Coordination Chemistry Reviews, 135/136 (1994) 65–92

Electrosynthesis of coordination compounds by the dissolution of sacrificial metal anodes

M.C. Chakravorti and Gampa V.B. Subrahmanyam
Department of Chemistry, Indian Institute of Technology, Kharagpur-721302 (India)

(Received 15 September 1992; accepted 9 August 1993)

CONTENTS

ABSTRACT

The article reviews the electrosynthesis of different kinds of coordination compound by the dissolution of sacrificial metal anodes into aqueous and non-aqueous media. The advantages of the method have been emphasized and a brief discussion on the mechanism has been included. The coverage of the literature is almost complete up to 1992 beginning from the early 1970s. In conclusion the article points out certain areas of electrosynthesis which deserve attention.

1. INTRODUCTION

Physicochemical studies on the behaviour of inorganic compounds at electrodes have attracted considerable attention The electrosynthesis of complex compounds

---

Correspondence to: M.C. Chakravorti, Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India.

0010-8545/94/$26.00
SSDI 0010-8545(93)01103-5

has not received its due attention, although rapid development of the electrosynthesis of organic compounds has taken place since the beginning of the present century. This is unfortunate, since the electrochemical method not using any oxidant or reductant and involving only electrons which can be removed from or added to a system avoids the complications that are often involved in the process with redox reagents. Thus contamination due to extraneous agents is less likely in this method. Electrosynthesis gives high selectivity for the reactions taking place, since it is possible to apply the preferred voltage by a preliminary determination of the potential at which the reaction takes place. Synthesis of compounds at this specific potential may give the expected final products or intermediates which are subsequently converted into the required compounds.

The electrosynthesis of simple salts of Cr^{2+}, Ti^{3+}, V^{3+} etc. by the reduction of higher valence metal ions or the formation of Mn^{3+}, Co^{3+} etc. by the oxidation of lower valence ions of the respective metals is well known. The electrolytic method for the large-scale preparation of many inorganic compounds has also been used for decades. However, the electrosynthesis of complex compounds has not been studied widely. Some familiar reactions involving electrochemical oxidation are the conversion of hexacyanoferrate(II) to hexacyanoferrate(III), manganate(VI) to manganate(VII), sulphate to peroxydisulphate etc. Interesting reactions involving the electrochemical oxidation of the ligand have also been described [1]. The electrosynthesis of partly oxidized bridged complexes of platinum has been reported [2].

The electrosynthesis of complex compounds by dissolution of a sacrificial metal anode has been practised for the last 20 years or so [3–6] and a few reviews on the subject have been published [3,7,8]. Tuck, a pioneer and active worker in this field has published a large number of papers describing the electrosynthesis of complex compounds as well as organometallic compounds. The experimental technique is very simple. The electrolytic cell is a beaker in which two electrodes are dipped, a platinum foil or wire constituting the cathode and the anode being the corresponding metal in the form of rod, foil, lump etc. Cells with partition between the electrodes have been used by a few workers. The electrolyte is an aqueous, non-aqueous or mixed solvent containing the appropriate ligand or the ligand precursor and sometimes also containing an inert electrolyte such as tetraalkylammonium perchlorate to increase the electrical conductivity of the solution. With the passage of electric current, the anode goes into solution and forms a complex which is quite often precipitated during the electrolysis itself. In some cases the residual electrolyte needs some work-up for the recovery of the complex. The process uses the metals directly, and thus contamination of the product by the anions which is often encountered in chemical methods using the metal salts is absent. The method is rapid, highly selective and in most cases comprises a single step. The reaction is usually carried out at room temperature. Although the procedures given are applicable for small-scale preparation of the compounds, many of these can be scaled up for the preparation of larger quantities of substances by the application of higher current, increasing the time of electrolysis and using several cells in series.

The method does not require metals in an ultrapure state. Many metals are available in reasonably pure state at a moderate cost. Some metals which are not readily available may be previously deposited by electrolysis on a platinum foil or graphite cathode which can subsequently be used as the anode for the electrosynthesis of complex compounds.

A brief account of the electrosynthesis of different kinds of coordination compound by the dissolution of sacrificial metal anodes is presented in the following pages. The coverage is almost complete beginning from the early 1970s. Examples of the preparation of a few relatively simple salts are also included. Much work on the electrosynthesis of organometallic compounds has appeared and to make our review complete a brief account of the synthesis of a few such common compounds has also been included.

2. ANHYDROUS METAL HALIDES, SOLVATES OF HALIDES AND HALIDE COMPLEXES

Tuck and co-workers [3,9–11] reported a convenient method for the electrosynthesis of many anhydrous halides including a few lower valence halides, e.g. $CrBr_3$, $InCl_3$, InI, $MoCl_2$ and VCl_2 by the anodic dissolution of the metals in a non-aqueous medium containing the halogens. The electrochemical cell may be represented as

$$Pt(-)/\text{non-aqueous solvent} + X_2/M(+)$$

The electrosynthesis is rapid at room temperature with a high yield. The method is claimed to be better than the existing process for the preparation of anhydrous metal halides. When the above electrolysis is carried out in the presence of solvents which can act as good donors, solvated complexes may separate out. The solvate $ThX_4 \cdot 4CH_3CN$ was obtained by the dissolution of thorium in the presence of $X_2(X \equiv Cl, Br)$ in CH_3CN medium [12]. However, $ThI_2 \cdot 2CH_3CN$ was obtained with iodine [13]. A uranium anode yields the solvates $UX_4 \cdot nCH_3CN$ or UO_2X_2 and $UO_2X_2 \cdot nL$ depending on whether the electrolysis is carried out in a nitrogen atmosphere or in oxygen [14]. Some of these may be easily converted into other adducts. The preparation of $InCl_3 \cdot 3DMSO$ (DMSO ≡ dimethysulphoxide), $InBr_3 \cdot 3DMSO$, $UI_4 \cdot 4DMF$ (DMF ≡ dimethylformamide) and $MnBr_2 \cdot MeCN$ has also been reported by the same method [5,11,14].

A large number of neutral and anionic halide complexes have been prepared by the dissolution of metal anodes (Table 1). The electrolyte consists of an aqueous or non-aqueous solution of tetralkylammonium halides and the corresponding halogen [11,12,14,16] or of HX [17–29]. In the latter case, alkali metal halides may be added to the electrolyte before or after the electrolysis when the anionic complexes crystallize out. If the electrolyte contains a very dilute solution of HX and L, adducts, namely MX_2L or MX_2L_2, are obtained [19–22] (Table 1). The ligand may also be

TABLE 1

Electrosynthesis of complex halides

Complex	Comment	Synthesis	Reference
$(Et_4N)_2[InCl_5]$	$X \equiv Cl$ or Br	Electrolysis in CH_3CN medium containing R_4NX and X_2	[11]
$(Et_4N)_2[ThX_6]$			[12]
$(Et_4N[AuCl_2]$			[15]
$(Et_4N)[AuBr_4]$			[15]
$(Et_4N)_2[SnBr_6]$			[16]
$(R_4N)[TiX_4]$			[16]
$(R_4N)_2[UX_6]$			[14]
$(R_4N)_2[UO_2X_4]$			[14]
$(R_4N)[GaX_4]$			[17]
$(Ph_3PH)_2[Ga_2X_6]$	$X \equiv Cl$, Br or I	Electrolysis in CH_3CN medium containing Ph_3P+HX	[18]
$(PH_3PH)_2[CoCl_4]$ $[Co(Ph_3P)_2Cl_2]$		Electrolysis in aqueous CH_3CN medium containing Ph_3P+HCl	[19]
$H_2[PtCl_6]$ $H[AuCl_4]$		Electrolysis in HCl medium	[20]
$MX(Ph_3P)_n$	$X \equiv Cl$ or Br; $M \equiv Cu$, Ag or Au; value of n depends on the mole ratio of M and PPh_3	Electrolysis of M in $CH_3CN+HX+Ph_3P$	[21]
$M_2[PdX_4]$	$X \equiv Cl$ or Br	Electrolysis in 6 M HX, and then NH_4X, CsX, Me_4NX, $bipyH_2X_2$ or $phenH_2X_2$	[22]
$(Me_4N)_2[PdX_4]$	$X \equiv Cl$ or Br		
$LH_2[PdX_4]$	$X \equiv Cl$ or Br; $L \equiv$ bipy or phen		
$(NH_4)_2[PdCl_6]$ $M_2[PdX_6]$	$X \equiv Cl$ or Br	Electrolysis in saturated NH_4Cl solution	[22]

$(Me_4N)_2[PdX_6]$	X ≡ Cl or Br	Electrolysis in 6 M HX, and then CsX, Me_4NX, $bipyH_2X_2$ or $phenH_2X_2$ and X_2; alternatively electrolysis in 6 M HX + CsX, Me_4NX, $bipyH_2X_2$ or $phenH_2X_2$ (bipy and phen compounds with X ≡ Br could not be prepared by the latter method)	[22]
$LH_2[PdX_6]$	L ≡ bipy or phen		
$[PdX_2(py)_2]$	X ≡ Cl or Br	Electrolysis in 0.2 M HX + py, bipy or phen; alternatively electrolysis in 0.2 M HX, and then the ligands	[22]
$[PdX_2L]$	X ≡ Cl or Br; L ≡ bipy or phen		
$[PdX_2(NH_2R)_2]$	X ≡ Cl or Br; R ≡ CH_3CH_2 or $C_6H_5CH_2$	Electrolysis in 0.5 M HX + CH_3CN or C_6H_5CN	[22]
$K_2[MoOF_5]$		Electrolysis in 20% HF, and then KF	[22]
$K_2[TiF_6]$		Electrolysis in 20% HF, and then KF	[24]
$K_2[VOF_4]$			
$K_3[MF_6]$	M ≡ Cr, Fe		
$K[MF_3]$	M ≡ Mn, Co, Ni		
$K_2[NbOF_5]\cdot H_2O$			
$K_2[TaF_7]$			
$Fe_2F_5\cdot nH_2O$	$n = 2,7$	Electrolysis in 20% HF; the compounds are obtained from the residue	[24]
$K_2[MnF_5]\cdot H_2O$		Anodic oxidation of $[MnF_3]^-$ (formed in situ as above) using platinum anode, and then KF	[24]

added after the electrolysis. An interesting case has been observed while using an acetonitrile or benzonitrile medium containing very dilute HX, when the nitriles undergo cathodic reduction to the amines, giving rise to the adducts MX_2L_2 (Table 1).

Many metals in pure state react with solutions of HX only very slowly. The application of a potential speeds up the reaction. The applied voltage is low (2–8 V) and the yield is very good. Anodic dissolution of metals thus affords a convenient method for the synthesis of complex halides. Adducts, namely $MX(PPh_3)_n$ ($M \equiv Cu$, Ag and Au) are also obtained if the electrolysis is conducted, replacing HX with organic halides such as benzyl chloride, methyl iodide or ethyl bromide [30]. It has been suggested that an organometallic halide is formed by electrolysis which then decomposes by subsequent reaction with an excess of the organic halide. Using a copper anode and an electrolyte containing alkyl halide and 2,2′-bipyridyl or tetraethylammonium halide, neutral or anionic halide complexes are synthesized [31].

3. SOLVATED COMPLEXES

The electrosynthesis of a large number of solvated complexes containing anions other than halides has been achieved. The electrolysis of a solution of silver perchlorate in CH_3CN using a tin anode has been used to synthesize the solvated complex $Sn(C10_4)_2 \cdot 2CH_3CN$ [32]. The electrolysis of $NaBH_4$ in liquid ammonia using a magnesium anode and a mercury cathode gives $Mg(BH_4)_2 \cdot 6NH_3$ with a 98% yield [33]. The ammonia molecules can be easily removed in vacuum at about 100°C to give the borohydride $Mg(BH_4)_2$. Electrosynthesis of $Al(BH_4)_3 \cdot 6NH_3$ has also been described [34]. The electrochemical oxidation of both transition and main group metals in the presence of DMSO or acetonitrile and HBF_4 gives the complexes $[M(Me_2SO)_6](BF_4)_n$ ($M \equiv V$, Cr, Mn, Fe, Co, Ni, Zn, Cd, or In; $n = 2$ or 3 depending on M) or $[M(NCMe)_6](BF_4)_3$ ($M \equiv Ti$ or In) and $[Cr(NCMe)_m](BF_4)_2$ ($m = 4$ or 6) [35]. The adduct $Th(NO_3)_4 \cdot 8DMSO$ has been obtained [36] from an electrolyte containing nitric acid, tributylphosphate and DMSO.

4. CYANIDE AND THIOCYANATE COMPLEXES

Electroplating grade $K[Au(CN)_2]$ has been prepared conveniently by the potentiostatic dissolution of gold in potassium cyanide solution at +0.345 V (with respect to a saturated calomel electrode (SCE)) using a H-type cell with partition [37]. The oxidation of silver and mercury electrodes in the presence of thiocyanate gives [38] AgSCN and $Hg(SCN)_2$. Anionic thiocyanate complexes of Zn, Cd, Ga(III), Co(II) and Au(III) have been synthesized [39] from a non-aqueous solution of thiocyanic acid using the metals as anode (Table 2). An obvious disadvantage of the method is that it uses thiocyanic acid which is not stable and has to be prepared fresh. A general method for the electrosynthesis of anionic and mixed ligand thiocyanato complexes of transition metals has been developed [40] by the oxidation of sacrificial metal anodes in aqueous or mixed aqueous ammonium thiocyanate solu-

TABLE 2

Electrosynthesis of thiocyanato complexes

Complex	Comment	Synthesis	Reference
$(R_4N)_2[Zn(NCS)_4]$		Electrolysis in non-aqueous medium containing HSCN	[39]
$(Ph_4P)_2[Zn(NCS)_4]$			
$(R_4N)_2[Cd(NCS)_4]$			
$(Bu_4N)_3[Ga(NCS)_6]$			
$(Et_4N)_2[Co(NCS)_4]$			
$(Et_4N)[Au(NCS)_4]$			
$(Me_4N)_3[Cr(NCS)_6]$		Electrolysis in aqueous NH_4NCS solution, and then Me_4NCl or $(Me_4N)NCS$; with Fe anode, electrolysis was *carried out in an* N_2 *atmosphere*	[40]
$(Me_4N)_2[M(NCS)_4]$	M ≡ Mn, Fe, Co, Cu, Zn or Cd		
$(Me_4N)_4[Ni(NCS)_6]$			
$(Me_4N)_4[Mo_2O_4(NCS)_6]$			
$(Me_4N)_3[Fe(NCS)_6]$		Anodic oxidation of $[Fe(NCS)_4]^{2-}$ (formed in situ as above) using Pt anode, and then Me_4NCl	[40]
$[M(py)_4(NCS)_2]$	M ≡ Mn, Fe, Co or Ni	Electrolysis in aqueous or aqueous ethanolic medium containing py, bipy or phen	[40]
$[M(py)_2(NCS)_2]$	M ≡ Cu, Zn or Cd		
$[Mo_2O_4(py)_4(NCS)_2]$			
$[ML_2(NCS)_2]$	M ≡ Mn, Fe, Co, Ni or Cd; L ≡ bipy or phen		
$[ML(NCS)_2]$	M ≡ Cu, Zn or Cd; L ≡ bipy or phen		
$[Mo_2O_4(NCS)_2L_2]$	L ≡ bipy, phen		

tion (Table 2). An advantage of this method lies in the fact that it uses an aqueous or mixed aqueous solvent at room temperature, while the common methods for the preparation of thiocyanate complexes often use non-aqueous solvents and sometimes involve reactions in the melt.

5. METAL CARBOXYLATES AND CARBOXYLATO COMPLEXES

The transition metal carboxylates $M(O_2CR)_n$ ($M \equiv Cr$; $R \equiv C_2H_5$ or C_6H_5; $n=3$) ($M \equiv Mn$, Fe or Ni; $R \equiv CH_3$, C_2H_5, C_6H_5 or n-C_7H_{15}; $n=2$) have been prepared [41] by oxidizing appropriate metal anodes electrochemically in solutions of RCOOH in acetonitrile. With cobalt and copper a wide range of carboxylic acids has been used successfully to give $M(O_2CR)_2$ [41–43]. The advantages of the method have been discussed. The preparation of $Cu(O_2CR)_2$ involves the prior formation of CuO_2CR at the anode, followed by oxidation by the solvent. The electrochemical synthesis of oxalato complexes of iron and copper has also been reported [44].

6. NEUTRAL METAL CHELATES WITH β-DIKETONATES, 8-HYDROXYQUINOLINATES etc.

The electrosynthesis of many neutral metal chelates by the dissolution of the metal anodes into solutions of β-diketones, 8-hydroxyquinoline, dimethylglyoxime etc. has been described [40,45–48]. In all cases the electrode reactions are given by the equations

cathode: $n\mathrm{HL} + n\mathrm{e} \rightarrow n\mathrm{L}^- + n\tfrac{1}{2}\mathrm{H}_2$

anode: $n\mathrm{L}^- + \mathrm{M} \rightarrow \mathrm{ML}_n + n\mathrm{e}$

Table 3 summarizes the procedures for the electrosynthesis of β-diketonates and their adducts. The electrolytic oxidation of titanium, vanadium and uranium in the complete absence of oxygen gives $Ti(acac)_3$, $V(acac)_3$ and $U(acac)_4$. In an atmosphere of oxygen the products are $TiO(acac)_2$, $VO(acac)_2$ and $UO_2(acac)_2$ or $UO_2(acac)_2 \cdot Hacac$ [49–51].

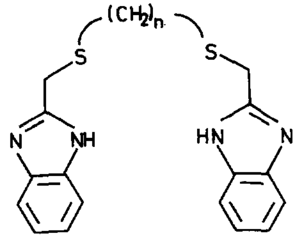
7. COMPLEXES WITH PYRAZOLES, IMIDAZOLES, PHTHALOCYANINES etc.

Chelated complexes ML_n with a large number of metals have been prepared by electrolysis of solutions containing pyrazoles [53–55], imidazoles [56–58] and phthalocyanine [59]. The electrochemical synthesis and physicochemical properties of neutral divalent transition metal (Ni, Co, Cu, Zn and Cd) complexes, $[ML] \cdot nH_2O$ ($H_2L \equiv$ 1,7-bis-(2-benzimidazolyl)-2,6-dithioheptane or 1,6-bis(2-benzimidazolyl)-2,5-dithiohexane; represented by **I** have been reported [60]. The dianionic ligands act as tetradentate ligands with both thioether sulphur atoms and deprotonated benzimidazole nitrogen atoms coordinating. Mixed ligand complexes of the type

TABLE 3

Electrosynthesis of β-diketonato complexes and their adducts

Complex	Comment	Synthesis	References
M(acac)$_2$ M(acac)$_3$ MO(acac)$_2$ UO$_2$(acac)$_2$ UO$_2$(acac)$_2$–Hacac	M ≡ Mn, Fe, Co, Ni, Cu or Cd M ≡ Ti, V, Cr or In M ≡ Ti or V	Electrolysis in non-aqueous medium containing acetylacetone + tetralkylammonium perchlorate	[4,11,12] [49–51]
M(benzacac)$_2$ U(benzacac)$_4$ UO$_2$(benzacac)$_2$	M ≡ Ni, Co, Cu, Zn or Cd	Electrolysis in non-aqueous medium containing the β-diketone + tetralkylammonium perchlorate	[51,52]
Th(acac)$_4$ Th(CF$_3$COCH$_2$COC$_3$H$_7$)$_4$		Electrolysis as above	[12]
Cd(RCOCHCOR′)$_2$L Cd(CF$_3$COCHCOC$_6$H$_5$)$_2$·phen	L ≡ bipy, phen or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine	Electrolysis as above in the presence of L or by the addition of L after electrolysis	[46]



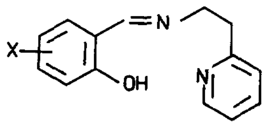
I

[ML(L′)] where L′ ≡ 2,2′-bipyridine and 1,10-phenanthroline have been obtained in a few cases when the electrolyte contained these ligands. The electrochemical oxidation of a metal anode in a nonaqueous solution of dpaH (dpaH ≡ 2,2′-dipyridineamine) under nitrogen gives M(dpa)$_n$ complexes (M ≡ Cu, Ag or Tl; $n = 1$) (M ≡ Zn or Cd; $n = 2$) with a high yield [61]. Copper yields Cu(dpa)$_2$ in the presence of oxygen. When the electrolysis is repeated in the presence of neutral ligands, adducts are obtained only for Cu(I) with phosphine donors.

8. SCHIFF BASE COMPLEXES

The electrochemical method has proven to be very useful for the synthesis of numerous neutral complexes with anions of Schiff bases of the composition ML or ML$_2$. Many of these are important from a structural point of view and have biological significance and could not be prepared by standard chemical methods. Much work in this area is being published by Sousa. The synthesis is based on the electrolysis of an acetonitrile or acetone solution of the preformed Schiff bases using the metal as anode where the complexes precipitate out as powders. Hydrogen is liberated at the cathode. The nature of the reaction at the anode is explained from the value of the electrochemical efficiency. Most of the complexes prepared have been characterized by IR, ^{1}H NMR and mass spectra.

A large number of complexes of different metals and Schiff bases derived from salicylaldehydes, monoamines and diamines have been prepared. The electrochemical synthesis of neutral Cu(II) complexes of Schiff bases derived from 2-(2-aminoethyl) pyridine and substituted salicylaldehydes (II) has been reported [62–64]. The electro-



II

chemical yield is close to 1 mol F^{-1}, indicating that the synthesis involves the processes

cathode: $LH + e^- \rightarrow L^- + \frac{1}{2}H_2$ (1)

and

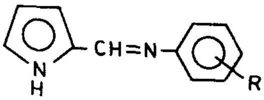
anode: $L^- + Cu \rightarrow [CuL] + e^-$ (2)

followed by the oxidation reaction

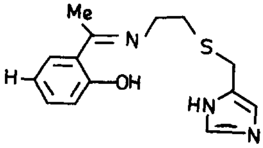
$CuL + HL \rightarrow [CuL_2] + \frac{1}{2}H_2$ (3)

Similar complexes of zinc and cadmium have also been synthesized electrochemically [65–67].

The electrochemical oxidation of cobalt in an acetonitrile solution of Schiff bases (HL) derived from H-pyrrole-2-carbaldehyde and substituted anilines (**III**) gives solutions from which [CoL_3] complexes are obtained [68]. When 1,10-phenanthroline or 2,2′-bipyridine is added to the electrolyte phase, crystals of [CoL_2(phen)] or [CoL_2(bipy)] are deposited. The electrochemical efficiency is close to 0.5 mol F^{-1}, implying that the primary product of anodic oxidation is Co(II) which gives crystals of [CoL_2(bipy)] or [CoL_2(phen)] in the presence of the coligands. However, in the absence of these ligands, subsequent aerial oxidation during evaporation gives the [CoL_3] complex. Sousa and co-workers [69] have also reported the electrosynthesis of neutral Cu(II) complexes of tetradentate Schiff bases derived from 4(5)-[(2-aminoethyl)thiomethyl]imidazole and *o*-hydroxy acetophenones (**IV**). These neutral complexes could not be prepared by a chemical method using copper(II) salts which resulted in only cationic complexes such as [Cu(HL)]$ClO_4 \cdot 2H_2O$ and Cu(HL)$O_2CCH_3 \cdot nH_2O$. The electrochemical synthesis and physicochemical properties of neutral Zn(II), Cd(II), Ni(II) and Cu(II)



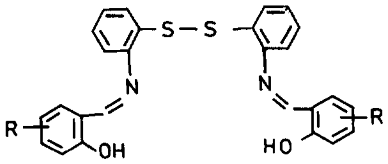
III



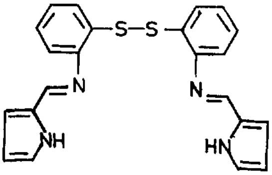
IV

complexes of Schiff bases derived from aminothioetherimidazoles and substituted salicylaldehydes have also been reported [62].

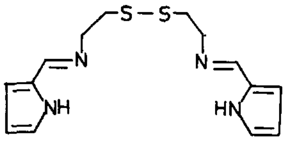
The electrochemical reductive cleavage of the disulphide bond present in preformed Schiff bases such as **V**–**VII** has been used to generate complexes of Ni(II), Cu(II), Zn(II), Cd(II) and Sn(IV) [69–71]. The electrochemical oxidation of tin in acetonitrile solutions of **V** yields compounds of formulation SnL_2, where LH_2 is represented by **VIII** [71]. Initially at the anode a tin(II) complex is formed and this is subsequently oxidized to the tin(IV) complex. The nature of the latter reaction is



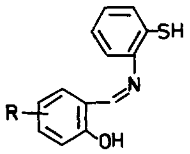
V



VI



VII



VIII

not clear. Under the same conditions, copper, however, gives the CuL complex. The electrochemical efficiency is close to 1.0 mol F^{-1}. It was postulated that the formation of Cu(I) at the anode is followed by oxidation to Cu(II) in solution. The mechanism, however, has not been explained. The complex derived from salicylaldehyde was shown to be identical with that prepared by conventional routes [72–75]. The introduction of nitrogeneous Lewis bases into the electrochemical cell gave the adducts CuL·L′ (where L′≡pyridine, 2,2′-bipyridine and 1,10-phenanthroline). Dissolution of nickel, copper, zinc and cadmium anodes in acetonitrile solutions of **VI** and **VII** gives the complexes of 2-[(2-mercaptophenyl)iminomethyl]pyrrole and 2-[(2-mercaptoethyl)iminomethyl]pyrrole by the cleavage of the Schiff bases H_2L_2 (**VI**) and H_2L_2' (**VII**). The complexes [ML], [ML′] or $[Zn(HL)_2]$ are otherwise difficult to prepare by conventional synthesis routes [76]. The electrochemical efficiency was found to be about 0.5 mol F^{-1} for nickel, zinc and cadmium. The reaction mechanism can therefore be written as

$$\text{cathode: } \tfrac{1}{2}H_2L_2 + 2e \rightarrow L^{2-} + \tfrac{1}{2}H_2$$

$$\text{anode: } L^{2-} + M \rightarrow [ML] + 2e \tag{4}$$

and

$$\text{cathode: } H_2L_2 + 2e \rightarrow 2HL^-$$

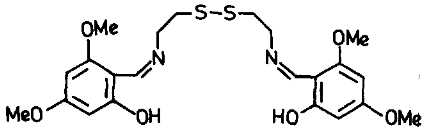
$$\text{anode: } 2HL^- + Zn \rightarrow [Zn(HL)_2] + 2e \tag{5}$$

for the [ML] and $[Zn(HL)_2]$ systems respectively.

The E_F values for the copper complexes are also close to unity.

However, the electrochemical oxidation of anodic zinc in acetonitrile solutions of the Schiff bases (H_2L_2) such as **IX** yields compounds of the formula ZnL_2 in which no reductive cleavage of the S–S bond has occurred [76].

The electrochemical synthesis of the *N,N*′-ethylene(monothioacetylacetoniminato)cobalt(II), copper(II), nickel(II) and zinc(II) complexes has been achieved by anodizing the corresponding metal microelectrodes at 60–70°C in an H-shaped cell with the anodic and cathodic compartments separated [77]. The electrolyte was an acetonitrile solution containing the free ligand and sodium acetate. The working potential was predetermined by recording the single-sweep voltammograms using the metal micro electrodes. Verification of the nature of the complex formed in situ



IX

in the electrolysed solutions was made by recording the cyclic voltammograms on the electrolysed solutions.

9. ALKOXIDES AND THIOLATES

Electrosynthesis is one of the most widely encountered methods for the preparation of metal alkoxides [7,78–81]. The method uses the electrolysis of an alcohol containing a supporting electrolyte using the metals as anode. Adducts with 2,2′-bipyridine, 1,10-phenanthroline and DMSO of the composition $Hg(OR)_2L$ have been isolated by electrochemical reactions of methanol or ethanol containing these ligands using a mercury anode [82]. Such adducts are not formed by refluxing the alkoxides with the ligands because the donor molecules are unable to rupture the alkoxide bridge. Recent electrochemical studies with catechol or other aromatic 1,2-diols have led to the synthesis of some new and structurally important compounds of a few metals in low oxidation states [83–85]. The electrochemical oxidation of anodic tin in non-aqueous solutions of aromatic diols $R(OH)_2$ gives rise to $Sn(O_2R)$ with a high yield [84]. The previous routes to such tin(II) compounds involve more laborious procedures. The adducts $Sn(O_2R)(phen)$ are obtained when the electrolyte contains 1,10-phenanthroline. The electrochemical efficiency is close to 0.5 mol F^{-1} which is consistent with either of the two following sets of electrode reactions involving the formation of monovalent or bivalent catecholate ion:

$$\text{cathode: } R(OH)_2 + 2e \rightarrow RO_2^{2-} + H_2 \qquad (6a)$$

$$\text{anode: } RO_2^{2-} + Sn \rightarrow Sn(O_2R) + 2e \qquad (6b)$$

or

$$\text{cathode: } 2R(OH)_2 + 2e \rightarrow 2RO_2H^- + H_2 \qquad (7a)$$

$$\text{anode: } 2RO_2H^- + Sn \rightarrow Sn(O_2R) + R(OH)_2 + 2e \qquad (7b)$$

The alkoxide $Sn(O_2R)$ undergoes oxidative addition reactions with iodine to give $Sn^{IV}I_2(O_2R)$ and with the substituted *o*-quinones $O_2C_6X_4$ ($X \equiv Cl$ or Br) to give the corresponding catecholates $Sn^{IV}(O_2R)(O_2C_6X_4)$.

The electrochemical oxidation of zinc and cadmium in the presence of diols also gives products similar to those obtained with tin [83]. With indium, however, unusual and new indium compounds In[OR(OH)] are obtained [85]. The electrochemical efficiency is close to 1 mol F^{-1} which, as in the case of tin, is compatible with two alternative sets of electrode reactions. An analogous thallium compound $Tl[OC_{12}H_8(OH)]$, derived from 2,2′-dihydroxydiphenyl, was earlier prepared by a chemical method [86]. Compounds with such oxohydroxo ligands are unusual and present a number of interesting structural problems for investigation. The In(I) compounds are susceptible to air oxidation and show reactions typical of In(I) chemistry. They undergo oxidative additive reactions with iodine to give

$In^{III}I_2[OR(OH)]$ and, by substituted *ortho*-quinone, $Br_4C_6O_2$ in the presence of 2,2′-bipyridine, giving six-coordinated In(III) compounds $In[OR(OH)](O_2C_6Br_4)(bipy)$. The reactions are analogous to those of tin(II) catecholates described above. The hydroxy-oxo ligand in InOR(OH) can be deprotonated by Et_3N to give the salts $Et_3NH[In(O_2R)]$. The electrochemical oxidation of copper in an acetonitrile solution of diols in the presence of nitrogen or phosphorus donor ligands gives adducts of Cu(I) catecholates [87].

Studies have been extended to substrates containing a carbonyl or O–R group ortho to a phenolic OH group [88,89]. The electrochemical oxidation of metals (M ≡ Zn, Cd, Hg, In or Sn) in non-aqueous solutions of 3-hydroxyflavone, 1′-hydroxy-2′-acetonaphthone or 2-ethoxy phenol (HL) gives ZnL_2, CdL_2, HgL, InL_3 or SnL_2. Adducts with 2,2′-bipyridine, *N,N,N′,N′*-tetramethylethanediamine (tmen) and triphenylphosphine have been prepared in some cases. With zinc, cadmium and tin anodes the electrochemical efficiency is close to 0.5 mol F^{-1} corresponding to the formation of products with the metals in the 2^+ state. For indium, however, $E_F = 1.02$ mol F^{-1}, implying the formation at the anode of In(I) species which subsequently undergoes disproportionation in solution as follows:

$$3InL \rightarrow 2In + InL_3$$

During the initial stages of electrolysis the formation of a yellow solid is observed. This quickly decomposes with the deposition of metallic indium in quantities required by the stoichiometry of the above reaction.

Metal derivatives ($M^{(II)} \equiv$ Zn, Cd, Sn or Cu; $M^{(III)} \equiv$ In) of 3-hydroxy-2-methyl-4-pyrone and their adducts have been prepared by a similar method [89]. The tin(II) compound shows the typical reactions of such low oxidation state species by reacting with iodine and ortho-quinones by oxidative additions.

Tuck and co-workers have shown that, as with alkoxides, the electrochemical method is very convenient for the direct synthesis of thiolates of both main group elements and transition metals. The products are the metal thiolates, their adducts or anionic cage complexes depending on the compositions of the electrolytic phase. The thiolato derivatives of transition metals have been the subject of considerable recent interest, because a number of these compounds are believed to serve as models for active metal–sulphur sites in metalloproteins [90]. The benzenethiolates of Sn(II), Pb(II) [91], Zn(II), Cd(II) and Hg(II) [92,93] can be easily prepared. Direct electrochemical synthesis of metal pentafluorothiophenolates has also been reported [94]. The processes taking place at the electrodes are described by the equations

anode: $n\mathrm{PhS}^- + M \rightarrow M(SPh)_n + ne$

cathode: $2PhSH + 2e \rightarrow 2PhS^- + H_2$

The electrochemical oxidation of tin first leads to the formation of $Sn(SR)_2$. In the presence of 2,2′-bipyridyl or 1,10-phenanthroline the initial product is oxidized to a Sn(IV) species, $Sn(SR)_4L$ [95]. With a lead anode the product is $Pb(SR)_2$ and no Pb(IV) species can be isolated. Cobalt(II) and nickel(II) thiolates $M(SR)_2$ and their adducts have been prepared with a number of thiols [96]. In the case of $[Co(SC_6H_5)_2(phen)_2]$, aerial oxidation leads to the formation of the cobalt(III) cation $[Co(SC_6H_5)_2(phen)_2]^+$ isolated as the perchlorate salt.

Copper and silver can be oxidized to give the M(I) thiolates with an excellent yield [97]. For copper, a variety of thiols give CuSR as air-stable insoluble compounds. When 1,10-phenanthroline is added to the electrolyte, the adducts CuSR.phen are obtained. Treatment of $CuSCMe_2Et$ or $CuSC_5H_{11}$ with carbon disulphide produces $Cu_8(SR)_4(S_2CSR)_4$ whose structure is based on an unusual Cu_8S_{12} cage having many interesting features [98]. As an extension to this work, adducts of various Cu(I) thiolates with bis(diphenylphosphino)methane(dppm), $(CuSR)_2 \cdot$dppm and $(CuSR)_2 \cdot 1.5$dppm have been prepared [99]. The crystal structure of the adducts $(CuSC_5H_{11})_2 \cdot$dppm reveals the presence of a novel central Cu_4S_4 ring, capped by two six-membered Cu_2SCP_2 rings in the boat form. The reaction between this compound and carbon disulphide gives the insertion product $CuS_2CSC_5H_{11} \cdot$dppm as noted above. Similar in-situ formation of the $RSCS_2$ derivative takes place with $CuSC_5H_{11}$ itself and also with $Cd(SR)_2(R \equiv n\text{-}C_4H_9$ or $C_6H_5)$ [100].

Unusual anionic thiolato complexes of zinc and cadmium, namely $[(C_2H_5)_3NH]_2[M_4(SC_6H_5)_{10}]$, have been prepared using an acetonitrile solution of benzenethiol, triethylamine and tetraethylammonium perchlorate as supporting electrolyte [92,101]. The structure of the anion is based on the M_4S_{10} kernel with both bridging and terminal thiolato groups [102–109].

Zinc, cadmium and mercury(II) thiolates $M(SPh)_2$ have also been prepared using disulphides [93]. In this case they are reduced at the cathode:

$$Ph_2S_2 + 2e \rightarrow 2PhS^-$$

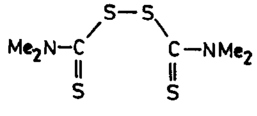
Polymeric alkanedithiolates of copper and silver, namely M_2S_2R, can be obtained with a high yield by electrochemical procedures [110]. Compounds of such ligands are of current biochemical importance. They also present some challenging structural problems. The electrochemical efficiency is close to 1 mol F^{-1}. When triphenylphosphine or bis(diphenylphosphino)methane is present in the solution, copper yields adducts whose stoichiometry apparently depends on R. The molecule $[Cu_2S_2C_3H_6 \cdot (C_6H_5)_2PCH_2P(C_6H_5)_2]_4 \cdot 4CH_3CN$ has a core Cu_4S_4 eight-membered ring, which is capped by six-membered Cu_2S_2 and Cu_2P_2CS rings and five-membered CuS_2C_2 rings. Reaction of $Cu_2S_2C_3H_6 \cdot 4PPh_3$ with carbon disulphide yields a material corresponding to the formula $Cu_2S_2C_3H_6 \cdot 4PPh_3 \cdot 3CS_2$, which, however, has not been structurally characterized. Electrochemical oxidation with solutions of alkanedithiols $R(SH)_2$ gives rise to MS_2R species and their adducts, for $M \equiv Zn$ and Cd [111] and to some unusual low oxidation state species for $M \equiv In$ [112].

Sousa and co-workers have achieved electrochemical synthesis of pyridine-

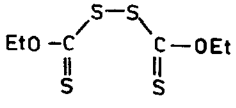
2-thionato complexes of some metals and their adducts. Such complexes are of current interest because of their important biological role and other wide-ranging applications [113]. Zinc, cadmium and nickel(II) complexes $M(pyt)_2$ have been prepared by the direct electrochemical oxidation of the metal into a solution of pyridine-2-thione (pytH) in acetonitrile [114,115]. Adducts are obtained by the addition of the ligands to the electrolyte. The electrochemical oxidation of nickel in pyrimidine 2-thione(pymtH) solution yields $Ni(pymt)_2$. Adducts with 2,2′-bipyridine and 1,10-phenanthroline can also be obtained [116]. In $[Ni(pymt)_2(bipy)]\cdot H_2O$ the nickel has a highly distorted octahedral coordination and the pyrimidine-2-thiolato ligand is bidentate, forming two four-membered chelate rings. The two sulphur atoms are as expected in the trans position. Complexes of Cu(I), Ag(I) and Ni(II), namely $[Cu(mimt)]_4$, [Ag(mimt)] and $[Ni(mimt)_2]$, have been electrochemically synthesized using the ligand 1-methylimidazoline-2(3H)-thione (mimtH) [117]. The copper (I) complex of thiazole-2-thionate [Cu(tzt)] has also been synthesized [117]. It appears that the synthesis of many novel thiolato and thionato complexes is possible by this electrochemical method.

10. COMPLEXES WITH XANTHATES AND OTHER SULPHUR LIGANDS

A general method for the direct electrochemical synthesis of *O*-ethylxanthato and *N*,*N*-dimethyldithiocarbamato complexes has been developed by Casey and Vecchio [118–120] by the electrolysis of an acetone solution of the oxidized form of the ligands (neutral ethyl dixanthogen (**X**) or tetramethylthiouram disulphide (**XI**)) using the metals as anode. Attempted preparations in the presence of various dithiocarbamate or xanthate anions failed or produced impure products. The complexes $[M(exa)_3]$ or $[M(me_2dtc)_n]$ are generally those of the metals in conventional oxidation states and have been previously known. Electrolysis of tin with ethyl dixanthogen produces the unusual pale yellow $[Sn(exa)_2S]_2$, while vanadium gives the oxo-vanadium(IV) complexes and cobalt gives the Co(III) derivatives directly.



X



XI

The current efficiencies were typically 0.1–1 mol F^{-1}, suggesting that some chain reaction follows the initial electrochemical step. It is believed that the neutral organic reagents undergo reduction to the ligand anions at the cathode. Dialkyldithiocarbamato derivatives $(R_2NCS_2)_nM$ of a number of metals have also been synthesized with almost quantitative yields by Tuck and co-workers [121] by the electrochemical oxidation of the metals in non-aqueous solutions of either the corresponding tetraalkylthiouram disulphide or a mixture of carbon disulphide plus the secondary amine [121]. The electrochemical yields in the hands of these workers were close to the theoretically expected value, implying the following electrode reactions for Fe, Co, Ni, Zn and Cd:

cathode: $(R_2NCS_2)_2 + 2e \rightarrow 2R_2NCS_2^-$

anode: $M + 2R_2NCS_2^- \rightarrow M(S_2CNR_2)_2 + 2e$

Silver and thallium give the complexes ML. Copper, indium, thallium and iron initially give CuL, InL, TlL and FeL_2 as the products at the anode, which subsequently undergo oxidative addition reactions to give the higher valence compounds:

$ML + L_2 \rightarrow ML_3 (M \equiv In \text{ or } Tl)$

$ML_2 + \frac{1}{2}L_2 \rightarrow ML_3 (M \equiv Fe)$

$ML + \frac{1}{2}L_2 \rightarrow ML_2 (M \equiv Cu)$

When a mixture of carbon disulphide, secondary amine and an appropriate solvent is used as the electrolyte, $R_2NC(S)SH$ is first formed. The following reactions then take place at the electrodes:

cathode: $nR_2NCS_2H + ne \rightarrow \frac{1}{2}nH_2 + nR_2CNS_2^-$

anode: $M + nR_2NCS_2^- \rightarrow M(S_2CNR_2)_n + ne$

Tuck and co-workers [121] have also achieved the electrosynthesis of analogous complexes of transition and main group metals with diethyldithiophosphate using $(EtO)_2PS_2H$ in the electrolyte. Adducts are obtained with 1,10-phenanthroline. Anodic dissolution of metals in nonaqueous solutions of 4-phenylthiosemicarbazide (HPTS) or 1,4-diphenylthiosemicarbazide (HDPTS) yields complexes of the composition $M(PTS)_n$ and $M(DPTS)_n$ with $n=1$ for Cu and 2 for Cd, Co, Fe and Zn. Adducts are obtained in the presence of 1,10-phenanthroline [122]. IR spectra show that the ligands are coordinated via thioenol and NH groups.

11. DIPHENYLPHOSPHIDO AND *O*-ALKYL PHOSPHITE COMPLEXES

Tuck and co-workers [123,124] have extended the electrochemical technique to prepare the diphenylphosphido derivatives, e.g. $M(PPh_2)$ ($M \equiv Cu$, Ag or Au), $M(PPh_2)_2$ ($M \equiv Co$, Zn or Cd) and $Ni(PPh_2) \cdot PPh_2H$. With a solution of Ph_2PH and bis(diphenylphosphino)methane (dppm) a copper anode gives

$Cu_4(PPh_2)_4(dppm)_2$ having interesting structural features. The oxidation of Co, Ni, Zn and Cd anodes in a solution of Ph_2PH and sulphur in an acetonitrile–toluene mixture gives $M(S_2PPh_2)_2$ complexes. The zinc compound was shown to be identical with that reported earlier [125]. The unusual nickel(I) complex $Ni(PPh_2)\cdot PPh_2H$ is oxidized by elemental oxygen, sulphur or selenium to give $[NiE_2(PPh_2)]$ ($E \equiv O$, S or Se). It also reacts with PhNCS to yield $[Ni\{PPh_2(SCNPH)\}_2]$, the structure of which consists of the square planar NiS_2P_2 core. Aluminium tris(*O*-alkylphosphites) with the alkyl group having one to 12 carbon atoms have been synthesized by the electrolysis of an aqueous solution of dialkylphosphites [126].

12. PEROXO COMPLEXES

A few reports on the electrosynthesis of peroxo complexes have been published very recently. A number of transition metal anodes dissolve in aqueous hydrogen peroxide in the cold. From the solution, different peroxo complexes, e.g. $K[VO(O_2)_2(H_2O)]$ and $K_3[VO(O_2)_3]\cdot 3H_3O$, have been isolated by raising the pH with KOH [127]. If the electrolysis is carried out in the presence of aqueous hydrofluoric acid, peroxofluoro complexes, e.g. $[MO(O_2)F_4]^{2-}$ ($M \equiv$ Mo or W), $[M(O_2)F_5]^{2-}$ ($M \equiv$ Nb or Ta) and $[VO(O_2)_2F]^{2-}$, are obtained [128]. Other heteroligand peroxo complexes, e.g. $[MO(O_2)_2L]$ ($M \equiv$ Mo or W; $L \equiv$ 2,2′-bipyridyl, 1,10-phenanthroline or 2,2′-bipyridyl-*N*,*N*′-dioxide), are obtained by the addition of the heteroligands to the solution left after electrolysis [129]. It appears that the electrochemical method may be general for the synthesis of a wide variety of peroxo complexes of various transition metals.

13. ORGANOMETALLIC COMPOUNDS

Organometallic compounds of both main group elements and transition metals and belonging to widely different classes have been prepared by the dissolution of metal anodes. The synthesis of metal derivatives of many C–H acids has been described. Ferrocene and other cyclopentadienyl complexes have been obtained in good yield by the electrochemical solution of iron and other metal anodes in a solution of Mcp ($M \equiv$ Li, Na, K or Tl) or cyclopentadiene (or its alkyl-substituted compound) itself in suitable organic solvents [130–133]. Several procedures [130,134] for the electrosynthesis of ferrocene have been claimed to be useful as industrial methods. An electrochemical method for the direct synthesis of phenylacetylides and their adducts of many metals has been given by Kumar and Tuck [135]. In a recent paper, Casey and Vecchio [136] have described detailed procedures for the electrosynthesis of a wide range of metallocenes, polymethylated metallocenes, "open metallocenes" (derivatives of 2,4-dimethylpentadiene), phenyl acetylides (including their adducts) and metal derivatives of fluorene and indene. Current efficiencies indicate faradaic behaviour. As the pK_a value increases, it becomes progressively more difficult to deprotonate these C–H acids with alkali, whereas the rupture of the C–H bond occurs readily through electrolysis. Thus the electrosynthesis provides a significant improvement over the conventional route via alkali metal salts of the carbon acids and it appears to be a general method applicable for all such weak acids.

Tetraethyllead is prepared on an industrial scale by the electrolysis of a solution of ethyl magnesium chloride and excess of ethyl chloride using a copper gauge cathode and lead granules as the anode [137]. It is considered [138,139] that the anodic reactions involved in the formation of many compounds with a metal–carbon bond takes place by a radical mechanism. Tuck and co-workers have studied extensively the direct electrochemical synthesis of organometallic halides of both main group elements and transition metals. The electrochemical oxidation of metals in a cell containing an alkyl or aryl halide results in the formation of organometallic halides mainly of the types RMX and R_2MX_2 which are stabilized by complex formation with suitable donors present in the solution giving compounds of the types RMX(bipy), R_2MX_2(bipy), $R_2MX_2 \cdot 2MeCN$ etc. [140,141]. These studies have been reviewed [3]. The organometallic halides may be converted to anionic species, e.g. $(Pr_4N)[RZnX_2]$, when the electrolysis is carried out in the presence of tetrapropylammonium halide [141].

14. MECHANISM

An important aspect which has remained neglected until now is the study of the mechanism of the reactions involved in the electrosynthesis of coordination compounds. By contrast, many mechanistic studies of the electrosynthesis of organic compounds and electrochemically induced reactions have been carried out. Two important parameters are measured as routine practice by the workers in this field: the chemical yield and the current efficiency, or the electrical yield or the electrochemical efficiency. The chemical yield is defined as the number of moles of the product divided by the number of moles of the metal dissolved and is expressed as a percentage. The electrochemical efficiency E_F is defined as the number of moles of the metal dissolved per faraday of electricity passed through the cell; this measurement is made at a controlled constant current. Most of the mechanisms proposed until now are based solely on the electrochemical efficiency and do not give much information beyond the overall reactions at the electrodes. For example, in the direct electrochemical synthesis of $[Ni(pyt)_2]$ where Hpyt is pyridine-2-thione, hydrogen is liberated at the cathode and the E_F value is close to 0.5 mol F^{-1}, from which the "reaction mechanism" has been proposed as follows [114,115]:

cathode: $2Hpyt + 2e \rightarrow H_2(g) + 2pyt^-$

anode: $2pyt^- + Ni \rightarrow [Ni(pyt)_2] + 2e$

In some cases a lower valence complex species is formed at the anode, which quickly undergoes disproportionation, giving the metal and a stable complex in the higher valence state of the metal. A calculation of the E_F value based on the loss in weight of the anode will naturally be much higher. As stated earlier, the electrosynthesis of some In(III) compounds gave E_F values of about unity, implying the formation at the anode of an In(I) species which subsequently undergoes disproportionation in solution as follows [88,89]:

$$3InL \rightarrow 2In + InL_3$$

An unusually high and non-integral E_F value (1–20 mol F^{-1}) observed in some electrosyntheses has been ascribed to chain reactions. For a variety of organometallic halide preparations from alkyl halides and metal the following simple reaction mechanism has been proposed [3,142]:

$$RX \xrightarrow{e-} [RX^-] \rightarrow R\cdot + X^- \tag{8}$$

Under the high applied potential (10–50 V), the halide ion migrates to the anode, where the proposed sequence of reactions is

$$X^- \rightarrow X\cdot + e^- \tag{9}$$

$$X\cdot + M \rightarrow MX \tag{10}$$

$$MX + RX \rightarrow RMX + X\cdot \tag{11}$$

in which reactions (10) and (11) obviously constitute a chain process, thereby explaining the high E_F value observed. Similarly in the electrosyntheses of metal halides from the halogen and the metal it is believed that the cathodic reduction of the halogen gives the dihalide ion X_2^-, i.e.

$$X_2 + e^- \rightarrow X_2^- \tag{12}$$

which migrates to the anode where the reactions are

$$X_2^- + M \rightarrow MX + X\cdot + e^- \tag{13}$$

$$M + X\cdot \rightarrow MX \tag{14}$$

followed by

$$MX + X_2 \rightarrow MX_2 + X\cdot \tag{15}$$

$$M + X\cdot \rightarrow MX \tag{16}$$

in which the chain process is clearly (15)+(16). The chain can be terminated by

$$X\cdot + X\cdot \rightarrow X_2$$

$$X\cdot + X_2^- \rightarrow X_3^-$$

or

$$MX + X\cdot \rightarrow MX_2$$

The nature of the final product MX_n depends on the interactions of M with the halide in question and may be influenced by stabilizing factors such as adduct formation and lattice energy [5].

The application of various spectroscopic methods to the electrolyte phase (particularly where the latter contains a number of components) may give useful information about the reactions. The electrochemical oxidation of some metals in acetonitrile containing PPh_2H and elemental sulphur yields the diphenylthiophinato compounds $[M(S_2PPh_2)_2]$ ($M \equiv Co$, Zn or Cd) [125]. The ^{31}P NMR spectrum of the electrolyte solution showed resonances assignable to $PPh_2(S)H$, $PPh_2(S)(SH)$ and some unreacted PPh_2H, suggesting the solution phase reactions

$$PPh_2H \xrightarrow{S} PPh_2(S)H \xrightarrow{S} Ph_2P(S)SH$$

The following electrochemical reactions have been suggested as important pathways to the electrosyntheses:

cathode: $2Ph_2PS_2H + 2e \rightarrow 2Ph_2PS_2^- + H_2(g)$

anode: $2Ph_2PS_2^- + M \rightarrow M(S_2PPh_2)_2 + 2e$

which are consistent with the E_F value of 0.5 mol F^{-1} and the fact that Ph_2PS_2H is much the strongest acid amongst PPh_2H, $PPh_2(S)H$ and $PPh_2(S)SH$.

There are very few kinetic studies on the dissolution of metal anodes in a medium containing a complexing agent. The kinetics of the anodic reaction of gold in aqueous alkaline cyanide in the potential range from −0.81 to +0.64 V were studied by means of potentiostatic and potentiodynamic measurements [143,144]. The reaction was identified as an adsorption reaction behaving in the manner predicted by the single reaction mechanism

$$Au + CN^- \rightarrow AuCN(ads)^-$$

$$AuCN(ads)^- \rightarrow AuCN(ads) + e^-$$

$$AuCN(ads) + CN^- \rightarrow [Au(CN)_2]^-$$

which is in agreement with the activation energies for each peak and with the effects of mass transfer [143].

15. OXIDATION STATES OBTAINABLE BY ELECTROLYSIS

Most of the workers in this field have applied the voltage arbitrarily without any pre-planning. As a result, the compounds synthesized are in normal or lower oxidation states of the metals. The method has been successfully utilized to synthesize some compounds of In(I), Ga(II), Th(II), Mo(II), Cr(II), Ti(III) etc. in a single step starting directly from the metals. In some cases the product initially formed at the anode undergoes subsequent change by disproportionation or reaction with the substances present in the electrolyte giving finally a different species. It is, however, possible to pre-determine the working potential required for achieving oxidation to a particular oxidation state by recording the single-sweep voltammograms using metal microelectrodes. Verification of the nature of the complex formed in situ in the electrolysed solutions may be made by recording the cyclic voltamograms of the electrolysed solutions. Unfortunately very few workers have applied this technique in order to simplify the procedure. Tuck [3] comments, in one paper, "One of the purposes of this paper will be to demonstrate that an ignorance of the detailed electrochemistry, and even of such fundamental parameters as E_0, need be no bar to the use of electrochemical methods in nonaqueous solvents in preparative chemistry." Besides the applied voltage, the nature of the electrolyte medium and its composition may also play an important role in influencing the oxidation state attainable. For example, $K_2[MnF_6]$ is unstable in dilute HF but is stable in 60% aqueous HF and so might be formed in it by anodic dissolution under appropriate applied voltage. The low solubility of the resulting compound may also drive oxidation to a higher state. Thus, while palladium anode dissolves in 6 M HCl or HBr to give $[PdX_4]^{2-}$, the oxidation proceeds to Pd(IV) in the presence of cations such as Cs^+ or $[(CH_3)_4N]^+$, giving rise to the sparingly soluble complexes $M_2[PdX_6]$ [25].

An attempt to achieve the electrosynthesis of compounds in higher oxidation states, e.g. Mn(III), Mn(IV), Ni(III) and Ni(IV), is worth undertaking, although it may not be very rewarding in the presence of the corresponding metal as anode. A better way to synthesize such compounds by anodic dissolution would be a subsequent electrolytic oxidation of the complex initially formed in situ after replacing the sacrificial metal anode with a platinum foil electrode. Several examples of this procedure have been mentioned earlier [26,40].

16. CONCLUSION

It is evident from the foregoing account that widely different kinds of coordination compound can be synthesized by the dissolution of a sacrificial metal anode. In order to avoid the complications arising owing to hydrolysis and the coordination of water, most of the work until now has been restricted to non-aqueous media, although a few electrosyntheses have been carried out in aqueous and mixed solvents. The electrochemical cell is very simple and a partition-type cell need not be used. The electrolysis is usually carried out at room temperature and rarely is it necessary to use a higher temperature. The voltage is often applied arbitrarily, although a few syntheses have been carried out where the oxidation of the metal anode is selectively conducted to a particular oxidation state by controlling the applied voltage through a prior determination of the potential at which the reaction takes place.

A few reports have been published in which the product formed in situ is subsequently oxidized by a second-stage electrolysis by replacing the sacrificial metal anode with an inert platinum electrode. This method looks promising for the electrosynthesis of compounds in higher oxidation states without necessitating the prior preparation of pure compounds in normal oxidation state. Most of the procedures use the ligands in the electrolyte phase. However, it is also possible to use the ligand precursor which is converted to the ligand during the course of electrolysis.

Until about a decade ago, electrosynthesis was mainly used to provide an alternative method for the preparation of compounds which were already well known. Very recently, efforts are being made to utilize the method for synthesizing structurally important compounds which could not be made earlier by chemical methods. As noted earlier, an important aspect which remains neglected until now is the study of the mechanism of the reactions involved. Another approach which is worth pursuing is the electrosynthesis of coordination compounds using electrolytes in the molten state.

REFERENCES

1 G.M. Brown, T.R. Weaver, F.R. Keene and T.J. Meyer, Inorg. Chem., 15 (1976) 190.
2 J.S. Miller, Inorg. Synth., 19 (1979) 1.
3 D.G. Tuck, Pure Appl. Chem., 51 (1979) 2005.
4 J.J. Habeeb, D.G. Tuck and F.H. Walters, J. Coord. Chem., 8 (1978) 27.
5 J.J. Habeeb, L. Nielson and D.G. Tuck, Inorg. Chem., 17 (1978) 306.
6 J.J. Habeeb and D.G. Tuck, J. Chem. Soc., Chem. Commun., (1975) 808.
7 V.A. Konev, V.Yu. Kukushkin and Yu.N. Kukushkin, Russ. J. Inorg. Chem., 31 (1986) 838.
8 B.L. Laube and C.D. Schmulbach, Prog. Inorg. Chem., 14 (1971) 65.
9 J.J. Habeeb and D.G. Tuck, Inorg. Synth., 19 (1979) 123.
10 J.J. Habeeb, C. Oldham and D.G. Tuck, J. Inorg. Nucl. Chem., 43 (1981) 2087.
11 J.J. Habeeb and D.G. Tuck, Inorg. Synth., 19 (1979) 257.
12 N. Kumar and D.G. Tuck, Can. J. Chem., 60 (1982) 2579.
13 N. Kumar and D.G. Tuck, Inorg. Chim. Acta, 22 (1983) 1951.
14 N. Kumar and D.G. Tuck, Inorg. Chim. Acta, 95 (1984) 211.
15 A.D. Goolsby and D.T. Sawyer, Anal. Chem., 40 (1968) 1978.
16 V.A. Shreider, A.Ya. Usyatinski, V.I. Bregadge, N.N. Godovinkov, and I.L. Knuhyants, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1987) 1106; Chem. Abstr., 107 (1987) 85980.
17 M.A. Khan, M.J. Taylor, D.G. Tuck and D.A. Rogers, J. Crystallogr. Spectrosc. Res., 16 (1986) 895.
18 M.J. Taylor and D.G. Tuck, Inorg. Synth., 22 (1983) 115.
19 C. Oldham and D.G. Tuck, J. Chem. Educ., 59 (1982) 420.
20 R.T. Khleborodova, P.V. Seliverstov, E.S. Avdeeva, A.N. Novikoda and A.I. Ryazanov, Tr. IREA, 46 (1984) 22; Chem. Abstr., 102 (1985) 228162.
21 V.A. Shreider and J.N. Volpin, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1988) 963.
22 M.C. Chakravorti and G.V.B. Subrahmanyam, Polyhedron, 11 (1992) 3191.
23 M.C. Chakravorti and D. Bandyopadhyay, Polyhedron, 7 (1988) 1135.
24 M.C. Chakravorti, G.V.B. Subrahmanyam and D. Bandyopadhyay, Polyhedron, 10 (1991) 2605.
25 H. Lehmkuhl, K. Mehler and G. Hauschild, Chem. Ber., 116 (1983) 438; Chem. Abstr., 98 (1983) 51729.

26 A. Kazantsev and V.A. Kuznetsov, Electrokhimiya, 20 (1984) 934; Chem. Abstr., 101 (1984) 119236.

27 K.I. Goloynya, L.M. Butorina, S.N. Puchkova, T.S. Petisova and A.I. Ryazanov, Tr. IREA, 46 (1984) 11; Chem. Abstr., 102 (1985) 228160.

28 R.T. Khleborodova, P.V. Seliverstov, A.N. Novikova and A.I. Ryazanov, Tr. IREA, 46 (1984) 28; Chem. Abstr., 102 (1985) 228163.

29 M.C. Chakravorti and G.V.B. Subrahmanyam, J. Chem. Educ., 68 (1991) 961.

30 M.A. Khan, C. Oldham and D.G. Tuck, Can. J. Chem., 59 (1981) 2714.

31 F.F. Said and D.G. Tuck, Can. J. Chem., 59 (1981) 62.

32 H. Schmidt, Z. Anorg. Allg. Chem., 271 (1953) 305.

33 G.F. Huff, A.D. McEroy and R.M. Adams, US Pat. 2355353, 1958; Chem. Abstr., 53 (1959) 1965.

34 J. Plesek, S. Hermanek and V. Gregor, Czech. Pat. 116107, 1965; Chem. Abstr., 65 (1966) 3354.

35 J.J. Habeeb, F.F. Said and D.G. Tuck, J. Chem. Soc., Dalton Trans., 1 (1981) 118.

36 N. Kumar and D.G. Tuck, Can. J. Chem., 62 (1984) 1701.

37 I. Rajagopal and S.R. Rajagopalan, Bull. Mater. Sci., 6 (1984) 165.

38 J.L.P. Garces and P.S. Batanero, Bull. Soc. Chim. Fr., 4 (1986) 526.

39 C. Oldham, M.J. Taylor and D.G. Tuck, Inorg. Chim. Acta, 100 (1985) L9.

40 M.C. Chakravorti and G.V.B. Subrahmanyam, Can. J. Chem., 70 (1992) 836.

41 N. Kumar, D.G. Tuck and K.D. Watson, Can. J. Chem., 65 (1987) 740.

42 J.S. Banait and P.K. Pahil, Polyhedron, 4 (1985) 1031.

43 J.S. Banait and P.K. Pahil, Bull. Electrochem., 5 (1989) 264.

44 D. Reinhard and H. Wiard, Prax. Naturwiss. Chem., 39 (1990) 41; Chem. Abstr., 112 (1990) 157271.

45 H. Lehmkuni and W. Eisenbach, Justus Liebigs Ann. Chem., 4 (1975) 672.

46 L. Bustos, J.H. Green, J.L. Hencher, M.A. Khan and D.G. Tuck, Can. J. Chem., 61 (1983) 2141.

47 Yu.A. Zhdanov, O.A. Osipov, N.M. Gontmaker, V.P. Grigor'ev, A.D. Garnovskii, O.N. Nechaeva, N.N. Bogdashev, Yu.E. Alekseev, V.G. Alekseeva and T.A. Yusman, Dokl. Akad. Nauk SSSR, 227 (1976) 882.

48 Yu.A. Zhdonov, O.A. Usipov, V.P. Grigor'ev, A.D. Gamovskii, Yu.E. Alekseev, N.M. Gontmaker, V.G. Alekseeva, I.A. Yusman, Y.U. Zaeltou, N.N. Boudashev and O.N. Nechaeva, Koord. Khim., 3 (1977) 3.

49 J. Grobe and H. Zimmermann, Z. Naturforsch., Teil B, 39 (1984) 808.

50 L. Matassa, N. Kumar and D.G. Tuck, Inorg. Chim. Acta, 109 (1985) 19.

51 N.N. Kostyuk, T.A. Kolevick, V.L. Shiroki and D.S. Umseiko, Koord. Khim., 15 (1989) 1704.

52 N. Arakelyan, A.B. Eremyan, Arm. Khim. Zh., 37 (1984) 591; Chem. Abstr., 102 (1985) 156836.

53 M.N. Arakelyan, S.A. Papyan, S.E. Isabekyan and E.G. Darbinyan, Electrokhimiya, 19 (1983) 940; Chem. Abstr., 99 (1983) 130280.

54 M.N. Arakelyan, S.A. Papyan and S.E. Isabekyan, Arm. Khim. Zh., 35 (1982) 202; Chem. Abstr., 97 (1982) 46445.

55 M.N. Arakelyan, S.A. Papyan, S.E. Isabekyan and E.G. Darbnyan, Arm. Khim. Zh., 35 (1982) 406; Chem. Abstr., 97 (1982) 152975.

56 N.N. Bogdashev, A.D. Garnovskii, O.A. Osipov, V.P. Grigor'ev and N.M. Gontmakher, Zh. Obshch. Khim., 46 (1976) 675.

57 O.A. Osipov, N.N. Bogdashev, V.P. Grigor'ev, A.D. Garnovskii and N.M. Gontmakher, USSR Pat. 485115, 1975.

58 O.A. Osipov, N.N. Bogdashev, V.P. Grigor'ev and A.D. Garnovskii, USSR Pat. 401674, 1972.

59 L. Griffiths, B.P. Straughan and D.J. Gardiner, J. Chem. Soc., Dalton Trans., 6 (1983) 1193.

60 R. Bastida, S. Gonzalez, T. Rodriguez and A. Sousa, J. Chem. Soc., Dalton. Trans., (1990) 3643.

61 R. Kumar and D.G. Tuck, Inorg. Chim. Acta, 157 (1989) 51.

62 N.M. Atherton, D.E. Fenton, G.J. Hewson, C.H. McLean, R. Bastida, J. Romero, A. Sousa and E.E. Castellano, J. Chem. Soc., Dalton. Trans., (1988) 1059.

63 A. Castineiras, J.A. Castro, M.L. Duran, J.A. Garcia-Vazquez, A. Macias, J. Romero and A. Sousa, Polyhedron, 8 (1989) 2543.

64 M.L. Duran, J.A. Garcia-Vazquez, A. Macias, J. Romero, A. Sousa and E. Rivero, Z. Anorg. Allg. Chem., 573 (1989) 215.

65 M.L. Duran, A. Rodriguez, J. Romero and A. Sousa, Synth. React. Inorg. Met.-Org. Chem., 17 (1987) 681.

66 T. Sogo, J. Romero, A. Sousa, A. Deblas, M.L. Duran and E.E. Castellano, Z. Naturforsch., Teil B, 43 (1988) 611.

67 C. Alvarino, J. Romero, A. Sousa and M.L. Duran, Z. Anorg. Allg. Chem., 556 (1988) 223.

68 J.A. Castro, J. Romero, J.A. Garcia-Vazquez, M.L. Duran, A. Sousa, E.E. Castellano and J. Zukerman-Schpector, Polyhedron, 11 (1992) 235.

69 R. Bastida, M.R. Bermejo, M.S. Louro, J. Romero, A. Sousa and D.E. Fenton, Inorg. Chim. Acta, 145 (1988) 167.

70 J. Castro, J. Romero, J.A. Garcia-Vazquez, M.L. Duran, A. Castineiras, A. Sousa and D.E. Fenton, J. Chem. Soc., Dalton. Trans., (1990) 3255.

71 E. Labisbal, A. deBlas, J.A. Garcia-Vazquez, J. Romero, M.L. Duran, A. Sousa, N.A. Bailey, D.E. Fenton, P.B. Lesson and R.V. Parish, Polyhedron, 11 (1992) 227.

72 Y. Muto, Bull. Chem. Soc. Jpn., 33 (1960), 1242.

73 K. Ison and E. Kokot, Aust. J. Chem., 23 (1970) 661.

74 A.W. Addison, T.N. Rao and E. Sinn, Inorg. Chem., 23 (1984) 1957.

75 W.W. Fee, J.D. Pulsford and P.D. Vowels, Aust. J. Chem., 26 (1973) 675.

76 H. Jadamus, Q. Ternando and H. Frefier, J. Am. Chem. Soc., 86 (1964) 3056.

77 C. Arnaido, R. Seeber, R. Cini and P. Zanello, Inorg. Chim. Acta, 53 (1981) L201.

78 V.A. Shreider, E.P. Turervkaya, N.I. Koziova and N.Ya. Turova, Inorg. Chim. Acta, 53 (1981) 273.

79 J.S. Banait and P.K. Pahil, Polyhedron, 5 (1986) 1865.

80 A.J. Bloodworth and J. Serlin, J. Chem. Soc., Perkin Trans., (1973) 261.

81 D.C. Bradley, R.C. Mehrotra and D.P. Gaur, Metal Alkoxides, Academic Press, New York, 1978.

82 J.S. Banait, S.K. Deol and B. Singh, Synth. React. Inorg. Met.-Org. Chem., 20 (1990) 1331.

83 M.E. Mabrouk, D.G. Tuck and M.A. Khan, Inorg. Chim. Acta, 129 (1987) 75.

84 H.E. Mabrouk and D.G. Tuck, J. Chem. Soc., Dalton Trans., (1988) 2539.

85 H.E. Mabrouk and D.G. Tuck, Can. J. Chem., 67 (1989) 746.

86 O.L. Brady and E.D. Hughes, J. Chem. Soc., (1933) 1227.

87 T.A. Annan, E.J. Kickham and D.G. Tuck, Can. J. Chem., 69 (1991) 251.

88 T.A. Annan, C. Peppe and D.G. Tuck, Can. J. Chem., 68 (1990) 423.

89 T.A. Annan, C. Peppe and D.G. Tuck, Can. J. Chem., 68 (1990) 1598.

90 W. Lovenberg (Ed.), *Iron–sulphur proteins*, Vols. I and II, Academic Press, New York, 1973.

91 J.L. Hencher, M.A. Khan, F.F. Said, R. Sieler and D.G. Tuck, Inorg. Chem., 21 (1982) 2787.

92 J.L. Hencher, M.A. Khan, F.F. Said and D.G. Tuck, Inorg. Nucl. Chem. Lett., 17 (1981) 287.

93 F.F. Said and D.G. Tuck, Inorg. Chim. Acta, 59 (1982) 1.
94 V.A. Shreider, Izv. Akad. Nauk SSSR, Ser. Khim., 8 (1984) 1832.
95 J.L. Hencher, M. Khan, F.F. Said, R. Sieler and D.G. Tuck, Inorg. Chem., 21 (1982) 2787.
96 R. Chadha, R. Kumar, J. Romero and D.G. Tuck, Can. J. Chem., 66 (1988) 2151.
97 R.K. Chadha, R. Kumar and D.G. Tuck, Can. J. Chem., 65 (1987) 1336.
98 R.K. Chadha, R. Kumar and D.G. Tuck, J. Chem. Soc., Chem. Commun., (1986) 188.
99 M.A. Khan, R. Kumar and D.G. Tuck, Polyhedron, 7 (1988) 49.
100 S.J. Black, F.W.B. Einstein, P.C. Hayes, R. Kumar and D.G. Tuck, Inorg. Chem., 25 (1986) 4181.
101 J.L. Hencher, M.A. Khan, F.F. Said and D.G. Tuck, Polyhedron, 4 (1985) 1263.
102 K.S. Hagen and R.H. Holm, Inorg. Chem., 22 (1983) 3171.
103 K.S. Hagen and J.M. Berg and R.H. Holm, Inorg. Chim. Acta, 45 (1980) L17.
104 K.S. Hagen, D.W. Stephan and R.H. Holm, Inorg. Chem., 21 (1982) 1928.
105 I.G. Dance and J.C. Calabrese, J. Chem. Soc., Chem. Commun., (1975) 762.
106 I.G. Dance, Inorg. Chem., 20 (1981) 2155.
107 I.G. Dance, J. Am. Chem. Soc., 101 (1979) 6264.
108 D. Coucouvanis, M. Kanatzidis, E. Simhon and N.C. Baenziger, J. Am. Chem. Soc., 104 (1982) 1874.
109 I.G. Dance, J. Am. Chem. Soc., 102 (1980) 3445.
110 T.A. Annan, R. Kumar and D.G. Tuck, Inorg. Chem., 29 (1990) 2475.
111 H.E. Mabrouk and D.G. Tuck, Inorg. Chim. Acta, 145 (1988) 237.
112 C. Geloso, H.M. Mabrouk and D.G. Tuck, J. Chem. Soc., Dalton Trans., (1989) 1759.
113 E.S. Raper, Coord. Chem. Rev., 61 (1985) 115, and references cited therein.
114 M.L. Duran, J. Romero, J.A. Garcia-Vazquez, R. Castro, A. Castineiras and A. Sousa, Polyhedron, 10 (1991) 197.
115 R. Castro, M.L. Duran, J.A. Garcia-Vezquez, J. Romero, A. Sousa, A. Castineiras, W. Hiller and J. Strahle, J. Chem. Soc., Dalton Trans., (1990) 531.
116 R. Castro, M.L. Duran, J.A. Garcia-Vazquez, J. Romero, A. Sousa, A. Castineiras, W. Hiller and J. Strahle, Z. Naturforsch. Teil B, 45 (1990) 1632.
117 E.S. Raper and T.R. Creighton, Inorg. Chim. Acta, 183 (1991) 179.
118 A.T. Casey and A.M. Vecchio, Transit. Met. Chem., 11 (1986) 366.
119 A.T. Casey and A.M. Vecchio, Inorg. Chim. Acta., 131 (1987) 191.
120 A.T. Casey and A.M. Vecchio, J. Coord. Chem., 16 (1988) 375.
121 C. Geloso, R. Kumar, J. Romero, L. Grado and D.G. Tuck, Can. J. Chem., 65 (1987) 928.
122 H.E. Mabrouk, A.A. Elasmy, T.Y. Alansi and M. Mounir, Bull. Soc. Chim. Fr., (1991) 309.
123 T.A. Annan, R. Kumar and D.G. Tuck, J. Chem. Soc., Chem. Commun., (1988) 446.
124 T.A. Annan, R. Kumar and D.G. Tuck, J. Chem. Soc., Dalton Trans., (1991) 11.
125 J.A. McCleverty, R.S.Z. Kowelsi, N.A. Bailey, R. Mulvancy and D.A. O'Cleirigh, J. Chem. Soc., Dalton Trans., (1983) 627.
126 L.M. Osadchenko and A.P. Tomilov, Electrokhimiya, 26 (1990) 898.
127 M.C. Chakravorti, S. Ganguly and M. Bhattacharjee, Polyhedron, in press.
128 M.C. Chakravorti, S. Ganguly, G.V.B. Subrahmanyam and M. Bhattacharjee, Polyhedron, 12 (1993) 683.
129 M.C. Chakravorti, S. Ganguly and M. Bhattacharjee, Polyhedron, 12 (1993) 55.
130 S. Valcher, Corsi Semin. Chim., 12 (1968) 37; Chem. Abstr., 72 (1970) 17834.
131 A.P. Giraitis, T.H. Pearson and R.C. Pinkerton, US Pat. 2960450, 1960; Chem. Abstr., 55 (1961) 8430.
132 V.L. Shirokii, A.B. Sutormin and Yu.A. Oldekop, Zh. Obshch. Khim., 53 (1983) 1892; Chem. Abstr., 99 (1983) 165728.

133 A.B. Sutormin, V.L. Shirokii, N.A. Maier and Yu.A. Oldekop, Vestai Akad. Nauk B. SSR, Ser. Khim. Nauk, 4 (1987) 53; Chem. Abstr., 108 (1988) 212436.
134 R. Yin, Huaxne Shijie, 28 (1987) 170; Chem. Abstr., 107, (1987) 6641.
135 R. Kumar and D.G. Tuck, J. Organomet. Chem., 281 (1985) C47.
136 A.T. Casey and A.M. Vecchio, Appl. Organomet. Chem., 4 (1990) 513.
137 I.L. Finar, *Organic Chemistry*, Vol. I, Oxford University Press, Oxford, 1989, p. 439.
138 G.A. Tedoradze, J. Organomet. Chem., 88 (1975) 1.
139 R. Galli, J. Electroanal. Chem., 22 (1969) 75.
140 F.F. Said and D.G. Tuck, J. Organomet. Chem., 224 (1982) 121.
141 J.J. Habeeb, A. Osman and D.G. Tuck, J. Organomet. Chem., 185 (1980) 117.
142 F.F. Said and D.G. Tuck, Can. J. Chem., 58 (1980) 1673.
143 C.P. Thurgood, D.W. Kirk, F.R. Foulkes and W.F. Graydon, J. Electrochem. Soc., 128 (1981) 1680.
144 D.W. Kirk, F.R. Foulkes and W.F. Graydon, J. Electrochem. Soc., 127 (1980) 1962.