Inorganica Chimica Acta, *156* (1989) 285–289

Synthesis of Triangular [$RhM_2cp_3(CO)_n$] Clusters (M = Ni, n = 2; M = Fe, n = 4; M = Mo, W, n = 6). [$RhMo_2cp_3(CO)_6$] as Catalyst Precursor in the CO Hydrogenation Reaction

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(Received January 15, 1988; revised July 28, 1988)

Abstract

Different synthetic routes to triangular clusters [$RhM_2cp_3(CO)_n$] (M = Ni, $n = 2$; M = Fe, $n = 4$; M = Mo, W, $n = 6$) were studied. The clusters obtained were characterized by spectroscopic means (IR, ^1H and ^{13}C NMR, MS). The behaviour of a [$RhMo_2cp_3(CO)_6$] cluster-derived catalyst in CO hydrogenation reactions was studied in comparison to appropriate conventionally prepared bimetallic and monometallic catalysts.

Introduction

Triangular metal clusters, although the most thoroughly investigated type of clusters of all [1], still enjoy considerable attention for many reasons. These include the development of synthetic strategies (e.g. [2–5]), the study of particular electronic states (e.g. [6–8]), the multisite activation of small molecules (e.g. [9, 10]), their application as homogeneous catalysts or catalyst precursors [11], their value as models for metal surfaces in the processes of chemisorption and catalysis [12] and as precursors of heterogeneous catalysts [13]. In the latter case, clusters are used to obtain high metal dispersions under mild conditions [14, 15], *i.e.* without reduction at higher temperatures, which could result in a sintering of the metal. Significant differences were observed in the catalytic behaviour of conventionally prepared catalysts, *i.e.* by impregnation of inorganic supports with metal salt solutions, and of cluster-derived catalysts [16]. For bimetallic catalysts, the application of heteronuclear clusters results in the formation of highly dispersed catalysts with an intimate contact between the different metal atoms [15].

This work presents the synthesis and spectroscopic characterization of triangular clusters containing a RhM_2 core (M = Ni, Fe, Mo, W). The interest in these clusters is based on the intention of applying these clusters as heterogeneous catalyst precursors in the CO hydrogenation reaction.

While homonuclear clusters of the type [$M_3cp_3(CO)_n$] have been intensively investigated (M = Nb, $n = 7$ [17]; Co [18], Rh [19, 20], Ir, $n = 3$ [21]; Ni, $n = 2$ [22]), heteronuclear clusters are still rare ([$CoFe_2cp'cp_2(CO)_4$] ($cp' = C_5Me_5$) [23], [$CoNi_2cp_3(CO)_2$] [24]).

Bimetallic catalysts containing rhodium are of major importance for the selective hydrogenation of CO to give oxygenated products. The composition of these catalysts and their structure have a significant influence on the activity and selectivity in CO hydrogenation [25–28]. Molybdenum oxide is known to enhance the activity and to favour the formation of oxygen containing compounds [29–32]. In these studies molybdenum was used as the MoO_3-support itself [31, 32] or as salts with Mo in a high oxidation state [30, 32]. No heteronuclear RhMo clusters have been used up till now. The present work reports on the catalytic behaviour in the CO hydrogenation at 1 MPa of a catalyst derived from the new $RhMo_2$ cluster, compared with a catalyst prepared by conventional impregnation of the support with metal salt solutions.

Results and Discussion

Preparation

Clusters of the type [$RhM_2cp_3(CO)_{2n}$] may be synthesized by the routes according to the following equation. The molar ratio of the reactants is 1:1 except for the synthesis of **1** where a 1:2 ratio was necessary to increase the yield because of the formation of [$Nicp_2$] as a byproduct. **2** was also obtained in low yield by treatment of [$RhcodCl$]$_2$ (cod = 1,5-cyclooctadiene) or $RhCl_3 \cdot xH_2O$, respectively, with two or three equivalents of K[$Fecp(CO)_2$].

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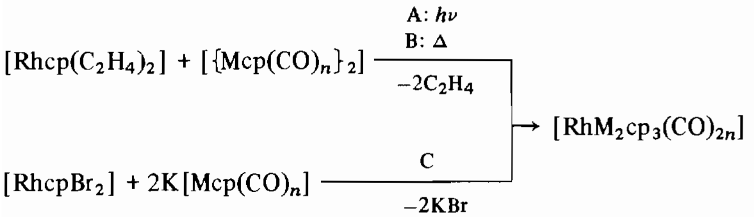

	1	2	3	4
M	Ni	Fe	Mo	W
n	1	2	3	3

The yields are generally low but the photochemical reactions have proved to be the best. Gentle heating to 55 °C improved the yield of **3** and **4** but not of **1** and **2**. The main reason for the low yield seems to be the formation of $[Rhcp(CO)_2]$ which is unable to form the clusters as proved by separate runs under the same conditions. In the analogous photochemical reactions of $[Ircp(C_2H_4)_2]$ with $[Mcp(CO)_n]_2$ (M = Ni, Fe, Mo) the formation of $[Ircp(CO)_2]$ dominated to such an extent that no clusters could be detected.

The thermal dissociation of the rhodium–ethylene bond needs about 115 °C (bond energy 130 kJ mol^{-1} [33]) but photochemically it takes place at room temperature. UV irradiation of $[Rhcp(C_2H_4)_2]$ in a CO saturated solution at room temperature quantitatively leads to $[Rhcp(CO)_2]$. Therefore, we believe that under photochemical conditions, loss of C_2H_4 occurs to form the unsaturated species [Rhcp]. This may attack the $[Mcp(CO)_n]_2$ complexes either forming the RhM_2 clusters or the byproduct $[Rhcp(CO)_2]$. A similar reaction pathway was discussed by Stone and coworkers [23] for the synthesis of CoM_2 clusters (M = Fe, Ru) with $[Cocp'(C_2H_4)_2]$ (cp′ = C_5Me_5) as precursor. The photochemical cleavage of the MM bond of the $[Mcp(CO)_n]_2$ complexes seems to be unimportant for these reactions because dinuclear RhM complexes and clusters with a Rh_2M core could not be found.

Characterization

1 forms deep-green, **2**–**4** form black crystals, which decompose without melting above 300 (**1**, **2**) and 200 (**3**, **4**) °C, respectively. In the solid state **1** and **2** remain stable in air for some days, **3** and **4** for some hours, but they are gradually decomposed in solution. For example, oxidation of **3** in $CHCl_3$ gives $[Rhcp(CO)_2]$ (ν(CO): 2051, 1987 cm^{-1} [34]) as well as the cyclopentadienyl molybdenum oxide derivatives $[MocpO_2]_2$, $[MocpO_2]O$ and $[MocpO_2Cl]$ (^1H NMR: δ 6.3–6.6 [35]) as indicated by the IR and NMR data, respectively.

Whereas the mass spectra (70 eV) of **3** and **4** do not exhibit the molecular peaks, the highest being those for $[RhMo_2cp_3]^+$ and $[RhW_2cp_3(CO)]^+$, respectively, those of **1** and **2** show the molecular peaks at 474 and 522 *m/e*, respectively, as well as the range of fragment ions resulting from the stepwise loss of carbonyl ligands.

The ^1H NMR spectra show a doublet for the cyclopentadienyl ligand attached to the rhodium atom due to the RhH coupling as well as a singlet of the intensity two for the cp ligands of both M atoms (Table 1).

TABLE 1. NMR and IR Data

	^1H NMR (δ (Hz))[a]			$^{13}C\{^1H\}$ NMR (ppm)[b]			IR (CH_2Cl_2 (cm^{-1}))[f]		
	Rhcp	^2J(RhH)	Mcp	t-CO	μ-CO	$μ_3$-CO	t-CO	μ-CO	$μ_3$-CO
1	5.48	0.8	5.28			not obs.			1746s
2	5.50	1.2	4.80		241.1 (Fe_2) 240.5 (RhFe)	266.6		1833vs 1767s, br	1673s
3	5.60	0.6	5.18	189.3, 187.7 (Mo)[c]	255.7 ($RhMo_2$)[d] 239.3, 239.7 227.7 (Mo_2)[c]		1978vs 1927s	1838vs 1752s	
4	5.53	0.5	5.30	187.3, 185.7 (W)[c]	246.9 (RhW_2)[e] 226.1, 223.5 216.2 (W_2)[c]		1970s 1920s	1830s 1750s	

[a] 1–3: CD_2Cl_2; 4: $CDCl_3$; [b] 1, 3, 4: CD_2Cl_2; 2: $CDCl_3$; [c] 193 K; [d] doublet, *J*(RhC) 22 Hz; [e] doublet *J*(RhC) 30 Hz; [f] s = strong, v = very, br = broad.

TABLE 2. Results of the CO hydrogenation of $RhMo/SiO_2$ [a]

Catalyst precursor	r (mmol g^{-1}, h^{-1}) CO cat.	C-selectivity (%)		
		h.c.	CH_3OH	C_2^+-oxyg.
$[RhMo_2cp_3(CO)_6]$	3.7	52	32	15
after reactivation (573 K air, 543 K H_2)	5.1	62	23	14
$RhCl_3 \cdot 3H_2O/(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	8.0	79	12	9
$RhCl_3 \cdot 3H_2O$	3.5	85	2	13
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	2.2	99	1	–

[a] 1.8 wt% Rh, atomic ratio Rh:Mo = 1:2, 523 K, 4000 h^{-1}, 1 MPa, $CO:H_2$ = 1:2.

The $^{13}C\{^1H\}$ NMR spectra of **1**–**4** (Table 1) at ambient temperature have two single resonances for the cp ligands in the intensity ratio 1:2. At 193 K **3** and **4** display three signals of equal intensity for these ligands (**3**: 94.5, 92.9, 92.7; **4**: 93.8, 92.5, 90.2 ppm) whereas these resonances remain essentially unchanged at low temperature in the case of the other compounds. No signal for the CO ligands of **1** could be observed even at 193 K but **2** gave resonances assigned to μ-CO and μ_3-CO ligands in the room temperature spectrum. The ^{13}C resonances of the CO ligands of **3** and **4** only appear in the low temperature spectra, and the six resonances are attributable to bridging and terminal CO ligands with one showing a ^{13}CRh coupling. The disappearance of these resonances at ambient temperature is probably due to a fast site-exchange of the bridging and terminal carbonyl ligands.

The IR spectra (Table 1) of **1** and **2** are similar to those of the analogous CoM_2 clusters [23, 24]. **1** exhibits only one CO band at 1746 cm^{-1} typical for a μ_3-CO coordination mode. **2** shows bands in the region of μ- and μ_3-CO ligands. These clusters are therefore described as $[RhNi_2cp_3(\mu_3\text{-}CO)_2]$ and $[RhFe_2cp_3(\mu_3\text{-}CO)(\mu\text{-}CO)_3]$, respectively. **3** and **4** have IR bands for terminal and bridging CO ligands.

The solid state spectra of both these clusters exhibit six bands by splitting both bands for the μ-CO ligands ((KBr) **3**: 1982 vs, 1903 s, br, 1836 s, 1811 s, 1766 s, 1745 s; **4**: 1979 vs, 1907 s, br, 1832 s, 1805 s, 1767 s, 1743 s) due probably, to lattice effects. No single cyrstals suitable for X-ray analysis have been obtained up to now.

CO Hydrogenation Reactions

The results of CO hydrogenation are summarized in Table 2. For comparison purposes we also included the corresponding results of the monometallic catalysts. The data in Table 2 show that the bimetallic salt-derived RhMo catalysts have a higher activity than the monometallic ones. Moreover, the selectivity towards oxygenated products is increased by the addition of Mo to the rhodium catalyst. This enhanced selectivity is due to the additional formation of methanol. While the C_2^+-oxygenates mainly consist of acetaldehyde in the case of the monometallic rhodium catalyst, on the bimetallic catalyst, ethanol is the main product. These results are in qualitative agreement with those of other authors with regard to the RhMo system [29–32]. The cluster-derived catalyst first decomposes in the reaction gas mixture. *In situ* FT-IR spectroscopic experiments showed that the primarily unchanged, weakly adsorbed cluster (Fig. 1a, b) is destroyed in flowing synthesis gas already at room temperature (Fig. 1c), [36]. During the decomposition another carbonyl compound is formed as a stable intermediate. According to the wave numbers at 2052 and 1987 cm^{-1} (Fig. 1c) it could be assigned to physically adsorbed $[Rhcp(CO)_2]$.

With increasing temperature the band doublet disappears (Fig. 1d) and at reaction temperature no more surface carbonyl species could be detected by infrared spectroscopy.

Decomposition processes were also observed at the beginning of the CO hydrogenation at 1 MPa in the flow reactor. Between 423 and 523 K decomposition products originating from the cyclopentadienyl ligands were obtained by GC analysis. At 523 K the decomposition is complete and the catalyst has a slightly smaller activity compared with the conventionally prepared samples but a significantly higher selectivity towards oxygenated products, reaching nearly 50% of the converted CO (Table 2). The enhancement of methanol formation is more pronounced than that of the C_2^+-oxygenates, which mainly consist of ethanol as in the case of the conventionally prepared bimetallic catalysts. At higher temperatures (573 K) the selectivity towards oxygenates decreases sharply (10%). A subsequent reactivation of the catalyst by oxidation in air (573 K) and reduction in flowing hydrogen (543 K) results in a

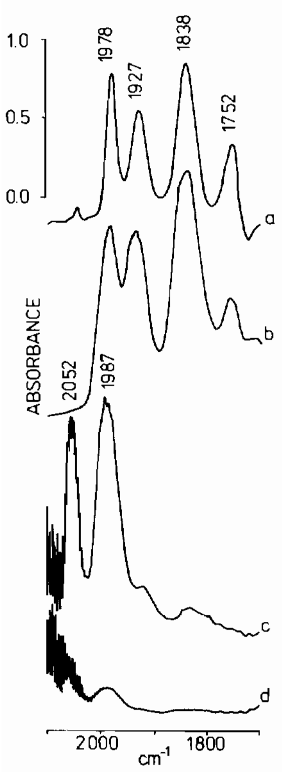

Fig. 1. Infrared spectra in the carbonyl stretching region: (a) [$RhMo_2cp_3(CO)_6$] in CH_2Cl_2 (×10); (b) [$RhMo_2cp_3(CO)_6$] on SiO_2 after evacuation at 298 K for 30 min; (c) after 10 min in flowing synthesis gas (0.1 MPa, CO:H_2 = 1:2, 21 h^{-1}) at 298 K; (d) after 30 min in synthesis gas at 373 K.

small decrease of the selectivity towards oxygenates, but it is still significantly higher than for conventionally prepared catalysts.

Experimental

Synthesis

All reactions were carried out anaerobically using conventional Schlenk techniques. Solvents were dried, deoxygenated, and distilled just prior to use. Starting materials were prepared according to known procedures: [$Rhcp(C_2H_4)_2$] [37], [$RhcpBr_2$] [38], [$M_2cp_2(CO)_n$] M = Ni [39], M = Fe [39], M = Mo [40], M = W [40], K[$Mcp(CO)_n$] M = Mo [41], M = W [41], [$Ircp(C_2H_4)_2$] [42].

The photochemical reactions were performed in an irradiation vessel (200 ml) fitted with an internal water-cooled quartz finger, to house the medium-pressure mercury lamp. The details for the preparation of **1**–**4** are given in Table 3.

Method A

[$Rhcp(C_2H_4)_2$] and [$Mcp(CO)_n]_2$ were dissolved in 200 ml THF, and the solution was irradiated for 50 h. Subsequently the solvent was removed *in vacuo*, and the residue was dissolved in a minimum quantity of CH_2Cl_2 and chromatographed.

Method B

The starting materials were refluxed in 70 ml of hexane (**1**) and toluene (**2**–**4**), respectively. The work-up was performed as described above.

TABLE 3. Preparation of **1**–**4**

No.	Method	[$Rhcp(C_2H_4)_2$] or [$RhcpBr_2$] (mg (mmol))	[{$Mcp(CO)_n$}$_2$] or K[$Mcp(CO)_n$] (mg (mmol))	Reaction conditions	Yield (%)	Analysis (%) found (calc.) C	H
1	A	200 (0.89)	540 (1.78)	UV, r.t.	3.5	42.69 (43.28)	3.38 (3.18)
	B	200	540	100 h	4.0		
2	A	200	316 (0.89)	UV, r.t.	9.0	43.91 (43.72)	2.67 (2.88)
	B	200	316	8 h	6.0		
	C	556 (1.5)	600 (3.0)	−60 °C	4.5		
3	A	224 (1.0)	490 (1.0)	UV, 55 °C	28.0	38.82 (38.28)	2.67 (2.28)
	B	224	490	8 h	10.0		
	C	500 (1.5)	850 (3.0)	−25 °C	1.4		
4	A	224 (1.0)	660 (1.0)	UV, 55 °C	27.0	29.96 (30.23)	2.01 (1.80)
	B	224	660	8 h	16.0		
	C	500 (1.5)	1115 (3.0)	−25 °C	2.0		

Method C

[RhcpBr$_2$] was added to the solution of the corresponding K[Mcp(CO)$_n$] in 70 ml THF, and the mixture was stirred for 30 min. The work-up was analogous.

Separation of the reaction products was achieved by column chromatography on silica gel (Merck 0.2–0.5 mm, column 2 × 30 cm). Three bands were eluted, the first (hexane) being a yellow band which was identified as [Rhcp(CO)$_2$] in a yield of up to 50%, the second red band (hexane/toluene 1:1) being [Mcp(CO)$_n$]$_2$ in about 50% yield, and the third either a dark-green (**1**) or brown (**2**–**4**) band (hexane/acetone 2:1) being the corresponding cluster. In the case of the preparation of **1** the first band is followed by an additional green band (hexane) of [Nicp$_2$] (yield of about 10%). **1**–**4** were recrystallized from CH_2Cl_2/heptane.

Catalyst Preparation and CO Hydrogenation Reactions

In order to prepare the heterogeneous catalyst, the RhMo$_2$ cluster was deposited on the support by anaerobic impregnation from a CH_2Cl_2 solution. The support used was Aerosil 200 (Degussa) with a surface area of 200 m^2 g^{-1}. The solvent was removed by evacuation at room temperature and the catalyst transferred to the reactor without air contact. The cluster-derived catalyst was used in the CO hydrogenation without further pretreatment.

The conventionally prepared catalysts were obtained by using the method of incipient wetness. An aqueous solution of $RhCl_3 \cdot 3H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was added to the silica and the solvent was removed by drying in air at 393 K. The dried catalysts were reduced in flowing hydrogen at 673 K for 2 h in a glass reactor.

A stainless-steel medium-pressure reactor was used to study the carbon monoxide hydrogenation. The reaction products were analysed in a GC system. All catalysts were measured under the following reaction conditions: $P = 1$ MPa, GHSV = 4000 h^{-1}, $H_2/CO = 2$.

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