

Catalysis with platinum carbonyl clusters

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In order to explain our interest in the selective reduction by proton and electron addition, and asymmetric hydrogenation, the historical background and the current status of carbonyl clusters as catalysts are briefly described. The unique redox chemistry of the anionic platinum carbonyl clusters (Chini clusters) has been utilized to design a model for the pH-driven transport of electrons through biological membranes. The platinum clusters have also been used as catalysts for the reduction of biological co-factors and proteins by dihydrogen. To overcome the water insolubility problem of the platinum clusters, two approaches have been adopted. In the first, a biphasic system consisting of water and a solution of the platinum cluster in a water immiscible organic solvent is used. In such a reaction system, by using a redox active dye such as Safranin O as the shuttle carrier for two electrons and one proton, the reduction of flavin and nicotinamide cofactors by dihydrogen could be effected. The regeneration of NADH from NAD⁺ by dihydrogen can be further coupled with lactate dehydrogenase catalysed reduction of pyruvate to lactate. In the second approach, the platinum clusters are anchored onto a biocompatible anion exchange resin such as QAE-SEPHADEX. The sephadex-supported material catalyses the reduction of flavin cofactors and CytC_{ox} by dihydrogen in water. The platinum clusters could also be anchored onto cross-linked polystyrene, functionalized with chiral quaternary ammonium groups. This material becomes an active heterogeneous hydrogenation catalyst after thermal decarbonylation, and reduces methyl pyruvate to methyl lactate with high enantioselectivity.

Introduction

In chemical literature the term 'cluster' is used to describe a very wide range of molecular level structures in the solid, liquid or gaseous phase. Zintl phases, polynuclear metal carbonyls, binuclear complexes with single or multiple metal-metal bonds, iron-sulphur cubanes, and a host of other metal complexes are examples of 'clusters' that are of special interest to inorganic chemists. In this article the term cluster is used only to refer to polynuclear metal carbonyl complexes with three or more metal atoms.

Simply put, the rationale behind the proposal that carbonyl clusters may have potential as novel catalysts is as follows. Certain carbonyl clusters may be expected to have co-ordinative unsaturation due to either the easy loss

of ligands, or because of their intrinsic electronic characteristics. Due to the presence of three or more metal atoms, the substrate activation may occur by more than one metal atom. Since such a mode of activation is not possible with *mononuclear* metal complexes, clusters may be able to catalyse reactions in solutions that fall strictly in the domain of heterogeneous catalysis¹⁻⁷.

In the early seventies, with what was perceived to be an imminent oil crisis, there was considerable interest in coal as a feed stock for chemicals. The gasification of coal to give synthesis gas (CO + H₂) and conversion of the synthesis gas into a mixture of hydrocarbons with heterogeneous Fischer-Tropsch catalyst are proven technologies. In a large number of clusters, both carbonyl and hydride ligands are present. Carbonyl clusters were thus expected to have potential catalytic activity or relevance in homogeneous CO hydrogenation reactions.

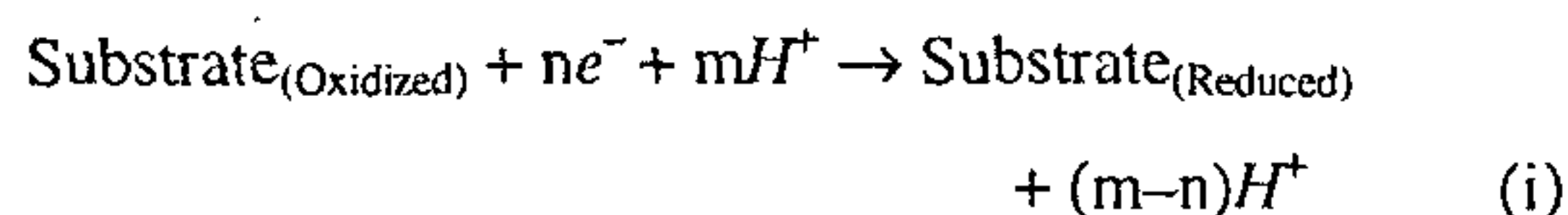
In the mid-seventies Mutterties reported the first example of homogeneous hydrogenation of CO to methane with Os₃(CO)₁₂ or Ir₄(CO)₁₂ as the precatalyst^{8,9}. Around the same time, Union Carbide also reported the selective hydrogenation of CO to ethylene glycol using soluble rhodium complexes as catalysts¹⁰. The possibility of rhodium clusters as catalytic intermediates was proposed but to date has not been proven. Although these original reports did generate a considerable amount of interest, subsequent research did not lead to the development of any cluster-based, high performance catalyst.

In the last two and a half decades, a very large number of carbonyl clusters with many interesting structural features have been made and characterized^{1,3}. Sophisticated theoretical models with considerable predictive power have been developed to rationalize the structures of clusters in the solid state and in solution. There are several monographs, review articles, and even an exclusive journal that deals with the chemistry of cluster complexes. A very recent book has comprehensively dealt with the theme of cluster catalysis¹¹. However, from this vast amount of literature it is clear that progress in terms of discovering cluster-based high performance catalysts for useful reactions at best has been modest¹¹⁻¹⁴.

Discussion on any catalyst – homogeneous, heterogeneous or enzymatic – must address two basic questions. What is the reaction that the catalyst is capable of catalysing and, in terms of activity and selectivity, what is its performance? From this perspective more than a decade and a half ago, we tried to identify reactions where we felt clusters may have unique catalytic potentials.

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The first reaction, shown by reaction (i), is the *selective* reduction of a given substrate by the addition of electrons and protons. The importance of this ubiquitous reaction in biological systems cannot be overemphasized. A homogeneous catalyst that uses *dihydrogen as the source of electrons and protons, but avoids over-reduction* would have obvious potential in catalytic reactions involving biomolecules. Since most biological reactions take place in an aqueous environment, the catalyst must also be able to function in such a medium.



It is important to note that there is a mechanistic difference between reaction (i) and conventional hydrogenation reactions. Many highly efficient homogeneous catalysts are available for the hydrogenation of unsaturated substrates such as alkenes, ketones, etc. In most of these reactions, metal hydrides are involved as catalytic intermediates. This however need not necessarily be and is very often not the case with the reaction (i).

The second problem that we wanted to address belongs to the area of asymmetric catalysis. We wanted to see if carbonyl clusters, placed in a chiral environment on a solid support, could act as precursors for asymmetric heterogeneous hydrogenation catalysts. As we will see, the advantage of this approach is that it allows the creation of a large library of potential catalysts with different combinations of metals, nuclearities and chiral environments. In this article we review our work in the two areas mentioned above.

Anionic platinum carbonyls

The platinum clusters of the general formula $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 1, 2, 3, 4, 5, 6$ and ~ 10) have come to be known as the 'Chini clusters'. The first report of the platinum clusters in fact could be traced back to the work of Chatt and Booth who had noticed that 'platinum dicarbonyl' dissolves in acetone in the presence of ammonia to give a dark-green solution¹⁵. However, at that time the intriguing molecular architecture of these clusters was neither recognized nor established. The rationale synthesis of these complexes by Chini and Longoni, using simple techniques and readily available starting materials, is a beautiful example of creative inorganic synthesis at its best¹⁶. These clusters are made from hexachloroplatinate salts by the careful reduction of Pt^{4+} in methanol.

The clusters can be isolated as tetraalkyl ammonium salts. As shown in Figure 1, the structures of all the clusters with more than three platinum atoms consist of metal triangles stacked over one another. In each triangle there are three terminal and three bridging carbonyl ligands. For the high nuclearity clusters ($n > 1$) there is some dis-

tortion from the ideal D_{3h} symmetry of the monomer. This is because some of the monomer units are rotated relative to the others. More than two decades ago, the unique structures of these clusters, both in the solid state and in solution, were established by single crystal X-ray and multinuclear NMR (^1H , ^{13}C , ^{195}Pt) studies respectively¹⁷⁻¹⁹. Theoretical bonding descriptions to rationalize the observed structures and spectroscopic properties have also been reported²⁰⁻²². The clusters with $n = 3, 4,$ and 5 have characteristic colours, and spectral (IR, UV-visible) signatures^{17,21-23}.

The platinum clusters have the unique ability to undergo a variety of redox reactions in a clean manner. In all these redox reactions the nuclearities of the clusters decrease in the case of reduction, and increase in the case of oxidation. The stoichiometries of the reactions with dihydrogen, hydroxide ion and water as the respective reducing agents are shown by eqs (ii) to (v) in Figure 1. Chini and Longoni had briefly reported these unusual reactions in their classic paper¹⁷.

In terms of reactivity there are two striking similarities between the platinum clusters and platinum colloids. First,

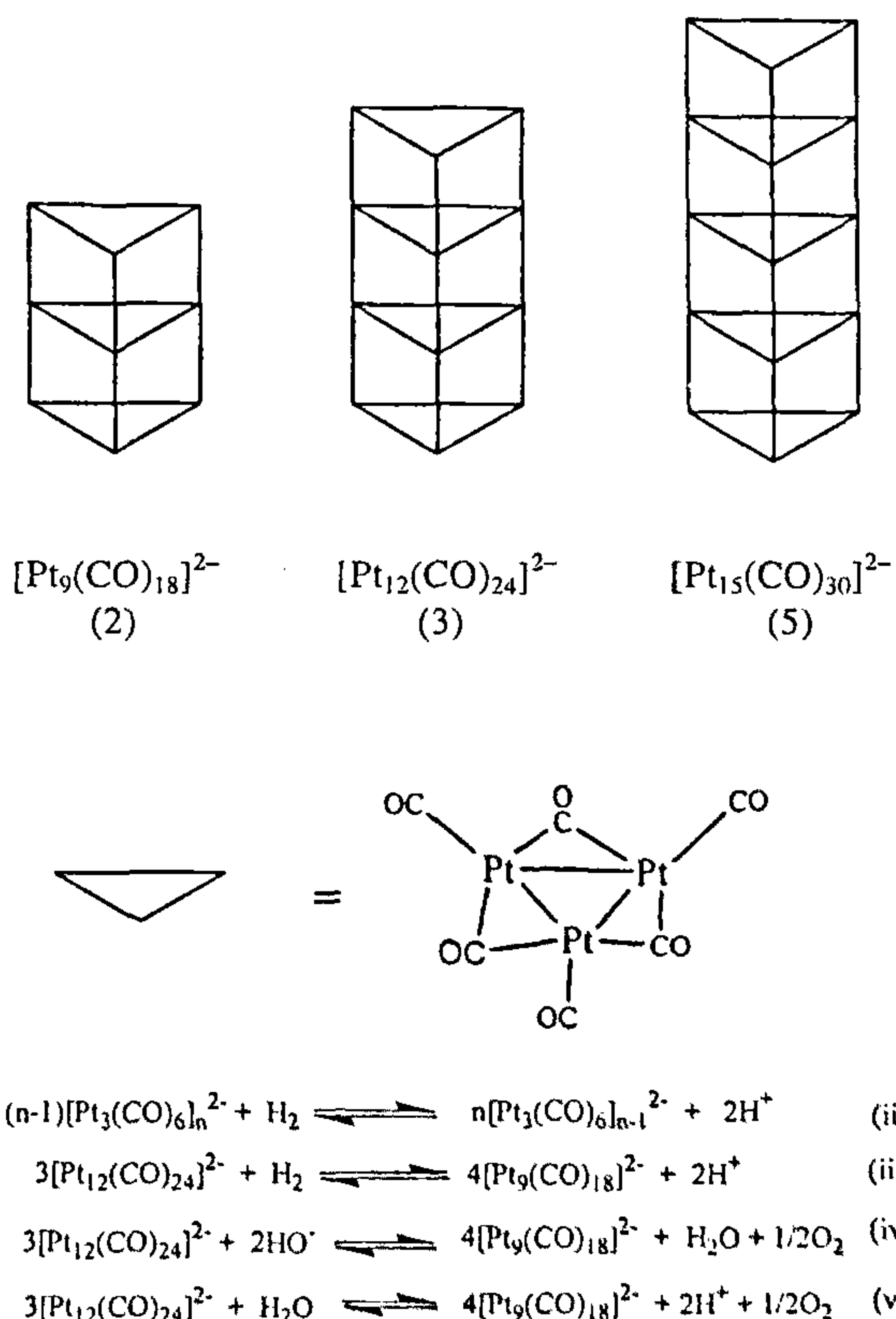


Figure 1. Top: Schematic structures of the Chini clusters with nine, 12 and 15 platinum atoms. For clarity the carbonyl groups and distortion from D_{3h} symmetry are not shown. Bottom: Stoichiometries of the redox reactions of platinum clusters with dihydrogen, hydroxide ion and water.

in most of the light-assisted water splitting systems, platinum colloids are used to catalyse the reduction of protons by a mediator such as methyl viologen radical cation^{24,25}. As we will see the reverse reaction, i.e. reduction of methyl viologen by dihydrogen, is catalysed by the platinum clusters. Secondly, it has recently been reported that aggregates of these carbonyl clusters are formed when carbon monoxide is reacted with platinum colloids²⁶.

In all the reactions studied by us, we have used the platinum clusters as the catalysts or precatalysts. We have explored their potential as homogeneous catalysts in solution. We have also anchored them onto organic supports and used them as *heterogenized homogeneous* catalysts. We first discuss those catalytic reactions where the cluster is used as a homogeneous catalyst, i.e. in solution. The liquid phase in these reactions may consist of a solution of the cluster and other reactants in a *single* solvent, or it may consist of *two immiscible liquids* such as water and a water immiscible organic solvent.

Platinum clusters as homogeneous redox catalysts

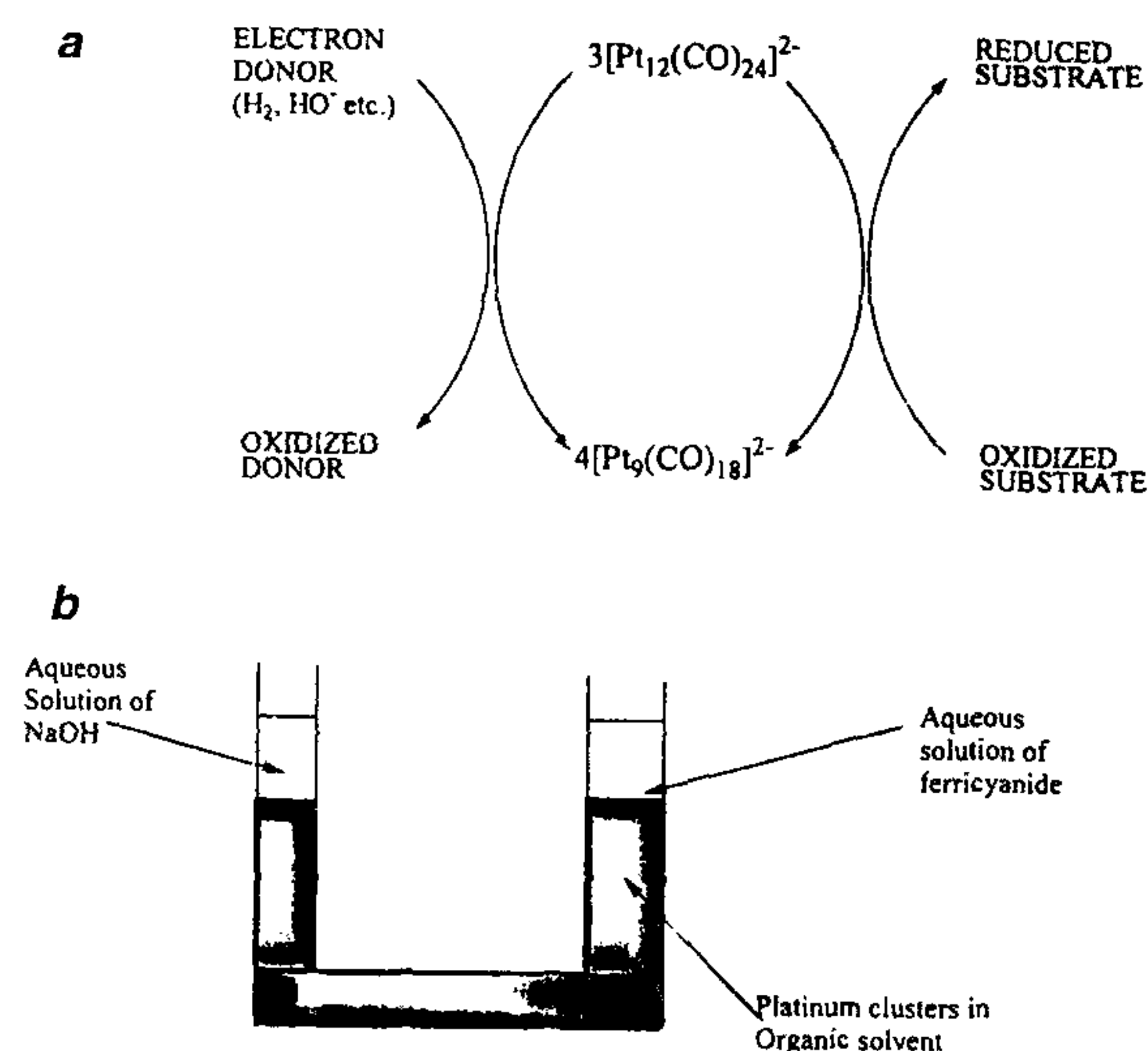
As shown in Figure 2 *a*, the idea of using the platinum clusters as redox catalysts would have some merit as long as it satisfies two obvious criteria. First, the oxidized substrate should not undergo reduction by the electron donor (HO^- , H_2O , or H_2) in the absence of the catalyst. Second, the oxidation of the cluster must be a clean one. In other words, over a modest number (greater than 10) of turnovers there should be no spectroscopically observable decomposition of the cluster.

Since conventional heterogeneous catalysts such as platinum on carbon over-reduce nicotinamide and flavin cofactors, the *selective* reductions of these cofactors are of special interest²⁷. We wanted to see if the clusters could be used as selective catalysts for these and related reactions. In evaluating the clusters as redox catalysts, the main difficulty lies in the solubility properties of the potential reactants. The clusters like most organometallic complexes are insoluble in water, while the cofactors are soluble only in water and insoluble in all common organic solvents.

In our early experiments we attempted to reduce FMN (or FAD) and NAD^+ directly, by reacting them with the reduced platinum cluster, $[\text{Bu}_4\text{N}]_2[\text{Pt}_9(\text{CO})_{18}]$ (1), in a biphasic system (water/dichloromethane, 50 : 50 by volume). No reduction of NAD^+ and very slow reduction of FMN and FAD were observed. In biochemical research $[\text{Fe}(\text{CN})_6]^{3-}$ is often used as an artificial electron acceptor. Since the results with the co-factors were disappointing, we evaluated the potential of $[\text{Fe}(\text{CN})_6]^{3-}$ as an electron acceptor, and found it to be satisfactory. UV-visible spectral monitoring of both the water and the organic layers showed clean isobesticities. The two absorbing species in water were $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, while in the orga-

nic solvent they were $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ (2) and $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ (3). The relatively easy reduction of ferricyanide compared to the co-factors may be partly due to the more favourable reduction potential of the former.

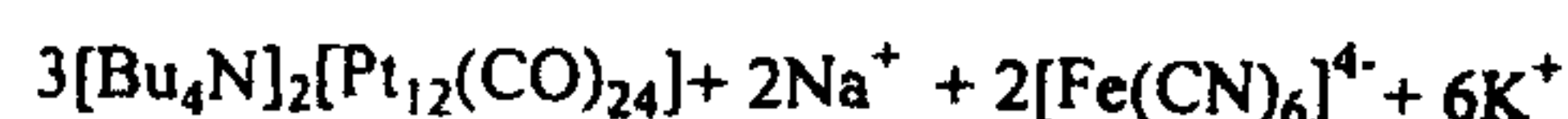
Based on these observations a model system for the pH-driven transport of electrons and alkali metal ions through an artificial membrane was constructed²⁸. In this model system, an aqueous solution of sodium hydroxide is separated from an aqueous solution of ferricyanide through an intervening layer of dichloromethane or ethyl acetate (see Figure 2). The platinum cluster $[\text{Bu}_4\text{N}]_2[\text{Pt}_{12}(\text{CO})_{24}]$ is dissolved in the organic layer. As shown in Figure 2 *b*, at the left and right phase boundaries the platinum clusters (3) and (2) undergo reduction by HO^- and oxidation by $[\text{Fe}(\text{CN})_6]^{3-}$, respectively. The net effect of these two reactions is the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ by



At the left interface:



At the right interface:



Net reaction:



Figure 2. *a*, Generalized catalytic cycle for the reduction of an oxidized substrate by dihydrogen or hydroxide ion; *b*, Cluster catalysed pH driven symport of electrons and sodium ions in a model system.

HO^- . In the process electrons and sodium ions are transported by (2) from the left to the right phase boundary.

Since the transport of electrons and sodium ions are in the same direction, the model mimics what is called 'symport' in a biological system.

The pH-driven model liquid membrane system cannot be used to effect the reduction of the cofactors. This is because, as already mentioned, in a biphasic system there is zero or negligible reduction of the cofactors by (2). Also, the reductions of NAD^+ and flavin cofactors require one and two protons respectively. Thus the catalytic reduction of NAD^+ and the flavin cofactors had to be based on an alternative strategy.

Our alternative strategy was based on the use of dihydrogen and a *shuttle carrier*. Dihydrogen supplies the reducing equivalents (two electrons and two protons), and the *shuttle carrier* transports the electrons and proton(s) from the organic to the aqueous phase³². The ubiquitous roles of various shuttle carriers in biological systems are well documented²⁹. Among their many functions they also facilitate the selective transport of electrons (and protons) across biological membranes. We decided to evaluate the potential of redox active dyes as shuttle carriers for electrons and protons.

We first established that, by using $[\text{Bu}_4\text{N}]_2[\text{Pt}_{12}(\text{CO})_{24}]$ as a precatalyst and dihydrogen as the reductant, a range of redox active dyes such as methylene blue (MB^+), safranineO (Saf^+), methyl viologen (MV^{2+}), etc. could be selectively reduced. Spectroscopic monitoring and reversible autoxidation established that in an organic solvent such as dimethyl formamide, MB^+ , Saf^+ , and MV^{2+} were selectively reduced to MBH , SafH and $\text{MV}^{+\bullet}$, respectively. Selective reduction of MB^+ and Saf^+ could also be effected in a biphasic system consisting of water, and a water immiscible organic solvent such as dichloromethane or ethyl acetate.

The mechanism for this reaction is shown in Figure 3 a. Reduction of (3) to (2) by dihydrogen takes place in the organic solvent. The oxidized dye (Dye_{ox}) has some solubility both in water and the organic solvent. In other words the oxidized dye partitions itself between the organic and the aqueous layers. Reduction of Dye_{ox} to Dye_{red} by (2) takes place in the organic layer. The reduced dye, like Dye_{ox} , is partitioned between the organic and the aqueous layers.

In traditional biochemical research, the use of redox active dyes as artificial electron acceptors is well established³⁰. The numbers of electrons and protons that the reduced dye may carry obviously depend upon the particular dye. The one-electron $\text{MV}^{2+}/\text{MV}^{+\bullet}$ couple has been widely used as an electron carrier in photo-assisted water-splitting systems^{24,25}. It has also been used with some success³¹ for the reduction of NAD^+ . We decided to use Saf^+/SafH couple as the shuttle carrier for three reasons. First, in contrast to $\text{MV}^{+\bullet}$, which is a single electron donor, SafH is a two electrons plus one proton donor. The

reduction of NAD^+ requires two electrons and one proton. Similarly, for the reduction of the flavin cofactors, two electrons and two protons are needed. Second, for the reduction of NAD^+ , compared to MB^+/MBH couple, the half-cell potential of Saf^+/SafH is thermodynamically more favourable. Third, the partition coefficients of Saf^+ and SafH in a biphasic system are adequate for them to function as efficient shuttle carriers. The molecular structures of Saf^+ and SafH are given in Figure 3 b.

For the reduction of NAD^+ by dihydrogen, we decided to use $[\text{Saf}]_2[\text{Pt}_{12}(\text{CO})_{24}]$ (4) as the precatalyst. This salt is easily made by adopting the literature reported synthetic procedure for the Bu_4N^+ salt of (3) and using Saf^+Cl^- in the place of $\text{Bu}_4\text{N}^+\text{I}^-$. The advantage of using (4) as the precatalyst is that the amount of the dye used is minimized. This in turn reduces the interference in the UV-visible spectra of the cofactors due to the presence of the dye.

The strategy of using Saf^+/SafH as shuttle carriers for electrons and protons was successful. Both NAD^+ and the flavin cofactors could be selectively reduced by dihydrogen in a biphasic (dichloromethane/water, 1 : 1) system³². Depending upon the pH of the aqueous layer and other reaction parameters, in both the cases 10–20 turnovers are obtained in an hour.

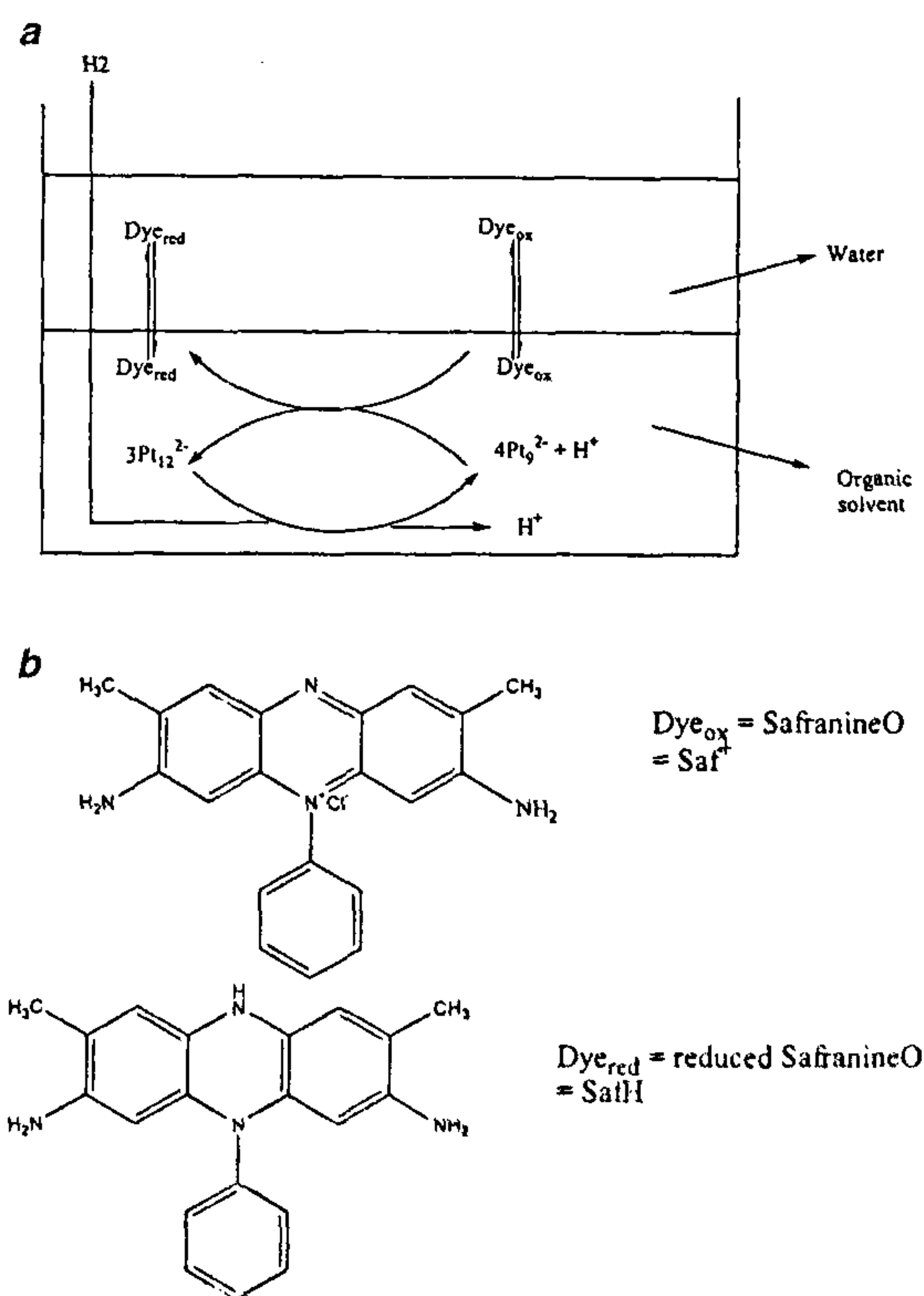


Figure 3. a, Mechanism of cluster catalysed catalytic reduction of methylene blue or safranineO by dihydrogen in a biphasic system; b, Structures of Saf^+ and SafH .

The importance of dehydrogenase-based enzymatic catalysis in industry and organic synthesis is well documented³³. An industrial process for the conversion of pyruvate to enantiomerically pure L-lactate involves the use of two dehydrogenase-based enzymes. One of the enzymes, lactate dehydrogenase (L-LDH), catalyses the reaction between pyruvate and NADH to give lactate and NAD⁺. The other enzyme, formate dehydrogenase (FDH), catalyses the regeneration of NADH from NAD⁺ using formate as the reductant.

The cluster-based catalytic system could be extended for the enzymatic reduction of pyruvate to lactate³². In this reaction only a single enzyme (L-LDH) is used. The cluster anions and the Saf⁺/SafH couple carry electrons and protons from dihydrogen to NAD⁺ for the continuous regeneration of NADH (see Figure 4). With a pyruvate to NAD⁺ to (4), molar ratio of 600 : 10 : 1, complete conversion of pyruvate to L-lactate could be achieved in less than 48 h.

In all the catalytic systems described so far, (2) and (3) are the only spectroscopically identifiable, organometallic species present during a given catalytic run. Their total absorbance remains constant during the course of such a run. These two observations suggest that (2) and (3) are the active catalytic intermediates, and there is no degradation of the clusters to colloidal platinum.

Catalysis with clusters supported on anion exchangers

The fact that the anionic platinum clusters could be tethered to commercial anion exchangers (Amberlite IRA 401)

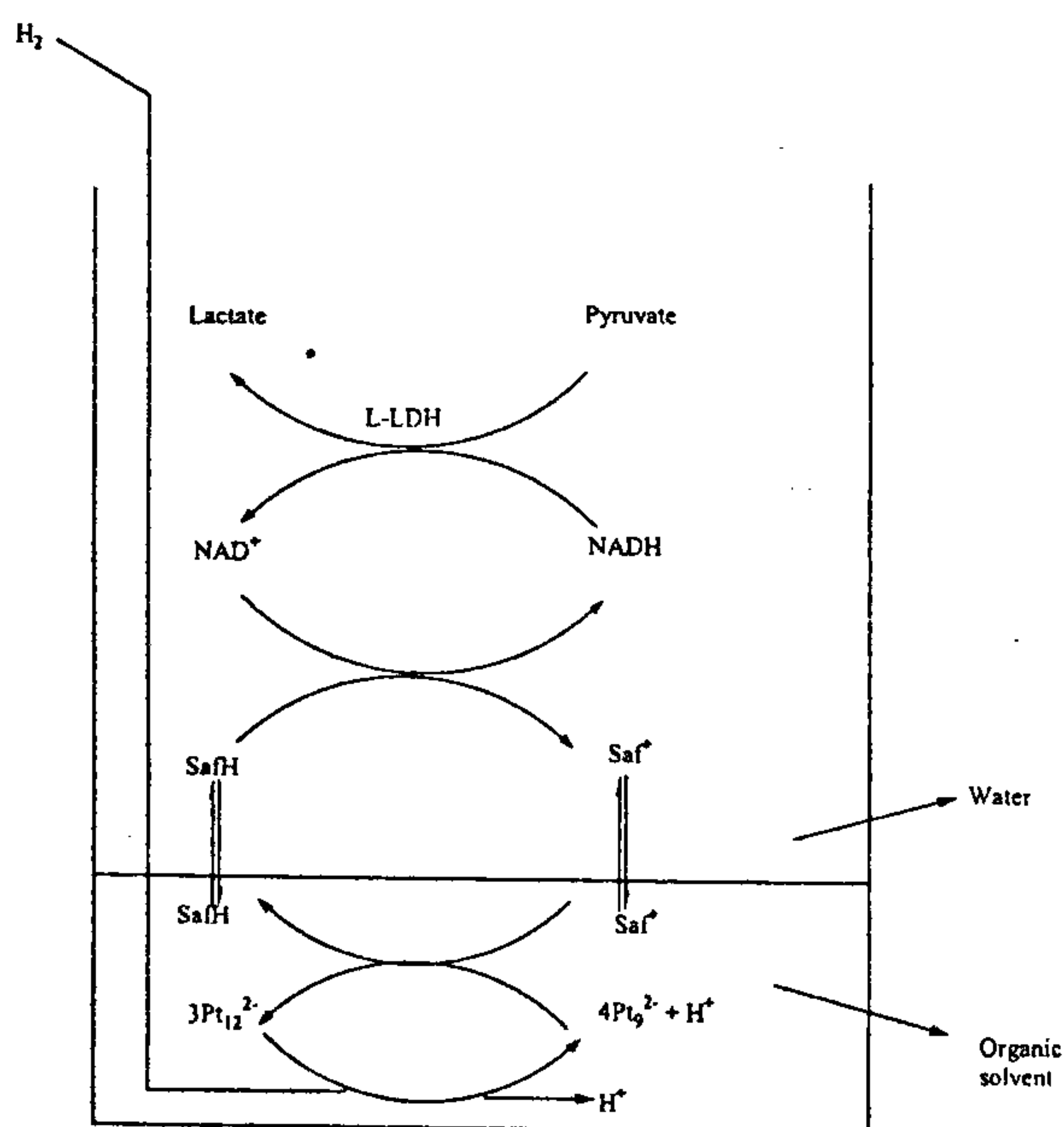


Figure 4. Coupling of cluster catalysed reduction of NAD⁺ by dihydrogen, with the enzymatic conversion of pyruvate to L-lactate.

without affecting their molecular structures and nuclearities was reported by Bhaduri and Sharma³⁴ many years ago. The structural evidence for the retention of nuclearities and molecular structure was based on analytical and spectroscopic (UV-visible, IR and ESCA) data, and initial studies had also established the following important conclusions. First, the supported cluster anions were sufficiently mobile and reaction (ii) could be effected on the resin surface. Second, on decarbonylation, the resin-supported cluster became an active hydrogenation catalyst.

The driving force of anion exchange is obviously the formation of ion pairs between the anionic cluster molecules and the cationic quaternary ammonium groups of the anion exchanger. We have used this general reaction to develop two novel catalysts (see Figure 5 a). With catalyst (6), dihydrogen is used as the electron (and proton) donor and a catalytic cycle similar but not identical to that of Figure 2 a is effected on a biocompatible resin surface. A resin with a chiral quaternary ammonium group such as cinchonine is used for catalyst (7). Here the supported cluster is *thermally decarbonylated*, and the decarbonylated material is used as a hydrogenation catalyst. We first discuss the catalytic applications where advantage is taken of the redox chemistry of the intact platinum clusters.

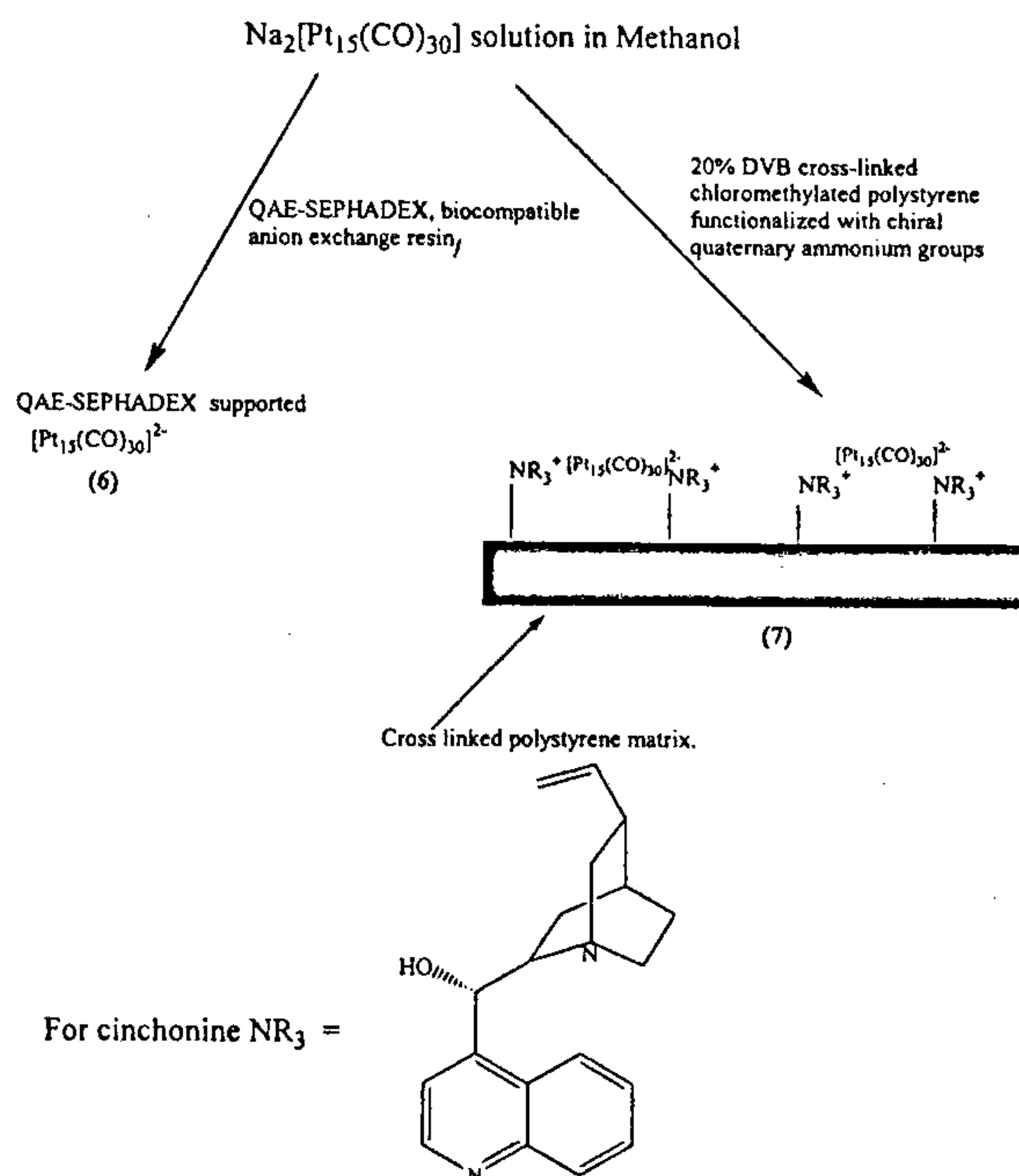


Figure 5. Two different types of polymer supported cluster catalysts. In (7), the cluster is in a chiral environment and on decarbonylation catalyses the asymmetric hydrogenation of methyl pyruvate. In (6), the cluster is on a bio-compatible resin and catalyses the reduction of selected proteins and flavin cofactors by dihydrogen in an aqueous environment.

Reduction of co-factors and proteins by dihydrogen

Our initial studies established that the anion exchanger, Amberlite IRA 401, was not compatible with biomolecules. It quickly denatured proteins such as CytCox and lipoamide dehydrogenase. We therefore chose a biocompatible, commercially available anion exchanger QAE-SEPHADEX (Sigma) as the support material. The cluster $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ (5) was anchored onto it by simply treating a methanolic solution of sodium salt of (5) with the resin for about 2 h.

The catalytic potential of sephadex-supported (5) for the reduction of bio-molecules in water by dihydrogen was evaluated. The resin-supported cluster was found to be effective in bringing about the selective reductions of flavin cofactors, lipoamide dehydrogenase and CytCox by dihydrogen³⁵. However, it showed near zero activity for the reduction of NAD^+ . This lack of activity is at least in part due to the thermodynamic demand of NAD^+/NADH couple. All the other oxidized substrates, FAD, FMN, CytC_{ox} have more favourable reduction potentials.

In mixed solvent systems such as DMF–water (more than 90% water), the extent of reduction of (3) to (2) by dihydrogen is insignificant and cannot be spectroscopically observed. Participation of (2) in the catalytic cycle is therefore unlikely. A plausible mechanism involves reduction of (5) to (3) by dihydrogen and oxidation of (3) back to (5) by the biomolecules.

Cluster-derived heterogeneous catalysts for asymmetric hydrogenation

Hydrogenation of methyl pyruvate ester with cinchona-modified platinum catalysts is known to give methyl lactate with high enantioselectivity^{36,37}. After the name of its inventor, this reaction is called the Orito reaction³⁸. As already mentioned, anionic carbonyl clusters of platinum (and other metals) could be supported on cross-linked polystyrene resin functionalized with quaternary *chiral* ammonium groups (see Figure 5). The semi combinatorial approach of ion pairing different chiral groups with anionic clusters of different metals, enabled us to create a library of potential asymmetric catalysts³⁹.

For the Orito reaction, ion pairing between (5) and cinchonine or quinine-derived quaternary ammonium groups gives the most effective (initial rate ~ 1–10 mmol/(min.g); enantiomeric excess ~ 75–80%) catalyst. Anionic carbonyl clusters of ruthenium and rhodium are found to be significantly less effective. Within experimental error, the catalysts derived from (2), (3) and (5) have very similar activity and selectivity. In other words the nuclearity of the cluster does not have an observable effect on the performance of the catalyst.

Kinetic studies on a number of catalysts all derived from (5) but ion paired with different quaternary ammo-

nium groups have been carried out⁴⁰. Data from such studies indicate that rapid pre-equilibrium leading to the formation of a catalyst–substrate complex precedes the rate determining step. It also shows that, among the different quaternary ammonium groups, the one derived from cinchonine is the most effective both in terms of activity and enantioselectivity.

As mentioned earlier, for any observable activity in these cluster-derived catalysts, thermal decarbonylation is an essential requirement. The nature of the active decarbonylated species is not known with any certainty. However, after use in a catalytic run, under CO pressure, the catalyst could be recarbonylated. The recarbonylated material has an IR spectrum that is identical to that of the freshly prepared catalyst. This reversible decarbonylation is probably indicative of retention of molecular structure by the decarbonylated cluster.

Conclusions and future outlook

The work described in this article shows that platinum carbonyl clusters do have considerable potential as redox catalysts both in a biphasic liquid medium and also on sephadex resin. Both these approaches are also useful for the efficient separation of the catalyst from the reaction products.

There are many questions that remain to be answered before the behaviour of these redox catalysts could be understood in a comprehensive manner. Detailed kinetic studies have been carried out on reaction (ii) and will be published soon. Similar data for each reaction step in Figure 4 is required. We have also carried out preliminary electrochemical (cyclic voltametry) studies on (2), (3) and (5) in DMF. Such data may provide a thermodynamic basis for the observed chemistry.

From a purely functional point of view, the ability of the clusters to equilibrate dihydrogen with two protons and two electrons, i.e. reaction (ii), is similar to that of the enzyme hydrogenase. In iron only hydrogenase, several iron sulphur clusters carry electrons to the so-called H-cluster where dihydrogen evolution is believed to take place⁴¹. We plan to evaluate the potential of the platinum clusters to catalyse a whole range of reactions normally encountered in an anaerobic ecosystem.

For the polystyrene-supported asymmetric catalyst, we plan to carry out detailed characterization studies on the active and used catalysts. Comparative evaluations of catalysts with chiral amines other than the cinchona alkaloids, and for the hydrogenation of prochiral substrates other than methyl pyruvate, are also planned.

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