

Some aspects of the chemistry of platinum carbonyl clusters

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Abstract. Different aspects of the work carried out on the Chini-clusters are reviewed here. These are: (1) the uses of platinum clusters for the synthesis of hetero-metal clusters, (2) platinum clusters as mediators in *pH*-driven transport of sodium ions and electrons through a liquid membrane, and (3) asymmetric hydrogenation of α -ketoesters with cluster derived heterogeneous catalysts.

Keywords. Platinum carbonyl clusters; Chini-clusters; asymmetric heterogeneous catalysts.

1. Introduction

The platinum carbonyl clusters of the general formula $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = \sim 10, 6, 5, 4, 3, 2, 1$) were first reported by Longoni and Chini (1976). Subsequently, other high nuclearity platinum carbonyl clusters that do not belong to this family have been synthesised, structurally characterised and studied (Roth *et al* 1992). We have studied the applications of the Chini-clusters in the synthesis of hetero-metal clusters, *pH* driven redox reactions and transport, and as precursors for asymmetric heterogeneous catalysts (Bhaduri *et al* 1984, 1987, 1992). In this paper we review some of these results.

2. Results and discussion

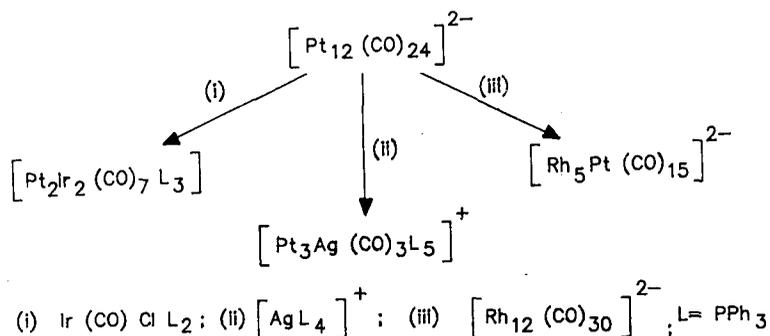
2.1 Heterometal clusters

As shown in scheme 1, the Chini-clusters are useful sources of platinum atoms for the syntheses of mixed metal clusters. Apart from the three clusters shown in the scheme, all of which were characterised by X-ray, other high nuclearity clusters are also formed. Thus reaction (ii) yields a 'Pt₆Ag' cluster while the reaction of Hg(OAc)₂ with $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ gives a cluster with a 'Pt₆Hg' core. Both these tentative formulations are based on analytical data. Suitable single crystals for X-ray structures have not yet been obtained.

2.2 *pH*-driven transport and redox reactions

Controlled transport of electrons and alkali metal ions across cell membranes is of fundamental importance in biological processes. Electron transport is known to be accompanied by a *pH*-gradient. The redox properties of the platinum clusters could

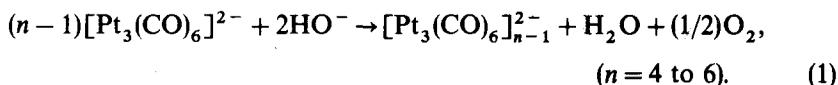
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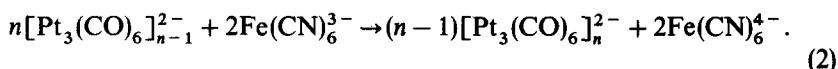
Scheme 1

be used to devise a system where transport of sodium ions and electrons in the same direction (symport) through a liquid membrane is achieved. A pH-gradient is used to drive this process.

Reductions of platinum clusters by HO^- proceeds according to



The reduced clusters could be oxidised by ferricyanide according to



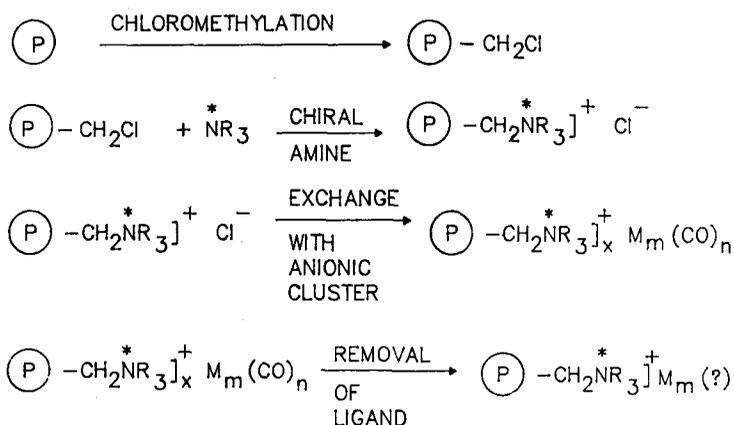
Both reactions (1) and (2) take place in biphasic systems consisting of HO^- or $\text{Fe}(\text{CN})_6^{3-}$ in water and $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ in CH_2Cl_2 or hexanol with trace quantities of dimethylformamide (see later).

Thus, the use of the clusters as redox catalysts to effect reaction (1) and (2) at the interfaces, result in the transport of electrons and sodium ions in the same direction. The overall chemical reaction i.e. reduction of $\text{Fe}(\text{CN})_6^{3-}$ by HO^- is thermodynamically favourable and has an approximate standard free energy of -25 kJ mol^{-1} .

Dichloromethane and *n*-hexanol have been used as the intervening liquid membranes. Due to the total insolubility of the platinum clusters in *n*-hexanol, very small quantities of dimethyl formamide have been added to solubilise the clusters. The extent of transport of sodium ion has been estimated by atomic absorption while electron transport is quantified by measuring the extent of reduction of $\text{Fe}(\text{CN})_6^{3-}$. For the latter the UV-visible spectral changes exhibit excellent isobesticity.

2.3 Platinum cluster derived asymmetric heterogeneous catalysts

While notable progress has been made in asymmetric homogeneous catalysis, examples of the effective use of heterogeneous catalysts in chiral syntheses are very few. The best example of such a transformation in a heterogeneous system is the catalytic hydrogenation of pyruvate esters. Using platinum catalysts modified with cinchona alkaloids, lactate esters with high enantioselectivities are obtained. This reaction was first reported by Orito and has subsequently been studied in considerable detail by others (Orito *et al* 1979; Garland *et al* 1990; Ibbotson *et al* 1992). We have studied



Scheme 2

Table 1. All reactions at 250°C, 500 psi H₂ with catalyst to substrate ratio 1:300.

$\textcircled{\text{P}} - \text{Cinchonine}] \text{Pt}_{15}(\text{CO})_{30}$

Substrate	Conversion	Enantioselectivity
	100	90S, 10R
	100	65R, 35S
	100	~ 52:2; 47:5

the 'Orito-type' and a few similar hydrogenation reactions with catalysts derived from the platinum clusters.

In 1984, we had shown that a wide variety of anionic carbonyl clusters including the Chini clusters could be ion-exchanged and supported on commercially available anion exchangers (Bhaduri and Sharma 1984). The scope of bringing clusters of different metal atoms of different shapes and sizes in close proximity to different chiral environments by this method is wide. This is so since the numbers of chiral quaternary nitrogen-containing groups and anionic clusters are many.

In scheme 2, the general methodology for synthesis of the chiral heterogeneous catalyst is shown. For high catalytic activities, removal of the CO ligands by thermal activation of the supported material is a *must*. In scheme 2, the material thus obtained is formulated as metal crystallites having the same nuclearity as the parent cluster. This of course is a gross-oversimplification.

Some of the results obtained with the catalyst derived from $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$, ion paired with polystyrene functionalised with cinchonine are shown in the table 1. It

is clear that enantioselectivity rapidly decreases with structural modification of the substrate.

Further work to expand the scope of the reaction and mechanistic studies are in progress.

3. Experimental

Most of the experimental details relevant to the work described in this paper could be found in our earlier publications (Bhaduri *et al* 1984, 1987, 1992).

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