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# Hydroformylation of 2,4,4-trimethyl-1-pentene catalyzed by the high nuclearity carbonyl cluster $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$

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## Abstract

The salt  $\text{Na}_2[\text{Rh}_{12}(\text{CO})_{30}]$  was used for the hydroformylation of 2,4,4-trimethyl-1-pentene in tetrahydrofuran under high pressures of  $\text{CO}/\text{H}_2$  (20–120 atm) in the temperature range 300–400 K. The reaction is highly chemoselective, approaching 100% selectivity to 3,5,5-trimethylhexanal, and only traces of 2,4,4-trimethylpentane and 3,5,5-trimethyl-1-hexanol are produced. Typical turnover numbers are 100–1000 mol olefin/mol cluster. The cluster precursor was transformed into derivatives of lower nuclearity,  $[\text{Rh}_6(\text{RCO})(\text{CO})_{15}]^-$  ( $\text{R} = (\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ ) or  $[\text{Rh}_5(\text{CO})_{15}]^-$ , as shown by infrared spectroscopy. The turnover numbers increase on lowering the catalyst to olefin ratio, and the order of the reaction with CO is positive. The dependencies of the rates versus CO and catalyst concentrations suggest that, irrespective of the actual species present in solution, all the clusters behave in the same way, probably through a CO-driven equilibrium of fragmentation.

*Keywords:* Rhodium; Hydroformylation; 2,4,4-trimethyl-1-pentene; Carbonyl cluster; High nuclearity

## 1. Introduction

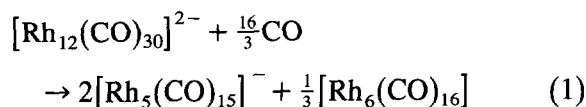
Neutral carbonyl clusters of low nuclearity can be obtained in large amounts and high purity, and the catalytic properties of the homometallic compounds were studied in detail; the results of these investigations have been thoroughly reviewed [1]. Nowadays, more than one hundred carbonyl clusters are known which possess more than twelve metal atoms, and they are conventionally included in the family of high nuclearity clusters. For several of these carbonylanionic species, experimental difficul-

ties precluded a detailed characterization, and the more reliable data were limited to their solid state structure. On the other hand, few high nuclearity clusters can be obtained easily and reproducibly [2].

In our laboratories, we have devoted many efforts to the synthesis and the structural characterization of anionic carbonyl clusters of almost all the metals of groups 7–10. Therefore, some of those prototypical compounds were studied for catalytic activity, in order to ascertain if some specific effects could be attributed to the cluster size, and to verify if some significant advantages could counterbalance difficulties in their preparation. For the first series of experiments we choose as catalytic precursor the well

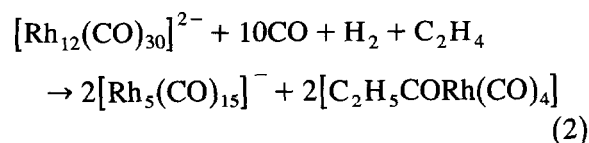
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known  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  [3] anion, for several reasons: (i) it can be prepared as salt of alkaline cations in high purity and high yields [4]; (ii) it was used recently, supported on  $\text{SiO}_2$ , for heterogeneous hydroformylation of ethylene, showing that surface-bound carbonylic species are still active for this reaction [5]; (iii) its chemical behavior is well established, and it is known to produce smaller clusters even at low pressures of CO, and at room temperature [6]:



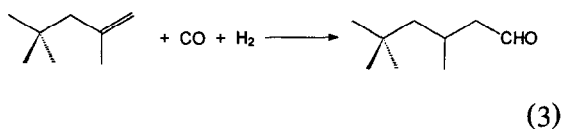
Instead, close-packed higher nuclearity species are formed by pyrolysis [7].

If Eq. (1) would be the only present under catalytic conditions,  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  would result to be an inconvenient precursor if compared, for example, to  $\text{Rh}_4(\text{CO})_{12}$  or  $\text{Rh}_6(\text{CO})_{16}$ . On the other hand it is conceivable that, in the presence of alkene and under high pressures,  $[\text{Rh}_6(\text{CO})_{16}]$  would not be formed and, therefore, stoichiometric amounts of mononuclear species of Rh(I) would be quickly generated in the solution, possibly with a reaction such as that depicted by Eq. (2) [8]:



However, as we shall see later, this possibility is not sufficient to explain our results, which indicate the possible participation of  $[\text{Rh}_5(\text{CO})_{15}]^-$  or other species.

The hydroformylation of several alkenes is presently under investigation. In this paper we report the catalytic reactions of 2,4,4-trimethyl-1-pentene, since a complete set of data was obtained.



The steric hindrance at the C=C double bond of the alkene slows down the reaction rate, making it possible to follow easily the dependence from the experimental parameters such as the CO pressure and the catalyst concentration. Both parameters suggest a decomposition of the cluster to (undetectable) active rhodium species of lower nuclearity.

## 2. Experimental

THF was freshly distilled from sodium/benzophenone ketyl, while all other reagents were used as commercially supplied.  $\text{Na}_2[\text{Rh}_{12}(\text{CO})_{30}]$  was prepared according to literature methods [4]. Hydroformylation experiments were carried out in a stainless steel autoclave (PARR 4841) equipped with a mechanical turbine stirrer, thermocouple, liquid sampling device and glass liner to avoid direct contact of solutions with the stainless steel.

In a typical experiment the substrate and the catalyst precursor were dissolved in 15 ml of THF in a Schlenk tube under nitrogen, then introduced into the autoclave, which was then purged three times with  $\text{CO}/\text{H}_2$  mixture and brought under pressure.

The reaction time was measured when the apparatus reached the selected temperature, and after 90 min the autoclave was removed from the heater. The reaction was then quenched by cooling the autoclave in an ice bath and depressurizing. During cooling, some vapors condensed outside the liner. This liquid was carefully collected and added to the catalytic mixtures in the liner. After addition of the internal standard (~160 mg of *p*-xylene) these mixtures were analyzed by gas chromatography on a Hewlett-Packard 4890/II equipped with a 3396/II HP integrator using a HP5 (5% phenylmethylsilicone) column (30 m × 0.53 mm). The products were identified using GC/MS HP 5971A. For the determination of the conversions as functions of time, the internal standard

Table 1  
The experimental parameters of significant catalytic runs

Run	g sub	mmol sub	T (°C)	P (atm)	mmol cat.	[cat.]	sub/cat.	mg aldehyde	mmol aldehyde	mg alcohol (%)	mmol alcohol	conv. (%)	select.	TON	TOF
27	2.66	23.75	100	20	2.59E-02	0.0017	916	226	1.59	0	0	6.7	100	61.3	0.68
14	2.6	23.21	100	40	2.18E-02	0.0015	1065	437	3.08	3	0.021	13.4	99.3	141.3	1.57
13	2.6	23.21	100	60	2.26E-02	0.0015	1026	821	5.78	0	0	24.9	100	256	2.84
26	2.66	23.75	100	80	2.40E-02	0.0116	988	1380	9.72	10	0.069	41.3	99.3	404	4.49
36	2.66	23.75	100	100	2.26E-02	0.0015	1050	1809	12.74	9	0.063	54.0	99.5	563	6.26
37	2.66	23.75	100	120	2.26E-02	0.0014	1072	1889	13.3	9	0.063	56.4	99.5	601	6.67
28	2.66	23.75	25	60	2.17E-02	0.0014	1096	0	0	0	0	0	—	0	0
29	2.66	23.75	50	60	2.36E-02	0.0015	1029	0	0	0	0	0	—	0	0
30	2.66	23.75	75	60	2.36E-02	0.0016	1008	98	0.69	0	0	2.9	100	29.3	0.033
13	2.6	23.21	100	60	2.26E-02	0.0015	1026	821	5.78	0	0	24.9	100	256	2.84
32	2.66	23.75	125	60	2.50E-02	0.0017	951	2007	14.13	117	0.813	62.9	94.6	566	6.29
13	2.6	23.21	100	60	2.26E-02	0.0015	1026	821	5.78	0	0	24.9	100	256	2.84
31	2.66	23.75	100	60	5.18E-02	3.50E-04	4582	498	3.51	0	0	14.8	100	677	7.52
35	2.6	23.75	100	60	2.36E-04	1.60E-04	10080	329	2.32	0	0	9.8	100	985	10.94
34	2.66	23.75	100	60	4.71E-04	3.1E-05	50398	296	2.08	0	0	8.8	100	4414	49.04
78	2.66	23.75	100	40	2.26E-02	0.0015	1050	350	2.46	2	0.014	10.4	99.4	109	1.21
79	2.66	23.75	100	50	2.21E-02	0.0015	1072	621	4.37	4	0.028	18.5	99.4	197	2.19
13	2.6	23.21	100	60	2.26E-02	0.0015	1026	821	5.78	0	0	24.9	100	256	2.84
80	2.66	23.75	100	70	2.21E-02	0.015	1072	1570	11.06	6	0.042	46.8	99.6	499	5.55
82	2.66	23.75	100	80	2.36E-02	0.0016	1778	121.52	7	7	0.049	52.9	99.6	531	5.9

was added at the beginning of the run, and samples of the liquid phase were spilled at fixed times. In this case the amounts of aldehyde are slightly underestimated, probably because of the different volatilities of the components.

Typical conditions are described for run 13, which was therefore chosen as reference reaction. In Table 1 are summarized the results obtained with  $\text{Na}_2[\text{Rh}_{12}(\text{CO})_{30}]$  as catalytic precursor under various experimental conditions.

### 3. Results

#### 3.1. The standard reaction

Run 13 was performed at  $100^\circ\text{C}$ , under 30 atm of  $\text{H}_2$  and 30 atm of CO, and an olefin/catalyst molar ratio of near 1000. After 90 min a conversion of 24.9% was observed, with a very high selectivity to the linear aldehyde 3,5,5-trimethylhexanal (> 99%). From these figures a turnover frequency (TOF) of  $2.84 \text{ mol mol}^{-1} \text{ min}^{-1}$  could be determined. All tests were stopped at constant reaction time, in order to compare the rates. Whenever the conversions are low (< 15%), it can be assumed that the amounts of the reagents (hence the rates) are constant. However, the reaction time could not be shortened below 90 min, since at the very beginning of the runs unrepro-

ducible data were obtained, probably because of the long time of heating of the apparatus.

Complete conversion of the substrate under standard conditions can not be reached even after 8 h. The percentages of alkene and products as a function of time are plotted in Fig. 1; the concentration of alcohol is negligible at the beginning of the reaction, but becomes detectable after 6 h.

#### 3.2. Ion pairing

The reactivity of transition metal carbonyl anions can be modified by the counterions: alkaline cations strongly interact with the CO oxygen atoms, reducing the electron density at the metal center, whereas the bulky  $[\text{N}(\text{PPh}_3)_2]^+$  cation has a large delocalized charge and is not involved in ion pairing. The coordination to alkaline ions is relevant in THF, a solvent with a low dielectric constant [9]. Therefore, some dependence from the cation was expected and confirmed by running two tests with the same molar amount of  $\text{Na}_2[\text{Rh}_{12}(\text{CO})_{30}]$  or  $[\text{N}(\text{PPh}_3)_2][\text{Rh}_{12}(\text{CO})_{30}]$  in identical conditions. The sodium salt was found to be more active (TOF 2.84 versus 2.0). Although the rate of CO insertion is increased by  $\text{Na}^+$  [9], the observed promotion is better explained considering that, the equilibrium of Eq. (1) being quickly attained, further demolition would be accompanied by build-up of negative charge on increasingly smaller metal complexes; the association with positive metal ions can offset this phenomenon, thus favoring formation of smaller fragments.

#### 3.3. Temperature dependence

The effect of the temperature is shown in Fig. 2. Under  $75^\circ\text{C}$ , the reactions have a negligible rate, and even at this temperature the products can be hardly detected. Above  $75^\circ\text{C}$  the effect is dramatic, and the TOF is increased by a factor of 2.21 by rising the temperature from 100 to

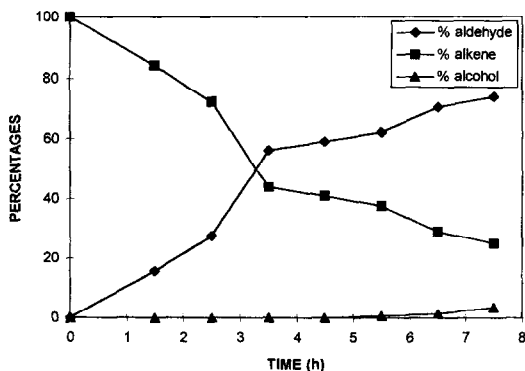


Fig. 1. The product distributions versus time.

RUN	Temp (°C)	mmol aldehyde	% conversion	% selectivity	TON	TOF
28	25	0	0	-	0	0
29	50	0	0	-	0	0
30	75	0.69	2.9	100	29.3	0.33
13	100	5.78	24.9	100	256	2.84
32	125	14.13	62.9	94.6	566	6.29

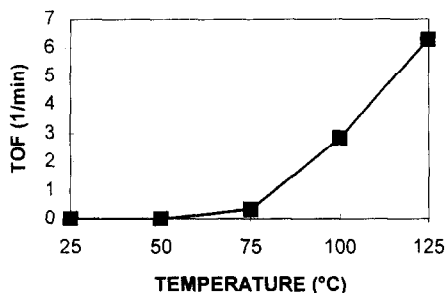


Fig. 2. The effects of temperature on the TOF.

125°C. However, loss of selectivity is also seen, and significant amounts of 3,5,5-trimethyl-1-hexanol are formed.

### 3.4. IR analyses

The reaction mixtures were routinely analyzed by IR spectroscopy *immediately* after depressurizing the autoclave. When low CO pressures were employed (10–20 atm), the prevalent cluster in solution was the acyl derivative  $[\text{Rh}_6(\text{RCO})(\text{CO})_{15}]^-$  ( $\nu(\text{CO})$  at 2080, 2040, 2020, 1820, 1785, 1775, 1725, 1655  $\text{cm}^{-1}$ ) [10], which is probably formed by oxidative addition of  $\text{H}_2$  to the precursor, with concomitant cleavage of the bridged Rh–Rh bond, followed by insertion of the olefin and CO. When higher CO pressures were used,  $[\text{Rh}_5(\text{CO})_{15}]^-$  ( $\nu(\text{CO})$  at 2044, 2010, 1871, 1840, 1787  $\text{cm}^{-1}$ ) was detected as the only carbonyl rhodium complex. This latter observation was expected, knowing the high stability of  $[\text{Rh}_5(\text{CO})_{15}]^-$  in the range 1–1000 atm of CO [11].

No bands in the IR spectrum could be assigned to mononuclear Rh species such as  $[\text{Rh}(\text{CO})_4]^-$  ( $\nu(\text{CO})$  at 1895  $\text{cm}^{-1}$ ) [12] or  $[\text{RCORh}(\text{CO})_4]$  ( $\nu(\text{CO})$  at 2111, 2065, 2039, 2020, 1698  $\text{cm}^{-1}$  in hexane) [13]. However, the latter complex decomposes rapidly at CO pressures lower than 20 atm [13], and its presence under catalytic conditions cannot be excluded.

### 3.5. Dependence from the partial pressure of CO

The effect of the pressure of carbon monoxide was studied running a series of reactions at constant  $p(\text{H}_2) = 30$  atm and varying the CO pressure in the range 10–50 atm. The results are shown in Fig. 3.

The hydroformylation reactions are usually inhibited by high pressures of CO, when using mononuclear catalysts [14,15]. Therefore, it has been established that the rate-determining step involves a dissociation of a carbonyl ligand from the precursor; however, if a cluster is used, a different kinetic equation can be observed; for example, Csontos et al. found that the order of reaction with respect to CO is 0, when using  $\text{Rh}_4(\text{CO})_{12}$  and an unreactive olefin, such as cyclohexene, and inferred that a pre-equilibrium, involving CO addition, was involved [14,16].

It is known that, even in a composite reaction, a bilogarithmic plot of the initial rate of reaction versus the concentration of the reagents should be linear, and the slope of the straight line gives the order of the reaction [17]:

$$v = k[\text{A}]^a[\text{B}]^b \dots \quad (4)$$

$$\ln v = \ln k + a \ln[\text{A}] + b \ln[\text{B}] \quad (5)$$

Therefore, we reported the turnover frequencies versus CO pressure in such a plot, and obtained a very good linear correlation ( $R = 0.98$ ) in the range 10–50 atm, with a slope of 1.02. This last value could not be taken for granted, since (a) the *average* rather than the *initial* rates were determined, and (b) it is highly unlikely that

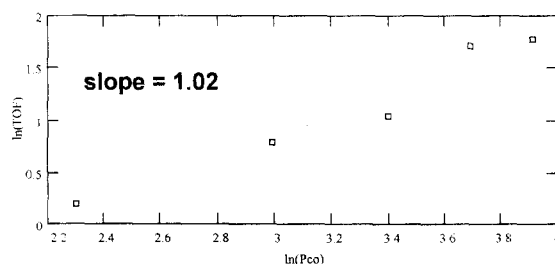


Fig. 3. The effect of the CO pressure on the TOF.

there is a linear relationship between the partial pressure of CO and the concentration of the gas in solution in the large range investigated. Nevertheless, our data quite convincingly show that the hydroformylation in these conditions is promoted by carbon monoxide.

This effect suggests that, before the rate-determining step, addition of CO and, presumably, breakage of Rh–Rh bonds occurs. However, because of the linear correlation of TOF with CO pressure, without any trace of saturation up to 50 atm, the fragmentation that is responsible for such a behavior can not be ascribed to the well known equilibrium in Eq. (1), which is completely displaced to the right hand side even at the lowest CO pressures.

We must conclude, therefore, that even the hexa- and penta- nuclear species which are always detected by infrared spectra, are degraded under catalytic conditions.

### 3.6. Pressure dependence

The effect of the total pressure is also remarkable and shown in Fig. 4; the consequences for the selectivity are negligible, whereas the conversions can be increased almost linearly in the range 20–100 atm. Above this total pressure, saturation occurs, and markedly smaller variations of rates can be observed.

RUN	P (atm)	mmol aldehyde	% conversion	% selectivity	TON	TOF
27	20	1.59	6.7	100	61.3	0.68
14	40	3.08	13.4	99.3	141.3	1.57
13	60	5.78	24.9	100	256	2.84
26	80	9.72	41.3	99.3	404	4.49
36	100	12.74	54.0	99.5	563	6.26
37	120	13.30	56.4	99.5	601	6.67

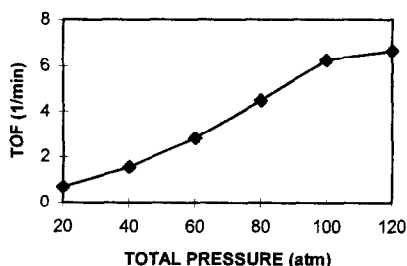


Fig. 4. The effects of the total pressure (CO/H<sub>2</sub> = 1) on the TOF.

RUN	olefin/cat	mmol aldehyde	%conversion	%selectivity	TON	TOF
13	1026	5.78	24.9	100	256	2.84
31	4574	3.51	14.8	100	677	7.52
35	10063	2.32	9.8	100	985	10.9
34	50313	2.08	8.8	100	4414	49.0

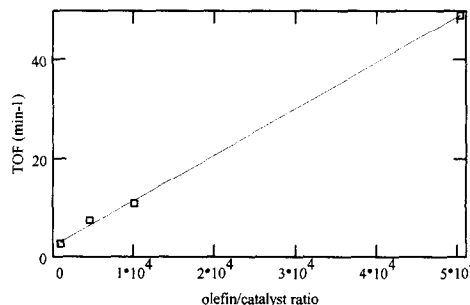


Fig. 5. The effects of the catalyst concentration on TOF.

### 3.7. Catalyst concentration

A decrease in turnover frequencies with increasing cluster concentration indicates that catalysis involves species of lower nuclearity since, on dilution, the equilibrium of fragmentation of a polynuclear species would be shifted to the right. Therefore, the dependence of TOF from precursor concentration was suggested as a diagnostic test to infer the real nature of the active catalyst [18].

The strictly linear plot of TOF versus the catalyst concentration is presented in Fig. 5. This nice dependence implies that the concentration (or nature) of the catalytically active species varies with dilution but it does not have other mechanistic relevance. Much more informative is the bilogarithmic plot of the conversion (the time of reaction being constant, this is a good estimate of the rate) versus the catalyst concentration. From least square fitting, the order of reaction toward the catalyst can be computed to be  $\sim 0.3$ , significantly lower than 1. This value is indeed indicative of fragmentation [19] and is therefore in keeping with the order toward CO. Also this behavior should be ascribed to the clusters which were detected by IR and not to  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ , which is virtually absent in solution.

#### 4. Conclusions

We have shown that  $\text{Na}_2[\text{Rh}_{12}(\text{CO})_{30}]$ , being readily and completely fragmented under mild conditions, is a valuable catalytic precursor for the hydroformylation of 2,4,4-trimethyl-1-pentene, yielding both high conversions and high selectivity. However, the equilibrium of Eq. (1) is not the only one responsible for the catalytic behavior. The order of the reaction toward CO, the increase of TOF when reducing the concentration of precursor, together with IR evidences lead to the conclusion that also  $[\text{Rh}_6(\text{RCO})(\text{CO})_{15}]^-$  and  $[\text{Rh}_5(\text{CO})_{15}]^-$  should participate to yield active species. The latter degradation, however, is far from being directly detectable, since the pentanuclear cluster is very robust under high pressures of CO.

The hydroformylation of the same olefin carried by pure, isolated,  $[\text{Rh}_5(\text{CO})_{15}]^-$  is currently investigated.

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