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Kinetics and Mechanism of the Reaction of the Tetranuclear Clusters $H_4Ru_4(CO)_{12}$ and $D_4Ru_4(CO)_{12}$ with Carbon Monoxide

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The title reaction at CO pressures up to 1 atm. gives rise quantitatively to $Ru_3(CO)_{12}$ and $Ru(CO)_5$. A kinetic study shows complicated dependence of the rate of the reaction on the concentration of the complex, of CO and of H_2. The isotopic effect, when the reactivity of the hydride and of the deuteride complexes are compared, suggests the contemporary breaking or weakening of Ru–Ru and Ru–H bonds as the rate-determining step. The proposed reaction mechanism points out the importance of a 'butterfly-shaped' Ru_4 intermediate, as a probable active form in many catalytic reactions involving tetranuclear ruthenium carbonyls.

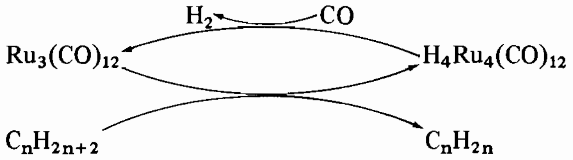
Introduction

Recently interest has been concentrated on the chemistry of the metal carbonyl clusters [1]. The greatest part of the efforts has been addressed to the synthesis and the structural analysis [2], and to the fluxional behaviour of the CO ligands by means of ^{13}C nmr spectroscopy [3]. Even if other fields are the subject of growing interest, (*e.g.* the vibrational properties, concerning in particular the metal core, have received increased attention by the present large availability of the Laser-Raman spectrophotometers [4]), there is a lack of kinetic and mechanistic studies on the basic reactions of these compounds. Work is needed to correlate the homogeneous and the heterogeneous catalysis and to propose the metal clusters as simple models of the metal surfaces in the chemisorption and in the catalytic processes [5]. Furthermore, the ability of a metal cluster to coordinate ligands on multicenter sites and to transmit the electronic effect across the metal–metal bond to the active catalytic centre have suggested the use of these compounds as catalysts in many important processes [6].

Ford [7] extensively studied the catalytic properties of the Ru_3 and Ru_4 hydrido carbonyl anions on the water gas shift reaction. He suggested several catalytic cycles, involving interconversion between the trinuclear and tetranuclear species, accompanied by CO coordination and H_2 elimination [8]. Furthermore Kaesz [9], taking into account the easy conversion of $Ru_3(CO)_{12}$ to $H_4Ru_4(CO)_{12}$ and *vice versa* according to the reaction (1)

$$Ru_3(CO)_{12} \underset{CO}{\overset{H_2}{\rightleftarrows}} H_4Ru_4(CO)_{12} \qquad (1)$$

suggested the possibility to engage these species in a catalytic cycle for the dehydrogenation of the hydrocarbons [10]:



Since the knowledge of a potential catalytic cycle is greatly improved by a more complete mechanistic understanding of the single steps, the kinetic study of the reaction of $H_4Ru_4(CO)_{12}$ with CO appears in this light very useful, as it implies, according to (1), declustering of a metal carbonyl hydride accompanied by H_2 elimination, both processes having been proposed as key steps in catalytic cycles involving Ru carbonyl clusters [8].

Experimental

Compounds and Solvents

All the manipulations were carried out under inert atmosphere, especial care being taken to exclude oxygen when preparing solutions for kinetic measurements. $Ru_3(CO)_{12}$ was obtained by the well-known procedure from the commercial ruthenium trichloride and CO at atmospheric pressure [11]. $H_4Ru_4(CO)_{12}$ and $D_4Ru_4(CO)_{12}$ were prepared by reacting a toluene solution of $Ru_3(CO)_{12}$ with H_2 or D_2 at atmospheric pressure respectively [9]. The reaction was carried out in a sealed glass vial and was completed after 24 hours at 70 °C. The solvents were dried on molecular sieves and distilled under nitrogen prior to use.

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Kinetic Measurements

The procedure for the rate determination has been fully described previously [12]. Basically the method consists of preparation for each kinetic measurement of a series of sealed glass vials, containing a measured volume of the complex solution saturated by CO or by 1:1 mixture of CO and H_2 at known pressure. The vials were kept in a thermostatted (±0.2 °C) bath during predetermined time intervals. The solution was then analyzed by means of i.r. spectrophotometry (see later).

The concentration of the dissolved CO at the reaction temperature, calculated on the basis of its solubility [13], has been considered to remain constant during the course of the reaction: the dissolved CO which has reacted can be easily supplied by the gaseous CO.

The large ratio (5–10) between the volume of the gas phase and the volume of the solution in each vial allowed the total amount of CO to be at least 50 times greater than that of $H_4Ru_4(CO)_{12}$.

I.R. Analysis of the Reaction Solution

The infrared spectra were recorded by a 580 B Perkin-Elmer i.r. spectrophotometer with a Data Station. The PE 580 Software, provided by Perkin-Elmer, solves the i.r. spectrum of the solution into separate components whose spectra were previously recorded on floppy disks. A typical analysis is given in Fig. 1.

Treatment of Data

The reaction rate was measured by following the progressive disappearance of the spectrum of the starting complex and by measuring the absorbance of the strong band at 2081 cm^{-1} ($H_4Ru_4(CO)_{12}$) or at 2080 cm^{-1} ($D_4Ru_4(CO)_{12}$). The linearity of the plots of $\ln A_t$ *vs.* time for 2–3 half lives indicates the absence of any induction period, and the first order of the rate with respect to the concentration of the starting complex. The slope of the best straight line, obtained by means of the least-squares treatment, gives the value of the observed pseudo-first-order rate constant k_{obs} (Table I). The error, calculated as standard deviation, was less than 10%. Similar results were obtained by observing the increasing absorbance of the $Ru_3(CO)_{12}$ spectrum and by plotting $\ln(A_\infty - A_t)$ *vs.* time, where A_∞ is the limiting value of the absorbance after several half-lives.

Results and Discussion

The i.r. analysis of the reaction solutions (Fig. 1) shows that the stoichiometry for the reaction of $H_4Ru_4(CO)_{12}$ with CO, as illustrated by eq. (1), is clearly false as the deconvolution of the spectrum indicates the presence of an unreported compound, characterized by the strong absorptions at 2036 and 2000 cm^{-1} which are absent at the beginning of the reaction and which increase together with those of

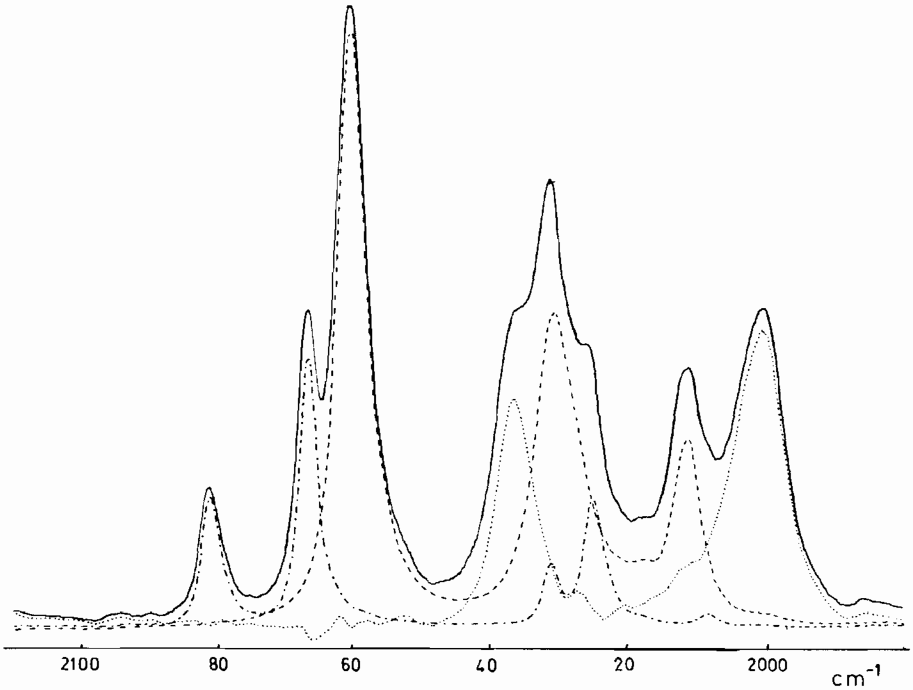


Fig. 1. Test i.r. spectrum of the reaction solution and its components: —— solution; – · – · $H_4Ru_4(CO)_{12}$; - - - - $Ru_3(CO)_{12}$; ····· $Ru(CO)_5$.

TABLE I. Values of the Observed Rate Constant of the Reaction of $H_4Ru_4(CO)_{12}$ and $D_4Ru_4(CO)_{12}$ with CO in n-Heptane.

Complex	t °C	$[CO]\cdot10^3$	$k_{obs}\cdot10^5$ sec^{-1}
$H_4Ru_4(CO)_{12}$	60.0	0.40	0.18
		0.58	0.21
		0.78	0.31
		1.1	0.32
		1.5	0.35
		2.4	0.42
		4.3	0.43
		5.2	0.44
		6.0	0.47
	70.0	0.30	0.58
		0.56	0.98
		0.60	0.97
		0.78	1.14
		0.83	1.08
		1.0[a]	0.22
		1.1	1.29
		1.4[b]	0.50
		1.4	1.70
		1.7[c]	0.78
		2.0	1.65
		2.1[d]	1.03
		3.0	1.91
		3.6	2.00
		4.3	2.08
	80.0	0.23	1.47
		0.35	1.95
		0.39	2.62
		0.60	3.0
		0.79	4.5
		0.95	4.4
		1.5	4.6
		1.9	5.6
		2.2	5.4
$D_4Ru_4(CO)_{12}$	60.0	0.69	0.18
		0.89	0.21
		1.1	0.24
		1.5	0.28
		2.4	0.37
		3.3	0.36
		4.2	0.41
		5.1	0.39
		6.0	0.41
	70.0	0.29	0.36
		0.30	0.39
		0.35	0.39
		0.42	0.51
		0.57	0.54
		0.80	0.71
		1.0	1.0
		1.3	1.12
		2.0	1.35
		3.0	1.28
		4.0	1.39
	80.0	0.29	2.0
		0.43	2.7
		0.61	3.3
		0.88	3.7
		1.2	4.1
		1.5	3.9
		2.0	5.0
		2.2	4.8

[a] $[H_2] = 1.5\times10^{-3}$. [b] $[H_2] = 1.9\times10^{-3}$. [c] $[H_2] = 2.4\times10^{-3}$. [d] $[H_2] = 3.0\times10^{-3}$.

$Ru_3(CO)_{12}$ when $H_4Ru_4(CO)_{12}$ disappears. The most obvious candidate is $Ru(CO)_5$, for which frequencies of 2035 and 1999 cm^{-1} have been reported [14]. The correct stoichiometry may be represented by eq. 2:

$$H_4Ru_4(CO)_{12} + 5CO \rightleftharpoons Ru_3(CO)_{12} + Ru(CO)_5 + 2H_2 \qquad (2)$$

Taking into account the volatility of $Ru(CO)_5$ and the ease with which it transforms into $Ru_3(CO)_{12}$ at low CO pressure, *e.g.* by the effect of light [14], it can be easily understood why $Ru(CO)_5$ was not detected when $H_4Ru_4(CO)_{12}$ reacted at high temperatures in a stream of CO [10]. Nevertheless, when the reaction occurs in a closed vessel at medium (0.5–1 atm) CO pressure and in absence of light, it is better described by eq. (2), to which our kinetic results must be referred.

The observed rate constant k_{obs} shows a clear dependence on the CO concentration, increasing linearly with [CO] at low [CO] values and reaching a limiting value when the [CO] is quite high. This behaviour, pointed out in Fig. 2 in which plots of k_{obs} *vs.* [CO] are reported, is simply expressed by the following equation:

$$k_{obs} = \frac{a[CO]}{1 + b[CO]} \qquad (3)$$

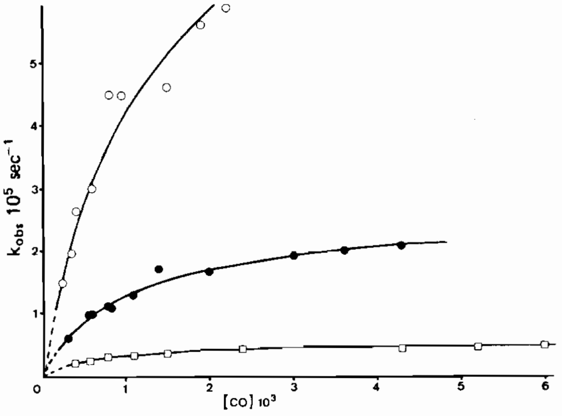


Fig. 2. k_{obs} *vs.* [CO] for the reaction of $H_4Ru_4(CO)_{12}$ with CO in n-heptane; open circles 80.0°, closed circles 70.0°, squares 60.0 °C.

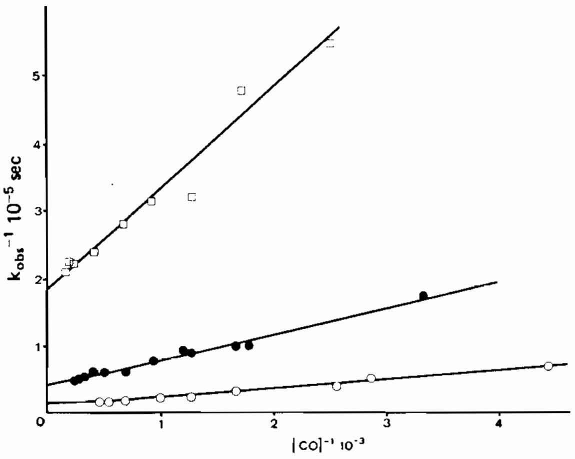


Fig. 3. $1/k_{obs}$ *vs.* $1/[CO]$ for the reaction of $H_4Ru_4(CO)_{12}$ with CO in n-heptane; for the symbols, see Fig. 2.

According to (3), plots of $1/k_{obs}$ *vs.* $1/[CO]$ should be linear, $1/a$ and b/a being the slope and the intercept, respectively. Fig. 3 illustrates this behaviour, so supporting the validity of eq. (3).

The simplest kinetic mechanism which fits the experimental data, is given by:

$$H_4Ru_4(CO)_{12} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [H_4Ru_4(CO)_{12}]^*$$

$$[H_4Ru_4(CO)_{12}]^* + CO \xrightarrow{k_2} \text{products} \qquad (4)$$

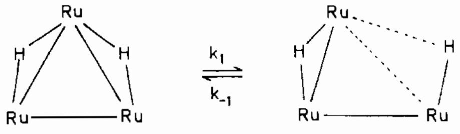
i.e. the starting complex $H_4Ru_4(CO)_{12}$ gives rise to an active intermediate, by means of a slow, rate-determining step (k_1). $[H_4Ru_4(CO)_{12}]^*$ can go back to $H_4Ru_4(CO)_{12}$ (k_{-1}) or can react rapidly with carbon monoxide (k_2) forming products, by means, of course, of several fast steps. If the velocity of the intermediate to react further is greater than that to give the starting complex, its concentration rapidly achieves a small but constant value and the steady-state approximation can be applied.

The rate of the reaction is expressed by eq. (5)

$$\text{rate} = k_{obs}[H_4Ru_4(CO)_{12}] = \frac{\frac{k_1k_2}{k_{-1}}[H_4Ru_4(CO)_{12}][CO]}{1 + \frac{k_2}{k_{-1}}[CO]} \qquad (5)$$

formally identical to the eq. (3), when $a = k_1k_2/k_{-1}$ and $b = k_2/k_{-1}$.

The best value of the slope and the intercept of the straight line $1/k_{obs}$ *vs.* $1/CO$ (Fig. 3), allow us to calculate the values of k_1 and k_1/k_2, which are reported in Table II. The first order rate determining step (k_1) is consistent with the activation of the starting complex via an internal dissociation. The form of the rate equation (5) and the dependence of k_{obs} on the CO concentration indicates that a dissociation of a CO group cannot play an important role on this reaction step. More probably it implies the dissociation of a Ru–Ru bond and/or a Ru–H bond, as illustrated in the following scheme, in which dotted lines indicate the possiblity that the bonds are weakened but not completely broken:



Scheme 1

To evaluate the role of the Ru–H bond, the reaction of the deuterium labelled compound $D_4Ru_4(CO)_{12}$ with CO was studied. Stoichiometry was the same and the kinetic expression was formally identical to that previously reported for $H_4Ru_4(CO)_{12}$ (eqs. (2) and (5)) (Figs. 4 and 5). Tables I and II also collect the values of the specific rate constants. Even if it is usually difficult to anticipate the kinetic isotope effect in a complex molecule, it can be expected, when the reaction involves Ru–H or Ru–D bond, that the light molecule reacts faster than the heavy molecule. This effect should be greater when the

TABLE II. Values of the Specific Rate Constants and of the Activation Parameters of the Reaction of $H_4Ru_4(CO)_{12}$ and $D_4Ru_4(CO)_{12}$ with CO in n-Heptane.

Complex	t °C	$k_1 \cdot 10^5$ sec^{-1}	$k_{-1}/k_2 \cdot 10^3$ *M*	ΔH_1 kJ mol^{-1}	ΔS_1 e.u.
$H_4Ru_4(CO)_{12}$	60.0	0.54 ± 0.04	0.77 ± 0.17		
	70.0	2.6 ± 0.2	1.02 ± 0.03	136 ± 12	15 ± 5
	80.0	9.3 ± 1.8	1.19 ± 0.27		
$D_4Ru_4(CO)_{12}$	60.0	0.50 ± 0.02	1.2 ± 0.2		
	70.0	2.0 ± 0.3	1.3 ± 0.1	119 ± 12	2 ± 5
	80.0	6.0 ± 0.4	0.56 ± 0.09		

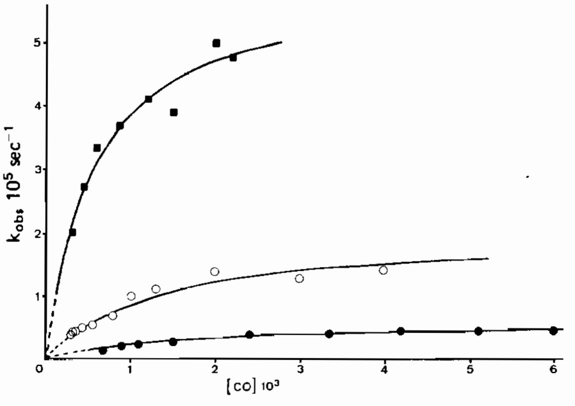


Fig. 4. k_{obs} *vs.* [CO] for the reaction of $D_4Ru_4(CO)_{12}$ with CO in n-heptane; closed squares 80.0°, open circles 70.0°, closed circles 60.0 °C.

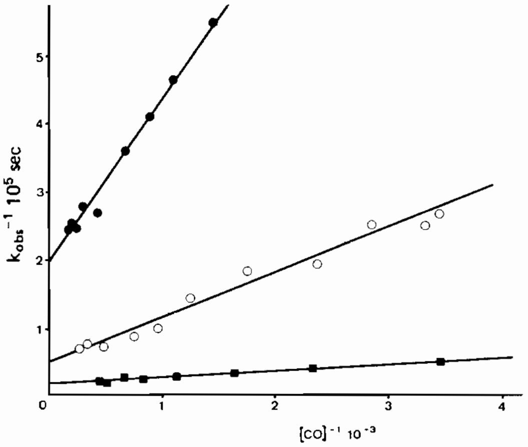


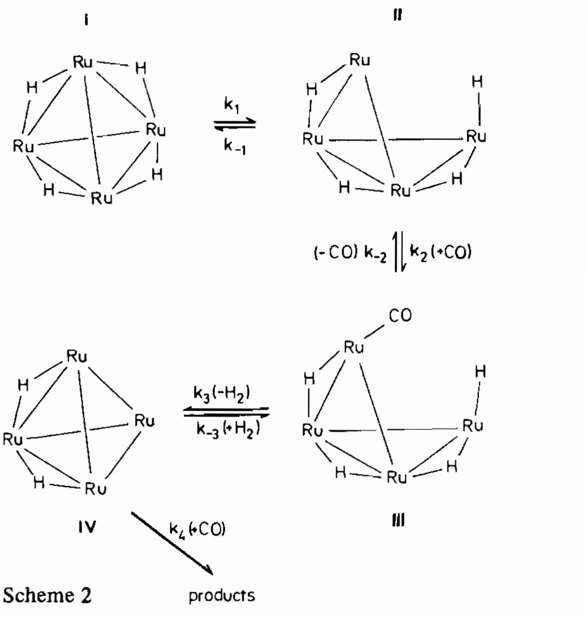
Fig. 5. $1/k_{obs}$ *vs.* 1/[CO] for the reaction of $D_4Ru_4(CO)_{12}$ with CO in n-heptane; for the symbols, see Fig. 4.

Ru–H or Ru–D bonds are completely broken in the activated state, whereas it is smaller in the case in which these bonds are weakened [15]. However, it is difficult to predict its magnitude because the geometry of the activated state might be such that the maximum isotope effect could be small. The ratio $k_1(H)/k_1(D)$ is *ca.* 1.1 at 60°, 1.3 at 70°, 1.6 at 80°. The isotopic effect is evident but not strong, and has different weights at different temperatures. It can thus be suggested that in the rate controlling step the Ru–H bond could be broken or considerably weakened, provided that breaking or weakening of the Ru–Ru bond too takes place. The average Ru–Ru bond energy in $H_4Ru_4(CO)_{12}$ can be easily calculated by the Wade method [16] as *ca.* 65 KJ/mol, taking into account the bond energy in the metal and the bond distance in the cluster [17]. The energy values of M–H bridged bond are not available, but they can hardly exceed 80–100 KJ/mol. So the values of the activation enthalpy are close to the sum of the presumable energies of the Ru–Ru and Ru–H bonds and can be reasonably related to a process in which simultaneous breaking or substantial weakening of both Ru–Ru and Ru–H bonds occurs. Nevertheless, this surprising agreement should not be emphasized, considering the uncertainty of the estimate of the bond energies on clusters. The $k_1(H)/k_1(D)$ values indicate that the Ru–H breaking contribution increases by increasing the temperature, whereas at low temperature the Ru–Ru bond breaking predominates. The low values of the activation entropy agree with the proposed mechanism, which does not imply a significant increase of the degrees of freedom.

In summary, all the kinetic data are consistent with a rate determining process implying the opening of the Ru_4 closed structure to a butterfly structure, in which a Ru atom has vacant coordination sites, easily available to the subsequent coordination of the carbon monoxide.

The effect of the free hydrogen gas on the reaction rate was determined by measuring the k_{obs} values of reactions in which free H_2 was initially introduced. Apart from the expected effect at the infinite time (the reactions do not go to completion, but reach equilibrium conditions in which different amounts of $H_4Ru_4(CO)_{12}$, $Ru_3(CO)_{12}$ and $Ru(CO)_5$ are present), the presence of free H_2 at the beginning of the reaction causes a significant decrease (50–70%) of the specific rate (see Table I). The retarding effect of H_2 is not shown by eq. (5), indicating that mechanism (4) is oversimplified and that the steps following the rate determining one can be better detailed.

In particular, a more complete scheme can be proposed in which, after the CO coordination (step 2), a reclosure of the butterfly structure III can occur, accompanied by H_2 elimination (step 3):



Scheme 2

The steady-state approximation applied to all the reaction intermediates allows to calculate the rate equation 6:

$$k_{obs} = \frac{k_1k_2k_3k_4\,[CO]^2}{k_4[CO]\,\{k_{-1}(k_{-2}+k_3)+k_2k_3[CO]\} + k_{-1}k_{-2}k_{-3}[H_2]} \qquad (6)$$

This equation takes into account the retarding effect of the free hydrogen and it is easily reduced to eq. (5), provided that $k_3 \gg k_{-2}$ and $[H_2] \approx 0$. The first condition is very likely, in that the reclosure of the unstable butterfly structure is more facile than is the loss of CO to maintain the same structure. The other condition is verified when hydrogen is only produced during the course of the reaction, so its concentration is clearly negligible.

The intermediate IV in Scheme 2 has the same formula as the well known compound $H_2Ru_4(CO)_{13}$, whose structure is strictly related to that of $H_4Ru_4(CO)_{12}$ [18], so the complex itself (or an excited form), can be considered the intermediate. The reactivitiy of $H_2Ru_4(CO)_{13}$ agrees with this suggestion, because the complex is known to react with H_2 to give rapidly and quantitatively $H_4Ru_4(CO)_{12}$ [9], and with CO by an S_N2 mechanism to give $Ru_3(CO)_{12}$ and $Ru(CO)_5$, much more rapidly than does $H_4Ru_4(CO)_{12}$ [19].

Catalytic cycles analogous to the previous scheme have been proposed for the homogeneous catalysis of the water gas shift reaction, promoted by Ru_4 and Ru_3 hydride carbonyl anionic species [8]. The reaction conditions are obviously different and involve cluster anions in many stages, so a comparison can be made with great care; nevertheless steps implying the opening and reclosure of Ru_4 tetrahedron to a butterfly structure, the CO trapping and the H_2 elimination from this structure seem to be fundamental paths in the reaction of ruthenium hydride clusters.

Finally, $H_4Ru_4(CO)_{12}$ is reported as catalyst of the isomerization of alkenes [20] and of the hydrogenation of alkynes [21], under experimental conditions very close to those described here. In both cases the addition of CO has a retarding effect on the rate of catalysis, which suggested that the Ru–CO bond dissociation was the rate-determining step. Scheme 2 can easily account for this behaviour, provided that the butterfly intermediate $H_4Ru_4(CO)_{12}$ is the active catalytic form, to which the organic substrates coordinate in competition with free CO. In the same way the retarding effect of the H_2 concentration on the alkene isomerization rate [20] can be explained.

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