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The electrochemical synthesis of inorganic and organometallic complexes in non-aqueous media

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There is a growing interest in the synthesis of coordination compounds by suitable reactions with the pure metal. It is in this context that the electrochemical dissolution of sacrificial metal anodes is an attractive procedure for the preparation of a large variety of complexes. The method, which is both rapid and selective, provides pathways to new compounds. For some compounds, electrosynthesis is more simple than conventional syntheses. The diversity of products synthesized suggests that electrosynthesis using a dissolving electrode has advantages for the preparative chemist. This work reviews developments of the direct electrochemical synthetic method for the preparation of inorganic and organometallic compounds in non-aqueous media. Electrosyntheses of metal halides, anionic metal halides, metal complexes derived from weak organic acids (e.g. alkoxides, glycolates, carboxylates, thiolates, azolates, phosphides), alkylmetal halides and metallocenes, are documented.

Nomenclature

acac	acetylacetonate
benzyl	$CH_2C_6H_5$
bipy	2,2′-bipyridine
Bu^n	n-butyl
Bu^t	t-butyl
bz	benzene
cp	cyclopentadienyl
DME	dimethoxyethane
DMF	dimethylformamide
DMSO	dimethylsulphoxide
dppe	diphenylphosphinoethane
dppm	diphenylphosphinomethane
en	ethylenediamine
Et	ethyl
i.r.	infrared
Iz	imidazolate
L	ligand or base of a weak acid
M	metal or metal ion
Me	methyl
MeCN	acetonitrile

NMR	nuclear magnetic resonance
OAc	acetate
Pc	phthalocyanine anion
Ph	phenyl
phen	1,10-phenanthroline
Pl′	2,4-dimethylpentadienyl
Pr^i	iso-propyl
py	pyridine
Pz	pyrazolate
R	alkyl or aryl
THF	tetrahydrofuran
tmen	tetramethylethylenediamine
tolyl	$CH_3C_6H_4$
X	halide

Symbols

(+)	anode
(−)	cathode

Non-SI unit

BM	$9.27 \times 10^{-24} \, J \, T^{-1}$

1. Introduction

Significant progress has been made in the last 10 years in the use of electrosynthesis for producing a variety of complexes. However, the vast potential of electrosynthesis in inorganic chemistry is often overlooked. Clearly, the advantages of the technique are either not widely known or readily considered by many researchers.

The electrosynthetic process offers several advantages over conventional methods. It is a productive technique incorporating inexpensive apparatus and raw materials. The method permits selective transformations on specific groups in a ligand or metal complex under mild conditions. It is sometimes possible to perform a reaction electrochemically which would otherwise be inhibited by kinetic constraints resulting from high activation energies. The highly reactive nature of several reaction intermediates may also prevent the isolation of the desired product. The direct electrochemical synthetic method has provided routes

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to some compounds not readily accessible by conventional methods, or has provided a more direct route than conventional syntheses. The products from electrosyntheses in non-aqueous media are obtained in an anhydrous state and can be used as starting materials for other reactions. In recent years, syntheses using a sacrificial anode have produced new complexes with reactive metals such as iron, cobalt, nickel and copper, and with more refractory metals such as titanium and hafnium.

Electrosynthesis can be performed in two modes: (i) using inert electrodes, and (ii) using participating electrodes. There is a vast literature on electrosyntheses using inert electrodes primarily focusing on the polarographic reduction of metal species [1–3]. Electrosyntheses of organometallic compounds [4–6] and inorganic complexes [7–10] using sacrificial anodes have been the subject of several reviews, and recent work [11–13] has discussed the use of sacrificial anodes in organic electrochemistry. Mechanistic models of the electrode reactions are also available [4, 14, 15]. Consequently, this review will concentrate on work reported in the post-1980 era. The aim is to present developments using a sacrificial metal anode and to illustrate the application to the production of a wide range of compounds by oxidation in an organic solution of a ligand or ligand precursor. It is apparent that this procedure is a valuable pathway for the synthesis of a variety of complexes, many of which cannot be readily obtained by conventional methods.

2. Apparatus for electrosynthesis using a sacrificial anode

The reaction vessel is typically a diaphragmless tall-form beaker [8, 13, 16]. An alternative design [17] incorporates a bottom outlet which permits solutions to be lead directly (if necessary) into a Schlenk apparatus for further manipulation. To maintain an inert atmosphere, air is purged from the cell by continuous flushing with either nitrogen or argon. This is particularly important in cases where air-sensitive material is being produced. The anode of the cell is a sacrificial metal and platinum is typically the cathode. Solutions are electrolyzed at ambient temperature at voltages of 5–50 V. A supporting electrolyte is added to the solution phase in the case of insufficient current flow.

The use of dry, non-aqueous solvents produces anhydrous products, thereby avoiding difficulties when products are dehydrated from aqueous solutions. Experiments in aqueous media impose restrictions which are often difficult to overcome, especially in organometallic experiments. The choice of a particular solvent or combination of solvents is made by considering such factors as the ease of purification and handling of the solvent, the chemical inertness towards solute species or electrochemical intermediates, the potential range available and the solubilities of the electroactive species. The supporting electrolytes offering the widest potential range are the tetra-alkylam

monium salts. These choices ensure that the reactions proceed satisfactorily, efficiently, and readily permit product isolation. Suitable solvents include MeCN, THF and acetone. The former two solvents are particularly good for organometallic work additionally and MeCN is a good conducting solvent.

3. Electrosynthesis using inert electrodes

The number of reactions involving electrosynthesis at inert electrodes is very extensive. Several selected examples from the recent literature are presented.

Preparation of organocorrinoid compounds [18], particularly organocobalt Costa-type B_{12} model complexes, is most conveniently carried out in aqueous or in aqueous alcoholic $NaBH_4$ solutions via the reduction of $Co(III)$ to $Co(I)$, followed by alkylation with alkyl halides. In particular, the electrochemical synthesis via reduction of $Co^{III}((DO)(DOH)pn)Br_2$ $((DO)(DOH)pn = N^2,N^{2'}$-propanediyl-bis(2,3-butanedione 2-imine 3-oxime) in $MeCN/Et_4NClO_4$ is feasible. Reduction in the presence of 2,2-bis(ethoxycarbonyl)propyl bromide (diester bromide) and recrystallization from acetone/water produces the orange cobalt(II) complex, $[H_2OCo((DO)(DOH)pn)diester]ClO_4$. This aqua derivative can be easily converted to other derivatives such as those with pyridine and 1,5,6-trimethylbenzimidazole. These complexes cannot be prepared by the $NaBH_4$ reduction method.

Molecular metals and superconductors derived from metal complexes of 1,3-dithia-2-thione-4,5-dithiolate (dmit) have attracted interest in the past few years [19, 20]. The reduction of $(Bu^n_4N)[Ni(dmit)_2]$ in a MeCN solution of TTF (TTF = tetrathiafulvalene) produces black, needle-like crystals of $(TTF)[Ni(dmit)_2]$ which was the first molecular superconductor with a transition metal. The reduction of (Bu^n_4N)-$[Ni(dmit)_2]$ in $CHCl_3$ in the presence of $DIPSPh_4$ (tetraphenyl dithiapyranilidene) gives blue crystals of $(DIPSPh_4)[Ni(dmit)_2]$ [21]. Several other related compounds with varying metal centres (e.g. Pt, Cu) can be prepared in this fashion. Anionic species such as $M[Ni(dmit)_2]_2$ (where M = Li, Na, K, Rb, Cs), can be produced by the addition of a salt to the electrolysis solution.

An extensive study of the electrosynthesis of metal carbonyl compounds has been conducted by Grobe et al. [22–26]. Reduction of $M(acac)_n$ (M = Fe(III), Co(III), Ni(II)) compounds at aluminium electrodes in the presence of CO produces a variety of anionic metal carbonyls [24]. The reduction of Fe^{m+} (m = 2 or 3) with carbon monoxide and PR_3 (R = Me, Ph) yields the iron carbonyl derivatives $[Fe(CO)_{5-n}(PR_3)_n]$ for n = 1, 2 [22]. Similar syntheses have been performed with cobalt and nickel carbonyl derivatives and phosphane ligands [22]. Cyclic voltammetry [25] of $M(CO)_6$ (M = Cr, Mo, W) in THF or pyridine in the presence of PR_3 (R = Me, Ph), produces the carbonyl compounds, $M(CO)_{6-n}(PR_3)_n$. The selective preparation of di- and trisubstituted metal carbonyls with the

formula $M(CO)_3(PR_3)_2$ or $M(CO)_4(PR_3)(PR'_3)$ was applied to $M(CO)_5PR_3$ (M = Cr, Mo, W).

4. Electrosynthesis using sacrificial cathodes

Upon cathodic dissolution of platinum in a MeOH/MeO$^-$ solution under a high pressure of CO, the platinum cluster compounds $[Pt_3(CO)_6]_n^{2-}$ (n = 3, 4) can be produced and isolated as salts with Bu_4N^+ [4]. The compounds contain layers of $Pt_3(CO)_6$ units in which three Pt atoms form an equilateral triangle with three bridging and three terminal CO groups. Similarly, the electrochemical dissolution of rhodium in MeOH/MeO$^-$ produces the cluster anion, $[Rh_4(CO)_{11}COOMe]^-$.

The reduction of tetraalkylammonium ions at sacrificial cathodes [27] gives rise to a series of metal alkyls with the formula, $[M(R_4N)]$ (M = Pb, Sn, Bi, Sb; R = alkyl) and $DMP(M)_5$ (M = Pb, Hg; DMP = dimethylpyrrolidinium)]. The compounds are formed by nucleation and growth mechanisms. The $DMP(M)_5$ compounds have been used as mediators in electroorganic syntheses.

5. Electrosynthesis using sacrificial anodes: inorganic metal salts and their derivatives

5.1. Anhydrous metal halides

Anhydrous halides of main group and transition metals are important precursors for the synthesis of organometallic compounds and neutral or anionic complexes. They are produced by a variety of pathways including dehydration of water-containing salts, reaction of metal elements, and reaction of metal oxides with HCl [28]. The single-step electrosynthesis of metal halides (Ti to Zn), can be achieved at room temperature by oxidation of the metal with a halogen (Cl_2, Br_2, I_2) dissolved in benzene/MeOH [8, 15, 29–32]. Adducts of the halides can be prepared in situ in the electrochemical cell or by subsequent reaction.

Similarly, $MoCl_2$ has been synthesized by the electrolysis of molybdenum in an MeCN solution of chlorine [33]. The solvated species $ThX_4 \cdot nMeCN$ has been obtained by the anodic dissolution of thorium in MeCN solutions of a halogen [34]. Oxidation of indium in an MeCN solution of CH_2X_2 (X = Cl, Br, I) has produced InX [35]. It has been reported [36, 37] that during the electrochemical preparation of organic materials using sacrificial metal anodes, anhydrous metal halides can be obtained. Zinc(II) dibromide has been obtained from a solution of 1,2-dibromomethane in CH_2Cl_2/DMF, and MCl (M = Cu, Ag, Hg) compounds have been obtained as by-products during the synthesis of polysilanes in DME [37].

Electrolytic reactions of coinage metals follow the general scheme:

$$Cu, Ag, Au \xrightarrow[\text{benzyl chloride} + HX]{\text{MeCN} + PPh_3} MX(PPh_3)_n$$
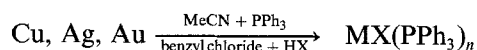
(where X = Cl, Br, I; n = 1, 1.5, 2; not all combinations) to produce triphenylphosphine adducts of uni-valent metal halides [38a]. Oxidation of copper in the presence of RX (R = Me, Ph, benzyl; X = Cl, Br, I, not all combinations) and either bipyridine or Et_4NX, gives rise to neutral or anionic copper(I) halide complexes. The current efficiency measurements imply that CuX is produced at the anode followed by complex formation processes [38b]. Despite the fact that gold is chemically resistant to attack by aqueous mineral acids, the metal is readily oxidized under electrochemical conditions in various media (see, for example, Sections 5.3.1, 5.3.2 and 6.3.1).

Fluoro compounds of transition metals are often synthesized using reactions that are carried out in the molten state [28]. Metals in the pure state react very slowly with aqueous HF even at elevated temperatures. In contrast, fluoro compounds can be prepared with relative ease by application of an electric potential to a cell with a metal anode in aqueous HF [39, 40]. In one such example, oxidation of an iron anode produces the yellow compound $Fe_2F_5 \cdot 7H_2O$.

5.2. Complexes derived from inorganic anions

Oxidation of thorium in either HNO_3/tri-n-butyl phosphate or N_2O_4/ethyl acetate/MeCN produces non-aqueous solutions of $Th(NO_3)_4$ species from which the anhydrous product can be isolated [41]. This is a significant improvement over conventional methods requiring the dissolution of $ThCl_4$ in ethyl acetate/N_2O_4 followed by thermal decomposition of the adduct [42]. It has been found that the oxidation of cobalt in MeCN/HNO_3 yields $Co(NO_3)_2$ [43].
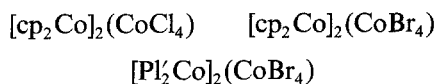
5.3. Anionic complexes

5.3.1. Anionic halides.
Anionic halide complexes of many metals have been successfully produced by the prior addition of tetraalkylammonium salts to the benzene/methanol/halogen (Cl_2, Br_2, I_2) phase of the electrolysis solution [8, 31, 34, 44–46]. Good yields of the salts of the anionic MX_n^{m-} complexes have been produced in a few hours at room temperature for metals such as Cd, Co, Au, Sn, Fe, In, Ti, Zr and Hf. Similarly, compounds such as $(Et_4N)_2[ThX_6]$ (X = Cl, Br) [34], $(Et_4N)[AuCl_2]$, and $(Et_4N)_2[SnBr_6]$ have also been prepared [8].

Several anionic metal halide complexes have been generated in acetonitrile containing a quantity of concentrated aqueous hydrohalic acid (HX) [47–49]. Experiments with gallium metal in solutions containing triphenylphosphine have produced the salts $[Ph_3PH]_2[Ga_2X_6]$ (where X = Cl, Br, I). The method produces the pure gallium(II) crystalline salt in a single step. The blue, crystalline $[Ph_3PH]_2[CoCl_4]$ complex [16] and the salts $[Ph_3PH]_2[NiX_4]$ (X = Cl, Br) and $[Ph_3PH]_2[FeBr_4]$ [50] have been obtained in the same way. The nickel complex is isolated as a blue–green complex with a magnetic moment of 3.8–4.2 BM and the bright orange tetrabromoiron(II) anion has a magnetic moment of 5.4 BM which indicates tetrahedral coordination.

A series of tetrahalocobaltate(II) salts with quaternary and diquaternary alkyl and arylphosphonium cations can be conveniently synthesized by the single-step electrochemical oxidation of cobalt in an MeCN-hydrohalic solution of the neutral tertiary or ditertiary phosphine [51]. Blue, crystalline anionic halo salts of cobalt have been isolated with the formula, $(R_3PH)_2[CoX_4]$ (R = Bu^n, Ph, 4-tolyl; X = Cl, Br) and $[HPPh_2(CH_2)_nPPh_2H][CoX_4]$ (X = Cl; n = 1, 2). I.r. absorptions and NMR spectra (^1H and ^{31}P) provide diagnostic criteria for confirming the presence of the phosphonium cation rather than the ligated phosphine. The magnitude of the $J(P\text{-}H)$ coupling constant is indicative of a quaternary phosphorus atom. Inspection of the $J(P\text{-}H)$ coupling constants [50], shows a progressive increase with increasing electronegativities of the substituents on the phenyl ring in triphenylphosphine.

$$(4\text{-}FC_6H_4)_3PH^+ > (4\text{-}tolyl)_3PH^+ \sim (2\text{-}tolyl)_3PH^+$$
$$> (3\text{-}tolyl)_3PH^+ > Ph_3PH^+$$
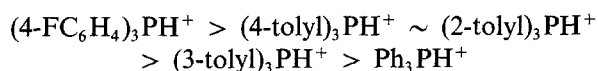
Other anionic species have been generated with organometallic cations (see also Section 6.3.2) by the addition of small amounts of acid to the electrolysis solution [52].

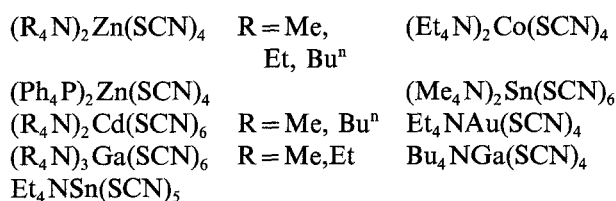$$[cp_2Co]_2(CoCl_4) \qquad [cp_2Co]_2(CoBr_4)$$
$$[Pl_2'Co]_2(CoBr_4)$$

Although the electrosynthesis of anionic fluoride complexes has been conducted without the use of an organic solvent mixture, its preparation is instructive. Iron has been oxidized in aqueous HF and subsequently reacted with KF or CsF to deposit crystalline materials with the formula, $M_3'(Fe_3F_6)$ (M' = K, Cs) [39, 40, 53]. The cell was constructed from polyethylene because of the corrosive nature of HF with soda glass. Similarly, salts of Ti(IV), VO(II), Cr(III), Mn(II, III), Co(II), Ni(II), Ta(V) and NbO(III) fluorides have also been prepared [40, 53]. The preparation of μ-oxo-fluoro complexes of Mo(IV) such as $K_2(MoOF_5)$, has been achieved by oxidizing molybdenum in a solution containing 20% HF, followed by addition of KF [54]. The product is recovered as a green, microcrystalline precipitate. Electrosynthesis is a significant improvement over the conventional method of mixing $MoO(OH)_3$ (the preparation of which is laborious) and alkali fluorides [54 and references therein].

5.3.2. Other anionic complexes. A convenient electrochemical route to metal thiocyanate complexes has been achieved using an MeCN solution of thiocyanic acid as the electrolyte [55]. The species $H_2Zn(SCN)_4$ and $H_3Ga(SCN)_6$ were generated. Crystalline products were obtained by the addition of a solution of potassium, alkylammonium or phosphonium thiocyanate, followed by solvent evaporation.

A solution of thiocyanic acid in MeCN shows the characteristics of a moderately strong acid, in that more electropositive metals such as zinc, are readily attacked and freely dissolve. The application of an electric potential increases the rate of dissolution and

also causes anodic metals which are otherwise attacked very slowly, or not at all, to be converted to the appropriate thiocyanate complex.

$(R_4N)_2Zn(SCN)_4$	R = Me, Et, Bu^n	$(Et_4N)_2Co(SCN)_4$
$(Ph_4P)_2Zn(SCN)_4$		$(Me_4N)_2Sn(SCN)_6$
$(R_4N)_2Cd(SCN)_6$	R = Me, Bu^n	$Et_4NAu(SCN)_4$
$(R_4N)_3Ga(SCN)_6$	R = Me,Et	$Bu_4NGa(SCN)_4$
$Et_4NSn(SCN)_5$		

5.4. Cationic complexes

Electrosynthesis has been used to obtain cationic species of vanadium, cobalt, nickel, zinc and cadmium [8, 44, 56]. Experiments in solutions of $HBF_4/DMSO$ in the presence of neutral ligands, yield a series of $[ML_6](BF_4)_n$ complexes which are readily obtained in crystalline form. One advantage of this direct synthetic method is that metal ions can be generated in low oxidation states.
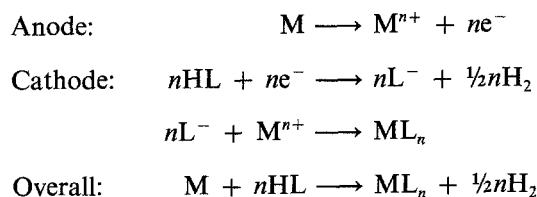
Other cationic species have been generated with organometallic anions [52] (see Section 6.3.2).

$$(cp_2Co)Br \qquad [(Me_5C_5)_2Co]PF_6$$
$$(Pl_2'Co)BF_4 \qquad [(Me_5C_5)_2Co]Br$$
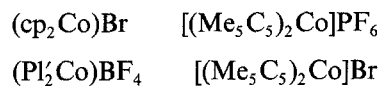
5.5. Complexes derived from organic anions (weak acids)

Electrosynthesis has successfully produced salts of weak acids which generally do not react directly with metals under thermal conditions. Conventional preparations often yield cationic complexes, whereas the electrochemical method facilitates the simple synthesis of electrically neutral compounds. The study of several of these salts has been prompted by current interests in metal–sulphur and metal–nitrogen bonds in biological systems.

Current efficiency calculations usually indicate the electrode processes. This is particularly the case in syntheses involving weak acids (HL) and carbon acids. The current efficiencies are equal to $(1/n)$ mol F^{-1} where n is the oxidation number of the metal. The general reaction scheme is given.

Anode: $\qquad M \longrightarrow M^{n+} + ne^-$

Cathode: $\quad nHL + ne^- \longrightarrow nL^- + \frac{1}{2}nH_2$

$\qquad\qquad nL^- + M^{n+} \longrightarrow ML_n$

Overall: $\quad M + nHL \longrightarrow ML_n + \frac{1}{2}nH_2$

5.5.1. Alkoxides, glycolates, carboxylates and their derivatives. Metal alkoxides, $M(OR)_n$ (for $n > 2$), are widely used in the preparation of various industrial oxide materials. The current methods of synthesis are mostly based on exchange reactions between MX_n (X = halogen, R, H, NR_2, $N(SiMe_3)_2$) and alkoxidizing reagents. These reactions are multistep processes

Table 1. Electrosynthesis of metal alkoxides, glycolates, catecholates and carboxylates.

| Metal	Substrate	Products	Ref.
Alkoxides and glycolates			
W	MeOH/EtOH	$W(OMe)_6$ $WO(OMe)_4$ $WO(OEt)_4$ $WO_2(OEt)_2$	[62]
M	ROH bz, MeCN, DMSO, DMF	$M(OR)_n$ (M=Ti, Zr, Ga, Se, Ge, Y, Nb, Ta, Fe, Co, Ni; R=C1–C4 alkyl; n = 2–5)	[59]
Hg	ROH	$Hg(OR)_2$ (R=Me, Et, Pr, Bu^n, C_5H_{11})	[64]
Cu	ROH	$Cu(OR)_2$ (R=Me, Et, Pr, Bu, Ph, pentyl, amyl, quinolyl)	[67, 68]
M	3-hydroxy-2-methyl–pyrone (HL)	ML_n (M=VO(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Sn(II), In(III))	[73, 74]
		$ML_2 \cdot$ tmen (M = Zn, Cd)	[73]
		$CuL_2 \cdot PPh_3$	[74]
M	HL	ML_n (M=Zn(II), Cd(II), Hg(II), In(III), Sn(II)) (HL=3- hydroxyflavone; 2-ethoxyphenol 1'-hydroxy-2'- acetonaphthone)	[75]
Diols and Catecholates			
Cu	$R(OH)_n$	$Cu(O_2R(OH)_{n-2})$ ($R(OH)_n$ = ethylene glycol; glycerol; 1,2-pro- panediol; phoroglucinol)	[66, 68]
Cu	$R(OH)_2$	$Cu(R(O)OH)$ ($R(OH)_2$ = catechol; 2,2'-dihydroxybiphenyl; tetrachloro-1,2-dihydroxybenzene)	[69]
In	$R(OH)_2$ MeCN	$In[OR(OH)]$ ($R(OH)_2$ = 1,2-dihydroxybenzene; 2,3-dihydroxy- naphthalene; 2,2'-dihydroxybiphenyl; 1,2- dihydroxytetrabromobenzene)	[70]
Sn	$R(OH)_2$	$Sn(RO_2)$	[71]
Zn, Cd	$R(OH)_2$ acetone	$M(RO_2)$ ($R(OH)_2$ = 1,2-dihydroxybenzene; 2,3-dihydroxy- naphthalene; 2,2'-dihydroxybiphenyl)	[72]
Zn, Cd	$o\text{-}C_6H_4(OH)_2$	$M(o\text{-}C_6H_4O_2)$	[72]
Carboxylates			
M	RCOOH MeCN	$M(RCOO)_2$ (M=Mn, Fe, Ni; R=Me, Et, Ph, $n\text{-}C_7H_{15}$) (not all combinations)	[82]
Cr		$Cr(RCOO)_3$ (R=Et, Ph)	[82]
Co, Cu	RCOOH	$M(RCOO)_2$ (R=Et; $c\text{-}C_3H_5$; $c\text{-}C_5H_9$; Ph; Bu^n; $n\text{-}C_7H_{15}$; 2-ethyl- hexanoic; oleic; linoleic)	[82]
Cu	RCOOH	$Cu(ROO)_2$ (ROOH=acetic, proprionic, n-butyric, benzoic, oxal- ic, succinic, phthalic, isobutyric, salicylic, tartaric, crotonic, glycine, alanine, histidine, aspartic, sodium pyruvate)	[68, 80, 81]
M	zinconH	$M(zincon)_2$ (M=Co, Ni, Cu, Zn, Cd, Sn, Pb)	[83]

and involve various by-processes which contaminate products and decrease their yields.

Electrolysis is an alternative method for preparing metal alkoxides (see Table 1). The distinct advantages are the increased purity of complexes and the simplicity of preparations. As early as 1906, Szilard [57] noted that copper or lead methoxides could be obtained by oxidizing the metal in a solution of sodium methoxide in methanol. In recent decades, the alkoxides of metals with atomic number 14 to 82 have been obtained by electrolysis in organic media (1–20 wt % benzene,

MeCN, DMSO or DMF) containing C_1 to C_4 alkyl alcohols [58]. The preparations of Si, Ti, Ge, Zr and Ta ethoxides by electrolysis of saturated alcoholic solutions of NH_4Cl has been patented [58]. Electro-synthesis has produced solid complexes of $Sc(OPr^i)_3$, $Y(OPr^i)_3$ and $Zr(OPr^i)_4$, and liquid complexes of the ethoxides of Ti(IV), Ge(IV), Nb(V), Ta(V) and the isopropoxides of Ga(II) and Ti(IV) [59, 60]. Lehmkuhl and Eisenbach [61] have described the high yield syntheses of Fe(III), Co(II) and Ni(II) alkoxides and phenoxides. Tungsten(VI) alkoxides have been isolated

from electrolyzed solutions of either MeOH or EtOH [62] and mercury(II) alkoxides and glycolates have been produced from MeCN solutions [63]. The mercury compounds have been isolated as air-stable, white–grey precipitates which are insoluble in common organic solvents [63, 64]. No coordination compounds can be obtained from refluxed solutions of these mercury complexes with bipy, phen or DMSO (= L) [63, 64]. However, $Hg(OR)_2 \cdot L$ complexes are easily isolated by electrolysing the alcohol solutions of these ligands at a mercury anode.

Copper, mercury and cadmium electrodes have been oxidized in solutions of polyhydric and monohydric alcohols [65–68]. These molecules have no acidic hydrogen but can lose protons to yield carbanions under suitable experimental conditions. A series of insoluble, hygroscopic, green copper(II) compounds have been synthesized from polyhydric alcohols such as ethylene glycol, glycerol, phoroglucinol and 1,2-propanediol [66, 68]. Cells were of the form:
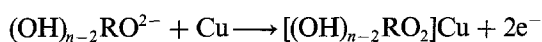
$$Pt_{(-)}/DMF + R(OH)_n + Bu_4NCl/Cu_{(+)}$$
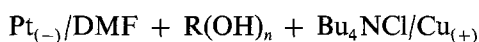
Measurements of current efficiencies indicate the following reaction mechanism,

Cathode:

$$R(OH)_n + 2e^- \longrightarrow (OH)_{n-2}RO^{2-} + H_2(g)$$

Anode:
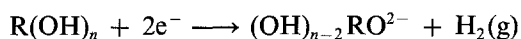
$$(OH)_{n-2}RO^{2-} + Cu \longrightarrow [(OH)_{n-2}RO_2]Cu + 2e^-$$

where $(OH)_{n-2}RO^{2-}$ is the dianion of the polyhydric alcohol. The oxidation of copper in a solution of 2-mercaptoethanol produces the compound $Cu(S(O)C_2H_4)$ by proton loss from both O—H and S—H groups [66].

The electrochemical oxidation of metals in ethyl cellosolve ($EtOCH_2CH_2OH$) or in a mixture with ethanol and the metal ethylate has been reported [65]. The introduction in the alkoxy group of the heteroatom with electron donor properties leads to the formation of soluble alkoxy derivatives of transition metals with low molecular structures.

Anodic dissolution of copper in an MeCN solution of an aromatic diol $R(OH)_2$ has produced the Cu-$(R(O)OH)$ species [69]. The previously unreported complexes of $In[OR(OH)]$ have been obtained by the oxidation of indium in an MeCN solution of $R(OH)_2$ (1,2-dihydroxybenzene; 2,3-dihydroxy-naphthalene; 2,2'-dihydroxybiphenyl; 1,2-dihydroxytetrabromobenzene). The oxidative addition reaction with iodine produces the cream–yellow indium (III) species, $InI_2[OR(OH)]$ [70]. Analogous experiments with tin [14, 17] produce $Sn(RO_2)$ species which undergo oxidative addition reactions with iodine to yield the tin(IV) compound, $SnI_2(RO_2)$ [71]. The electrosynthesis of zinc and cadmium catecholates in acetone [72] is a particularly useful procedure in view of the facile redox reactions of catechol and other 1,2-arenediols in aqueous solution. The ease of generation and isolation of products from organic media contrasts with conventional syntheses of metal diolates and catecholates

via the alkali salt of RO_2^{2-}, in which a strictly anaerobic environment is essential because of the extreme sensitivity of alkaline solutions of the diols [72 and references therein]. As a result, the products are dark green or black in colour whereas the products from electrosynthesis have been obtained as clear to light coloured substances which darken upon prolonged exposure to air.

Electrochemical oxidation of metals in solutions of 3-hydroxy-2-methyl-4-pyrone(HL) produces several neutral metal complexes [73, 74]. I.r. spectra show no $v(O—H)$ band at $3262\,cm^{-1}$ as found in the parent acid. The preparation of ZnL_2, a potential agent for the treatment of anemia, has been carried out via the reaction of $ZnCl_2$ with maltol in chloroform; InL_3 has also been synthesized from $InCl_3$ and maltol in acetone–MeOH, but there are no reports of the preparation from the metallic element other than by the electrochemical route. The products of the electrosyntheses of d^{10} metal ions with derivatives of anionic bidentate oxygen donors such as 3-hydroxyflavone, 1'-hydroxy-2'-acetonaphthone, and 2-ethoxyphenol [75] have been isolated as white to yellow solids. The distinct advantage over conventional methods are the ease of preparation and purity of products.

The direct reaction of acetylacetone (Hacac) with a metal is rarely possible, except for alkali metals, but this reaction is accessible when the metal is oxidized in a non-aqueous solution of the parent acid [74, 76]. Similar preparations have been carried out by Lehmkuhl and Eisenbach [61] who have described the continuous production of $M(acac)_2$ compounds in high yield. Preparations are simple and rapid, producing gram quantities of the complex. Other metal complexes have been generated from electrolyzed solutions of dimethylglyoxime, 8-quinolinol and C-heteroaryl substituted monosaccharides [74]. A summary is presented in Table 2 and includes work with cadmium and β-diketones [77]. Oxidation of copper in the presence of aldehydes and ketones produces copper(II) glycolates. In addition, organocopper (II) species can be isolated from solutions containing ketones [68] (see also Section 6.1). Electrochemical reactions of diethyl malonate, ethyl cyanoacetate and cyano acetamide yield mercury(II) alkoxides/glycolates [63]. The absence of a $v(Hg—C)$ absorption band in the i.r. spectra indicates that these products may be formed through resonance forms. In contrast, copper produces organometallic compounds with these particular organic molecules [68].

Oxalato complexes of Fe(III) and Cu(II) have been synthesized in an oxalic acid solution with a carbon cathode [78]. Subsequent reaction with KCl and cooling, produces the compounds, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ and $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$. $Pb(OAc)_4$ is a well known reagent in organic chemistry. It is used in many reactions: oxidation of double bonds and acetoxylation of various types of activated methylenes and methyl groups. Conventional preparations require mixing red lead oxide (Pb_3O_4), acetic acid (HOAc) and acetic anhydride (Ac_2O). Instead, lead tetra-acetate can be

Table 2. Electrochemical products of ketones, aldehydes and other organic molecules with abstractable protons

Metal	Substrate	Products	Ref.
Cu	RCHO	Cu(glycolate)$_2$ (RCHO=benzaldehyde, cinnamaldehyde, dihydrocinnamaldehyde, salicylaldehyde)	[68]
Cu	RR'CO	Cu(RR'CO)$_2$ (RR'CO=acetone, ethyl methyl ketone, isobutyl methyl ketone)	[68]
M	Hacac MeOH or acetone	M(acac)$_n$ (M=Ti(III), TiO(II), Zr(IV), Hf(IV), V(III), VO(II), Cr(III), MO(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II))	[74, 76]
Cu, Hg	Hacac	M(acac)$_2$	[61, 63, 68]
Cd	H(RCOCHCOR'),L	Cd(RCOCHCOR')$_2 \cdot$ L (L=bipy, phen, TMED R=Me, R'=Me; R=CF$_3$, R'=Me, Pr^i, Bu^i, Bu^t, Ph, 2-napthyl)	[77]
Hg	H$_2$R	Hg(RH)$_2$ (H$_2$R=diethylmalonate, ethyl cyanoacetate, cyano acetamide, malonitrile)	[63]

easily prepared by the oxidation of lead in an acetic acid solution of lead diacetate and KOAc [79].

Preparative studies show that the technique of direct electrochemical oxidation is a convenient and simple route to a variety of transition metal carboxylates [68, 80–82]. The compounds include the salts of both short- and long-chained carboxylic acids (including the C$_{17}$-chain oleic and linoleic acid), and benzoic acid for metals ranging from chromium to copper. The recommended procedures are based on dissolving metal hydroxides or carbonates in an aqueous solution of the carboxylic acid. Crystallization may yield either anhydrous or hydrated materials. Clearly, the electrochemical methods offers substantial advantages, both in simplicity of experiment and in purity of product.

A number of copper(II) carboxylates have been synthesized [80]. Electrolysis of mono- and di-, substituted and unsaturated carboxylic acids, yields copper(II) carboxylates which are isolated as blue–green solids [68, 81]. Two approaches are typically used in conventional preparations. For the higher molecular weight acids which are relatively insoluble in water, mixing alcohol solutions of copper acetate with the carboxylic acid leads to precipitation of Cu(RCOO)$_2$. For very high molecular weight acids, reactions involving aqueous solutions of RCOONa and a suitable metal salt are required. The application of the electrosynthetic procedure is not restricted by the type of carboxylic acid used, and is more simple and direct than other methods.

Recently, divalent main group and transition metal complexes of zincon (2-hydroxy-5-sulphonyl az-obenzylidene hydrazinobenzoic acid) have been prepared in acetone [83]. Zincon is known to function as an analytical reagent for the zinc ion. The ligand acts as a dibasic tetradentate chelating agent, coordinating through NH, N=N, COOH and OH by proton loss from the two latter groups. The spectra of the metal complexes show the absence of the O—H absorption bands and the replacement of the C=O vibra-

tion by a band assigned to the carboxylate group. This indicates metal attachment to the carboxylate oxygen.

5.5.2. Phosphides. The synthetic routes reported in the literature for the preparation of M(PR$_2$)$_n$ compounds include alkane elimination between MR and HPR$_2$, the elimination of Me$_3$SiCl between NiCl$_2$ and Me$_3$-SiPPh$_2$ or the reaction of MR with dppm and trans-metallation with LiPR$_2$. The direct electrochemical method is far simpler and gives high yields compared with other methods [84, 85]. Diphenylthiophosphina-to compounds have been obtained in 80–90% yield by the prior addition of sulphur to the solvent medium. These phosphides are more air stable than the PPh$_2$ analogues [84] (see Table 3).

5.5.3. Thiolates. Oxidation of a metal with a thiol or disulphide ligand precursor in an organic solvent has generated a considerable number of metal alkylthiola-tes, arylthiolates, alkyldithiolates, dialkyldithiophos-phates, xanthates and dithiocarbamates [86–101] (see Tables 4 and 5). The simplicity of the technique and the high yields obtained, contrast with the typical metathetical preparations of this class of compounds. The number of reported crystal structures make a worthy contribution to the understanding of metal-sulphur bonding, especially in view of their similarities to metalloproteins. Additionally, the impetus for the study of copper(I) coordination is reinforced because of the number of compounds used in synthesis and as catalysts in organic processes.

Cells for the electrosynthesis of metal thiolates are typically of the form:

$$Pt_{(-)}/MeCN + RSH \ (or \ R_2S_2)/M_{(+)}$$

(or acetone) (+ bipy or phen)
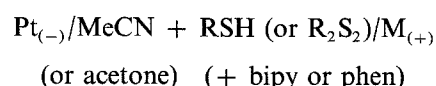
The salts [Et$_3$NH]$_2$[M$_4$(SPh)$_{10}$] (where M = Cd, Zn) have been produced by the oxidation of the metal in an MeCN solution of triethylamine and benzenthiol [86, 87]. Similarly, oxidation of zinc, cadmium and mercury in an MeCN solution of the parent thiol or

Table 3. Electrosynthesis of metal phosphido complexes

Metal	Substrate	Products	Ref.
M	$Ph_2PH + S$ MeCN/toluene	$M(S_2PPh_2)_2$ (M=Zn, Cd, Ni, Co)	[84]
M	Ph_2PH, MeCN	$M(PPh_2)_n$ (M=Cu, Ag, Au; $n = 1$) (M=Co, Zn, Cd; $n = 2$)	[84, 85]
Ni		$Ni(PPh_2)PPh_2H$	[84]
Cu	$Ph_2PH + dppm$ MeCN	$Cu_4(PPh_2)_4(dppm)_2$	[85]

disulphide produces $M(SR)_2$ complexes [88]. Oxidation of lead and tin in solutions of RSH (R = phenyl, 2-tolyl, 3-tolyl) produces the analogous thiol complexes [89]. Tin compounds have been isolated with either oxidation state two or four. The electrolysis of copper and silver in solutions of RSH yields the insoluble M(SR) species [90]. When zinc or cadmium are oxidized in the presence of α,ω-alkanedithiols, i.e., $HS(CH_2)_nSH$ (n = 2–6), the $M[S_2(CH_2)_n]$ species are produced in high yield [91]. The red–brown thioxanthato species $[Cu_8(SC_5H_{11})_4(S_2CSC_5H_{11})_4]$ has been generated in solutions of $C_5H_{11}SH$ (where C_5H_{11} =

2-methyl-2-butyl) followed by the addition of CS_2 [92]. The yellow phosphine adducts, $CuS_2CSC_5H_{11} \cdot 2phos$ (where phos = Ph_3P, $(C_6H_{11})_2PPh$) have been recovered from solutions containing the phosphine. The adduct with dppm, $Cu_4(SC_5H_{11})_4(dppm)_2$, contains a novel Cu_4S_4 ring in which the sulphur atoms are below the Cu_4 plane. The compound $In(SPh)_3$ has been easily obtained by electrosynthesis [99] from a solution of PhSH. This is a distinct advantage over the only known preparation by metathesis of $InCl_3$ and NaSPh, or thermal reaction of indium metal and Ph_2S_2 in refluxing toluene.

Table 4. Electrochemical synthesis of metal thiolate complexes

Metal	Substrate	Products	Ref.
Alkane- and arenethiols			
Ni	RSH MeCN or acetone	$M(SR)_2$ (R=Ph; 2-tolyl; $2\text{-}C_{10}H_7$; $2,3,4,5\text{-}C_6F_4H$)	[96]
Co	RSH MeCN or acetone	$M(SR)_2$ (R=Ph; 2-tolyl; $2\text{-}C_{10}H_7$)	[96]
Cu	RSH	CuSR (R=Ph; $C_{10}H_7$; CPh_3; C_6F_4H; 2-tolyl; CMe_2Et)	[97, 98]
Cu, Ag	RSH	M(SR) (R=Bu^n; 2-methylbutyl; Ph_3C; 2- or 3- or 4-tolyl; $C_{10}H_7$; $2,3,4,5\text{-}C_6F_4H$)	[90]
Zn, Cd, Hg	RSH	$M(SR)_2$ (R=Ph; Bu^n; Bu^t)	[95]
Zn, Cd	Et_3N, PhSH	$[Et_3NH]_2[M_4(SPh)_{10}]$	[86, 87]
Sn	RSH + bipy/phen	$Sn(SR)_2$ $Sn(SR)_4 \cdot L$ (R=Ph; tolyl)	[89]
Pb	PhSH, MeCN	$Pb(SPh)_2$	[89]
In	RSH, MeCN	InSR (R=Et; Bu^n) $In(SR)_2$ ($R=2\text{-}C_{10}H_7$; CMe_2Et) $In(SR)_3$ (R=Ph; C_6F_5)	[99]
Tl	RSH	TlSR (R=Ph; 2-tolyl; 3-tolyl; $2\text{-}C_{10}H_7$)	[99]
Dialkyldithiophosphates			
M	$(EtO)_2P(S)SH$ MeCN	$M[(EtO)_2PS_2]_n$ (M=Fe(ii), Co(ii,iii), Ni(ii), Cu(i), Ag(i), Zn(ii), Cd(ii), Hg(ii), In(iii), Tl(i))	[95]
	+ phen	$M[(EtO)_2PS_2]_n \cdot phen$ (M=V(ii), Mn(ii), Co(iii), Zn(ii), Ga(i)) $Fe[(EtO)_2PS_2]_2 \cdot 2phen$	
Alkanedithiols			
Cu, Ag	$R(SH)_2$ MeCN	M_2S_2R ($R=1,2\text{-}C_2H_4$; $1,2\text{-}C_3H_6$; $1,3\text{-}C_3H_6$; $1,4\text{-}C_4H_8$; $2,3\text{-}C_4H_8$; $1,5\text{-}C_5H_{10}$; $1,6\text{-}C_6H_{12}$)	[100]
Zn, Cd	$HS(CH_2)_nSH$ (n = 2–6)	$M[S_2(CH_2)_n]$	[91]
In	$R(SH)_2$, MeCN	$In[SR(SH)]$	[101]
Tl	$R(SH)_2$	$Tl_2(S_2R)$ ($R=1,2\text{-}C_2H_4$; $1,2\text{-}C_3H_6$; $1,3\text{-}C_3H_6$; $2,3\text{-}C_4H_8$; $1,5\text{-}C_5H_{10}$; $1,6\text{-}C_6H_{12}$)	[101]

Table 5. Metal thiolate complexes derived from ligands with disulphide bonds

Metal	Substrate	Products	Ref.
Disulphides			
Zn, Cd, Hg	$(Bu^t)_2S_2$, MeCN	$M(SBu^t)_2$	[88]
Cu, Au	Ph_2S_2, MeCN	M(SPh)	[90]
Au	$(Bu^n)_2S_2$, MeCN	$Au(SBu^n)$	[90]
Dixanthogen			
M	$(Et_2OCS_2)_2$ acetone	$M(Et_2OCS_2)_n$ (M=VO(IV), Cr(III), Mn(III), Fe(III), Co(III), Ni(II), Cu(I), Zn(II), Cd(II), Ag(I), In(III), Sn(IV), Pb(II), Bi(III), Te(IV))	[17, 93, 94]
Thiuram disulphides			
M	$(Me_2NCS_2)_2$ acetone	$M(Me_2NCS_2)_n$ (M=VO(IV), Cr(III), Mn(III), Fe(III), Co(III), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), In(III), Tl(III), Sn(IV), Pb(II), Bi(III), Te(IV))	[93–95]
M	$(Et_2NCS_2)_2$ MeCN	$M(Et_2NCS_2)_n$ (M=Fe(III), Co(II), Ni(II), Cu(II), Ag(I), Au(I), Zn(II), Cd(II), In(III), Tl(I,III))	[95]
Cu	$CS_2 + R_2NH$ MeCN	$Cu(R_2NCS_2)_2$ (R=Et, Pr^i or R_2NH=piperidine)	[95]
Cd	$CS_2 + R_2NH$ MeCN	$Cd(R_2NCS_2)_2$ (R=Et or R_2NH=piperidine)	[95]
Tl	$CS_2 + Et_2NH$	$Tl(Et_2NCS_2)$	[95]

Oxidation of a metal in an organic solution of ethyl dixanthogen or tetraalkylthiuram disulphide is a convenient route to metal xanthates and dithiocarbamates [17, 93–95] (see Table 5). The single step synthesis is an alternative to metathetical preparations, or prolonged refluxing of the metal powder (Co, Zn, Hg, In, Pb, As and Bi) and dixanthogen for up to 30 h [102].

5.5.4. Amines, pyrroles, azoles and hydrazones. Electrochemical synthesis of heterocyclic amino complexes and their derivatives, is clearly of general applicability. Habeeb *et al.* [74] have prepared neutral complexes with 2-acetyl-pyrrole (HL) to give CrL_3, CoL_2, NiL_2 and CuL_2 complexes. The compound tris(formylpyrrolato)–indium has also been obtained. Electrolysis of metals in a non-aqueous solution of 2,2'-dipyridylamine [103] has produced compounds of Cu(I), Ag(I), Tl(I), Zn(II) and Cd(II). The conventional preparative routes to metal pyrrolates are not simple, due to the relative instability of the parent pyrrole. In the case of the synthesis of the chromium compound, hexacarbonylchromium(o) is required [104]. Electrosynthesis is by far the most economical option.

Metal azolates model metalloproteins such as histidine and azurin. Metal pyrazolates are used in epoxy resins, PVC stabilizers, electrical insulation and as anticancer reagents. Pyrazole and its derivatives are weak acids ($pK_a \sim 14$) and susceptible to N–H bond rupture under electrolysis. As a result, the electrochemical synthesis of neutral transition metal complexes of imidazole, pyrazole and their derivatives, has been accomplished at room temperature by the oxidation of the metal at a controlled potential of 40–50 V, in an acetone solution containing 0.1–0.5 M of the diazole [50]. Polymeric complexes precipitate during the electrolysis and are of the general formula, $[M(Dz)_n]$ (where M=Cr(III), Mn(III), Fe(III), Co(II, III),

Ni(II), Cu(I, II), Zn(II), Ag(I); Dz = Iz, Pz, 4-MeIz, 2-(2'-pyridyl)imidazole, 4-ClPz, 4-IPz, 3-5-Me$_2$Pz, 3,5-Me$_2$-4-BrPz (not all combinations)). This method is an improvement over that requiring the synthesis of a charged metal halide salt, e.g. $M(3(5)\text{-MePzH})_nX_2$ followed by treatment with alkali [105]. A comparative electrolytic synthesis of neutral metal pyrazolate complexes of cobalt, copper and zinc requires electrolyzing aqueous solutions of divalent metal complexes in 0.05% NaCl containing 3(5)-methylpyrazole, to give polymeric $[M(3(5)\text{-MePz})_2]_n$ compounds [106–108]. Obviously, the previous method of direct reaction of the metal and the ligand is more practical. These complexes display high melting points and insolubility in all common solvents which is consistent with polymeric structures. Magnetic measurements of cobalt complexes show temperature dependent moments of tetrahedral species and indicate metal–metal interactions across the molecule. The susceptibility results are compatible with antiferromagnetic interaction between copper(II) or cobalt(II) ions in the lattice. This suggests that the polynuclear arrangement consists of a one-dimensional linear chain and is supported by the magnetic susceptibility data for copper(II) complexes fitting a Heisenberg model, and data for cobalt(II) complexes fitting an Ising model.

Osipov *et al.* [109–111] have patented several electrochemical preparations of metal (Co, Ni, Cu) azolates by anodic dissolution of the metal in a MeOH solution of benzimidazole, benzotriazole and 2-(2'-pyridyl)benzimidazole.

The electrosynthetic technique may be applied to preparations involving other similar compounds with acidic N–H bonds such as the heterocyclic ligand pyridine-2-carbaldehyde pyridin-2'-ylhydrazone (papyH) and its derivatives [50].

H   H
| |
C=N—N
pyridine structure

papyH
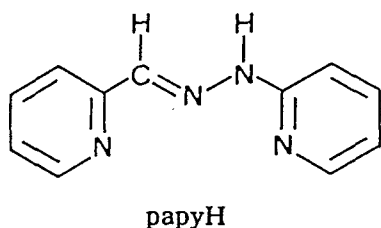
The M(papy)$_2$ compounds are mostly obtained as red-green dichroic substances due to the extended π-conjugation system in the anionic ligand. A study of the magnetic data of the octahedral cobalt chelates fits well to a known model expression for the susceptibility of a $^2E \longrightarrow {}^4T_1$ crossover system.

Divalent metal complexes (Zn, Cd) have been obtained with MeCN solutions of pyridine-2-thione (pytH) [112]. Although Zn(pyt)$_2$ has been synthesized by conventional routes, the complexes Cd(pyt)$_2$, Zn(pyt)$_2$ · bipy, Zn(pyt)$_2$ · phen and Cd(pyt)$_2$ · phen have not been previously prepared. Again, deprotonation was confirmed by the absence of N—H stretching bands at 3160 cm^{-1}. The X-ray structure of 1,10-phenathroline-bis(pyridine-2-thionate)zinc(II) represents the first example of an octahedral complex of zinc(II) with thiolate ligands, which contrasts with the tetrahedral geometry commonly observed in other zinc thiolate complexes. This is of interest since these compounds model the Zn—S bonds in DNA and RNA binding proteins. Nickel(II) complexes of pyrimidine-2-thiolate have been prepared by electrosynthesis [113]. Although Ni(pymt)$_2$ has been prepared by conventional methods, adducts with bipy, phen and py have not been previously synthesized. The ligand pyrimidine-2-thione is able to coordinate to metal centres in both thiolate and thione forms. The i.r. spectra show the absence of the N—H stretching frequency.

The complex [Cu(mimt)]$_4$ has been electrochemically synthesized in MeCN using a copper anode, a platinum cathode and the parent ligand, 1-methylimidazoline-2(3H)-thione (mimtH) [114]. The complex is isolated as colourless, diamagnetic crystals. Analogous syntheses have isolated Ni(mimt)$_2$ and Ag-(mimt) as well as the copper(I) complex of thiazole-2-thionate, Cu(tzt). Anions of these ligands are formed through proton loss from the N—H moiety. Syntheses have been carried out with tetradentate thioether-benzimidazole-containing ligands [115]. The oxidations of metals (Cu, Ni, Co, Zn, Cd) in acetonitrile-absolute ethanol solutions of 1,7-bis(2-benzylimidazolyl)-2,6-dithiaheptane and 1,6-bis(2-benzylimidazolyl)-2,5-dithiahexane (H$_2$L) yields complexes with the formula ML · nH$_2$O. These ligands have two imidazole-nitrogen atoms and two thioether sulphur atoms available as potential donors. Consequently, these ligands are useful in the synthesis of metal complexes that, in the case of copper, may be considered to model sites present in blue proteins. The dianionic ligands act as tetradentate ligands with both thioether sulphurs and both deprotonated benzimidazole nitrogens coordinating. All compounds are

four-coordinate in tetrahedral or distorted tetragonal geometries, except for the nickel complexes, in which the effect of magnetic interactions produces a distorted-octahedral geometry around the metal.

Anodic oxidation of Fe, Co, Cu, Zn and Cd in acetone solutions of 4-phenylthiosemicarbazide (HPTS) or 1,4-diphenylthiosemicarbazide (HDPTS) yields complexes with the composition M(PTS)$_2$ and M(DPTS)$_2$ (M = Fe, Co, Zn, Cd), Cu(PTS) and Cu(DPTS) [116]. The metal complexes of thiosemicarbazides have attracted special attention due to their cancer inhibiting properties. Analysis of i.r. spectra show that enethiolization takes place upon release of a proton from N—H. Thiol sulphur and amino nitrogen participate in bonding. The electrical conductivity of Cu(PTS) · phen is in the range for semiconductors.

5.5.5. Schiff bases. The synthesis and crystallographic study of neutral metal complexes of Schiff bases has provided valuable information about model systems in nature. Complexes have been synthesized electrochemically by various reactions of the ligand:

(i) O—H bond cleavage [117–121]
(ii) O—H bond cleavage and S—S bond rupture [122, 123]
(iii) O—H bond cleavage and no S—S bond rupture [124]
(iv) N—H bond cleavage [125]
(v) N—H bond cleavage and S—S bond rupture [126]

The variety of complexes prepared is presented in Table 6. The weakly acidic nature of many Schiff bases can be attributed to such moieties as the N—H group of the pyrrole ring and the O—H group of aldimines. The i.r. spectra of the neutral metal complexes show no bands attributable to v(O—H) or v(N—H) in the deprotonated Schiff bases.

Coordination complexes of different metals and Schiff bases derived from salicylaldehydes and mono and diamines have been obtained [117—121]. Attempts to form neutral complexes by reaction of the preformed cationic species with methanolic NaOH have been unsuccessful [119]. The structures of bis{N-[2-(6-methylpyridyl)-salicylideneiminato}copper(II) and bis{N-[2-(3-methylpyridyl)]-5-methoxysalicylideneiminato}copper(II) [118] show that the metal adopts a square-planar geometry and the pyridyl atoms are not coordinated. An example of electrosynthesis involving O—H bond cleavage and S—S bond rupture is the copper complex of the Schiff base derived from salicylaldehyde and bis-(2-aminophenyl)disulphide [126]. Difficulties are encountered in conventional syntheses because the presence of copper(II) causes oxidation of the Schiff base with accompanying reduction of copper. This is easily overcome by direct anodic reaction of the metal with the Schiff base. Cleavage of the disulphide bond does not occur in the case of zinc(II) complexes of 2-(2-mercaptophenyl)-imino-phenols [124]. Cobalt(II) and cobalt(III) complexes with arylpyrrol-2-aldimines deposit crystals during electrolysis [125]. The ease of preparation of CoL$_3$

Table 6. Electrosynthesis of complexes derived from Schiff bases

Schiff base	Metals	Ref.
salicylaldehyde and 2-(2-pyridyl)ethane	Ni(II)	[117a]
substituted salicylaldehyde and 2-(2-pyridyl)ethane	Zn, Cd(II)	[117b]
substituted salicylaldehyde and 2-aminopyridine	Cu(II)	[118]
o-hydroxyacetophenone and 4(5)-[(2-aminoethyl)thiomethyl]-imidazole	Cu(II)	[119]
substituted salicylaldehydes and 2-(2-aminoethyl)pyridine	Cu(II)	[119]
salicylaldehyde and methyl derivatives of 2-aminopyridine	Zn, Cd(II)	[120]
salicylaldehyde and alkyl- and arylamines	Zn(II)	[121]
salicylaldehyde and bis-(2-aminophenyl)disulphide	Sn(IV)	[122]
salicylaldehyde and bis-(2-aminophenyl)disulphide	Cu(II)	[123]
salicylaldehyde and bis-(2-aminophenyl)disulphide	Zn(II)	[124]
2-pyrrole carbaldehyde and substituted analines	CO(III)	[125a]
2-pyrrole carbaldehyde and substituted anilines	Ni(II)	[125b]
2-pyrrole carbaldehyde and bis(2-aminophenyl)disulphide	Ni, Cu, Zn, Cd(II)	[126]
2-pyrrole carbaldehyde and cysteamine	Ni, Cu, Zn, Cd(II)	[126]

complexes contrasts with that of cobalt(II) salicylal-diminates for which oxidation to cobalt(III) is difficult even in the presence of hydrogen peroxide. The crystal structure of tris{2-[(2-methylphenyl)iminomethyl] pyrrolato}cobalt(III) consists of monomeric molecules in which the central CoN_6 unit has a slightly distorted octahedral geometry. The ML complexes of 2-[(2-mercaptophenyl)iminomethyl]pyrrole [126] are difficult to prepare by synthetic routes.

6. Electrosynthesis using sacrificial anodes: organometallic compounds

6.1. Alkyl metals

The use of sacrificial anodes in synthetic electrochemistry was first encountered in the early 1920s when lead and bismuth alkyls were obtained by electrolysis of the metal anode in Et_2Zn and Et_3Al solutions of ethylsodium [11]. This pioneering work was followed in the 1950s by a thorough study by Ziegler and Lehmkuhl on the anodic dissolution of aluminium in the presence of organic halides and/or various organometallic species [6]. Since then, several syntheses of organometallics using sacrificial electrodes have been developed and exploited commercially, e.g. the manufacture of tetraethyllead. Electrosynthesis is an efficient mode of production compared with the other major commercial synthesis of these compounds by the interaction of a Na–Pb alloy with MeCl or EtCl in an autoclave at 80–110 °C [127].

Electrolyses of (i) nitromethane, nitroethane, MeCN, cyanoacetamide, and (ii) malonitrile, diethyl malonate and ethyl cyanoacetate in DMF, have been carried out at a copper anode to yield blue–green organocopper(II) complexes [68, 128]. The organic precursors have abstractable protons and the carbanions are stabilized by resonance. Group (i) organic precursors contain only one functional group having electron withdrawing properties, so that the carbon bearing the negative charge is less stable and the abstraction of one proton is possible. Thus, compounds with the general formula $Cu(CR)_2$ are produced. In the case of group (ii) organic molecules, both func-

tional groups attached to the carbon bearing the negative charge are highly electron-withdrawing, and thus it is possible to remove two protons to form organometallic species of the general formula $Cu(CR)$. The presence of the Cu—C bond is confirmed by infrared.

Aldehydes and ketones produce radical anions at the cathode which dimerize to give anions. At a copper anode, copper(II) glycolates are produced [68] (see Section 5.5.1.). In the case of ketones, the radical anions are comparatively stable and a small fraction may react to give organocopper(II) compounds. Compounds with the general formula $Cu(RR'CO)$ have been produced from DMF solutions of ethyl methyl ketone and isobutyl methyl ketone [68].

6.2. Alkylmetal halides

The electrochemical approach has been applied to the synthesis of organometallic halides of a number of main group elements and transition metals. The products are sometimes conveniently stabilized *in situ* as adducts with neutral donors (e.g. bipy, phen, tmen) or as the tetraalkylammonium salts of the corresponding anionic complexes.

6.2.1. Titanium, zirconium and hafnium. Oxidation of titanium, zirconium and hafnium (= M) in a cell containing either an MeCN or MeOH solution of organic halide RX, results in the formation of organometallic halides which may be conveniently isolated as adducts with MeCN or bipy [129]. These complexes are formulated as $R_2MX_2 \cdot 2L$ (L = MeCN, $\frac{1}{2}$bipy). The mechanism proposed for these and analogous reactions involves the cathodic reduction of an organic halide followed by migration of the halide ion to the anode where MX is formed. This may then undergo a variety of oxidative insertion reactions yielding, R_2MX_2 species stabilized *in situ* by neutral donors.

6.2.2. Zinc and cadmium [130, 131]. Zinc is more reactive towards alkyl halides than is cadmium, therefore, the direct reaction of RX and zinc is possible, but this

Table 7. The electrochemical synthesis of organozinc and organocadmium halides [130, 131]

Metal	Substrate	Products
Zn	RX	RZnX
		(R=Me, Et, Ph, benzyl, CF_3, C_3H_3
		X = Cl, Br, I; not all combinations)
Zn, Cd	RC_6H_4X, bipy	$RC_6H_4MX \cdot$ bipy
	MeCN	(R=o-NC; X=Cl, Br
		R=o-NO_2; X=Cl, I)
Zn	$Pr_4^n NX$	$Pr_4^n N(RZnX_2)$
		(R=Me, Et, Ph, CF_3; X=Cl, Br, I)

procedure cannot be used with aryl halides. Electrolytic processes produce organozinc halides irrespective of the type of alkyl halide used. Application of the techique in the presence of either alkyl or aryl halides and certain perfluoro analogues, gives the corresponding RMX compounds (M = Zn, Cd; R = alkyl, aryl; X = Cl, Br, I) which are conveniently stabilized as the addition compounds with bipy or as the anionic species $(RMX_2)^-$. Nitro and cyano substituted phenyl compounds are also isolated. The successful outcome of syntheses using substituted aryl species such as perfluorophenyl, demonstrates that the electrosynthetic method is in no way restricted by the type of organic halide used. Some reactions are summarized in Table 7.

6.2.3. Magnesium. The electrochemical oxidation of magnesium in MeCN containing alkyl or aryl halides (RX) and bipy, yields the neutral adducts [RMgX · bipy] [132]. With α,ω-dihalides $(X(CH_2)_nX)$, the products are the corresponding $[XMg(CH_2)_nMgX \cdot 2bipy]$ compounds. The preparation proceeds equally well with either alkyl or aryl compounds and with chloride, bromide and iodide anions, but the resultant adducts show none of the typical reactions of Grignard reagents other than alkane elimination with mineral acids. Solutions containing RX and $R_4'NX$ produce the salts $[R_4'N(RMgX_2 \cdot MeCN)]$ which also lack typical Grignard reagent chemistry.

6.2.4. Indium. Complexes of the type R_2InX and R_2InX_2 have been produced [133]. Anodic dissolution of indium in benzene/MeOH with RX and bipy has yielded $R_2InX \cdot$ bipy and $R_2InX_2 \cdot$ bipy (R = Et, Ph, benzyl, C_6F_5; X = Cl, Br, I) [133]. Anionic complexes of the type $R_4N(R_2InX_2)$ and $R_4N(RInX_3)$ have also been prepared by the prior addition of tetraalkylammonium halides to the solution. Oxidation in solutions of CH_2X_2 (X = Br, I) yields X_2InCH_2X. The advantage of the electrolytic technique is that low oxidation states of indium can be produced.

6.3. Complexes derived from carbon acids

Organometallic compounds of transition metals are of much technical and preparative interest. There are several organic compounds with moderately weak C—H bonds which rupture upon the addition of base to form carbanions, e.g. acetylenes, dienes and so on.

Under suitable conditions, an electric current can cause the cleavage of the C—H bond. In these circumstances, the advantages of the electrochemical method of synthesis are:

- electrical rather than chemical rupture of the C—H bond,
- activation of metal by electric potential,
- thermolytic procedures are unnecessary,
- isolation of high purity compounds in a relatively short time.

As a result, an electrochemical route to many transition metal metallocenes and derivatives has been established (see Table 8).

6.3.1. Acetylides. The phenylacetylides of copper, silver and gold (= M) have been synthesized by the application of electric potential to a solution of phenylacetylene in MeCN to give PhC≡CM complexes [52, 134]. Highly reactive phenylacetylide complexes with other metals have been stabilized against hydrolysis by the addition of imine ligands. Under the electrochemical conditions employed, Au(I) phenylacetylides are easily produced. The single-step electrosynthesis at room temperature is a cost effective alternative to typical transmetallation reactions.

6.3.2. Metallocenes and derivatives. In conventional syntheses, alkali metals are used to abstract the proton in carbon acids. In typical metallocene preparations, cyclopentadiene is metallated using strong basic lithium reagents. An alternative preparation requires the condensation of cyclopentadiene with metal vapours at liquid nitrogen temperatures. Some carbon acids have very high pK_a values and are difficult to metallate. An apparently fruitful approach is the reaction of the activated metal with weak protonic acids, particularly perhaps, in the formation of complexes with olefins where the pK_a value may range from 20 to 25. As an example of this approach, successful preparations of a range of metallocenes and methylated metallocenes have been achieved directly from the metal (Fe, Co, Ni) and cyclopentadiene in DME/MeCN, THF/MeCN or MeCN [52, 135–137] (see Table 8). The use of electrolysis is far superior to the conventional use of the alkali salt of the diene, which is both a tedious and time consuming approach to these compound. Complexes are isolated as pure products of excellent purity and crystallinity. Anionic and cationic species can be produced by the introduction of small quantities of acid to the solution phase [50, 52]. The species, (cyclopentadienyl)(tetraphenyl-butadiene)cobalt(I) has been synthesized in quantities of 30–50% by oxidation of cobalt (with a stainless steel cathode) in an MeCN solution of diphenylacetylene and RcpH (R=H, Et, Pr^i) [138, 139].

Oxidation of transition metals in the presence of o-carborane and its C-alkyl derivatives has produced a series of C-metallo-o-carboranes and complex salts of the anions such as 7,8-dicarbaundecaborate; 7,10- and 9,11-dicarba–nido-dodecarborate [140].

Electrolysis has generated complexes of these metals

Table 8. Organometallic complexes produced by electrosynthesis

Metal	Substrate	Products	Ref.
M	PhC≡CH	M(PhC≡C)$_n$	[52, 136]
	MeCN	(M=Cu(I), Ag(I), Au(I), Fe(III), Ni(II), Co(III), Zn(II))	
	+ phen	M(PhC≡C)$_n$ · phen	
		(M=Cu(I), Ag(I), Au(I), Fe(II), Zn(II))	
	+ bipy	M(PhC≡C)$_n$ · bipy	
		(M=Ag(I), Fe(II), Zn(II))	
M		M(cp)$_2$	[24]
		(M=Fe, Co, Ni)	
M	cpH, CO	(cp)$_n$M(CO)$_m$	[135]
		(M=Fe, Co, Ni, Ti, V)	
M	cpH	M(cp)$_2$	
	MeCN/THF	(M=Fe, Ni, Co, Zn)	
	cpH	M(cp)$_2$	[135]
	THF	(M=Fe, Co, Ni)	
	cpH, CO	cp$_n$M(CO)$_m$	[24, 135]
	THF or py	(M=Ti, V, Fe, Co, Ni)	
	MecpH	M(Mecp)$_2$	
		(M=Fe, Ni)	
	Me$_5$C$_5$H	M(Me$_5$C$_5$)$_2$	
		(M=Fe, Co, Ni, Zn)	
	indene	Fe(indenyl)$_2$	
	fluorene	M(fluorenyl)$_2$	
		(M=Fe, Ni)	
	Pl'H	M(Pl')$_2$	
		(M=Fe, Ni, Co, Zn)	
Co	cpH	Co(cp)$_2$I$_3$	[136]
	DMSO		
Fe, Co	Alkylcp, indene	M(alkylcp)$_2$	[141]
	MeCN or DMSO	M(indenyl)$_2$	

with 2,4-dimethylpentadiene (so called 'open metallocenes') [52]. Calculations of current efficiency for these types of reaction indicate Faradaic behaviour. It appears that the reasonable yields obtained, the simplicity of the operations and the low cost of the reagents employed, permit the recommendation of this method as an alternative synthesis of metallocenes. Although complexes are typically prepared by metallation with strongly basic lithium reagents, electrosynthesis requires only a change in metal anode in order to prepare a variety of organometallic complexes.

6.4. *Carbonyls*

An extensive study of the electrochemical preparation of metal carbonyls has been conducted [4, 24, 26, 76, 135]. Electrolysis of organic solutions of monomeric cpH and CO at metal anodes has successfully yielded metal carbonyls of Fe, Co, Ti and V. Cyclopentadienyl metal carbonyls have been prepared at 383 K using titanium and vanadium anodes in pyridine, monomeric cpH, and CO at > 10 MPa [4]. The high temperature counteracts the dimerization of cpH and the high pressure of CO aids in reducing material decomposition at 383 K which is otherwise encountered under normal pressure. The greater solvating properties of CO at high temperatures and pressures (i.e., supercritical fluid characteristics) may account for the unsuccessful preparation of carbonyl compounds using CO at atmospheric pressure [52].

7. Applications

The direct electrochemical synthesis of compounds from metal anodes has wide application in organometallic chemistry [6, 10, 11–13]. It is the predominant method for the preparation of a variety of technological materials such as catalysts [4, 13]. A new and interesting coupling of anodic dissolution of various metals (Mg, Al, Zn) to cathodic reactions involving organic halides catalyzed by nickel complexes has been proposed recently for the performance of various electrosyntheses [13]. Sacrificial zinc anodes are commonplace in organic electrosynthesis. Reaction with allylic chlorides has produced several organozinc species [142] and many other examples exist in the literature.

Many examples of the deposition of metal in superconductors by repeated electrolysis in aqueous solutions are cited in the literature. Recent work [143] describes an alternative technique involving the insertion of an alkali metal into a ceramic superconductor,

$$n\text{M}^+ + n\text{e}^- + \text{YBa}_2\text{Cu}_3\text{O}_7 \longrightarrow \text{M}_n\text{YBa}_2\text{Cu}_3\text{O}_7$$
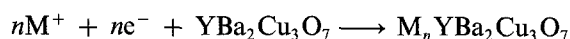
where M denotes lithium or sodium ions. The synthesis is carried out in solutions of LiClO$_4$ or NaClO$_4$ in propylene carbonate. The superconductor forms the cathode and sodium or lithium metal as the counter electrode. The electrochemical technique is an efficient and economic alternative to conventional synthesis which requires butyllithium. The advantage of electrolysis in organic media is that oxygen insertion into

the crystal lattice cannot be readily achieved. Electrosynthesis using an active anode is also an alternative method for thin film solar cell processing [144, 145].

Anodic dissolution of tungsten in acetic acid electrolyte [146] has been conducted to enable ellipsometry to be used to study the optical properties of the oxide.

The phthalocyanine radical complex of lithium (PcLi*) is a member of the class of intrinsic molecular semiconductors. Its synthesis has been little reported, but two recent accounts [147, 148] describe a convenient and efficient electrochemical process which directly converts phthalonitrile into pure PcLi* in high yields. A gold cathode and a platinum anode formed the electrodes of a cell containing absolute EtOH, LiCl and phthalonitrile (PN). The electrolysis produces $PcLi_2$ according to the equation:

$$4PN + 2Li^+ + 2e^- \longrightarrow PcLi_2$$
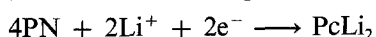
Purification with hot absolute ethanol produces PcLi* in 70% yield. This procedure has also been successfully applied for the synthesis of octasubstituted phthalocyanines (dihydrogen PcH_2 and radical lithium PcLi* forms). Yields of isolated materials are in the 50–70% range, and generally better than those obtained using conventional chemical procedures.

8. Future applications

Although the primary aim of electrosynthesis is to further the study of preparative chemistry, there is scope for its application to the physical sciences. Examples of potential applications include, studies of the kinetics of dissolution, reaction mechanisms, or modeling battery electrodes (e.g. Al [149], Ni, Cd, Mn, Pb).

The electrochemical method is capable of replacing the application of redox reagents in favourable cases. It allows for the use of raw materials, and product isolation and processing is simple. The generation of species in non-aqueous media is advantageous, especially since many chemical systems are incompatible with water. The method is conducted at room temperature thus avoiding thermolytic routes to complexes. The generation of reactive intermediates from which complexes may be prepared is very practical. In particular, the activation of acidic hydrogens has been shown to be quite effective. The wide variety of successful applications of electrosynthesis in inorganic chemistry is destined to open the way to other areas of synthetic chemistry. The pedagogical value of electrosynthesis is that the experiment shows the simple and rapid formation of complexes directly from a metal.

Acknowledgement

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