

Stoichiometric and Catalytic Hydrogenation of the $[\text{Co}_2(\text{CO})_6(\mu_2\text{-}\eta^2\text{-alkyne})]$ Complexes

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Abstract

The $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')]_n$ complexes ($\text{R}, \text{R}' = \text{H}, \text{Me}, \text{Et}, \text{Pr}^n$) react with molecular hydrogen under mild conditions of temperature and pressure, at low but appreciable rates. The effect of the steric hindrance of the substituents and the strength of the metal–carbon bonds are discussed. The kinetic data measured for $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$, suggest that both H_2 -coordination and CO -dissociation are involved in the rate-determining step of the overall hydrogenation process.

The catalytic activity of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ in the homogeneous hydrogenation of acetylene is described. At low substrate/catalyst ratio the initial hydrogenation rate is equal, within experimental error, to that found for the stoichiometric reaction; on increasing the acetylene concentration, cyclotrimerization to benzene becomes the dominant process. Interestingly C_4 hydrocarbons (mainly butadiene and 1-butene) are produced in measurable yield ($\leq 8\%$). The formation of these products is interpreted as the result of the hydrogenation of the elusive $[\text{Co}_2(\text{CO})_5(\text{HC}_2\text{H})_2]$ complex, an unstable intermediate in the cyclotrimerization chain.*

Introduction

Molecular metal clusters represent an attractive model of metallic surfaces for chemisorption and heterogeneous catalytic phenomena [1]. Among these the hydrogenation of the triple bond is an interesting type of process, as has been shown by Muettterties [2] for the hydrogenation of alkynes coordinated to transition metal clusters.

Even in the simplest alkyne-dimetal compounds there is an extensive rehybridization of the carbon

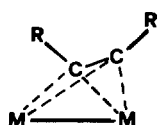


Fig. 1. M_2C_2 tetrahedral framework.

orbitals; the most common structural feature is the triple bond bridging the two metals in a crosswise manner, so that the M_2C_2 framework describes a distorted tetrahedron ($\mu_2\text{-}\eta^2$ bonding mode).

Recently it has been shown that acetylene is also rehybridized when chemisorbed at low temperature on transition metal surfaces [3]. Furthermore acetylene and molecular hydrogen co-adsorbed onto a clean $\text{Cu}(110)$ surface undergo a very efficient reaction to selectively give ethylene [4]. Thus this kind of study can provide some insight into the analogy between homogeneous and heterogeneous hydrogenation from a kinetic point of view.

In each of the $\mu_2\text{-}\eta^2$ -alkyne-dimetal complexes so far studied, the triple bond is strongly reduced upon coordination, as confirmed by the C–C bond lengthening (beyond 1.30 Å) and supported by several spectroscopic evidence [5]. Muettterties suggested that this bond order reduction is, in principle, sufficient to activate the alkyne for hydrogenation [6]. The reactivity towards molecular hydrogen should depend upon the energy barrier required to reach an 'unsaturated' transition state. Indeed, among the number of isostructural $\mu_2\text{-}\eta^2$ -alkyne-dimetal compounds tested for stoichiometric hydrogenation, only the coordinatively unsaturated (32 electrons) complexes $[\text{Ni}_2(\text{COD})_2(\text{PhC}_2\text{Ph})]$ and $[\text{Fe}_2(\text{CO})_6(\text{Bu}^t\text{C}_2\text{Bu}^t)]$ react under mild conditions of temperature and hydrogen pressure [7]. Within the class of coordinatively saturated (34 electrons) complexes, $[\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})]$, $[\text{CoNiCp}(\text{CO})_3(\text{PhC}_2\text{Ph})]$ and $[(\text{Ni}_2\text{Cp}_2)(\text{PhC}_2\text{Ph})]$ show no reaction with hydrogen up to 60°, 80° and 120 °C respectively [7, 8], whereas from $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\text{EtC}_2\text{Et})]$ *cis*-3-hexene

*Non – S.I. unit employed: 760 Torr = 101325 Pa.

TABLE I. Values of the Observed Initial Rates R of the Stoichiometric Hydrogenation of Organo-cobalt Complexes in *n*-Octane at 60 °C and $P_{H_2} = 760$ Torr.

Complex (25.0 mM)	R (mmol h ⁻¹ × 10 ⁴)	C% (% h ⁻¹)	Initial Products ^a %
Co ₂ (CO) ₆ (HC ₂ H)	106	21.2	$\begin{cases} H_2C=CH_2 & 91 \\ H_3C-CH_3 & 9 \end{cases}$
Co ₂ (CO) ₆ (HC ₂ Me)	63	12.6	1-C ₃ H ₆ >95 ^b
Co ₂ (CO) ₆ (HC ₂ Et)	53	10.7	1-C ₄ H ₈ >96 ^b
Co ₂ (CO) ₆ (HC ₂ Pr ⁿ)	46	9.2	1-C ₅ H ₁₀ >94 ^b
Co ₂ (CO) ₆ (MeC ₂ Me)	22	4.4	2- <i>cis</i> -C ₄ H ₈ >90 ^b
Co ₂ (CO) ₆ (MeC ₂ Et)	19	3.8	2- <i>cis</i> -C ₅ H ₁₀ >93 ^b
Co ₂ (CO) ₆ (PhC ₂ Ph)	0	0	—
Co ₄ (CO) ₁₀ (HC ₂ H)	6	1.2	$\begin{cases} H_2C=CH_2 & 86 \\ H_3C-CH_3 & 14 \end{cases}$
Co ₃ (CO) ₉ (C-CH ₃)	4	0.8	$\begin{cases} H_2C=CH_2 & 77 \\ H_3C-CH_3 & 23 \end{cases}$

^aMean of three gc measures at low conversion (within 1 h). ^bAlong with the corresponding isomers and trace of alkane.

is slowly obtained above 100 °C [9]. These isoelectronic and isostructural compounds, having internal alkynes with bulky substituents (Ph or Bu^t) are certainly easier to handle, but their reactivity is probably so low and the corresponding olefins so difficult to detect by gc analysis that the measure of the hydrogenation rates is hardly feasible. Whereas [Co₂(CO)₆(PhC₂Ph)] does not react at all with H₂, we report that the [Co₂(CO)₆(RC₂R')] complexes (R, R' = hydrogen or alkyl group) undergo stoichiometric and catalytic hydrogenation at low but measurable rates.

Results and Discussion

Stoichiometric Hydrogenation

The [Co₂(CO)₆(HC₂R)] and [Co₂(CO)₆(RC₂R')] complexes react at 60 °C with molecular hydrogen (760 Torr) forming the corresponding 1-olefin and *cis*-olefin respectively (see Table I). The hydrogenation is stereospecific at low conversion of the complex; as the reaction is carried on, the olefin isomerizes to attain thermodynamic equilibrium [10] and small amounts of alkane are produced. Since [Co₂(CO)₆(alkyne)] complexes are not able to catalyze any isomerization process (see blank tests in the Experimental), these side-reactions may be accounted for in terms of a catalysis operated by trace of HCo(CO)₄, a very efficient catalyst always present in a mixture of cobalt carbonyls and hydrogen [11, 12].

During the stoichiometric hydrogenation extensive reactions occur in the solution; the following stoichiometric equations hold for [Co₂(CO)₆(HC₂-

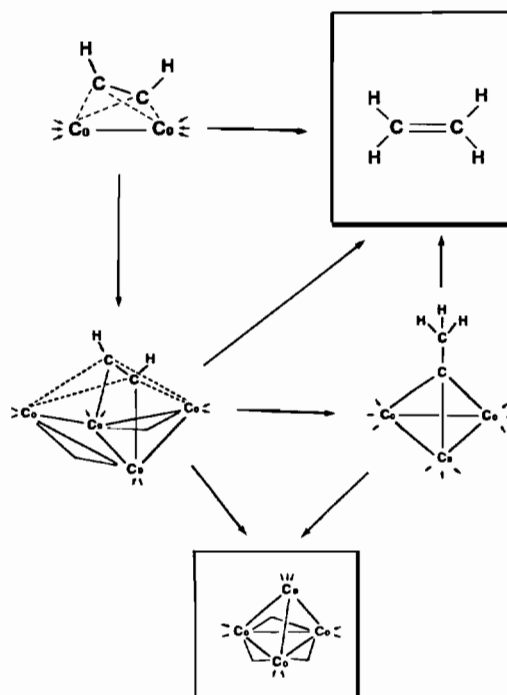
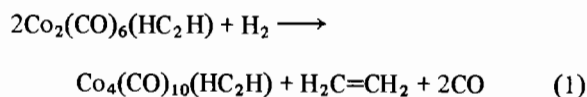


Fig. 2. Transformations occurring in the reactant solution of [Co₂(CO)₆(HC₂H)] during the stoichiometric hydrogenations. Final products in rectangles.

H)] on the basis of material balance by gc and tlc analyses and IR monitoring:



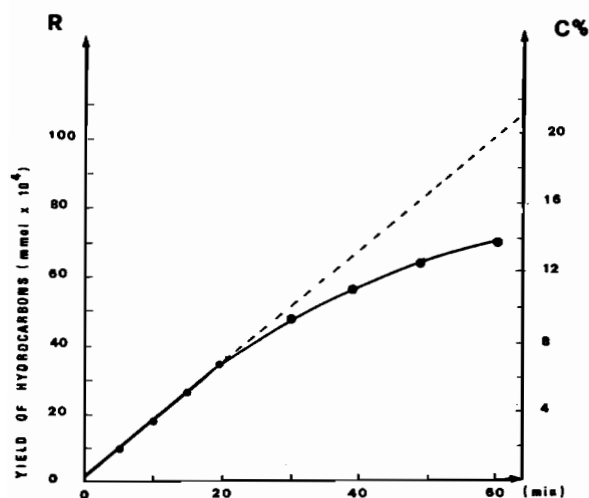
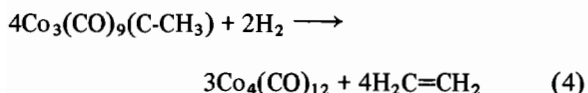
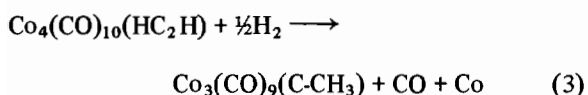
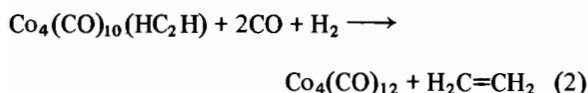


Fig. 3. Representative hydrocarbons yield plot for stoichiometric hydrogenation of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ (60°C ; [complex] = 25.0 mM , 2 ml ; $P_{\text{H}_2} = 760\text{ Torr}$). Initial hydrogenation rate $R = 106 \times 10^{-4}\text{ mmol h}^{-1}$; conversion $C = 21.2\%$.



Eqns. 1–4 are for the terminal alkyne complexes, whereas eqns. 1–2 only hold in the case of internal alkyne complexes.

The overall hydrogenation scheme of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ is depicted in Fig. 2.

Since the higher nuclearity compounds result to be inert towards further hydrogenation (see Table I), the above-mentioned transformations cause a marked decrease in the overall reactivity of the solution. After several half-times (*ca.* 24 h) the originally coordinated acetylene results to be only up to $\sim 60\%$ hydrogenated.

When the hydrogenation of the $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{R})]$ complexes is brought about for several days $\text{Co}_4(\text{CO})_{12}$ and $[\text{Co}_3(\text{CO})_9(\text{C-CH}_2\text{R})]$ are the products recovered (20–40% depending on R). This synthetic method for $[\text{Co}_3(\text{CO})_9(\text{CCH}_2\text{R})]$ compounds is very similar to that recently reported by Bergman *et al.* [13], where the use of additional $\text{Co}_2(\text{CO})_8$, which prevents extensive hydrogenation, further increases the yield of the alkylidyne complexes.

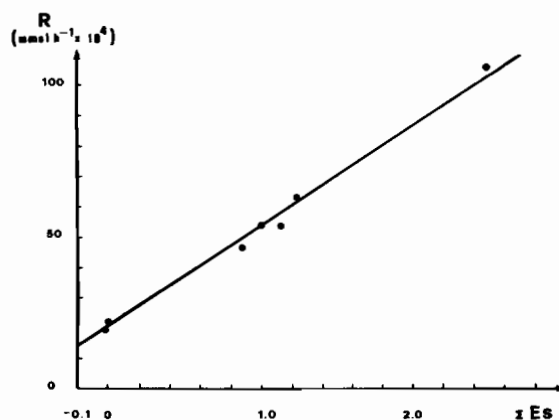


Fig. 4. Plot of the rate of several $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')]$ complexes against the sum of the Taft E_s values of the substituents R and R'.

The absolute yield of hydrocarbon products is obtained by their gc peak area integration with respect to that of the internal standard, n-hexane. The slope of the best straight line obtained by means of the least-squares treatment of the data at low conversion, represents the tangent of the curve at $t = 0$ and hence the initial hydrogenation rate R. Figure 3 shows a typical plot of the stoichiometric hydrogenation of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$; an alternative scale (on the right) indicates the C% conversion of the complex as a function of the reaction time.

The initial hydrogenation rates R of several organocobalt complexes are reported in Table I along with the hydrocarbon distribution at low conversion.

For alkyne-dicobalt complexes the rates strongly depend on the substituents. Two effects could be responsible for this behaviour, the inductive effect, which is able to vary the electron density at the metal atoms and hence the Co–CO bond order, and the steric effect.

The inductive effect is quite similar for all the alkyl substituents and cannot explain the dramatic decrease of hydrogenation rate for the $[\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})]$ complex. The steric effect can be evaluated using the Taft E_s values [14], which are inversely proportional to the Van der Waals radii of the substituents [15]. A good linear relationship is obtained by plotting the initial hydrogenation rates R vs. the sum of the E_s values of the substituents in the corresponding complex, as shown in Fig. 4.

Within the class of acetylene-cobalt complexes, the trend expected for the C–C activation, using the bond distance criterion [2], would be: $[\text{Co}_3(\text{CO})_9(\text{C-CH}_3)] > [\text{Co}_4(\text{CO})_{10}(\text{HC}_2\text{H})] > [\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$. The ethane/ethylene ratio in the products is in agreement with this potential activation. On the contrary the trend of the hydrogenation rates is exactly the opposite. Probably the strength of the

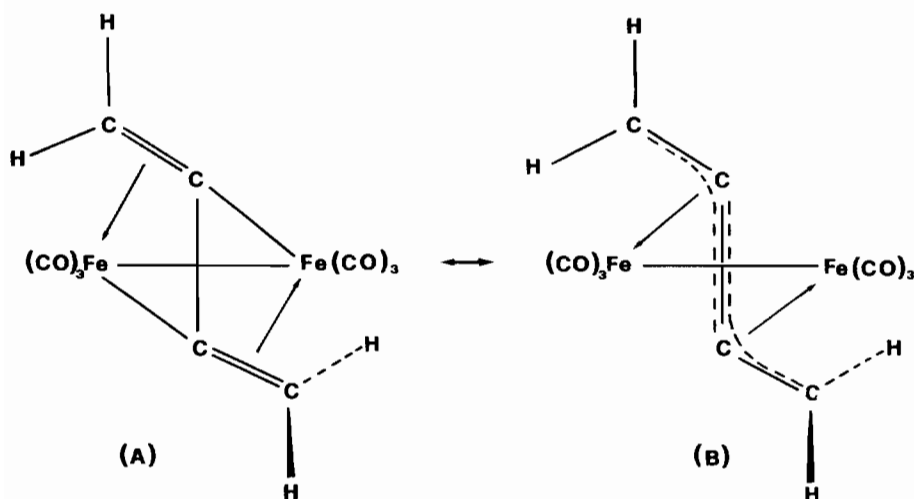


Fig. 5. Two valence-bond descriptions of the $[\text{Fe}_2(\text{CO})_6(\mu\text{-butatriene})]$ molecule. In the former (A) the organic chain is regarded as a di- σ -trans-butadiene, in the latter (B) as a bis(η^3 -allyl) system.

metal-carbon bonds, which must be broken in order to release the olefin produced, plays an important role in the overall hydrogenation process.

Interestingly the $[\text{Fe}_2(\text{CO})_6(\mu\text{-H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2)]$ complex, isoelectronic with the $[\text{Co}_2(\text{CO})_6(\mu\text{-alkyne})]$ series, undergoes no hydrogenation in the same experimental conditions.

On the basis of X-ray investigation [16] and theoretical studies [17] two valence-bond descriptions have been suggested for this molecule.

In spite of the high *potential* reactivity of the butatriene chain, the presence of strong Fe-C interactions in the complex prevents its hydrogenation. The ground electronic state and structural features of the alkyne-clusters are a general guide for their susceptibility to hydrogenation [2], but other fine parameters such as the steric encumbrance of the substituents and the metal-carbon bond strength have also to be considered.

Further information on the hydrogenation process can be extracted from the study of the factors affecting the rate of the simplest alkyne-dicobalt complex, namely $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$. Unfortunately the initial hydrogenation rate, $R = d(\text{hydrocarbons})/dt$, represents the final result of a sequence of elementary steps, including H_2 coordination, H-H bond cleavage, carbon-hydrogen bond formation and metal-carbon elimination, so that the interpretation of the kinetic data is not straightforward. Since the $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')]_2$ complexes are coordinatively saturated (at least in the usual E.A.N. formalism) the first event in the hydrogenation sequence might involve the formation of a vacant site. This can be achieved by:

- simple CO-dissociative path
- cleavage of the Co-Co bond to give a diradical species

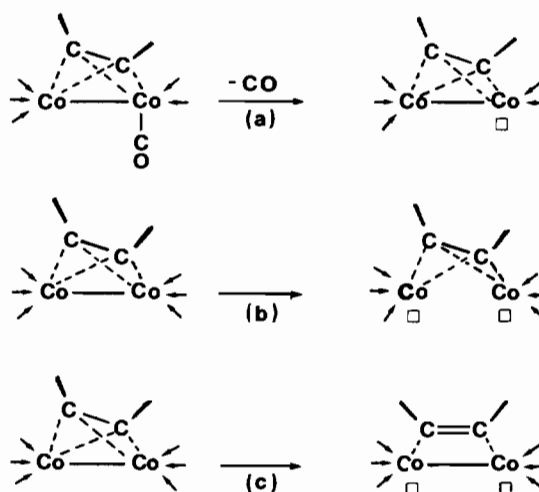


Fig. 6. Likely paths for the creation of vacant site/s (\square) in the $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')]_2$ complex.

c) formal rotation of the C-C and Co-Co vectors to give the isomeric 1,2-dimetallocyclobutene.

The first mechanism has been postulated for the substitution reaction of $[\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})]$ with phosphorus donor ligands, covering a wide range of nucleophilic character [18].

Process *b* occurs in *heterolytic* mode to give a diradical anion when $[\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})]$ is reduced chemically or electrochemically [19].

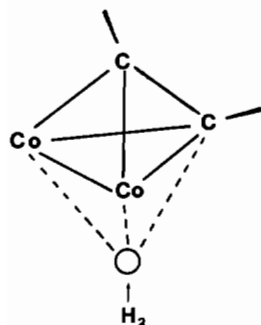
The formal rotation of the alkyne (*c*), originally proposed by Iwashita *et al.* [20], is not very likely, since recent theoretical calculations suggest that a very high energy barrier has to be overcome [21].

An alternative and attractive picture of these complexes has been recently proposed by Jaouen *et al.*

TABLE II. Values of the Observed Initial Rates R of the Stoichiometric Hydrogenation of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ in *n*-Octane.

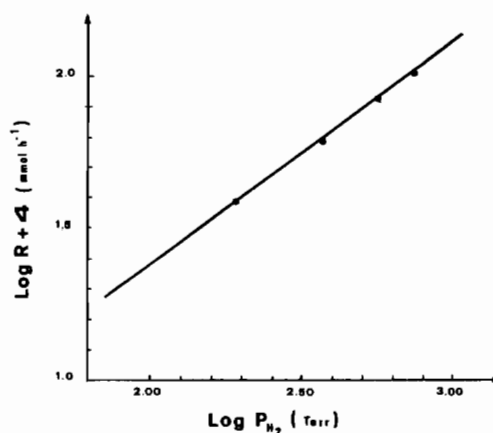
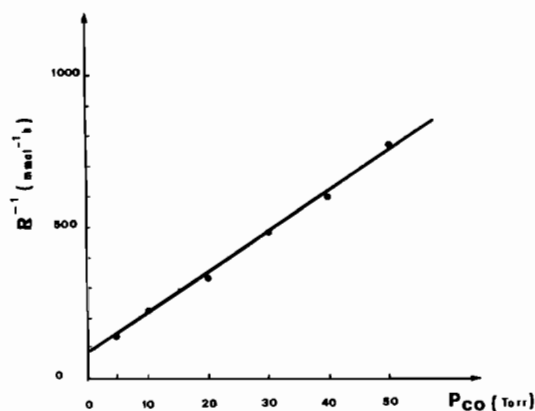
[Complex] (mM)	t (°C)	P_{H_2} (Torr)	R ($\text{mmol h}^{-1} \times 10^4$)	CO added (Torr)
50.0	60	760	214	
37.5	60	760	158	
25.0	60	760	106	
12.5	60	760	54	
25.0	60	570	90	
25.0	60	380	63	
25.0	60	190	40	
25.0	60	760(D ₂)	81	
25.0	60	760	69	5
25.0	60	760	45	10
25.0	60	760	30	20
25.0	60	760	21	30
25.0	60	760	17	40
25.0	60	760	13	50
25.0	55 ^a	760	71	
25.0	65 ^a	760	166	

^aThe variation of solubility of H_2 in *n*-octane within this range of temperatures is ca. 5% by interpolation from the literature data.

Fig. 7. View of the $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')]$ complex in the P.S.E.P. theory as a *nido*-trigonal bipyramid. \circ = vacant apex.

[22]. In the PSEP (Polyhedral Skeletal Electron Pair) theory developed by Mingos and Wade [23] the tetrahedral ' M_2C_2 ' complexes, having 6 skeletal electron pairs and 4 skeleton atoms, are regarded as *nido*-trigonal bipyramids with a missing vertex. This concept of vacancy on the polyhedral surface can explain the easy fluxionality of the chiral $[\text{NiCoCp}(\text{CO})_3(\text{RC}_2\text{R}')]$ complexes [22] as well as that of the $[\text{Co}_2(\text{CO})_4\text{DPM}(\text{alkyne})]$ series (DPM = bis(diphenylphosphino)methane) [24]. This hypothesis can explain the facile addition of suitable addenda as the ' $\text{Fe}(\text{CO})_3$ ' fragment to the alkyne-dimetal complexes to give trinuclear mixed-metal clusters [25].

Also in the hydrogenation process the incoming H_2 molecule could be coordinated in the vacant vertex without any previous bond cleavage.

Fig. 8. Relationship between hydrogenation rate of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ and partial pressure of H_2 through the differential method. Least-squares analysis of data: correlation: 0.998; slope: 0.730.Fig. 9. Plot of $1/R$ vs. P_{CO} (60 °C: [complex] = 25.0 mM; P_{H_2} = 760 Torr).

The hydrogenation rate shows first order dependence on the concentration of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$, whereas the dependence of the partial pressure of H_2 has a non-integral order (0.7 ± 0.1 , estimated from differential method, see Fig. 8). The addition of CO into the vials causes a large suppression of the hydrogenation process. Figure 9 shows the inverse relationship between the hydrogenation rate and the partial pressure of the CO added.

When D_2 is used in place of H_2 the rate decreases and the kinetic isotope effect is 1.3 ± 0.1 (60 °C, P_{H_2} or P_{D_2} = 760 Torr).

A rough evaluation of the activation energy of the overall hydrogenation process can be directly obtained from the initial hydrogenation rates, measured within a narrow range of temperatures, through the Arrhenius law. The resulting E_a value (18 ± 3 Kcal mol^{-1}) is too low for a simple Co-CO dissociative path (a) as the rate-determining step [26] of the overall process.

TABLE III. Initial Rates, Turnover Rates and Hydrocarbon Distribution for the Homogeneous Acetylene Hydrogenation Catalyzed by $\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})$ Varying the Substrate/Catalyst Ratio (60 °C; $[\text{complex}] = 0.025 \text{ M}$, 2 ml; $P_{\text{H}_2} = 760 \text{ Torr}$).

Acetylene/Catalyst Ratio	Initial Hydrogenation Rate $\text{mmol h}^{-1} \times 10^4$	Turnover Rate for Hydrogenation $\text{mol} (\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6) / \text{mol}(\text{catalyst}) \cdot \text{h}$	Hydrocarbons Distribution ^a		
			C_2H_4	C_2H_6	C_4H_6
0	106	—	91	9	trace
0.2	104	0.21	92	6	1
0.5	84	0.17	74	3	20
1.0	67	0.13	60	1	31
5.0	30	0.06	24	trace	71

^aMean of three gc measures at low conversion (within 1 h).

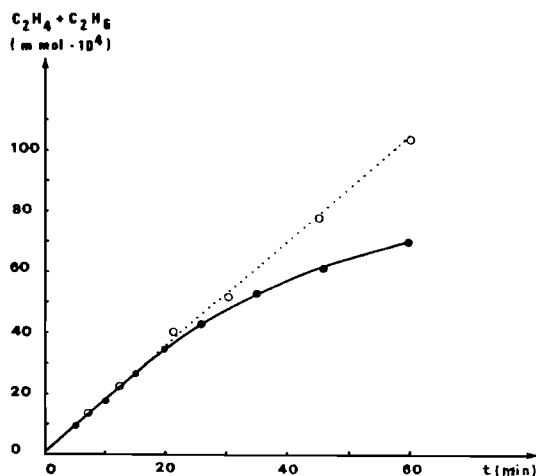


Fig. 10. Representative hydrocarbon yield plot for stoichiometric (\bullet , heavy line) and catalytic (\circ , dashed line) hydrogenation test. Experimental conditions: 60 °C; $[\text{complex}] = 25.0 \text{ mM}$, 2 ml; $P_{\text{H}_2} = 760 \text{ Torr}$; free acetylene in the catalytic run: 10 mmol.

The bulk of the kinetic data indicates that the hydrogenation process cannot be accounted for by the oversimplified *a*, *b* or *c* mechanisms.

The influence of the steric hindrance of the substituents, the dependence of the hydrogenation rate on the partial pressure of H_2 and the low but meaningful [27] isotopic effect suggest that both the incipient coordination of H_2 (possibly in the vacant vertex of the polyhedral surface) and the cleavage (or at least the weakening) of a $\text{Co}-\text{CO}$ bond are involved in the transition state.

Catalytic Hydrogenation

In a typical stoichiometric hydrogenation of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ the yield of the hydrocarbon products (ethylene and ethane in a molecular ratio *ca.* 10:1) is proportional to the reaction time, within 20 min. The least-squares treatment of the data in this interval gives the initial hydrogenation rate *R*. When free acetylene is added to the reactant system (substrate/catalyst = 0.2), the initial hydrogenation rate is equal, within experimental error, to that of the stoichiometric reaction but the hydrocarbon yield remains proportional to the reaction time until the free acetylene is consumed (*ca.* 1 h) (Fig. 10). IR analysis of the reactant solution shows that $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ is the sole species detectable in this interval; at longer reaction times the reactant solution undergoes the same chemical transformations as in the stoichiometric run. It follows that the title complex is the effective catalyst for this homogeneous hydrogenation, being immediately reformed as the originally coordinated acetylene moiety is hydrogenated and then released. This represents one of the few examples of the use of kinetic

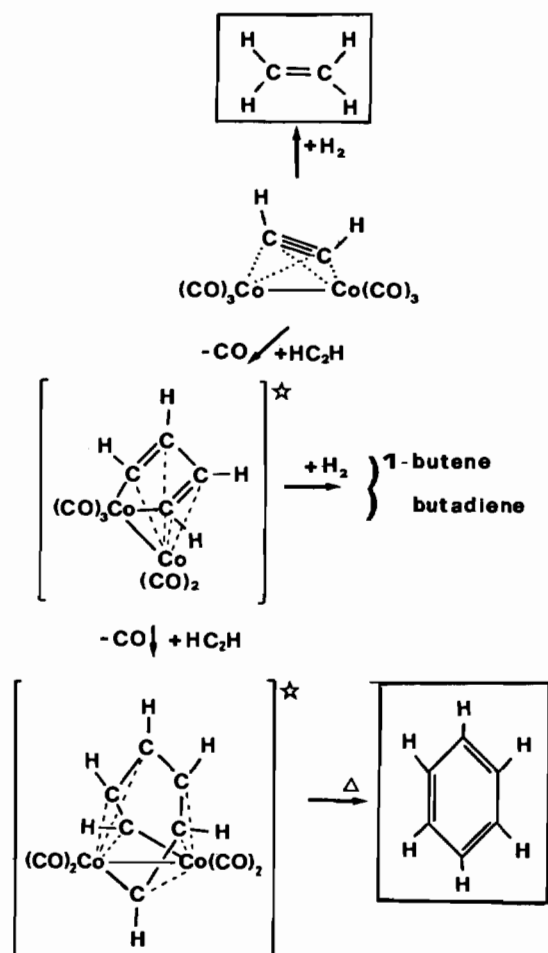


Fig. 11. Suggested mechanism of formation of various hydrocarbons during the catalytic hydrogenation. *Postulated intermediates.

studies to assess the nature of the actual catalyst [28].

However, the turnover rate for the hydrogenation is very low (see Table III). By increasing the substrate/catalyst ratio (0.5–5.0) the known cyclotrimerization of acetylene to benzene [29] becomes the most important process and the turnover rate for the hydrogenation decreases proportionally. Moreover, the ethane–ethylene ratio decreases, suggesting that the coordination of free acetylene competes with the addition of hydrogen to the activated complex, so that further hydrogenation to alkane is strongly limited.

Interestingly, C_4 hydrocarbons (mainly butadiene and 1-butene, in a molecular ratio *ca.* 1:1, at low conversion) are produced in appreciable amounts. As the reaction proceeds, butadiene and 1-butene smoothly turn into a mixture of butene isomers which reach the thermodynamic [10] equilibrium value ratio within 24 h. These side-reactions, *i.e.* butadiene hydrogenation and 1-butene isomerization,

may again be accounted for in terms of a catalysis operated by trace of $\text{HCo}(\text{CO})_4$.

The C_4 hydrocarbons should derive by direct coupling of two acetylene moieties followed by subsequent hydrogenation. An alternative pathway, represented by the reaction of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ with ethylene (the main product of the hydrogenation) to give firstly butadiene, has to be discarded on the basis of the careful work of Pauson *et al.*, who reported that the sole products of the reaction of $\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R})$ complexes with ethylene are cyclopentenones [30]. Furthermore, only traces of these C_4 hydrocarbons are present in the stoichiometric run *i.e.* in the absence of free acetylene.

The $\text{Co}_2(\text{CO})_8$ catalyzed cyclotrimerization of alkynes is believed to proceed stepwise via $[\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R})]$ (I), $[\text{Co}_2(\text{CO})_5(\text{RC}_2\text{R})_2]$ (II) and $[\text{Co}_2(\text{CO})_4(\text{RC}_2\text{R})_3]$ (III) as intermediates; the chemical or thermal degradation of the last compound gives ultimately benzene [29]. Although complexes of type II and III have not been isolated for acetylene itself, structural determinations have been carried out on homologous ‘cobaltacyclopentadiene’ complexes such as $[\text{Co}_2(\text{CO})_5(\text{cyclooctyne})_2]$ [31] and ‘fly-over bridged’ complexes such as $[\text{Co}_2(\text{CO})_4(3,3,3\text{-trifluoropropyne})_3]$ [32].

Furthermore the role of type II compounds as intermediates in the alkyne cyclotrimerization has been already recognized for $[\text{Mo}_2(\text{OR})_6(\text{py})(\text{C}_2\text{H}_2)_2]$ [33], $[\text{Rh}_2(\text{CO})_4(\text{PPh}_3)(\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ [34] and $[\text{Rh}_2(\text{PF}_3)_5(\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ [35].

Thus C_4 hydrocarbons may be viewed as the results of the hydrogenation of the elusive $[\text{Co}_2(\text{CO})_5(\text{C}_2\text{H}_2)_2]$ complex, an unstable intermediate in the cyclotrimerization process (Fig. 11). A careful analysis of the IR spectra of the reaction solution (substrate/catalyst > 1) shows the growing of new bands, which disappear when the free acetylene is consumed. The resulting spectrum of this intermediate [νCO bands at 2090(m) 2035(vs) 2021(s) and 1982(s) cm^{-1}] shows a pattern similar to that reported for the $[\text{Co}_2(\text{CO})_5(\text{cyclooctyne})_2]$ complex [31]. Several attempts to isolate this intermediate were unsuccessful: it immediately decomposed to metallic residue on SiO_2 or Al_2O_3 tlc plates, even in N_2 atmosphere, and only $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ could be eluted. We were unable to monitor the reaction in a sealed tube at 60 °C by ^1H NMR, because of line broadening increasing with the reaction time, possibly due to paramagnetic species that are formed in these experimental conditions.

In order to get some insight into this proposed pathway, we carried out a stoichiometric hydrogenation test of $[\text{Fe}_2(\text{CO})_6(\text{HC}_2\text{H})_2]$, a stable ferracyclopentadiene complex isoelectronic with the postulated intermediate [36] (Fig. 12).

Indeed $[\text{Fe}_2(\text{CO})_6(\text{HC}_2\text{H})_2]$ reacts very slowly with molecular hydrogen (80 °C; [complex] = 0.025

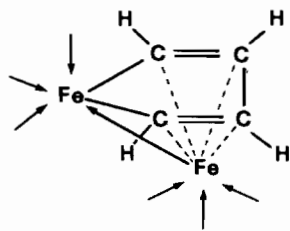


Fig. 12. Molecular structure of the 'ferrole' complex $[\text{Fe}_2(\text{CO})_6(\text{HC}_2\text{H})_2]$.

M, 2 ml; $p_{\text{H}_2} = 760$ Torr; conversion *ca.* 5% within 24 h) forming butadiene and 1-butene in a molecular ratio of *ca.* 1:1, a pattern very similar to that found in the aforementioned catalytic tests.

In conclusion the $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ complex in presence of both acetylene and hydrogen is able to catalyze three different processes:

- hydrogenation of acetylene, mainly to ethylene
- cyclotrimerization of acetylene to benzene
- dimerization of acetylene followed by subsequent hydrogenation to give ultimately butene isomers in their thermodynamic equilibrium ratio.

A careful choice of the reaction parameters may increase the relative importance of a desired process.

Experimental

Material

n-octane was distilled from sodium, stored on molecular sieves and saturated with dry nitrogen prior to use. Hydrogen, carbon monoxide, n-hexane and all the C_2 – C_5 hydrocarbons were Carlo Erba pure grade. Acetylene was passed over a trap maintained at -78°C to remove the acetone stabilizer. $[\text{Co}_2(\text{CO})_6(\text{Alkyne})]$ [37] complexes, $[\text{Fe}_2(\text{CO})_6(\text{butatriene})]$ [38] and $[\text{Fe}_2(\text{CO})_6(\text{HC}_2\text{H})_2]$ [36] were synthesized according to the reported procedures. Their purity was checked by IR and ^1H NMR spectroscopy.

All the n-octane standard solutions of the complexes under investigation were saturated with N_2 and added with an appropriate amount of n-hexane as internal standard for gc measurement.

The required volumes (2 ml) of the solutions were introduced into glass vials (estimated volume of 80 ml) equipped with a gc septum. The vials were connected to a vacuum line, degassed by two freeze–pump–thaw cycles, filled with the desired gas mixture and finally sealed hermetically. The ampoules were wrapped in aluminum foil and immersed in a thermostatic bath at $60 \pm 0.2^\circ\text{C}$. Samples of the gas above the reactant solution were withdrawn at regular intervals by a syringe and analyzed quantitatively by gc. In the catalytic runs the overall amount of benzene produced (not completely vaporized at 60°C) was extrapolated according to the Clausius–Clapeyron equation. Material balance between

acetylene consumed and products formed showed that the errors were less than $\pm 10\%$.

Analyses

The gas phase was analyzed on a Carlo Erba 4200 FID gas chromatograph with $2\text{ m} \times 4\text{ mm}$ columns filled with n-octane (Porasil C 100/120 mesh) or with SE30 2% on Chromosorb W AW 60/80 respectively, using N_2 as carrier gas.

The reactant solutions were checked by TLC and IR spectroscopy. The IR spectra were recorded on a 580 B Perkin-Elmer instrument with a Data Station. The PE 580 software, provided by Perkin Elmer, solved the IR spectrum of the reactant solution into separate components whose pure spectra were previously recorded on floppy disks. ^1H NMR spectra were recorded on a Jeol C60-HL instrument.

Blank Tests

A large ampoule equipped with gc septum was connected to a vacuum line and filled with 1-butene, *cis*-2-butene and *trans*-2-butene in molecular ratio *ca.* 1:1:1 (checked by gc analysis) up to a total pressure of 760 Torr. Required volumes of this C_4H_8 gaseous mixture were transferred into the vials by a syringe through the gc septa.

$[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ as Isomerization Catalyst

A n-octane solution of $[\text{Co}_2(\text{CO})_6(\text{HC}_2\text{H})]$ (0.025 M, 2 ml) was sealed in a vial under N_2 and added with 1 ml (0.04 mmol) of the C_4H_8 gaseous mixture. After 1 day at 60°C , gc analysis showed no change in the hydrocarbon composition, within the experimental error.

$\text{Co}_2(\text{CO})_8$ – $\text{Co}_4(\text{CO})_{12}$ as Catalysts

A mixture, obtained from 1 ml each of two n-octane 0.025 M solutions of $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ was sealed in a vial under 760 Torr of H_2 and added with 1 ml of the C_4H_8 mixture. After 1 day at 60°C moderate isomerization and little hydrogenation was detected by gc. In these experimental conditions the active species is probably $\text{HCo}(\text{CO})_4$.

Attempt to Hydrogenate $[\text{Fe}_2(\text{CO})_6(\mu\text{-butatriene})]$

A n-octane solution of $[\text{Fe}_2(\text{CO})_6(\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2)]$ (0.025 M, 2 ml) was sealed in a vial under 760 Torr of H_2 . After a week at 60°C no hydrocarbons were detected by gc analysis. IR monitoring showed no change in the solution.

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