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The homogeneous hydrogenation of carbon–carbon multiple bonds with heteronuclear platinum clusters

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The heteronuclear platinum clusters

$$Pt_2Co_2(CO)_8(PPh_3)_2 \quad \text{and} \quad Pt(C_6H_{11}NC)_2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$$

are poor catalysts for the hydrogenation of olefins and internal acetylenes, but they show a reasonable activity for the hydrogenation of terminal acetylenes. In this latter case the selectivity towards olefins is low.

Whereas the $PtMo_2$ cluster can be recovered unaltered from the reaction mixture, the Pt_2Co_2 cluster undergoes rather complex molecular rearrangements, which take place under the catalytic conditions.

Finally the Pt_2Co_2 cluster, under well defined conditions, may act as a catalyst for the selective hydrogenation of diphenylacetylene to *cis*-stilbene.

1. Introduction

In the last few years molecular metallic clusters have been proposed as models of very small metallic particles such as those of highly dispersed supported metallic catalysts (Basset & Ugo 1977). However, even for a relatively simple catalytic reaction such as the hydrogenation of C–C multiple bonds it was reported that the activity of polynuclear metal clusters is usually less than that found for mononuclear metal complexes or for heterogeneous metallic catalysts. In addition, firm evidence that the original metal frame of the cluster is maintained unaltered under the catalytic conditions is difficult to acquire (Laine 1982; Smith & Basset 1977).

Metal clusters act as homogeneous catalysts usually under rather severe conditions (e.g. high temperature, high pressure, or both); this low intrinsic activity can be attributed to various factors. A major cause of the lack of catalytic activity of metal clusters under mild conditions could be the coordinative saturation of the metal atoms in the cluster frame (Norton 1977; Laine 1982). With this in mind, we have carried out an investigation on the hydrogenation of unsaturated C–C bonds catalysed by some heteronuclear platinum clusters that have one or more formally coordinatively unsaturated platinum atoms. Examples are the butterfly structure of $Pt_2Co_2(CO)_8(PPh_3)_2$ and the linear structure of *trans*-PtL_2M_2, ($L = C_6H_{11}NC$, pyridine or pyridine derivatives, $M = Co(CO)_4$, $Fe(NO)(CO)_3$, $Mo(CO)_3(\eta^5\text{-}C_5H_5)$) or the triangular structure of $PtCo_2(CO)_7DPE$ (Braunstein & Dehand 1970; Braunstein *et al.* 1970, 1975; Dehand & Nennig 1974; Barbier & Braunstein 1978; Pearson & Dehand 1969).

The choice of mixed heteronuclear platinum clusters was prompted by the report that the formation of heteronuclear platinum–metal bonds (e.g. Pt–Sn bonds) enhances the properties of platinum complexes as hydrogenation catalysts (Coffey 1970).

2. Hydrogenation of olefins

We studied the clusters listed above under the following range of the reaction parameters: variation of temperatures from 25 to 100 °C; variation of hydrogen pressures up to 100 atm; variation of molar ratio of substrate to catalyst from 10 to 100 and variation of reaction times from few hours up to 40 h.

Table 1. Hydrogenations catalysed by $Pt_2Co_2(CO)_8(PPh_3)_2$

($[Cat] = 3.3 \pm 0.5$ mm; $[Sub]/[Cat] = 110 \pm 10$; $T = 50$ °C; the solvent was toluene unless otherwise stated.)

substrate	reaction time/h	pressure/atm	percentage conversion†	percentage isomerization	percentage hydrogenation
1-octene	40	33	47	43	4
cyclohexene	40	35	6 ± 1	—	6 ± 1
cyclooctene‡	20	50	4 ± 1	—	4 ± 1
1,3-cyclooctadiene‡	20	50	1.5	—	1.3 (0.2)§
1,5-cyclooctadiene‡	20	50	6.4	2 (0.9)¶	3.3 (0.2)§
styrene	20	50	3–4	—	3–4†

† In some catalytic runs higher conversions (*ca.* 10–30 %) have been obtained, but data were not reproducible and a metallic solid separated.
‡ With benzene as solvent.
§ Double hydrogenation to alkane in parentheses.
¶ Isomerization to 1,4-cyclooctadiene in parentheses.

Table 2. Hydrogenations catalysed by $Pt(C_6H_{11}NC)_2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$

($[Cat] = 3.0 \pm 0.4$ mm; $T = 50$ °C; reaction time = 20 h; $[Sub] = 0.3 \pm 0.04$ M; the solvent was toluene unless otherwise stated; pressure = 48 ± 2 atm.)

substrate	percentage conversion	percentage isomerization	percentage hydrogenation
styrene†	2.6	—	2.6
1,3-cyclooctadiene‡	2.9	—	2.9
1-octene§	8	6.5	1.5

† With a reaction time of 65 h the conversion rises to 10.5 %; under a pressure of 70 atm for 20 h the conversion rises to 13 ± 1 %.
‡ With benzene as solvent.
§ $[Sub]/[Cat] = 50$.

Some compounds (e.g. $PtL_2[Fe(NO)(CO)_3]_2$ and $PtL_2[Co(CO)_4]_2$, where L = $C_6H_{11}NC$ or pyridine, and $PtCo_2(CO)_7DPE$) do not show any catalytic activity for isomerization or hydrogenation of olefins under all the reaction conditions investigated. $Pt_2Co_2(CO)_8(PPh_3)_2$ (**1**) isomerizes 1-octene under 1 atm of hydrogen at room temperature. More drastic conditions increase both the hydrogenation and isomerization properties of **1** and $Pt(C_6H_{11}NC)_2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (**2**). We have examined in detail the behaviour of these two catalysts by carrying out an extended investigation on the hydrogenation of non-activated and activated terminal monoolefins, of cyclic internal olefins and of cyclic diolefins under the following standard conditions: temperature about 50°C, hydrogen pressure about 50 atm, molar ratio of substrate to catalyst about 100, reaction time between 20 and 40 h. The results are reported in tables 1 and 2. Both clusters are very poor hydrogenation catalysts towards all olefins studied, although they catalyse the isomerization of 1-octene to a major extent.

Catalyst **2**, with a $PtMo_2$ metallic frame, can be completely recovered; infrared and thin-layer investigations did not show formation of any other metal complexes. On the other hand, an extended transformation and rearrangement was found for catalyst **1**, which has the Pt_2Co_2 metallic frame. The examination of the nature of the metal complexes recovered after the catalytic runs showed the quantitative transformation of the original cluster **1** into the known platinum cluster $Pt_5(CO)_6(PPh_3)_4$ (Barbier *et al.* 1978) and a series of cobalt complexes.

We could not isolate other platinum complexes, even in trace quantities. This unusual kind of disproportionation of the original heteronuclear Pt_2Co_2 cluster cage is not only independent of the nature of the olefin, but occurs only in the presence of both excess of olefin and of hydrogen pressure. In fact cluster **1** remains rather stable when maintained under 50 atm H_2 at 50 °C for 20 h (but in the absence of olefin) or when the olefin is added (but the pressure of H_2 is replaced by a similar pressure of N_2).

TABLE 3. HYDROGENATIONS OF TERMINAL ACETYLENES

([Cat] = 2.9 ± 0.3 mM; [Sub]/[Cat] = 110 ± 10; T = 50 °C; pressure = 50 atm; time = 20 h; the solvent was toluene.)

catalyst	substrate	percentage conversion	percentage monohydrogenation	percentage dihydrogenation	percentage oligomerization
$Pt(C_6H_{11}NC)_2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$	$PhC{\equiv}CH$	98	63	33	2
$Pt(3Mepy)_2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$	$PhC{\equiv}CH$	45†	9.5	0.5	35
$Pt(C_6H_{11}NC)_2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$	$nC_6H_{13}C{\equiv}CH$	95	34	61	—
$Pt_2Co_2(CO)_8(PPh_3)_2$	$Ph\text{-}C{\equiv}CH$	39†	19	3.2	16.8
$Pt_2Co_2(CO)_8(AsPh_3)_2$	$Ph\text{-}C{\equiv}CH$	40†	10	1.3	28.7
$Pt_5(CO)_6(PPh_3)_4$	$Ph\text{-}C{\equiv}CH$	100†	3	53	44
$Pt_2Co_2(CO)_8(PPh_3)_2$	$nC_6H_{13}C{\equiv}CH$	98†	55	43	—
$Pt_5(CO)_6(PPh_3)_4$	$nC_6H_{13}C{\equiv}CH$	98	10	88	—

† The i.r. spectrum (ν_{CO}) of the catalyst after the reaction is changed.

TABLE 4. HYDROGENATIONS OF DIPHENYLACETYLENE†

([Cat] = 2.9 ± 0.3 mM; [Sub]/[Cat] = 110 ± 10; T = 50 °C; pressure = 50 atm; time = 20 h; the solvent was toluene.)

catalyst	percentage conversion	percentage monohydrogenation	percentage dihydrogenation
$Pt(C_6H_{11}NC)_2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$	2.4	2.4‡	—
$Pt_2Co_2(CO)_8(PPh_3)_2$§	24	23‡	1
$Pt_5(CO)_6(PPh_3)_4$§	55	52.5‡	2.5

† The substrate $EtOOC\text{-}C{\equiv}C\text{-}COOEt$ is not hydrogenated; no oligomers are found in the hydrogenation of $Ph\text{-}C{\equiv}C\text{-}Ph$ under these conditions.
‡ Selectivity of more than 95 % to the *cis* isomer.
§ The i.r. spectrum (ν_{CO}) of the catalyst after the reaction is changed.

Because the only platinum product formed in this transformation is the cluster $Pt_5(CO)_6(PPh_3)_4$ (**3**), we have examined its catalytic properties under our standard conditions. The results are comparable with those found by using **1** as catalyst, but $Pt_5(CO)_6(PPh_3)_4$ can be recovered unaltered from the reaction mixture. Infrared and thin-layer investigations did not show the presence of any other complexes. Under our conditions, the decomposition of the platinum clusters to metals is negligible, but we observed extensive decomposition at higher temperatures and pressures.

Although it is very difficult to ascertain the presence of very small amounts of very dispersed colloidal metals (Laine 1982), in few experiments the formation of very limited amounts of colloidal metals was confirmed by using the Maitlis methodology (Hamlin *et al.* 1980). We did find some hydrogenation activity due to metal left on the cellulose, but the product distribution was so different from that found with the original or recycled metal complexes that the catalytic activity shown in tables 1 and 2 must be ascribed mainly to a true homogeneous process. In addition, we could not detect any hydrogenation of the aromatic rings either of styrene or of the aromatic solvents (toluene or benzene). This observation supports a true homogeneous process, because it is known that colloidal or very dispersed platinum particles are active catalysts for aromatic hydrogenation under our standard reaction conditions.

3. HYDROGENATION OF ACETYLENES

The results of the catalytic hydrogenations of terminal acetylenes ($C_6H_5C{\equiv}CH$ and n-$C_6H_{13}C{\equiv}CH$) and internal acetylene (C_6H_5-$C{\equiv}C$-C_6H_5) by catalysts **1**, **2** and **3** are given in tables 3 and 4. The internal acetylene ($COOC_2H_5$-$C{\equiv}C$-$COOC_2H_5$) was not hydrogenated by any of the clusters that we examined. All the clusters used are rather active in the hydrogenation of the terminal acetylenes. Whereas catalyst **2** is recovered unaltered from the reaction mixture, catalyst **1**, and its $AsPh_3$ homologue, and catalyst **3** transform into new species with very different infrared spectra in the ν_{CO} region.

We have so far been unable to characterize the nature of these new species; it is interesting that these new metal carbonyl complexes are also good hydrogenation catalysts for mono-olefins because they readily hydrogenate styrene. This explains why catalysts **1** and **2** are not selective catalysts for hydrogenation of terminal acetylenes to olefins, although this would be expected in view of their poor ability to hydrogenate olefins. The fast *in situ* formation of new catalytic species before hydrogenation of acetylenes to olefins is supported by the complete absence of any isomerization of 1-octene, a reaction that is easily catalysed by both original catalysts **1** and **2**.

In conclusion, we propose that new species are formed by the interaction between the original clusters and the terminal acetylenes; these new complexes are the active hydrogenation catalysts.

We have also observed during the hydrogenation of $C_6H_5C{\equiv}CH$ with catalysts **1** and **3** a secondary reaction that causes the oligomerization of phenylacetylene. Such oligomerization reactions do not occur with n-$C_6H_{13}C{\equiv}CH$, suggesting that the acidity of the acetylenic hydrogen must play a role in controlling the oligomerization process. With catalyst **2**, which has the linear $PtMo_2$ frame, the selectivity of the hydrogenation is also quite poor, but we could not detect any oligomerization with any of the terminal acetylenes investigated. Because the original complex was always recovered unaltered, the lack of selectivity is quite unexpected in view of its poor hydrogenating properties towards olefins (see table 2). We suspect that this catalyst develops, in the presence of terminal acetylenes, a specific activity for olefin hydrogenation. Catalysts **1** and **3** are active towards the hydrogenation of internal acetylenic compounds such as diphenylacetylene C_6H_5-$C{\equiv}C$-C_6H_5 (table 4). They show a remarkable and selective formation of *cis*-stilbene, together with a complete absence of any oligomerization reaction.

Catalyst **2** has poor activity, although it has a high selectivity towards *cis*-stilbene. It must be pointed out also that although catalyst **2** is recovered quantitatively from the reaction mixture catalysts **1** and **3** transform into new carbonyl species. We suppose that these new species, which are generated by the interaction of diphenylacetylene with catalysts **1** and **3**, are related to the real hydrogenation catalytic entities.

4. CONCLUSION

This investigation was initiated on the basis that the presence of coordinatively unsaturated metal atoms in a molecular metal cluster could cause high catalytic activities. However, our work does not confirm that the presence of coordinatively *open* platinum atoms in the cluster cages is related to high activities. In fact, under conditions used for olefin hydrogenation, the original cluster rearranges to new clusters that do not have coordinatively *open* platinum atoms in its metallic cage. Obviously in this case a low catalytic activity is expected. With terminal and internal acetylenes the interaction of the substrates with the original clusters produces new species, which are quite active towards the hydrogenation of acetylenes and olefins. Although we could not characterize these new active species, the disappearance in their i.r. spectra of bridging carbonyl groups suggests that mononuclear species are formed. The relatively high catalytic activities observed can be attributed to such species. In conclusion, we could not confirm our hypothesis because the original clusters are unstable under catalytic conditions.

The particular case of the high activity for the hydrogenation of terminal acetylenes by catalyst **2**, with a linear $PtMo_2$ frame, is worthy of discussion because the original cluster structure is maintained unchanged.

We could not find a parallel high activity for the hydrogenation of internal acetylenes. We therefore conclude that the slightly acidic hydrogen atom of the acetylene must be involved in the catalytic process as a 'co-catalytic' entity. This is not unexpected because it is well known that weak protonic substances may act as co-catalysts in homogeneous catalytic processes. In our case we suspect that the co-catalytic action must be related to the facile oxidative addition of the terminal acetylene to the formally platinum (II) centre to form an active platinum hydride when compared with the known difficult oxidative addition of the hydrogen molecule to platinum (II) centres (Roundhill & Jonassen 1968). This suggestion would explain the low activity displayed by catalysts **2** towards olefins and internal acetylenes (difficult activation of molecular hydrogen) compared with the high activity found with thermal acetylenes (easy formation of an intermediate active metal hydride). It is well known that the formation of active metal hydrides is necessary for a catalytic activity of hydrogenation.

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