

## Electroprotic reactions

ANIMESH CHAKRAVORTY

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,  
Calcutta 700032, India, and  
Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560012, India

**Abstract.** Reactions involving the coupled transfer of electrons and protons are called electroprotic reactions. In this article we briefly describe some of our experiences with electroprotic reaction as a tool for executing interesting chemical transformations.

**Keywords.** Electroprotic reactions; two-electron transfer; isomerisation; proton switch; organic refunctionalisation.

### 1. Introduction

The reaction below represents a general electroprotic transformation (Ghosh and Chakravorty 1984; Chakravorty 1985)



Here  $n$  electrons and  $m$  protons are transferred to molecule  $A$  in a “concerted” or “coupled” manner. In this article we present a few instances where electroprotic reactions lead to interesting chemistry.

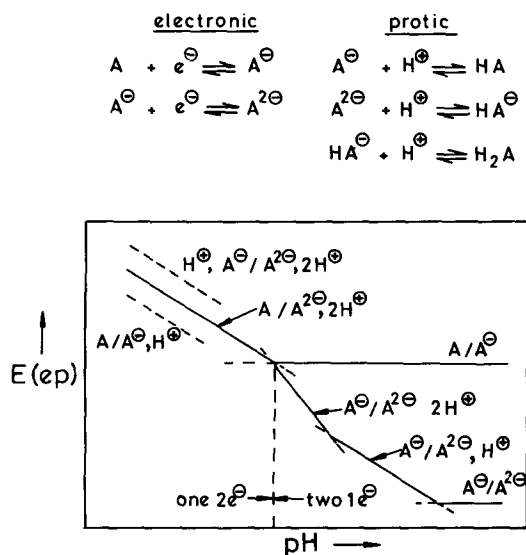
### 2. One-step $2e$ transfer

The  $m = 0$  case of (1) corresponds to pure electron transfer which usually occurs in discrete one-electron steps. In the presence of proton transfer, say  $m = n = 2$ , the process of (1) could proceed as a single step particularly under low  $pH$  conditions (figure 1). The physical basis for this is the proton-affinity order  $A^{2-} > A^- > A$ .

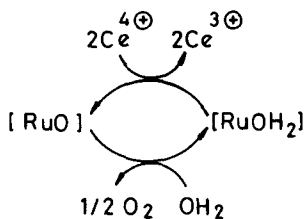
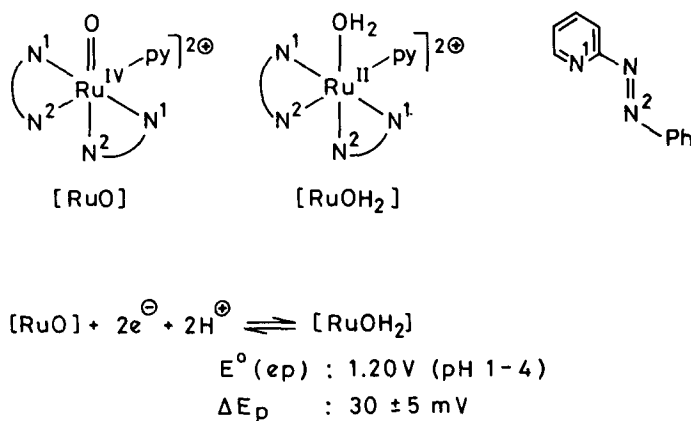
A good example of this situation is shown in figure 2 (Goswami *et al* 1982). Here the two-electron step is realised in the  $pH$ -range 1–4 ( $py$  = pyridine). The formal potential of the two-electron couple (figure 2) is 1.20 V vs s.c.e. and the cyclic voltammetric peak-to-peak separation is 30 mV as expected for two-electron transfer. The two-electron oxidation process can be chemically brought about by  $Ce(IV)$ . The  $Ru^{IV}O$  complex is a rare species that is able to oxidise water to oxygen.

### 3. A proton switch

In some cases a sluggish proton can control the flow of electrons in one direction. A case is provided by the strongly antiferromagnetic ( $S = 1/2$ ) trinuclear copper(II)



**Figure 1.** Plot of observed potential vs pH for the electroprotic reaction having  $m = n = 2$ ; the single-step two-electron process starts at the top of the vertical dotted line.



**Figure 2.** A single-step two-electron electroprotic reaction of a ruthenium complex and water oxidation by the oxidised complex.

isonitrosoketonates (Beckett and Hoskins 1972; Baral and Chakravorty 1980; Butcher *et al* 1981; Gross *et al* 1991).

The results are depicted in figure 3. The X=O species display a reversible  $\text{Cu}^{\text{III}}\text{Cu}_2^{\text{II}}/\text{Cu}_3^{\text{II}}$  couple in MeCN and MeOH ( $E^0 \sim 0.3\text{ V}$ ). On the other hand, the  $\text{Cu}_3\text{OH}$  complexes do not show any oxidative response upto 1.0 V but these are reversibly

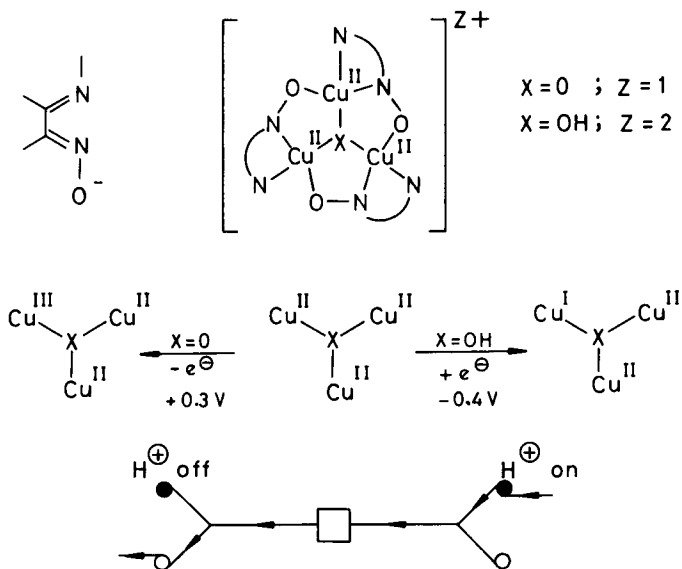


Figure 3. Trinuclear copper species with proton switch action.

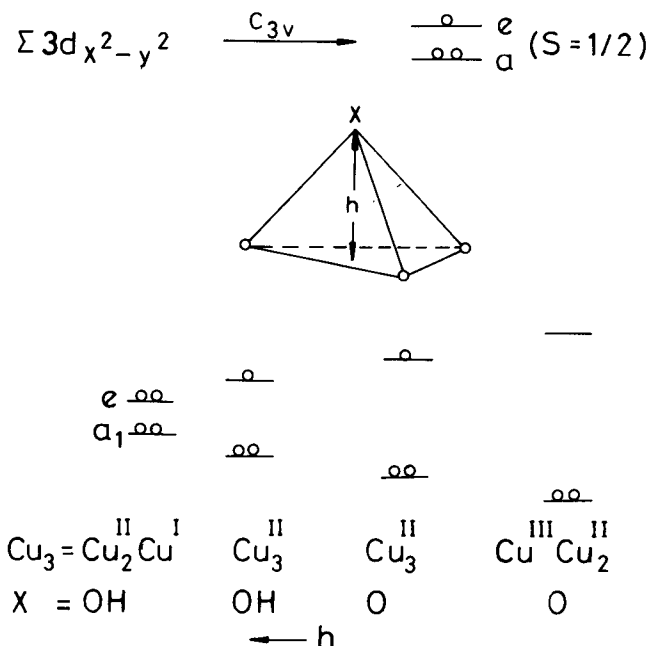


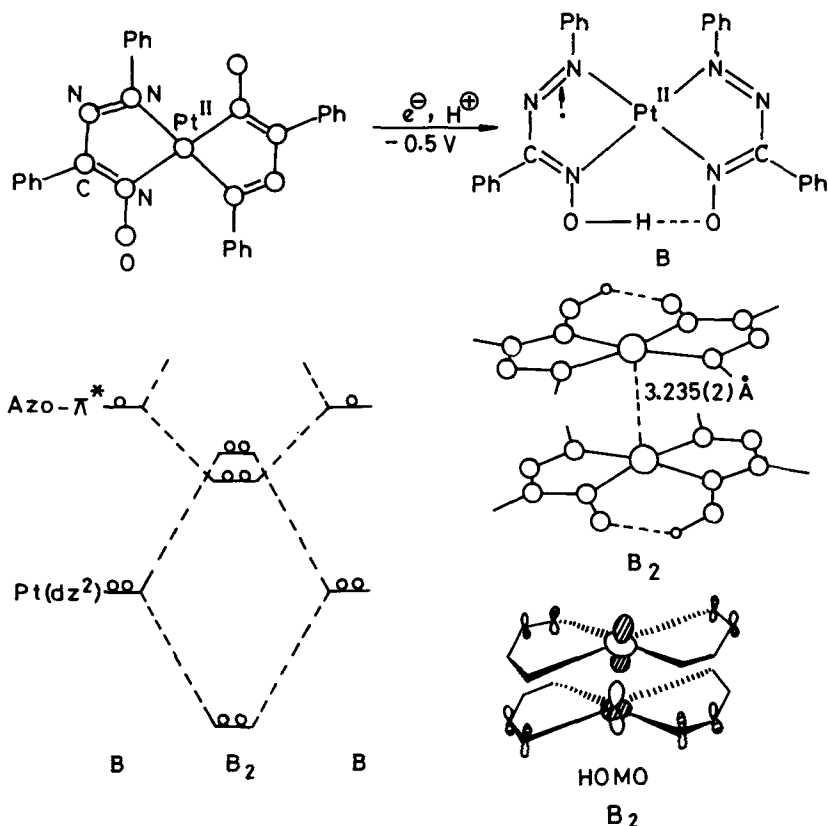
Figure 4. Interaction within the  $\text{Cu}_3\text{X}$  group in trinuclear copper species.

reducible:  $\text{Cu}_3^{\text{II}}/\text{Cu}_2^{\text{II}}\text{Cu}^{\text{I}}$  ( $E^0 \sim 0.4 \text{ V}$ ). In effect, the proton in  $\text{Cu}_3\text{OH}$  acts as a switch allowing an extra electron to come in but blocking the removal of any of the original electrons (Datta *et al* 1981; Datta and Chakravorty 1982, 1983).

While the weak acidity of the  $\text{Cu}_3\text{OH}$  moiety is a factor, the electronic interactions within the  $\text{Cu}_3\text{X}$  fragment are believed to play an important role. The oxygen-mediated intermetal interaction increases as the pyramid height  $h$  decreases (figure 4). In  $C_{3v}$  symmetry the  $d_{x^2-y^2}$  orbitals of the  $\text{Cu}_3$  unit furnish molecular orbitals of  $e$  and  $a_1$  symmetry. The relative energies of the  $e$  level of  $\text{Cu}_3\text{OH}$  and  $\text{Cu}_3\text{O}$  suggest that the oxidation of the former should occur at a higher potential than that of the latter. This shift will be further augmented by the charge of the proton. In practice, no oxidation is observed for  $\text{Cu}_3\text{OH}$ . By the same logic, reduction of  $\text{Cu}_3\text{OH}$  should be easy and that of  $\text{Cu}_3\text{O}$  difficult. We thus have a molecular basis for the proton switch action.

#### 4. Geometrical isomerisation

We cite here an example of spontaneous isomerisation associated with an electroprotic reaction (figure 5). The *trans* planar arylazooximate of bivalent platinum adds



**Figure 5.** Isomeric transformation of platinum arylazooximates; structure and bonding in the *cis* dimer.

an electron to an azo group and a proton to an oximato oxygen. There is concomitant isomerisation to the paramagnetic *cis* complex B. It reversibly dimerises in solution affording diamagnetic B<sub>2</sub> which alone is present in the crystalline *cis* complex. The Pt...Pt distance is 3.235(2) Å and extended Hückel treatment of B<sub>2</sub> reveals that the HOMO is primarily metal *d*<sub>z<sup>2</sup> in character (Chattopadhyay *et al* 1993).</sub>

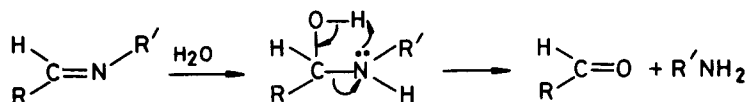
## 5. Organic refunctionalisation

Two examples will be considered here where metal bound organic functions are transformed via electroprotic pathways.

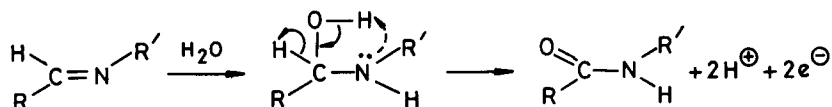
Addition of water to a Schiff base function normally leads to hydrolysis affording an aldehyde and an amine. An electroprotic transformation to the amide function can be conceived (figure 6) but it is difficult to achieve in practice (Chum and Helene 1980). We have employed metal binding as a tool for achieving this end. Through selection of the donor D and the charge *z*<sup>+</sup> on the metal, C–N cleavage which is crucial for hydrolysis could be bypassed making amide formation facile. A particular reaction is shown in figure 7. Here [Re<sup>IV</sup>] represents the Re<sup>IV</sup> analogue of the Re<sup>III</sup> precursor. The reactant and the product have been structurally characterized and the reaction rate is found to be first order with respect to the water concentration (Menon *et al* 1994).

A fascinating case of thioether activation by cobalt is depicted in figure 8. Oxidation of the metal from the bivalent to the trivalent state is attended with the deprotonation of an α-methylene group. When the SS chelate ring is six-membered, the carbanionic

### Hydrolysis (common)



### Oxidation (required)



### Strategy

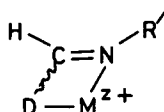


Figure 6. Two possible modes of transformation of the Schiff base function and strategy for achieving the electroprotic pathway.

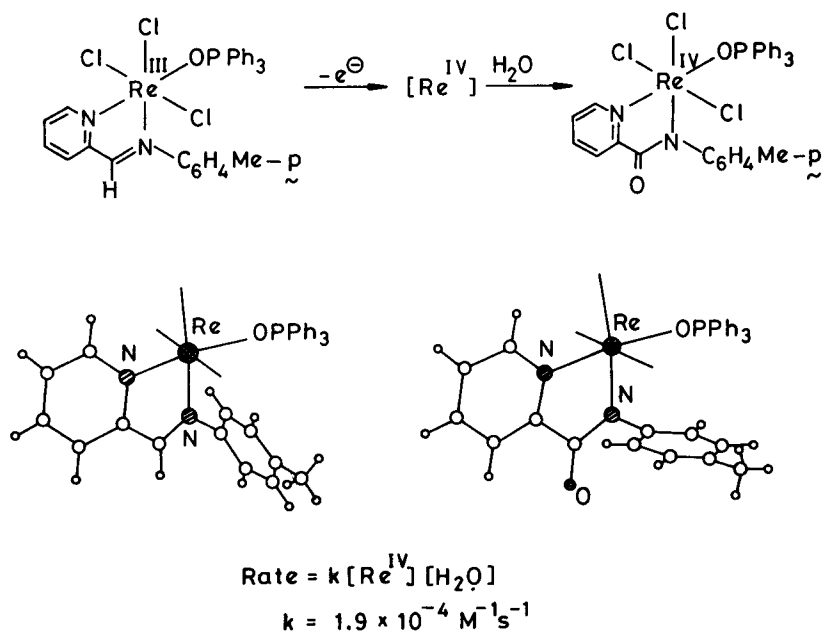


Figure 7. Oxidation of Schiff base to amide in a rhenium complex; structure and rate.

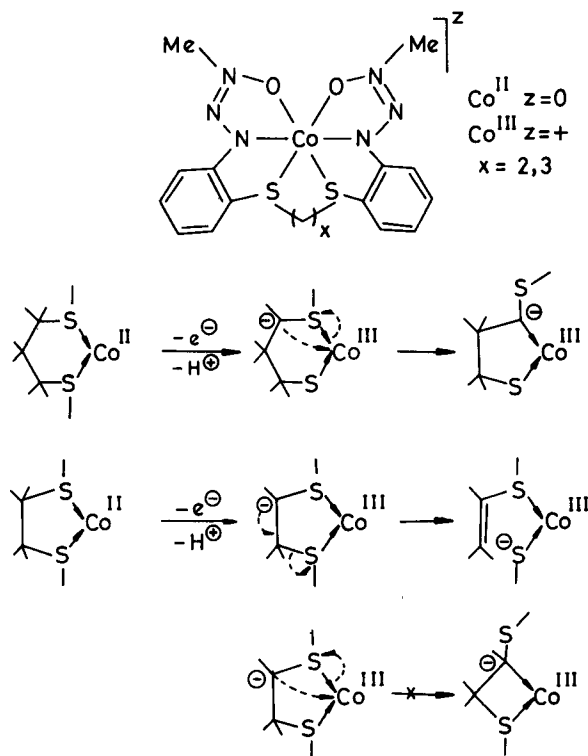
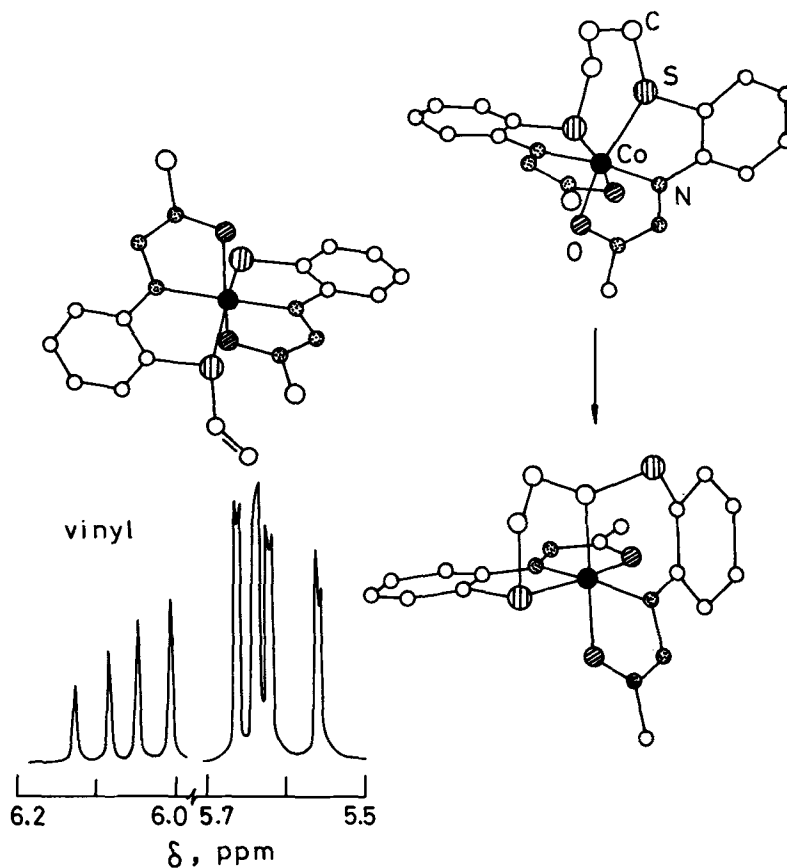


Figure 8. Thioether activation via electroprotic change in cobalt complexes.



**Figure 9.** Structures of parent and transformed cobalt species and proton nmr of the vinyl group in the cleaved complex in  $\text{CDCl}_3$ .

site displaces a thioether function affording cobalt(III) organometallics. When the SS ring is five-membered this does not happen since the organometallic ring would be four-membered. Instead a C–S bond is cleaved leading to coordinated thiolate. The transformation is thus ring-size specific (Chakraborty *et al* 1993, 1994). The products from both types of reactions have been fully characterized (figure 9). The reaction scheme of figure 8 has helped rationalisation of apparently disparate literature results (Blake *et al* 1989; Bennet *et al* 1992; Kofod *et al* 1992).

## 6. Conclusions

We have demonstrated that electroprotic reactions can be a source of fascinating chemistry. It can effect geometrical isomerisation, single-step multielectron transfer and organic refunctionalisation. In one case, the proton is shown to act as a switch that can control the direction of electron flow.

**Acknowledgements**

I express my deep indebtedness to the students who did the many electroprotic experiments and whose names appear in the references cited. I am thankful to Prof. E D Jemmis for helping with our Hückel calculations. Financial support received from the Department of Science and Technology, New Delhi and Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged.

**References**

- Baral S and Chakravorty A 1980 *Inorg. Chim. Acta* **39** 1  
Beckett R and Hoskins B F 1972 *J. Chem. Soc., Dalton Trans.* 291  
Bennet M A, Goh L Y and Willis A C 1992 *J. Chem. Soc., Chem. Commun.* 1180  
Blake A J, Holder A J, Hyde T I, Küppers H -J, Schröder M, Stötzel S and Wieghardt K 1989 *J. Chem. Soc., Chem. Commun.* 1600  
Butcher R J, O'Connor C J and Sinn E 1981 *Inorg. Chem.* **20** 537  
Chakravorty P, Chandra S K and Chakravorty A 1993 *Organometallics* **12** 4726  
Chakravorty P, Karmakar S, Chandra S K and Chakravorty A 1994 *Inorg. Chem.* **33** 816  
Chakravorty A 1985 *Comments Inorg. Chem.* **4** 1  
Chattopadhyay S, Pal C K, Sinha C and Chakravorty A 1993 (unpublished results)  
Chum H L and Helene M E M 1980 *Inorg. Chem.* **19** 876, and references therein  
Datta D and Chakravorty A 1982 *Inorg. Chem.* **21** 363  
Datta D and Chakravorty A 1983 *Inorg. Chem.* **22** 1611  
Datta D, Mascharak P K and Chakravorty A 1981 *Inorg. Chem.* **20** 1673  
Ghosh P and Chakravorty A 1984 *Inorg. Chem.* **23** 2242  
Goswami S, Chakravarty R and Chakravorty A 1982 *J. Chem. Soc., Chem. Commun.* 1288  
Gross M, Gisselbrecht J P, Boudon C, Metz B, Louis R and Agnus Y 1991 *Inorg. Chem.* **30** 3155  
Kofod P, Larsen E, Petersen C H and Springborg J 1992 *Acta Chem. Scand.* **46** 1149  
Menon M, Choudhury S, Pramanik A, Deb A K, Chandra S K, Bag N, Goswami S and Chakravorty A 1994a *J. Chem. Soc., Chem. Commun.* 57  
Menon M, Pramanik A, Bag N and Chakravorty A 1994b *Inorg. Chem.* **33** 403