equatorial carbon atoms. The back-donation towards the cobalt is provided by the 2*s* orbital of each carbon atom, which loses 0.24*e* in the apical ligand and 0.17*e* in the equatorial ligand. This σ-donor effect is partially counterbalanced by an increase in the $2p\sigma$ population of 0.09*e* for the carbon atoms.

If we compare these charge transfers with those obtained by CNDO, it is observed that the σ-donor and π-acceptor effects are extended to the oxygen atoms, with little change in the population of the 2*s* O orbital. This can be explained by the fact that this latter orbital does not intervene in the higher MO's of the free CO molecule. For the carbon atoms also, the CNDO method enhances the electron transfers. A very large σ-donor effect from the 2*s* orbitals decreases this population by 0.53*e* for the equatorial carbon, and by 0.55*e* for the apical one; this effect is not compensated by a large variation of the $p\sigma$

TABLE 3

AB INITIO ATOMIC POPULATIONS OF $HCo(CO)_4$ AND $HCo(CO)_3$ (The CNDO values are in brackets)

	Co	C(1)	O(1)	C(4)	O(4)	H
$HCo(CO)_4$						
$4s/2s61s$	0.43	1.46	1.79	1.39	1.79	1.29
	(0.49)	(1.19)	(1.71)	(1.17)	(1.71)	(1.23)
$4p\pi/2p\pi$	0.32	1.27	2.94	1.30	2.93	
	(1.00)	(1.58)	(3.11)	(1.51)	(3.15)	
$4p_z/2p\sigma$	0.23	1.06	1.57	1.06	1.56	
	(0.49)	(1.06)	(1.37)	(1.09)	(1.32)	
$3d_z{}^2$	0.76					
	(1.07)					
$3d_{xz} + 3d_{yz}$	3.73					
	(3.15)					
$3d_{x^2-y^2} + 3d_{xy}$	3.05					
	(2.57)					
Charges	+0.59	+0.21	−0.30	+0.25	−0.28	−0.29
	(+0.23)	(+0.17)	(−0.19)	(+0.23)	(−0.18)	(−0.23)
$HCo(CO)_3$						
$4s/2s/1s$	0.45	1.47	1.79			1.29
	(0.45)	(1.21)	(1.75)			(1.15)
$4p\pi/2p\pi$	0.33	1.28	2.94			
	(0.98)	(1.93)	(3.06)			
$4p_z/2p\sigma$	0.17	1.06	1.58			
	(0.28)	(0.78)	(1.39)			
$3d_z2$	0.61					
	(0.92)					
$3d_{xz} + 3d_{yz}$	3.87					
	(3.41)					
$3d_{x2-y} + 3d_{xy}$	3.06					
	(2.45)					
Charges	+0.63	+0.19	−0.30			−0.29
	(+0.50)	(+0.08)	(−0.19)			(−0.15)

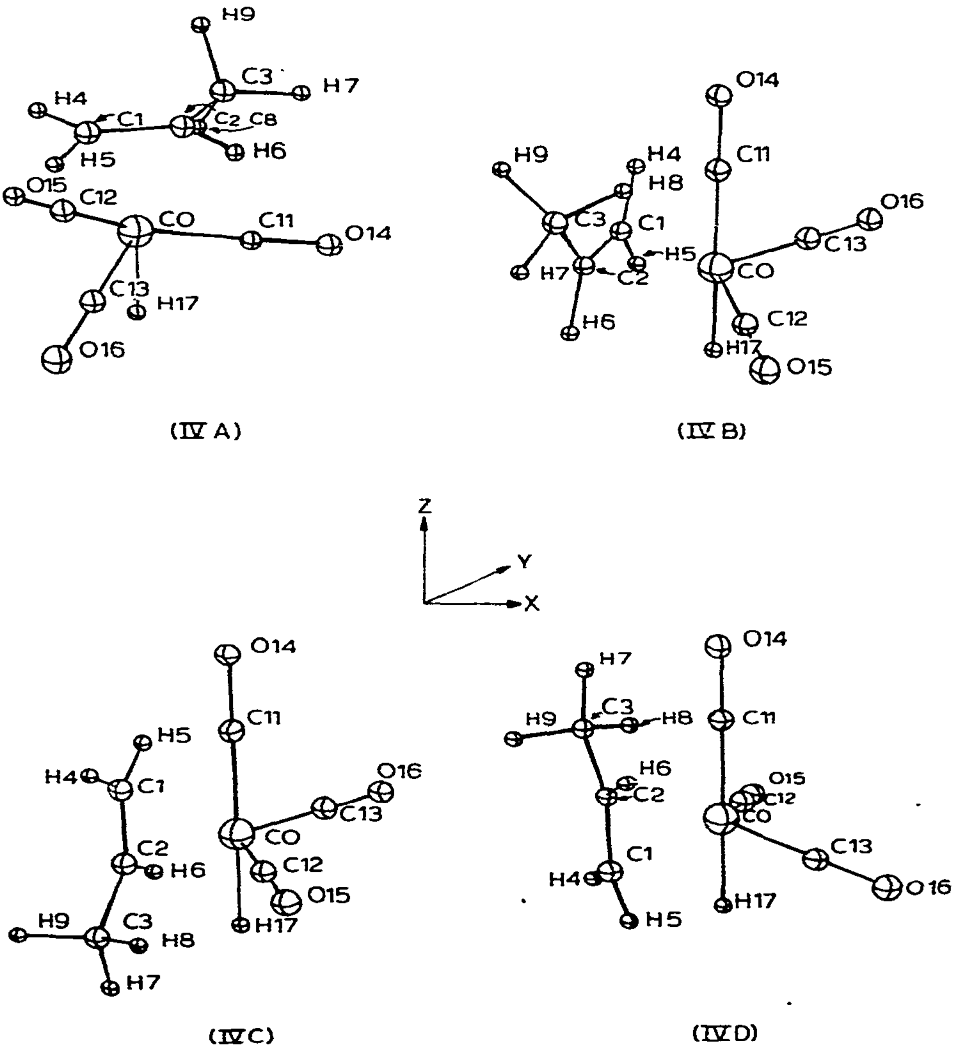
population. The π-acceptor effect corresponds to an increase of $0.39e$ for the apical carbon and $0.46e$ for the equatorial one.

Comparison of the molecules $HCo(CO)_4$ and $HCo(CO)_3$ shows a decrease in the electronic population along the z axis (favouring therefore a σ-donation from an olefin), and an increase in the d_{xz} and d_{yz} orbitals, making the latter available for π-back donation towards an olefin.

Reaction 2

π-Complex formation. We have studied the most widely accepted scheme, that is the attack of an olefin on the $HCo(CO)_3$ molecule, leading to the π-complex $HCo(CO)_3RCHCH_2$, and we have performed CNDO calculations for the reaction $C_3H_6 + HCo(CO)_3$. The incoming propylene attacks at the site previously occupied by the CO ligand. The trigonal bipyramid structure IVA thus obtained can rearrange easily to give geometries of the type IVB, IVC or IVD, where the olefin and the hydrogen are in *cis* positions. These conformations are necessary for the intramolecular alkylation leading to the σ-complex.

The energies obtained by CNDO for the complexes IVA, IVB, IVC, IVD are very similar, structure IVA being the most stable. These results and the optimiz-



(IV A) (IV B)

(IV C) (IV D)

Fig. 4. Possible configurations for the complex $HCo(CO)_3C_3H_6$. A: TBP (trigonal bipyramid) configuration with the olefin in apical position. B: TBP configuration with C(1), C(2), Co, C(12), C(13) in the equatorial plane. D: TBP configurations with C(1)—C(2) parallel to the apical axis of the TBP.

ed geometries are summarized in Table 4. Structural studies on several complexes seem to favour a IVB type structure [18]. However, in our case, the comparison with complexes involving a much heavier metal is difficult, and we are not dealing with a stable molecule, but rather with a transition state. Moreover, it is seen that the energies are closely similar, the maximum difference being 20 kcal/mole; this indicates that the rearrangement from a *trans* to a *cis* complex should occur readily under the conditions of the reaction.

A study of the electronic structure of the Co—olefin bond was carried out with the help of ab initio calculations on $HCo(CO)_3C_2H_4$ (Va). The Co—olefin

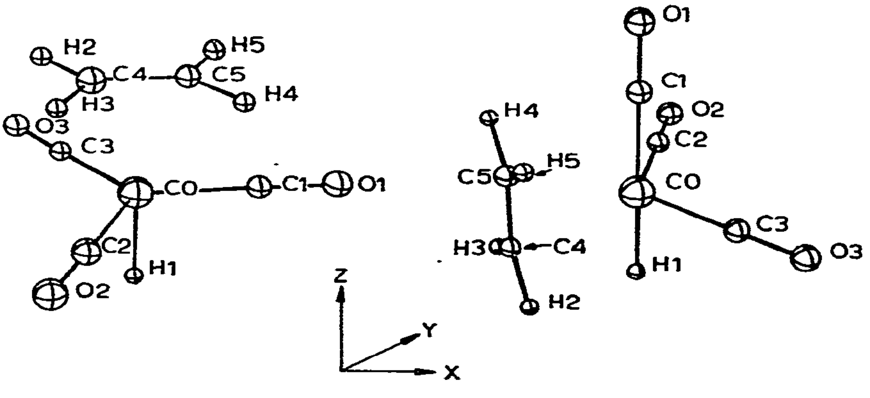
TABLE 4

$HCo(CO)_3C_3H_6$ CALCULATED GEOMETRIES

Interatomic distances (Å)	IVA	IVB	IVC	IVD
Co—CO	1.76	1.76	1.76	1.76
C—O	1.23	1.23	1.23	1.23
Co—H(17)	1.62	1.62	1.62	1.62
Co—olefin plane	1.78	1.79	1.77	1.77
C(1)—C(2)	1.33	1.33	1.33	1.33
C(2)—C(3)	1.46	1.46	1.46	1.46
C(1)—H(4), C(1)—H(5), C(2)—H(6)	1.10	1.10	1.10	1.10
C(3)—H(7), C(3)—H(8), C(3)—H(9)	1.12	1.12	1.12	1.12
Angles (°)				
C(1)—C(2)—C(3)	124.5	124.5	124.5	124.5
C(2)—C(1)—H(4), C(2)—C(1)—C(5)	120	120	120	120
C(1)—C(2)—C(6), C(3)—C(2)—H(6)	117.5	117.5	117.5	117.5
C(2)—C(3)—H(7), C(2)—C(3)—H(8), C(2)—C(3)—H(9)	109.4	109.5	109.5	109.5
C(12)—Co—C(13)	120	114	118	118
H—Co—C(12), H—Co—C(13)	79	90	90	82
H—Co—C(11)	79	180	180	180
Energies in a.u.	—125.994	—125.960	—125.977	—125.970

distance was optimized to 1.99 Å, by maintaining the other geometric parameters unchanged throughout the process of complexation. The electronic population analysis for both complexes with propylene and ethylene are summarized in Tables 5 and 6. It is thus possible to compare the description of the Co—olefin bond by both methods.

In ab initio, the HOMO's include mainly *d* orbitals from Co. If we consider the atomic charges, the $HCo(CO)_3$ moiety is electrodonating towards ethylene,



(VA) (VB)

Fig. 5. Possible configurations for the complex $HCo(CO)_3C_2H_4$. A: TBP configuration with the olefin in apical position. B: TBP configuration with the olefin in equatorial position.

TABLE 5

CNDO ATOMIC POPULATIONS OF $HCo(CO)_3C_3H_6$ (IVA) (Values for propylene alone are brackets)

	Co	C	O	H(17)	C(1)	C(2)	C(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)
$4s/2s/1s$	0.48	1.22	1.75	1.18	0.94 (1.05)	0.90 (1.01)	1.01 (1.02)	0.96 (0.99)	0.96 (0.99)	0.98 (1.00)	0.97 (1.00)	1.00 (0.94)	1.02 (0.99)
$4p_\pi/2p_x$	0.98	1.98	1.96		1.00 (1.01)	1.00 (1.02)	0.99 (0.99)						
$2p_y$					0.93 (0.94)	0.96 (0.97)	1.01 (1.02)						
$4p_z/2p_z$	0.48	0.70	1.52		1.20 (1.05)	1.17 (0.97)	0.92 (0.97)						
$3d_{z^2}$	1.06												
$3d_{xz} + 3d_{yz}$	2.93												
$3d_{x^2-y^2} + 3d_{xy}$	2.55												
Charges	+0.52	+0.10	−0.24	−0.18	−0.06 (−0.06)	−0.02 (+0.03)	+0.06 (0.0)	+0.04 (+0.01)	+0.04 (+0.01)	+0.02 (0.0)	+0.03 (0.0)	+0.0 (0.06)	−0.02 (+0.01)

TABLE 6

AB INITIO ATOMIC POPULATIONS OF $HCo(CO)_3C_2H_4$ (VA) (Values for ethylene alone are in brackets)

	Co	C(1)	O(1)	C(2), C(3)	O(2), O(3)	H(1)	C(4)	C(5)	H(2), H(3)	H(4), H(5)
$4s/2s/1s$	0.47	1.44	1.79	1.46	1.79	1.25	1.19 (1.16)	1.20 (1.16)	0.80 (0.80)	0.80 (0.80)
$4p_x/2p_x$	0.17	1.06	1.57	0.77	1.51		1.09 (1.08)	1.09 (1.08)		
$4p_y/2p_y$	0.16	0.66	0.46	0.95	1.54		1.18 (1.16)	1.18 (1.16)		
$4p_z/2p_z$	0.19	0.61	1.49	0.61	1.46		1.00 (1.00)	1.00 (1.00)		
$3d_{z^2}$	0.71									
$3d_{xz} + 3d_{yz}$	3.74									
$3d_{x^2-y^2} + 3d_{xy}$	3.04									
Charges	+0.63	+0.24	−0.30	+0.21	−0.30	−0.25	−0.45 (−0.40)	−0.47 (−0.40)	+0.20 (+0.20)	+0.20 (+0.20)

since it bears a charge of 0.12e. This electronic transfer is accepted by the $2s$ ($2 \times 0.04e$) and $2p_y$ ($2 \times 0.02e$) AO's of C(4) and C(5). Examination of the overlap populations shows that the cobalt—olefin bond is mainly described by the interaction of the $3d_{z^2}$, $4p_z$ and $3d_{yz}$ AO's of the cobalt with the $2s$, $2p_z$ and $2p_y$ AO's of the carbons. The bond is strengthened by a weaker interaction between the cobalt $3d_{xz}$ AO and the carbon $2p_z$ AO's.

The CNDO charges are much weaker than the ab initio ones, especially for the olefinic carbons, but this is a general trend of our CNDO calculations. In both *cis* and *trans* complexes, the $HCo(CO)_3$ moiety is negatively charged but, as in ab initio, the olefinic double bond is an acceptor.

The cobalt—olefin bond is mainly described in CNDO by the interaction of the $4s$ and $4p_z$ AO's of the cobalt with the $2s$ AO's of C(1) and C(2). It is strengthened by an acceptor π type bond, comprised by the interactions of the $3d_{xz}$ cobalt AO with the antibonding $2p_z$ AO's of the carbon double bond. The latter appears to be stronger in CNDO than in ab initio, but this is a characteristic feature of the CNDO method. With respect to the olefin alone, C(1) and C(2) are donor by the $2s$ AO's (of $2 \times 0.11e$) and acceptor by the π $2p_z$ AO's (of 0.15e and 0.20e).

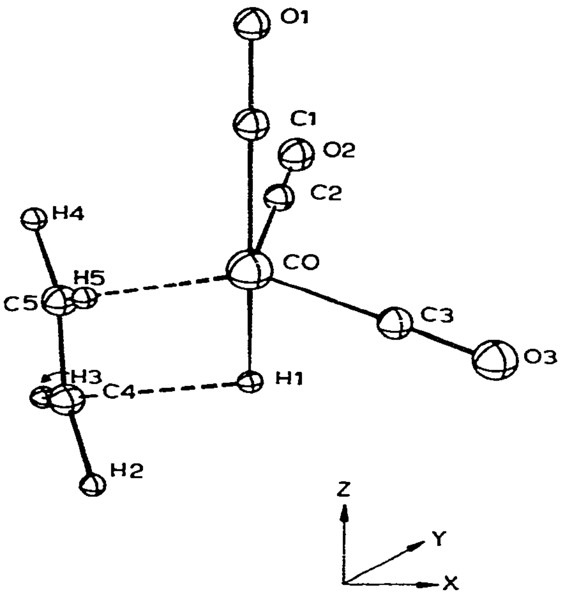
The electronic structure of the olefin does not appear to be profoundly modified as a result of complexation and this trend has also been pointed out for $[Pt(C_2H_4)Cl_3]^-$ from SCF Xα calculations [19]. In our case, the geometry of the olefin has been kept unchanged through complexation, and the electronic changes could be found more important if the deformation of this moiety was taken into account; structural results on other complexes [18] indicates in many cases a non planearity of the olefin. The propylene shows a strong *trans* effect, since the trans Co—H bond is weaker in $HCo(CO)_3C_3H_6$ than in $HCo(CO)_4$.

Alkylation reaction. A dehydrogenation process has recently been developed which allows the production of internal olefins, which have thus become cheaper. However, a disadvantage of the oxo synthesis lies in the fact that only non-linear products are formed if isomerisation giving rise to terminal alkenes has not been carried out previously. It is thus very important to have a stereospecific system which favours the formation of linear products.

There are two main possible isomerisation steps in the synthesis; the first involves the π-complex $HCo(CO)_3$olefin, and the second corresponds to the stage of the carbonyl insertion in the alkyl—cobalt bond. It is currently accepted that isomerisation takes place mostly during the first stage. A configuration inversion by an olefin rotation or a sigmatropic transformation, for example, can then occur very easily.

The most probable hydrogenation scheme for the *cis* complexes proceeds via a four-center transition state obtained by the olefin shift towards the hydrogen.

In order to check the feasibility of such a mechanism, we performed ab initio calculations on the $HCo(CO)_3C_2H_4$ complex (VI). With respect to the initial complex VB, the ethylene has shifted towards H(1) in a direction parallel to the Co—H(1) bond, until C(5) is in the plane of the cobalt and equatorial carbonyl groups. The Co—C(5) distance is then 1.99 Å which is relatively close to the value typical for a standard σ Co—C bond. Moreover, the H(1)—C(4) interatomic distance is not greater than 2.00 Å. The geometry of the olefin was kept identical to that of ethylene. Although the geometry of the complex was not



(VI)

Fig. 6. Geometry of the transition state of $HCo(CO)_3C_2H_4$ for the alkylation reaction.

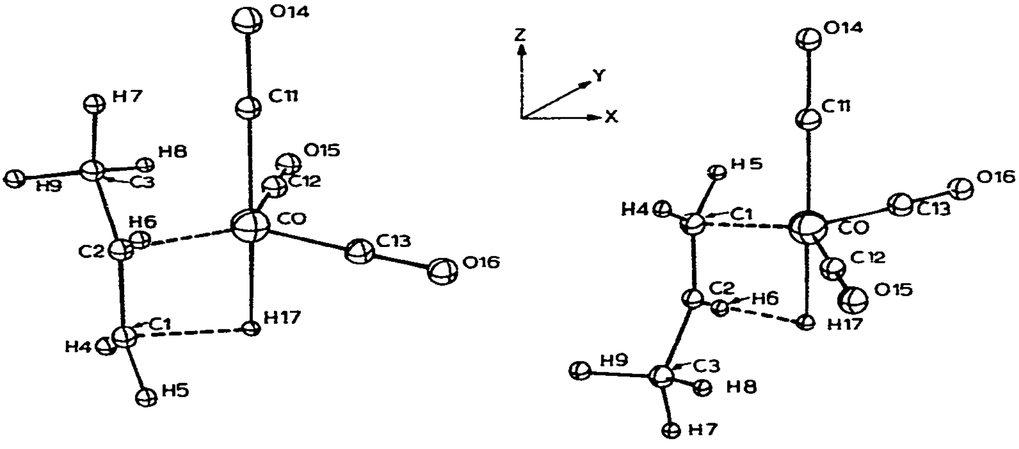
fully optimized, the activation energy obtained for this shift is less than 20 kcal/mol. It would thus appear easy to obtain a geometry conductive to hydrogen migration.

With regard to the electronic changes, it is observed that the H(1) charge changes from —0.35*e* to —0.07*e* under the influence of the strong negative charge of C(4), which also decreases. The $3d_{z^2}$ population of the cobalt AO decreases from 1.62*e* to 1.01*e*. The olefin therefore induces a charge transfer of 0.28*e*, amplified by the $3d_{z^2}$ AO, from H(1) towards C(1), C(2) and C(3); the atomic charges go from 0.21*e* to 0.08*e* for C(1) and from 0.20*e* to 0.11*e* for C(2) and C(3).

A weak interaction between H(1) and the olefin, described by the AO's $2p_x$ of C(4) and 2*s* of H(1), appears in the MO N° 28 and lowers its energy.

Thus, according to ab initio results, a four-center transition state appears likely, an activation energy of less than 20 kcal/mol being required for such an intermediate. Moreover, we observe a shortening of the Co—H(1) bond and the formation of a weak interaction between C(4) and H(1). However, the ab inito calculations performed on an ethylene complex do not allow a differentiation between Markovnikov and anti-Markovnikov type addition. This important point was examined in detail with the aid of the CNDO method for the propylene complex (IVC, IVD).

First, the olefin was shifted, as in the case of ab initio, to obtain the VIIC and VIID complexes. The distances Co—C(1), C(2)—H(17) (in VIIC) and Co—C(2), C(1)—H(17) (in VIID) were set equal to 1.77 Å, i.e. the distance of a σ(Co—C)



(VII D) (VII C)

Fig. 7. Possible geometries of the transition state of $HCo(CO)_3C_3H_6$ for the alkylation reaction.

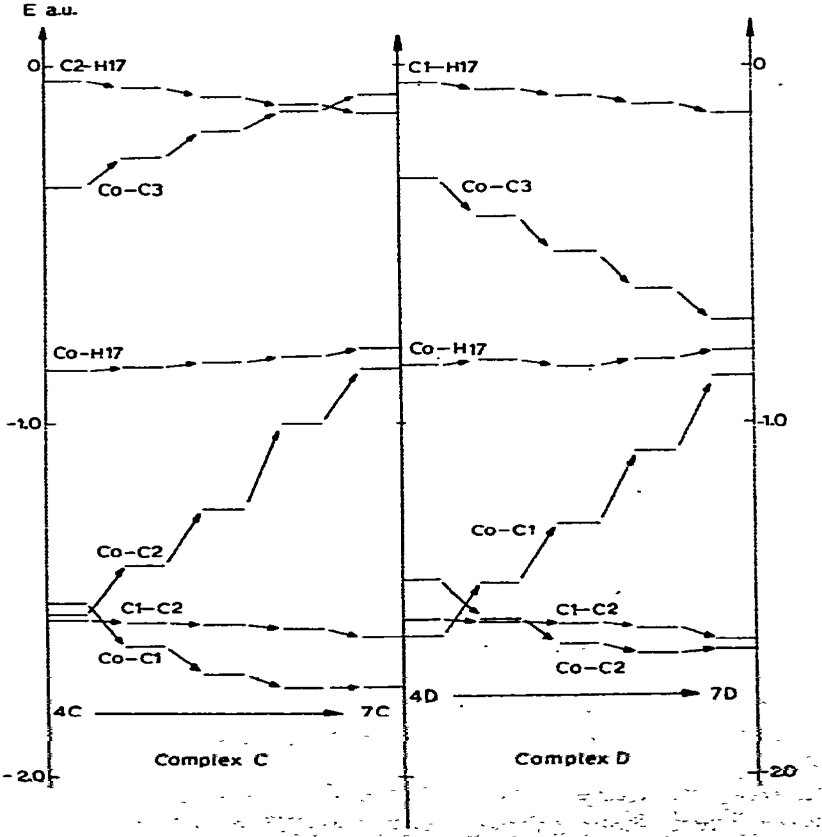


Fig. 8. Variations of bonds electronic energies for the alkylation reactions IVC → VIIC and IVD → VIID.

bond optimized by the CNDO method for the compound $Co(CO)_3C_3H_7$. The second stage we considered was the displacement of H(17) from the metal towards the olefin.

Examination of the modifications of the bonds electronic energies (EE) when passing from IVC to VIIC (Fig. 8) shows a sharp decrease between Co and C(2) and a smaller increase between Co and C(1). This energy is highly dependent

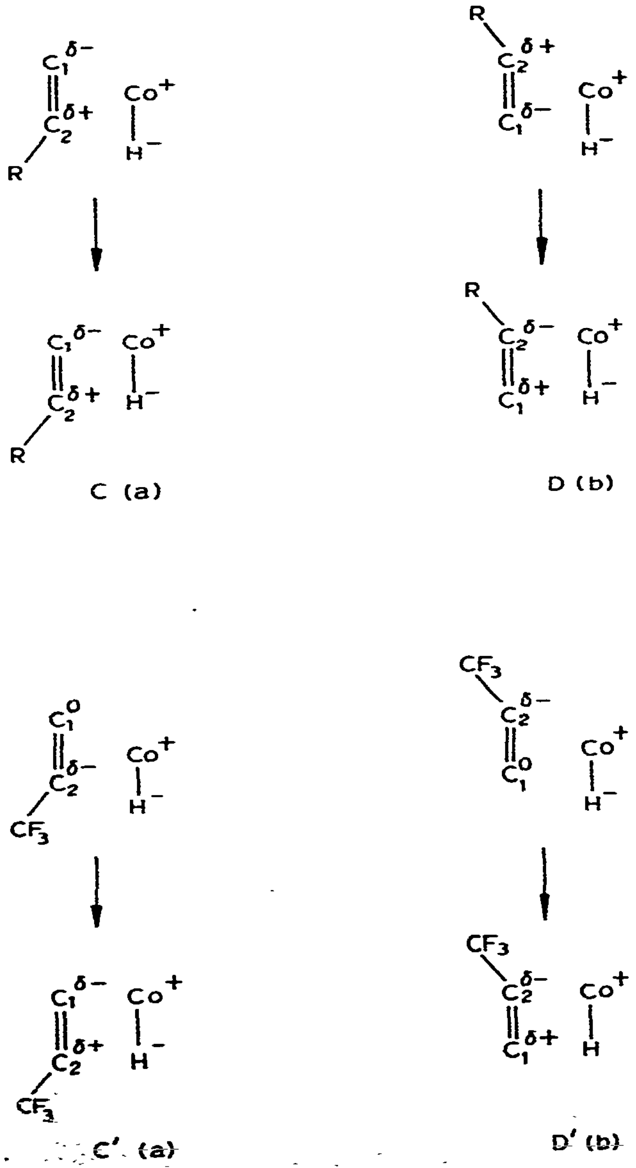


Fig. 9. Charges patterns obtained during the alkylation reaction: (a) leads to linear products, (b) leads to ramified products.

upon the value of the C(1)—C(2) bond length. A perceptible interaction appears between C(2) and H(17), and the Co—H(17) bond is slightly weakened at this stage. The main modifications for these latter bonds occur in the second stage. The same trends are observed in complex VIID, in which C(2) is replaced by C(1). The only difference is that the value of the EE for the Co—C(3) bond

TABLES 7—10

VARIATIONS OF THE ATOMIC CHARGES IN THE COMPLEXES $HCo(CO)_3C_3H_6$ (C AND D) AND $HCo(CO)_3C_3H_3F_3$ (C' AND D') DURING THE ALKYLATION REACTION

TABLE 7

$HCo(CO)_3C_3H_6$ (C)

	Complex IVC	→		Complex VIIC	→	Complex σ[a]
Co	+0.64	+0.62	+0.59	+0.55	+0.51	+0.44
H(17)	–0.27	–0.24	–0.21	–0.18	–0.17	+0.05
C(1)	–0.02	–0.04	–0.04	–0.05	–0.07	–0.05
C(2)	+0.01	+0.03	+0.06	+0.09	+0.14	+0.10

[a] Corresponds to the complex $Co(CO)_3C_3H_7$ obtained by CNDO (linear)

TABLE 8

$HCo(CO)_3C_3H_6$ (D)

	Complex IVD	→		Complex VIID	→	Complex σ[a]
Co	+0.62	+0.62	+0.63	+0.61	+0.57	+0.47
H(17)	–0.19	–0.11	–0.19	–0.17	–0.16	+0.07
C(1)	–0.02	–0.01	0.00	+0.03	+0.08	+0.06
C(2)	+0.01	0.00	0.00	–0.01	–0.01	–0.04

[a] Corresponds to the σ-complex $Co(CO)_3C_3H_7$ obtained by CNDO (branched).

TABLE 9

$HCo(CO)_3C_3H_3F_3$ (C')

	Complex IVC'	→			Complex VIIC'
Co	+0.64	+0.62	+0.59	+0.55	+0.51
H(17)	–0.25	–0.22	–0.19	–0.16	–0.15
C(1)	–0.01	–0.02	–0.02	–0.03	–0.05
C(2)	–0.07	–0.06	–0.04	–0.01	+0.04

TABLE 10

$HCo(CO)_3C_3H_3F_3$ (D')

	Complex IVD'	→			Complex VIID'
Co	+0.64	+0.62	+0.59	+0.55	+0.51
H(17)	–0.25	–0.22	–0.19	–0.16	–0.15
C(1)	–0.01	–0.02	–0.02	–0.03	–0.05
C(2)	–0.07	–0.06	–0.04	–0.01	+0.04

increases, whereas it decreases in complex C.

The stereospecificity control can be best studied by examining the variations of the atomic charges. In complex VIIC (see Fig. 9), the charge pattern after the olefin shift corresponds to two dipoles of opposite sign. Indeed, our calculations for the passage of complex IVC to complex VIIC show a decrease of the strong charges localized on Co and H(17), together with an increase of the olefin charges (Table 7). This leads to a more balanced charge repartition and favours the formation of linear products. For complex D, the olefin shift leads to an unfavourable situation for the two dipoles. However, our calculations indicate that the strong atomic charges on Co and H(17) induce an inversion of the C(1) and C(2) charges, leading to the same pattern as observed in complex C (see Table 8). Higher energy, required to invert the olefinic dipole sign, is then necessary to obtain the complex leading to a ramified alkyl group. The influence of this electronic effect is very clear and rather important. It can be verified by replacing the hydrogen of the methyl group by fluorine atoms. The latter induce a strong negative charge on C(2), with the result that complex D′ is favoured with respect to complex C′ and therefore the reaction leads to branched products. When the olefin in complex C′ shifts, the negative charge C(2) decreases and is finally inverted (Table 9).

However, the CNDO energies favour the formation of complex VIID (hence the production of branched alkyls). This result is in agreement with some experiments which indicate that the reaction of propylene with $HCo(CO)_3$ may mainly lead to branched alkyl products under specific conditions [1]. Since the olefinic charges obtained by our calculations are very low, there is no contradiction between the two indications. The production of linear alkyls can thus be favoured by replacing the apical carbonyl by a more electrodonating ligand which serves to induce a strong negative charge on the *trans* hydrogen H(17).

Discussion and conclusions

We have first considered the formation of the $HCo(CO)_3$ complex (reaction 1), which appears to be very reactive (on steric and electronic grounds) towards an incoming olefin. If allowance is made for the hydroformylation reaction conditions (temperature, pressure), the activation energy found (45 kcal/mol) indicates a very low stability of $HCo(CO)_3$. This value appears to be in contradiction with the fact that the stoichiometric hydroformylation reaction can be performed under normal conditions [20]. However, there is a large uncertainty in the calculated value, in view of the fact that the $HCo(CO)_3$ geometry was not fully optimized and the basis set used was small.

Nevertheless, proof of the existence of $HCo(CO)_3$ is still lacking and there are only two strong indirect indications of the existence of this intermediate. The work of Heck and al. [21] showed that there is an inhibiting effect of CO on the rate of hydroformylation, but other steps in the mechanism may involve a CO deficient species [1]. The kinetics of the decomposition of dissolved $HCo(CO)_4$ [22] can be interpreted by a scheme involving the $HCo(CO)_3$ complex, with a calculated activation energy of ca. 14 kcal/mol. However recent IR investigations [23] indicate that under hydroformylation conditions there is no additional absorption which could be attributed to the presence of $HCo(CO)_3$.

Thus, if this complex exists, its concentration must be very low (<1%) with respect to that of $HCo(CO)_4$.

In our case, both ab initio and CNDO results indicate very low stability of $HCo(CO)_3$. It appears impossible in the present time to make a definitive statement and we think that the problem of the existence of $HCo(CO)_3$ merits additional experimental investigation.

Several other mechanisms are possible for the formation of the π-complex. The first involves the addition of an olefin to $HCo(CO)_4$: the reaction proceeds via the octahedral π-tetracarbonyl complex $HCo(CO)_4RCHCH_2$. CNDO results indicate that this reaction is the most favourable energetically. However, this method leads to unreliable results when the energies of non isoelectronic molecules are compared. The most highly coordinated complexes are favoured with respect to less coordinated ones. However, the interpretations offered by Falbe [24] (the reaction proceeds via a hexacoordinated $HCo(CO)_4RCHCH_2$ intermediate) or by Piacenti et al. [25] (two catalytically active species are present during the reaction, differing only in the number of carbonyls bonded to the cobalt atom) should not be ruled out, on the basis of energetic considerations.

Another mechanism which must be considered involves a concerted reaction between $HCo(CO)_4$ and an approaching olefin arriving in the plane of the equatorial carbonyls. Repulsion of the adjacents ligand and serving of the cobalt—carbonyl bond in *trans* position leads to the formation of the $HCo(CO)_3RCHCH_2$ complex. In fact, the CNDO results do not predict CO departure, but lead to the previous octahedral complex.

The mechanism we have considered in this paper is the most widely accepted one, and our calculations show that the direct fixation of the incoming olefin on $HCo(CO)_3$ leads to a π-complex in which the olefin is *trans* to the hydrogen atom attached to the metal. Such an intermediate can rearrange easily, leading to a configuration in which the hydrogen and the olefin are in *cis* positions.

Moreover, the most probable hydrogenation scheme, whatever the number of coordinated carbonyls, involves a four-center transition state which favours hydrogen migration towards the olefin.

The stereospecificity control of the resulting alkyl depends on electronic and steric factors. Our calculations show that the electronic effect favours the formation of linear products. This effect should be increased by replacing the apical carbonyl *trans* to the Co—H bond by a more basic ligand, such as a phosphine group, and this is consistent with experimental results [26].

Further information may be obtained on request.

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