1979

DIRECT ELECTROCHEMICAL PREPARATION OF SELECTED TRANSITION AND NON-TRANSITION METAL COMPLEXES.

FAROUQ F. SAID
University of Windsor

Recommended Citation
SAID, FAROUQ F., "DIRECT ELECTROCHEMICAL PREPARATION OF SELECTED TRANSITION AND NON-TRANSITION METAL COMPLEXES." (1979). *Electronic Theses and Dissertations.* Paper 1750.

National Library of Canada
Collections Development Branch

Canadian Theses on
Microfiche Service

Bibliothèque nationale du Canada
Direction du développement des collections

Service des thèses canadiennes
sur microfiche

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE

Ottawa, Canada
K1A 0N4

NL-339 (Rev. 8/80)

DIRECT ELECTROCHEMICAL PREPARATION OF SELECTED TRANSITION AND NON-TRANSITION METAL COMPLEXES

by

© Farouq F. Said

B.Sc., University of Baghdad, 1967

M.Sc., University of NewcastleUponTyne, 1970

A Dissertation

Submitted to the Faculty of Graduate Studies through
the Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy

at

The University of Windsor
Windsor, Ontario, Canada
1979

723798

To Dina,

Our Beloved Daughter

FOREWORD

The following account is the result of a research investigation undertaken in the chemical laboratories of the University of Windsor, Ontario, between 1975 and 1979: Professor D.G. Tuck, under whose supervision this work performed is sincerely thanked for his willing guidance, valuable help and enthusiasm throughout the research.

Special thanks to my committee, Dr. R.C. Rumfeldt, Dr. J.E. Drake, Dr. D.F. Watt and my external examiner Dr. C.H. Brubaker, Jr. (Michigan) for their reading and comments on this dissertation.

Many thanks are also due to the members of 362 Essex Hall, those of special mention are Messrs A. Osman, L. Victoriano, S. Zhandire, to Dr. R. Steevensz and Dr. J. Habeeb for many helpful discussions and much needed stimulation, and to Dr. C. Trudell for her help with the preparation of this manuscript.

Acknowledgements are also directed to the faculty members of the chemistry department, the members of the technical staff, the secretaries and the many graduate students who helped during this project and made my stay a pleasant and valuable experience.

For help in typing this dissertation I wish to thank Mrs. Selina Wong.

A word of eternal gratitude to my wife Layla Khasrou for so much patience, help and inspiration through these four years away from our distant motherland.

Finally, the Indium Coorporation of America, the National Research Council of Canada and University of Windsor are thanked for the partial financial support.

F. Said

Windsor 1979

ABSTRACT

The contents of this dissertation report investigations utilizing a direct electrochemical synthetic technique for the preparation of some inorganic and organometallic compounds. In each case, the metallic element under investigation was used as the sacrificial anode of an electrochemical cell which resulted in dissolution of the metal to produce compounds of the metal in question. The counter electrode employed was a platinum wire and the solution phase in the majority of cases was a non-aqueous organic solvent or mixture of solvents. Applied voltages ranged between 1-50 volts, as dictated by the solution conditions.

Some neutral and anionic chloro- and bromo- complexes of titanium, zirconium and hafnium were prepared by this method. The electrochemical oxidation of the metal in the presence of a solution of chlorine or bromine (X_2) in acetonitrile (L) leads directly to the neutral $MX_4.L_2$ species. These compounds are easily transformed into other neutral adducts. For neutral complexes, a small amount of a tetraalkylammonium salt was added to the solution phase to assist current flow. On addition of large quantities of the appropriate tetraalkylammoniumhalide to the solution phase, the products are the salts $[R_4N][MCl_5]$ or $[R_4N]_2[MBr_6]$, except that with

titanium $[Et_4N][TiBr_4]$ was also produced under some specific conditions. Attempts to prepare similar neutral and anionic iodo-complexes of the three elements by the same method were unsuccessful.

Similarly, compounds of the type $InX_3.nMeCN$ and related complexes (X = Cl or Br, n = 3; X = I, n = 2) were prepared by oxidation of indium metal. In contrast to the Ti, Zr and Hf systems, the electrochemical reaction of indium with iodine was found to proceed smoothly, producing the acetonitrile adduct. The infrared spectra of the acetonitrile adducts show that the iodide is both structurally and stoichiometrically different from its lighter congeners.

The electrochemical method was also used to prepare some neutral titanium, zirconium, hafnium and indium organometallichalide and some anionic organoindiumhalide complexes. Electrochemical oxidation of these metals in alkyl or aryl halides (RX) and non-aqueous organic solvent(s) and the presence of a ligand (L) produced, in general, neutral compounds of the type $R_2MX_2.L$ (M = Ti, Zr or Hf; X = Cl, Br or I and L = 2,2'-bipy or 2MeCN) or $RInX_2.bipy$ (X = Cl, Br or I). When Et_4NX is present instead of 2,2'-bipyridine, indium gave the salts $[Et_4N][RInX_2]$. There are, however, some notable variations found, especially when RX = MeI. These results

are discussed and a mechanism is suggested.

A variety of tetrafluoroborate salts of cationic complexes of selected transition and main group elements have also been prepared by these methods. The metals can be oxidized electrochemically in cells containing aqueous (48%) tetrafluoroboricacid or $HBF_4.OEt_2$ solution in dimethylsulfoxide or acetonitrile; the direct products are the $[M(dmso)_6]^{n+}$ or $[M(MeCN)_6]^{n+}$ salts with BF_4^-, but products such as $[M(bipy)_3]^{n+}$, $[M(phen)_3]^{n+}$ and $[M(en)_3]^{n+}$ can be obtained by subsequent reactions. The infrared spectra of the dmso complexes show that they contain ionic tetrafluoroborate.

The possibility of applying the electrochemical method to olefin polymerization by generating the catalyst as an organotitanium compound directly in the cell in the presence of the olefin (styrene and vinylacetate) was briefly investigated.

The compounds which have been prepared were studied by standard methods; such as elemental analysis, infrared, proton magnetic resonance, mass spectrometry, and conductivity measurements. The current efficiency of a system, expressed as the number of moles of metal dissolved per Faraday of electricity passed through the cell,/was measured for a few systems at constant current. This method gave evidence for the proposed reaction mechanisms.

TABLE OF CONTENTS

Page

Page

LIST OF TABLES

LIST OF ABBREVIATIONS

bipy	2,2'-bipyridine
Bu	n-butyl
Bu^i or i-Bu	isobutyl
Bz	benzyl
COT	cyclooctatetraene
Cp	cyclopentadienyl
diphos	1,2-bis(diphenylphosphino) ethane
dmso or DMSO	dimethylsulfoxide
EDTA	ethylenediaminetetraacetate
E_F	current efficiency
en	ethylenediamine
Et	ethyl
F	Faraday constant
^1H NMR	proton nuclear magnetic resonance
I	current
IR	infrared
Me	methyl
Pent	n-pentyl
Ph	phenyl
Phen	1,10-phenanthroline

Pr	n-propyl
py	pyridine
R	organic moiety
STP	standard temperature and pressure
t	time of electrolysis
terpy	terpyridine
THF	tetrahydrofuran
TMEDA	N, N, N', N'-tetramethylethylenediamine
TMMDA	N, N, N', N'-tetramethylmethylenediamine
TMPDA	N, N, N', N'-tetramethylpropylenediamine
TMS	tetramethylsilane
Λ_M	molar conductivity

CHAPTER I

PREPARATIVE ELECTROCHEMISTRY

I. 1. Introduction

The electrochemical technique represents the simplest and most direct method of carrying out oxidation or reduction reactions. The application of this principle in inorganic and organometallic chemistry is well documented in the extensive literature describing the reaction of solute species at inert electrodes, which effectively act as the source or sink of electrons in the reduction or oxidation of solute species to yield either direct products or intermediate species which subsequently decompose to some other required compound(s). Leadtetraacetate, for example, was prepared by the oxidation of $Pb(OAc)_2$ at a platinum mesh anode in glacial acetic acid.[1]

When one or two of the electrode metals is electroactive and undergoes oxidation or reduction along with the oxidation or reduction of solute species present in solution phase, they serve not only as the source of electrons, but in addition, undergo reaction with species present in solution, or generated in solution as electrolysis proceeds. It is usual to refer to such cells as having a sacrifical anode or cathode, and the metal can serve as the starting material of a synthesis. A sacrificial anode type of cell has been used in almost all of the preparations described in this dissertation.

The solution phase of a preparative electrochemical cell could be either aqueous or non-aqueous. In the preparation of some inorganic and organometallic compounds, aqueous media impose restrictions which it is often impossible to overcome, and the use of organic solvents becomes a necessity. Some salts such as tetraalkylammonium halides or perchlorates are used in this case to assist in the current flow. A number of solvents and supporting electrolytes have been used in non-aqueous media. The solvents most often used have been, acetonitrile, dimethyl formamide, dimethyl sulfoxide tetrahydrofuran, dimethoxy ethane and propylene carbonate, because of their resistance to either reduction or oxidation. The supporting electrolytes that offer the widest potential range are the tetraalkylammonium halides and perchlorates, but salts containing the tetrafluoroborate and tetraphenylborate anions have also been used. The choice of suitable solvents and electrolytes depend on some factors, which can be summarized as follows:[1]

- Chemical inertness toward starting materials, electrochemical intermediates and final products.
- The solubilities of the solute and the supporting electrolyte.
- Solvents and supporting electrolytes should form systems of

sufficient electrical conductivity.

- Ease of purification and handling of the solvent and supporting electrolyte.

Basically two different types of cells have been used in preparative electrochemistry. In one type, the reduction or oxidation reactions take place in unseparated areas. In the other type, the catholyte and anolyte are separated by a diaphragm, so that reduction and oxidation take place in spatially separated areas. The latter type of cell has been used when the organometallic complex formed by cathodic reduction is more readily oxidizable than the metal itself, in which case, the desired reaction may be reversed by anodic oxidation of the product. An example of this is the reaction of aluminium metal with dialkyl mercury[2]

$$2\ \mathrm{Al} + 3\ \mathrm{Hg\ Et_2} \rightleftharpoons 2\ \mathrm{Al\ Et_3} + 3\ \mathrm{Hg}$$

The free energy of this reaction has been estimated to be $-50\ \mathrm{kJ\ mol^{-1}}$, so that the equilibrium lies to the right. Electrolysis of triethyl aluminium results in formation of diethyl mercury at a mercury anode, and simultaneously metallic aluminium is deposited at the cathode. Thus the anolyte and catholyte must be separated in order to prevent the dimethyl mercury formed at the anode reaching the cathode, where the normal reaction between aluminium and dimethyl mercury would occur. This can also be considered as an example of a reaction which does not proceed in the desired direction, for thermodynamic reasons, but which can still be carried out by electrolysis.

Some advantages of the method

- In electrochemical reactions, one normally works at, or near, room temperature.
- The simplicity of the procedure is such that one usually requires relatively unsophisticated apparatus.
- The method involved is a direct one in which the product(s) precipitate during the electrolysis in many cases.
- In the direct electrochemical syntheses, the metals used as starting materials are generally stable, easily stored and available in high purity. And while the other materials (solvent, organic halides, etc.) are generally used in excess, these remain available for further operations if needed. The chemical yields are generally high in terms of metal consumption, and the amounts used are convenient for normal laboratory working.
- It has been noted that it is sometimes possible to perform electrochemically a reaction which is not possible by direct reaction of the compounds because of kinetic restraints resulting from high

activation energies. Thus, the preparation of NiCOT has been achieved electrochemically,[2] but the direct synthesis of the compound from solid nickel and cyclooctatetraene has not yet been accomplished. Finally, it is of interest in preparative electrochemistry in non-aqueous solvents, that an ignorance of the detailed electrochemistry, and even of such fundemental parameters as E_o, need not be a serious hindrance in preparative chemistry.

I. 2. Literature Survey of preparative Electrochemistry

With non-aqueous solution electrochemistry, as with aqueous systems, thorough reviews[1, 2, 3] of the field suggest that more effort has been devoted to the study of phenomena such as current-voltage relationships than to the preparative applications of the processes involved. Despite the inherent simplicity and despite the amount of information available from polarographic studies and other physical measurements, it still appears that the method has not been used for preparation of inorganic and organometallic compounds to the extent which might have been expected. Although the method of preparation of organometallic compounds began to attract attention fairly recently, some developments had already been made in this field. The electrochemical synthesis of tetraethyllead has been carried out industrially.[4] Such syntheses of organometallic compounds occur as the result of both anodic and cathodic processes. Tafel, the first to observe the dissolution of cathodically polarized mercury during electrolysis of acetone and to obtain an organomercury product, called this phenomenon a "strange formation of alkyl mercury"[5].

This section will attempt to outline the range of applicability of electrochemical methods in the synthesis of organometallic compounds, and to consider the possible mechanisms of the processes leading to formation of the carbon-metal bond reported in the literature. Emphasis will be placed on non-aqueous systems, and it will be more convenient to discuss the cathodic and anodic processes separately.

I. 3. Direct Synthesis At Sacrificial Cathodes

Electrochemical preparations of organometallic compounds from unsaturated substances, ketones and organo halides, can often be carried out at the cathode, starting from a metal and organic substance in non-aqueous solvents. The metals used include mercury, lead and tin and special emphasis has been placed on lead alkyls, and particularly tetraethyllead because of the industrial importance of this compound which has been used as a fuel anti-knock additive. A number of similar preparations in aqueous or mixed aqueous/organic media have also been reported.[2,3,5]

Reduction of Carbonyl compounds

The electrochemical reduction of ketones at a sacrificial mercury or lead cathode gives rise eventually to an organometallic compound. In most of these reactions the electrolysis has been carried out in aqueous acid. A reaction of the type represented by the following equation was first carried out be Tafel and Schmitz[6]

$$2\ R_2CO + M \xrightarrow[-2H_2O]{6H^+,\ 6\bar{e}} (R_2CH)_2M$$

This reaction was studied later in some detail[7] and on the basis of some available evidence, aliphatic and alicyclic ketones most readily form organometallic compounds by this procedure. Extensive disintegration of the zinc cathode used during acetone reduction was attributed to formation of unstable organo-zinc compound.[5]

There is less information available on the reduction of aldehydes, although dibenzylmercury was obtained from benzaldehydes,[8] Attempts to prepare similar compounds with anisaldehyde and some other aldehydes with lead, mercury and cadmium did not succeed.

Reduction of Unsaturated Compounds

When methylvinylketone is reduced at a mercury cathode in acidic medium, the C-C double bond and not the carbonyl group is affected[9] and an organomercury compound is obtained. A carbon-metal bond is formed at the site where the double bond breaks, and one of the carbon atoms undergoes protonation. This type of reaction was studied in detail for the case of electro-reduction of unsaturated nitriles.[10] The first synthesis of a metal-olefin complex using an electrochemical method in non-aqueous medium was carried out in 1966. Bis - (1, 5-cyclooctadiene) Copper (I) perchlorate was obtained as a result of electrolysing copper (II) perchlorate in the presence of 1, 5-cyclooctadiene between copper electrodes.[11] This method has been used extensively for the synthesis of transition metal cycloolefin complexes. The general principle is the cathodic reduction of mixtures of readily accessible transition metal compounds and suitable olefins.[12]

Reactions involving organohalides

The preparation of alkyl metal compounds by the irreversible electrochemical reduction of an organic halide as represented by the following equation

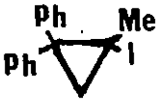
$$RX \xrightarrow{e^-} [RX^-] \longrightarrow R^{\bullet} + X^-$$

is an important class of reactions. The fate of the radical $R^{\bullet}$ may include formation of the dimer R_2, a process which has found a number of synthetic applications. More importantly the reaction

$$M + nR \longrightarrow MR_n$$

which may well occur in consecutive steps, gives rise to a series of important metal alkyl compounds. This reaction was used first for preparation of tetraethyllead by electro-reduction of ethyl iodide at a lead cathode in alkaline alcohol,[5] but has only been closely investigated in the past few years. The electrochemical reductions of benzyl bromide and substituted benzyl bromides ,[14] benzyl iodide,[15] allyl bromide[16] and 1-iodo-1-methyl-2, 2 diphenyl cyclopropane[17,18] at a mercury cathode yielded organo-mercury compounds. Bis (pentafluorophenyl) mercury was the result of pentafluoroiodobenzene reduction at a mercury cathode.[5] Electro-reduction of β -iodo propionitrile yielded cyanoethyl derivatives of tin, mercury, lead thallium[19] and indium.[20] Table 1.1. lists some typical examples of such syntheses[21].

Table 1.1. Formation of Metal Alkyls From Sacrificial Cathodes in Non-Aqueous Media

Substrate	Cathode, supporting electrolyte, solvent	Product	Reference
$RC_6H_4CH_2Br$	Hg, LiBr, MeOH	$Hg(CH_2C_6H_4R)_2$	14
	Hg, Me_4NBr, MeCN	HgR_2	17, 18
EtBr	Sn, Et_4NBr, MeCN	$SnEt_4$	22
RX	Sn, various, MeOH or MeCN	SnR_4	23, 24, 25
EtBr	Pb, Et_4NBr, propylene carbonate	$PbEt_4$	26, 27
EtBr	Pb, various salts, propylene carbonate	$PbEt_4$	28
EtBr	Pb, Et_4NBr, various solvents	$PbEt_4$	26
EtBr	Pb, LiBr, various solvents	$PbEt_4$	22
MeCl, Br, I EtCl, I	Pb, Et_4NBr MeCN	PbR_4	22
MeI	In, $NaClO_4$, MeCN	Me_2InI	20
$\underset{CN}{CH_2}CH_2I$	In, $NaClO_4$, MeCN	$(CNCH_2CH_2)_2InI$	20
$\underset{CN}{CH_2}CH_2I$	Tl, $NaClO_4$ MeCN	$(CNCH_2CH_2)_2TlI$	20
MeI	Tl, $NaClO_4$	Me_2TlI	20
EtI	Tl, $NaClO_4$ MeCN	Et_2TlI	20

Some Miscellaneous Reactions at Sacrificial Cathode

There are also other known cases of organo-metallic compounds being formed through cathodic reductions; for example, the reduction of diphenyl iodonium hydroxide and its 4,4'-dimethyl and 4,4'-dimethoxy derivatives at a mercury cathode yielded diphenyl mercury, bis (p-tolyl) mercury and bis (4-methoxyphenyl) mercury[29]. respectively, according to the following reaction

$$2PhI^+ + Hg \xrightarrow{2\bar{e}} Ph_2Hg + 2phI$$

The electrolysis of organometallic compounds themselves gives many possibilities and the fate of the species produced in the electrochemical reduction of various organometallic compounds has been reviewed by Lehmkuhl,[12] following a scheme proposed by Dessy.[30,31] Examples of such reactions are given in Table 1.2., and clearly represent simple synthetic routes to, a number of useful compounds.[21]

Table 1.2. Other Reactions involving Sacrificial Cathodes

Reactions	References
$2\ RHgBr + Hg_{(-)} \longrightarrow R_2Hg + HgBr_2$	18
$2Ph_3PbCl + 4Hg_{(-)} \longrightarrow 3Ph_2Hg + 2Pb + HgCl_2$	32
$Ph_2PbCl_2 + 3Hg_{(-)} \longrightarrow Ph_2Hg + Pb + HgCl_2$	32
$2CpTl + Hg_{(-)} \longrightarrow Cp_2Hg + 2Tl$	33
$Mn_2(CO)_{10} + Hg_{(-)} \longrightarrow Hg(Mn(CO)_5)_2$	34
$Re_2(CO)_{10} + Hg_{(-)} \longrightarrow Hg(Re(CO)_5)_2$	34

I. 4. On the Mechanism of Carbon-metal Bond Formation During Cathodic Process

Most of the workers who studied the dissolution of metal during the electrolysis are of the opinion that the formation of the carbon-metal bond is due to the primary generation of organic radicals by reduction of organic compounds, followed by reaction of the radicals with the cathode metal to give organometallic compounds.[12,21,35,36] Thus, the electroreduction process of 1-bromo-1-methyl-2,2 diphenyl cyclopropane in acetonitrile at a mercury cathode[14] is believed to occur according to the following equations

$$R - Br + \bar{e} \longrightarrow (R^{\bullet} - Br^{-})$$

$$(R^{\bullet} - Br^{-}) \longrightarrow R^{\bullet} + Br^{-}$$

$$R^{\bullet} + Hg_n \longrightarrow R - Hg_n^{\bullet}$$

$$2R - Hg_n^{\bullet} \longrightarrow R - Hg - R + Hg_{n-1}$$

The competing reaction is the combination of two radicals to give the hydrocarbon R_2

$$2R^{\bullet} \longrightarrow R_2$$

In the first step the electron is transferred to the σ-anti-bonding orbital of the C-Br bond to form the anion radical, which on the mercury surface can dissociate to the radical $R^{\bullet}$. The radicals are absorbed on the mercury surface and dimerized to the dialkylmercurial.

A similar mechanism is suggested for the reduction of alkyl halides with a labile halogen atom, such as benzyl iodide and alkyl bromide at a mercury cathode. Thus, it has been established by polarographic investigations[37,38] that the benzyl mercury iodide obtained in the reaction is further reduced to the radical $BzHg^{\bullet}$ which dimerizes with separation of mercury to dibenzyl mercury. The same argument is used for formation of diallyl mercury from alkyl bromide.

Mann et al[17] during their investigations of the electro-reduction of pentafluoroiodo benzene in dimethyl formamide, obtained bis (pentafluorophenyl) mercury quantitatively at a mercury cathode, and at a copper cathode decafluorodiphenyl was obtained, so that dimerization of the radical or reaction with the cathode material depends on the nature of the electrode. The following mechanism is suggested for the reaction with mercury cathode:

$$PhI + \bar{e} \longrightarrow (Ph\dot{I}^{-})$$

$$PhI^{-} \longrightarrow Ph^{\cdot} + I^{-}$$

$$2Ph^{\cdot} + Hg \longrightarrow Ph_2Hg$$

Furthermore the electrochemical transformation of pentafluorophenylmercuric bromide at a mercury cathode was observed by Ershler et al[39]. By means of polarographic and chronopotentiometric methods, the authors found that PhHgBr gives two polarographic waves, one of which is believed to correspond to the formation of bis (pentafluorophenyl) mercury and the other to the products of further reduction decafluorobiphenyl and mercury.

The most comprehensive work concerned with the investigation of the formation of the carbon-metal bond during electroreduction of alkyl halides at a lead electrode was done by Ulery.[40] From the polarographic half-wave potentials of alkyl bromides at a lead cathode in acetonitrile in the presence of Et_4NBr, a mechanism analogous to the SN2 reaction for the alkyl metal compounds was derived. It is assumed that the cathode acting as a nucleophilic agent, attracts the carbon atom bonded to halogen. The rupture of the C-Br bond is compensated to some extent by the formation of a new C-M bond.

I.5. Direct Synthesis At Sacrificial Anodes

For the majority of the organometallic compounds which have been prepared from sacrificial anodes, exchange of one metal in an organometallic compound by another from the anode was necessary, and usually the first stage of such a synthesis is the preparation by chemical means of a more readily obtainable compound such as a Grignard reagent, triethylaluminium or complexes of the type $MX.AlR_3$ or $MR.AlR_3$ (where M is a univalent metal, X is a halogen or hydrogen).

Organometallic compounds of aluminium, boron, lead, phosphorus and some other elements have been prepared by the electrolysis of Grignard reagents. French and Drane[41] during their study of the electrolysis of solutions of Grignand reagents in ethers observed dissolutions of aluminium, zinc and cadmium anodes and deposition of magnesium on the cathode. Later, it was suggested by Evans and Lee[42] that dissolution of an aluminium anode in ethyl magnesium bromide yields triethyl aluminium. Table 1.3. contains some typical examples of organometallic compounds obtained from the electrolysis of Grignand reagents.

Table 1.3. Electrolysis of Grignard reagents

Anode	Electrolyte	Solvent	Product	References
Aluminium	EtMgI	Diethyl ether	$Al(Et)_3$	43
Boron	RMgCl	"	BR_3	5
Zinc	$C_6H_{13}MgBr$	Hexyl ether of diethylene glycol	$(C_6H_{13})_2Zn$	5
Lead	EtMgBr	Diethyl ether	$PbEt_4$	5

The earlier experiments of Hein[44] showed that mixtures of alkyl compounds of the alkali metals in dialkylzinc or trialkylaluminium give good conducting solutions, which was explained by the formation of the dissociating complex

$$NaZnEt_3 \rightleftharpoons Na^{\oplus} + ZnEt_3^{\ominus}$$

Such solutions yield alkyl radicals on anodic oxidation; these may attack the anode to yield compounds which may be stable metal alkyls, or which may disproportionate.

Ziegler in 1956,[45] using the complex $NaF.2AlEt_3$ as electrolyte, prepared tetraethyllead electrochemically at a lead anode. Similarly when a complex of the type $NaAlEt_4$ was electrolysed on an aluminium anode, $AlEt_3$ was produced on the anode and sodium deposited on the cathode.[46] Although the emphasis has very much been on lead and aluminium, other elements such as B, Mg, Hg, Bi, Sn, Zn, Sb, Si, Ge, In and Ti[5,21] have been successfully alkylated in this way.

In spite of the fact that by electrolysis of aluminium complexes it is possible to synthesize a large number of different alkyl metal compounds, the use of these compounds presents significant difficulties due to their high reactivity. The organoboron complexes of the type $MR.BR_3$ on the other hand are of interest in that they are safe compounds with which to work and a number of alkyl metal compounds can be prepared by electrolysis in ether.[47] Some typical examples of such syntheses are included in Table 1.4.

Table 1.4. Electrolysis of Aluminium and Boron Complexes

Anode	Electrolyte	Product	References
Aluminium	$NaAlEt_4$	$AlEt_3$	48
Magnesium	$NaAlEt_4$	$MgEt_2$	48
Zinc	$NaF.2AlEt_3$	$ZnEt_2$	43
Tin	$NaF.2AlEt_3$	$SnEt_4$	43
Antimony	$NaF.2AlEt_3$	$SbEt_3$	43
Mercury	$NaF.2AlEt_3$	$HgEt_2$	49
Cadmium	$NaAlEt_4$+KCl	$CdEt_3$	50
Bismuth	$NaAlEt_4$+KCl	$BiEt_3$	50
Indium	$NaF.2AlEt_3$	$InEt_3$	43
Lead	$NaBMe_4$	$PbMe_4$	47
Mercury	$NaBEt_4$	$HgEt_2$	47
Bismuth	$NaBEt_4$	$BiEt_3$	47

Some other organo aluminium compounds have also been synthesized by using soluble aluminium anodes in non-aqueous solvents. Thus, electrolysis of AlI_3 in MeI produced $MeAlI_2$ [51]. When dichloromethane was used instead of MeI, the main electrolysis product was bis (dichloro aluminium) methane ($Cl_2AlCH_2AlCl_2$).[52] The preparation of cyclopentadienyl complexes is formally similar to some of the cathodic reactions noted earlier. Thus the electrochemical synthesis of dicyclopentadienyl iron Cp_2Fe has been reported.[53] The method is based on the electrolysis of CpTl in dimethyl formamide with an iron anode. Cp_2Ni[54] and di-1, 5-cyclooctadiene nickel[55] were also prepared by a similar method. Of the same reaction type is the formation of complex manganese compounds during electrolysis of cyclopentadienyl with manganese salts, or in their absence, with the use of soluble manganese anodes. Table 1.5. shows some of these reactions.

Table 1.5. Some Other Complexes from Sacrificial Anodes

Anode	Starting Substances	Product	References
Iron	CpTl	$FeCp_2$	53
Manganese	Methyl cyclopentadienyl sodium	$MnCp_2$	13
Manganese	Indene + LiBr + $Mn(MeCOO)_2$ + $Co_4(CO)_{12}$	Indenyl manganese tricarbonyl	5

More recently, Tuck et al have developed a direct preparative electrochemical method[21] using sacrificial anodes. Although it was possible to synthesize a number of inorganic and organometallic compounds by this method, emphasis was placed on systems where reduction of alkyl or aryl halide is followed by oxidation of the metal which forms the anode of the cell.

Table 1.6. includes some examples of such syntheses.

Table 1.6. Formation of Organometal Halide Complexes

Reactions	References
$Cd_{(+)} \xrightarrow[\text{acetone}]{RX,\,L} RCdX.L$ R = Me, Et, n-Bu, ph, C_6F_5 X = Cl, Br, I. L = bipy, phen, diox	56, 57
$Cd_{(+)} \xrightarrow{RX,\,Pr_4NX} Pr_4N(RCdX_2)$ R = Me, Et, n-Bu, Ph, C_6F_5 CF_3 X = Cl, Br, I	56, 58
$Zn_{(+)} \xrightarrow[\text{MeCN}]{RX,\,L} RZnX.L$ R = Me, Et, Ph, C_6F_5, Bz X = Cl, Br, I L = bipy.	58
$Sn_{(+)} \xrightarrow[\text{MeOH},\,C_6H_6]{RX,\,L} R_2SnX_2.L$ R = Me, Et, n-Bu, Ph X = Cl, Br, I L = bipy, phen, diphos, or 2 dmso, 2 MeCN	59
$Pd_{(+)} \xrightarrow[L]{PhBr} PhPdBr.L$ L = diphos or 2 Et_3P, 2py	60

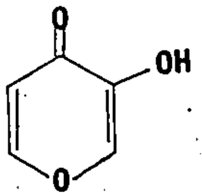
Tuck, Walters and Habeeb were able, by the same method to produce a number of neutral compounds involving anions of chelating ligands.[61] Table 1.7. contains examples of such syntheses.

Table 1.7. Electrochemical Synthesis of Metal-Chelate Complexes

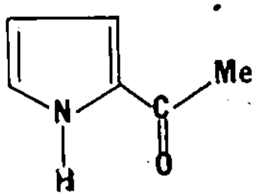
Reactions

$$M_{(+)} \xrightarrow[N_2]{\text{HL, MeOH or acetone}} ML_n$$

$MeCOCH_2COMe \longrightarrow TiL_3,\ ZrL_4,\ HfL_4,\ VL_3,\ CrL_3,\ MnL_2,\ FeL_3,\ CoL_2,\ NiL_2,\ CuL_2,\ ZnL_2,\ InL_3$



$\longrightarrow FeL_3,\ CoL_2,\ NiL_2,\ CuL_2,\ InL_3$



$\longrightarrow CrL_3,\ CoL_2,\ NiL_2,\ CuL_2,\ InL_3$

Similar preparations have also been carried out for Fe, Co and Ni /acac by Lehmkuhl and Eisenbach.[62]

The same method of synthesis also provided a facile route for preparations of a number of anhydrous halides, neutral adducts and anionic halogeno complexes.

Table 1.8. shows some of the compounds prepared by the direct electrochemical method.

Table 1.8. Electrochemical Preparation of Anhydrous Metal Halide adducts and Halogeno Complexes

Compounds	References
$CrBr_3$	63
VCl_2, VBr_2, VI_2	64
$MnBr_2$	65
$FeCl_2$, $FeBr_2$, FeI_2	65
$CoBr_2$	65
$NiCl_2$, $NiBr_2$, NiI_2	65
$CuBr$, $CuBr_2$	65
$ZnBr_2$	65
InI, $InCl_3$, $InBr_3$, InI_3	66.
$InX_3.3dmso$ ($X = Cl, Br$)	
$(Et_4N)(FeBr_4)$	67
$(Et_4N)_2(InBr_5)$	67
$(Et_4N)_2(SnBr_6)$	67

The reaction of cathodic mercury with M-M bonded dinuclear carbonyls giving rise to M-Hg-M systems was noted earlier (Table 1.2.). The electrochemical behaviour of dinuclear carbonyls and similar compounds has been extensively investigated in polarographic and related experiments, from which it is known that reduction may yield $M(CO)_n^-$ anions.[34] Migration to and reaction at a sacrificial anode can then give $M'[M(CO)_n]_2$.

Table 1.9. contains the species which Tuck and Zhandire[21] were able to prepare by reduction of carbonyl compounds on sacrificial anodes.

Table 1.9. Electrochemical Synthesis of M-M at Sacrificial Anodes

Reaction

$$M_{(+)} \xrightarrow[C_6H_6+MeOH+bipy]{Mn_2(CO)_{10}} M(Mn(CO)_5)_2.bipy$$

(M = Zn, Cd)

$$Cd_{(+)} \xrightarrow{Co_2(CO)_8} Cd\ (Co(CO)_4)_2$$

$$M_{(+)} \xrightarrow{Co_2(CO)_8\ +\ L} M(Co(CO)_4)_2.L$$

(M = Zn, Cd,
L = bipy, TMED)

I. 6. On the Mechanism of Carbon-Metal Bond Formation During Anodic Processes

Anodic oxidation of organometallic compounds containing carbanions, is believed to involve the oxidation of the carbanion to generate organic radicals; followed by reaction with the anode metal.[5,21] For instance during the electrolysis of the complex $Na(Zn(Et)_3)$, the $Zn(Et)_3^-$ ions are discharged at the anode

$$Zn(Et_3)^- \xrightarrow{-e} Zn(Et)_2 + Et^\bullet$$

and these ethyl radicals react with the anode material

$$M + nEt^\bullet \longrightarrow MEt_n$$

The work of Evans on the electrolysis of Grignard reagent solutions in ethers[68] supports the radical nature of the anodic process. He established that the electrolysis of Grignand reagents at insoluble anodes yields compounds whose formation can be due to disproportionation or dimerization of the initially formed radicals and their interaction with the solvent.

It was also shown that the composition of anodic gases during the electrolysis of organometallic complexes depends significantly on the anode material. For example, during the electrolysis of solutions of the complex $NaF.2AlEt_3$ in $AlEt_2H$, H_2, C_2H_6, C_4H_{10} and C_2H_4

gases were evolved on the anode.[69] The greatest ethane yield was observed at Pd anode and the dimerization of radicals with formation of butane occurred most effectively at an Fe anode, and at a Cu anode hydrogen was predominent. A similar conclusion was derived in electrolysis of $NaGePh_3$ in liquid ammonia.[70]

CHAPTER II

EXPERIMENTAL

II. 1. Introduction

In this chapter the electrochemical technique used for the syntheses of all compounds reported in this dissertation, the isolation of products, analyses and some physical measurements used are described in general terms. Further details are given in the appropariate parts of the dissertation.

II. 2. The Electrolysis Cell

The cell which has been used for electrochemical syntheses, basically consists of a reaction vessel closed off with a rubber stopper and with two electrodes inserted through the stopper. Because of the nature of the majority of the compounds synthesized, and the necessity of avoiding contact with the atmosphere, the electrolysis and all subsequent operations were performed under a stream of nitrogen or in a nitrogen dry-box. Fig. 2.1. shows a photograph of the cell set up and the dry-box used for this purpose. The reaction vessel is a pyrex or plastic beaker, 200-500 cm^3 in capacity. A platimum wire (~ 1 mm diam.) normally forms the cathode of the cell. The form of the anode depended upon the properties of the metal concerned. In some cases, the metal (1-2 g) was suspended and supported on a platinum wire. Indium, which is a soft metal, was hammered onto the platinum support to form a plate. In the case of hafnium, iron, and copper a suitable length of wire was used without modification; other metals such as titanium and zirconium were suitably cut and shaped to form plates normally 1 x 1 cm^2 in dimensions. Both electrodes were supported by a rubber bung fitted tightly into the neck of the vessel. The rubber stopper also allowed the use of gas inlet and outlet tubes, to maintain the system under nitrogen during the electrolysis. The outlet tube in its turn is connected to a gas bubbler. Fig. 2.2. shows a schematic diagram of the cell. In the preparation of metal chlorides, chlorine gas was bubbled into the solution phase with nitrogen carrier gas at a rate of approximately 25 cm^3/min,

II. 3. The Power Supply.

The power supply used was a Coutant LQ 50/50, capable of supplying at maximum 50V, D.C., and 500 mA. Applied voltages were 1-50 V, as dictated by solution conditions, given that a current of 10-300 mA, normally produced a reasonable rate of reaction without over heating the solution, In some cases, a cooling external water bath was used, especially when halogens were used in the reaction.

II. 4. The Solution Phase

Organic solvents plus the solute formed the solution phase. Small amounts (~ 30 mg) of tetraalkylammonium halide or perchlorate were used to improve and assist the current flow in the preparation of neutral compounds, but excess of the salt was present when anionic complexes were being prepared.

All solvents had to be free of moisture and were dried either over activated molecular sieves or over freshly pressed sodium and often distilled under nitrogen.

II. 5. Isolation of Products

In some cases, the products of the electrochemical reactions precipitated in the reaction vessel, in others, subsequent addition of diethyl ether or other organic solvents, and/or reducing the total volume was necessary. All operations, such as filtration, were done in a dry-box. Volume reductions and sample dryings were done in vacuo. Details are given in the appropriate parts of the dissertation.

II. 6. Analysis

Halide: The Volhard method was used for halide analysis. The Oakdale and Thompson method[71] was used occasionally when samples were not sufficiently soluble.

Volhard method: Samples (~ 30 mg) were dissolved in 100 cm^3 distilled water and 2 cm^3 concentrated nitric acid was added, followed by a known excess of standard silver nitrate, 5 cm^3 nitro benzene and 2 cm^3 ferric alum indicator solution. Excess $AgNO_3$ is then titrated with standard potasium thiocyanate until the colour of $Fe\,SCN^{2+}$ is permanent for one minute.

Oakdale and Thompson method: The apparatus (Fig. 2.3.) consists of a 100 cm^3 Kjeldahl flask (A) fitted with a condenser (B). The tube (C) is attached to the top of the condenser; (D) represents a bulb of 10 cm^3 capacity for additions to (A). The gas wash-bottle (E) of 500 cm^3 capacity has an attachment (F) to an aspirator to allow control of the pressure inside the apparatus. The tap (G) allows atmospheric pressure to be reached inside the apparatus after the experiment.

The method consists of placing a weighed sample (0.2 - 0.5 g) in the Kjeldahl flask, with 100 cm^3 of 10% sodium hydroxide in (E). The tap (G) is closed and a slight vacum applied. 20 cm^3 fuming sulphuric acid is added slowly through the dropping funnel and the mixture boiled for 30 minutes, care being taken to prevent vapours from ascending the condenser. When the solid has been digested, 30 cm^3 of sulphuric acid is added and the solution is then drained from the condenser and ~ 10 cm^3, 30%

hydrogen peroxide is added carefully through the dropping funnel; the liberated halogen is driven through the apparatus by boiling the solution. The addition of peroxide and the heating are continued intermittently until all the halide has been liberated and absorbed in the sodium hydroxide solution.

The apparatus is then disconnected and the contents of (E) are transferred to a 600 cm^3 beaker and carefully acidified with concentrated nitric acid, after which the halide determined by the Volhard method.

Metal Analysis

Analytical methods used for different metals are discussed separately for each metal in related chapters.

Current Efficiency

The current efficiency is defined as the number of moles of metal dissolved per Faraday of electricity. The measurement is made at a controlled constant current, under the same conditions as the preparative experiment. The electrode which undergoes dissolution is weighed before and after electrolysis, and the number of moles dissolved so calculated.

The amount of electricity passed through the cell in Faradays is also calculated.

$$\text{Number of Faradays} = \frac{I\ (\text{Amp}) \times t\ (\text{Sec})}{F}$$

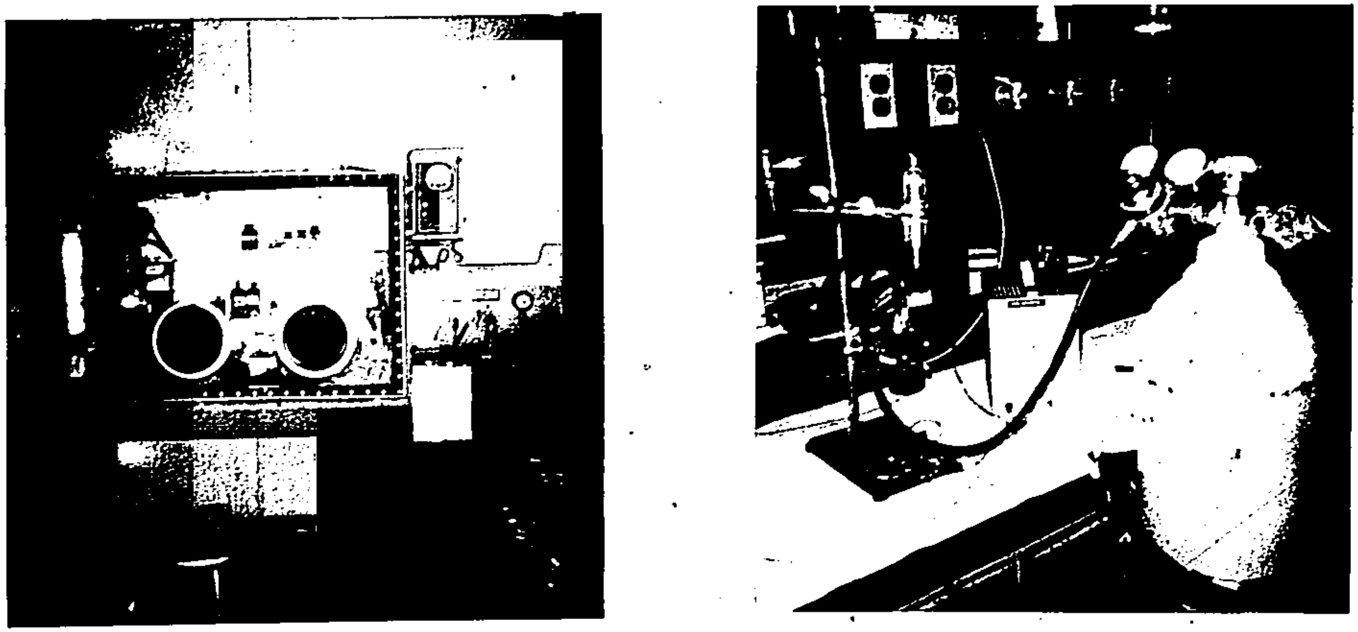
I = the controlled constant current

t = the time of electrolysis

and I x t = the number of Coulombs

F = Faraday's constant = 96500 Coulombs

$$\text{Then } E_F = \frac{\text{number of moles dissolved}}{\text{number of Faradays}}$$



A

B

Fig. 2.1. A - A photograph of the dry-box

B - A photograph of the electrolysis set up

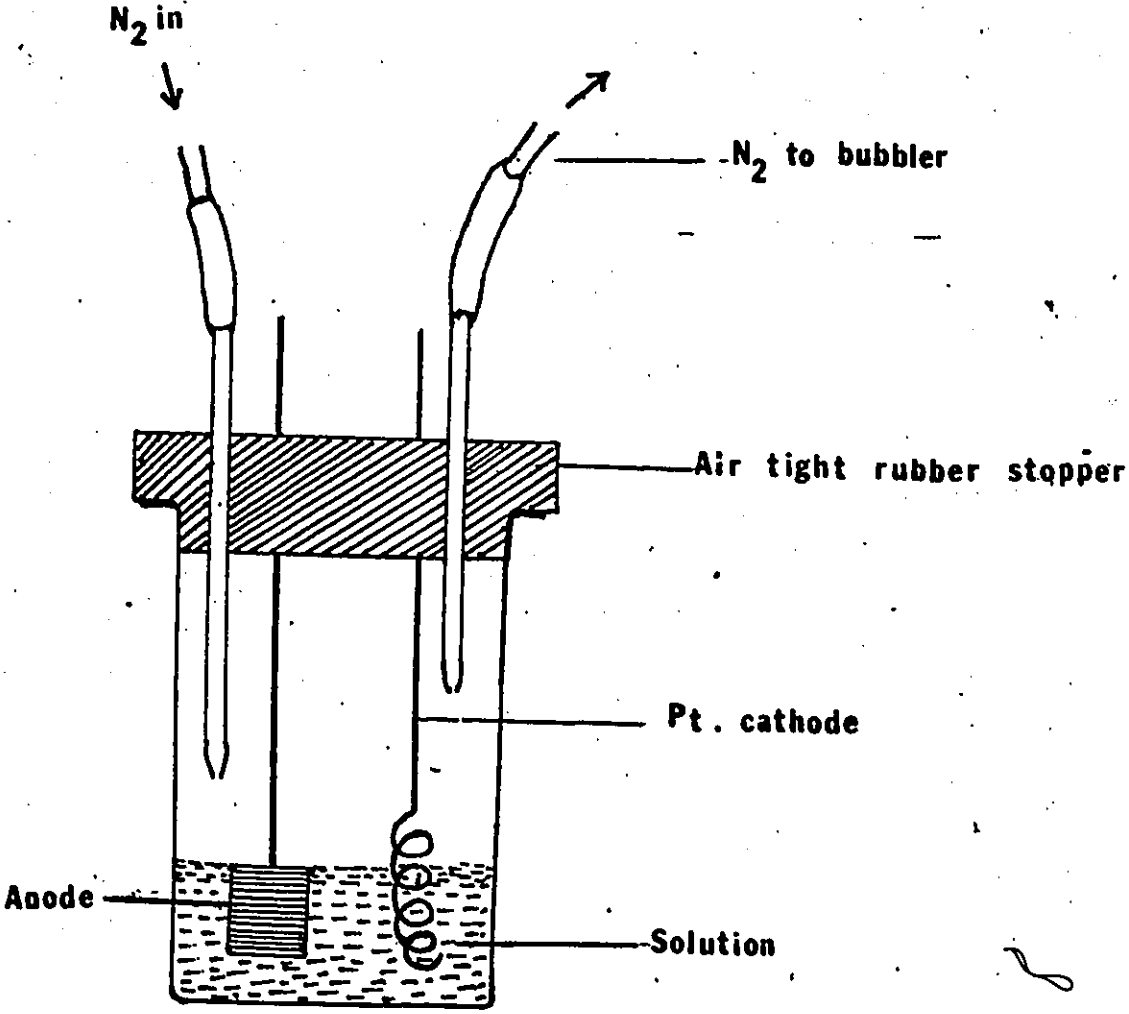
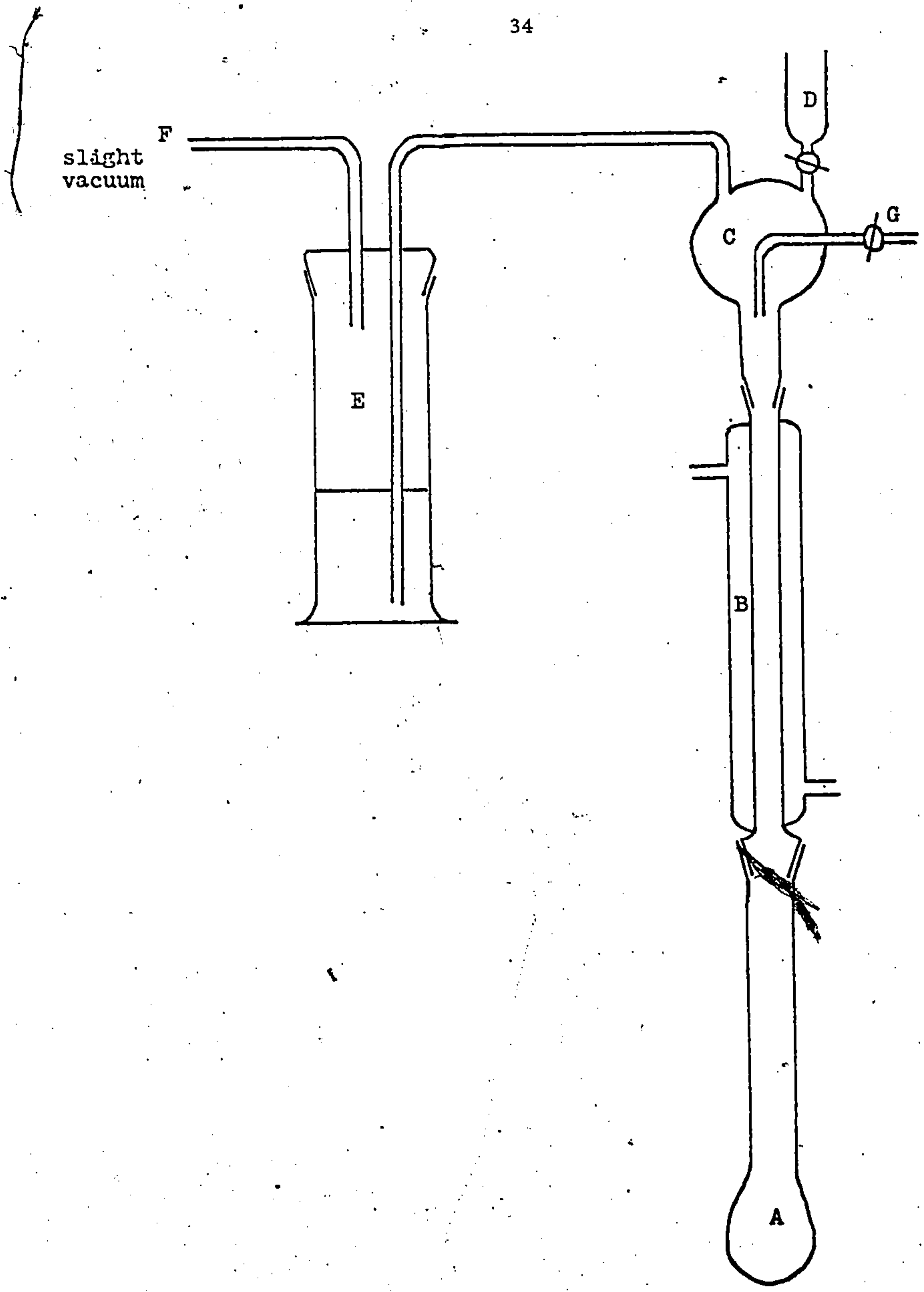


Figure 2.2 Electrochemical Cell.


F
slight
vacuum
D
C
G
E
B
A

CHAPTER III

NEUTRAL AND ANIONIC CHLORO- AND BROMO-COMPLEXES OF TITANIUM, ZIRCONIUM, AND HAFNIUM

III. 1. Introduction

Titanium, the lightest member of the d-block transition elements, is a silvery ductile metal with a considerable industrial potential owing to its rare combination of properties. It is less dense than iron, much stronger than aluminium and almost as corrosion resistant as platinum. These properties make it ideal for use in engines, air craft frames, missiles, some marine equipment, etc., where light weight, strength, and the ability to withstand extremes of temperature are important. Titanium was discovered in 1791 by William Gregor who gave it the name titanium after the Titans who, in Greek methology, were the sons of the earth. It is the ninth most abundant element in the earth's crust, and almost always occurs in igneous rocks, and in the sun, stars and meteorites.

Titanium cannot be obtained in the pure form by the usual method of reduction of the oxide with carbon, since this route yields a very stable carbide. In practice, the basis of the preferred methods for producing the pure metal is via reduction of tetrachloride, even though this reagent must first be prepared from one of the two major titanium ores, rutile (TiO_2) or ilmenite ($FeTiO_3$). The purest titanium is obtained by the method of Van Arkel and de Boer[72], in which impure titanium is allowed to react with iodine at 150-200°C, followed by decomposition of the resultant titanium tetraiodide vapour on an incandescent tungsten filament at $\sim$ 1300°C.

Zirconium and hafnium, on the other hand, are both hard metals which resemble titanium in appearance. Zirconium has good mechanical properties combined with resistance to corrosion and very low neutron absorption character which give the metal an important role in nuclear reactor technology. Unfortunately, hafnium, which may constitute two percent impurity in zirconium metal, has a very large cross-section for thermal neutrons, so that the production of hafnium-free zirconium is a matter of interest, but the close chemical similarity of zirconium and hafnium makes the separation of zirconium from hafnium a tedious process (see ref. 72) and for most purposes the hafnium content is ignored.

Zirconium metal was isolated by Berzelius in 1824 by potassium reduction of a fluoride, but was not obtained pure until 1925 by Van Arkel and de Boer using the iodide method. The presence of hafnium in zirconium had remained undetected by ordinary chemical methods and its presence was first demonstrated by X-ray spectroscopy and it was separated in 1923 after a laborious fractional crystallization of the complex fluorides of zirconium and hafnium. The pure hafnium salt was isolated and elemental hafnium obtained by sodium reduction.[73]

The metal chemistry, composition, sources, uses and production of titanium, zirconium and hafnium have been discussed in a number of articles, texts and reviews.[74,75,76]

III. 2. The General Chemistry of Ti, Zr and Hf

The electronic configurations of the three elements in their ground states are:

Ti	Ar	$3d^2 4s^2$
Zr	Kr	$4d^2 5s^2$
Hf	Xe	$4f^{14} 5d^2 6s^2$

The highest oxidation state of the three elements is therefore four, Ti(IV) is the most stable and common oxidation state, but compounds in lower oxidation states (-1, 0, II, and III) are known, and are readily oxidized to Ti(IV) by air, water, or other reagents. The most important difference between titanium on the one hand, and zirconium and hafnium on the other, is that the lower oxidation states of zirconium and hafnium are of minor importance, and few compounds are known.

III. 3. The halides of Ti, Zr and Hf

As the main consideration of this chapter is the electrochemical syntheses of some neutral and anionic complexes of the metal halides, the discussion will be largely restricted to the halides and their complexes.

Tetrahalides (other than fluorides)

Titanium tetrachloride is one of the most important titanium compounds, since it is the usual starting point for the preparation of other titanium compounds. It is prepared by treating the dioxide at 900 - 1000°C with chlorine gas in the presence of a reducing agent such as carbon black or charcoal.[77]

$$TiO_2 + 2Cl_2 + 2C \longrightarrow TiCl_4 + 2CO$$

However, a number of other methods are available, including reaction of the dioxide with chlorinating agents such as $CHCl_3$ or CCl_4[77]. The tetrabromide may be prepared by direct reaction of the metal with bromine in a sealed evacuated tube, by distillation of the tetrachloride in small quantities into an excess of liquid HBr, or by passing bromine vapour over a mixture of carbon and the dioxide at 650 - 700°C.[78] The tetraiodide may be prepared by direct reaction of the elements at 25°C, by the action of gaseous HI on liquid $TiCl_4$, or by disproportionation of the triiodide.[79]

The tetrachlorides and tetrabromides of zirconium and hafnium are obtained by a variety of chlorination or bromination procedures starting with the metal, the dioxide, the carbide ... etc.[77] A relatively new method for preparation of $ZrBr_4$ involves halogen exchange between $ZrCl_4$ and BBr_3 at room temperature.[80]

$$3ZrCl_4 + 4BBr_3 \longrightarrow 3ZrBr_4 + 4BCl_3$$

The tetraiodides may be prepared by three main methods,[81] direct reaction of the elements, action of AlI_3 on the metal dioxide at 400°, or halogen exchange, preferably between AlI_3 and $ZrCl_4$.

Properties

All the tetrahalides are diamagnetic, extremely hygroscopic, They are powerful Lewis acids and form extensive series of addition compounds. $TiCl_4$ is a colorless liquid with a pungent odour, fumes strongly in moist air, and is vigorously, though not violently, hydrolyzed by water. $TiBr_4$ and TiI_4 are similar to $TiCl_4$, but crystalline at room temperature. The tetrahalides of zirconium and hafnium are also crystalline solids, which react readily with water to form oxyhalides $MOX_2.8H_2O$. $ZrCl_4$ resembles $TiCl_4$ in its chemical properties. It is a white solid, which fumes in air and sublimes at 331°. The three titanium halides are monomeric tetrahedral species in all physical states,[82, 83] but solid

$ZrCl_4$ consists of zigzag chains of $ZrCl_6$ octahedra,[84] and the compounds $ZrBr_4$, $HfCl_4$ and $HfBr_4$ are isotypic.

Halides of lower oxidation states.

Halides in other oxidation states other than +4 are represented by MCl_2, MBr_2, ZrI_2, MCl_3, MBr_3 and MI_3 (M = Ti, Zr or Hf). Titanium monochloride is known in the gaseous state and certain physical properties have been established. The methods of preparation, properties and other physical constants of lower halides are discussed in Ref. 77.

Mixed halides

When $TiBr_4$ is mixed with $TiCl_4$ the chlorobromides $TiCl_3Br$, $TiCl_2Br_2$ and $TiClBr_3$ are all formed in solution.[85,86] However, the chlorobromides have never been obtained separately, and in the solid state the tetrachloride and tetrabromide form a continuous series of mixed crystal.

III. 4. Complex Formation

As has already been mentioned, the tetrahalides of those elements and especially $TiCl_4$ and $TiBr_4$ are powerful Lewis acids which form addition compounds with electron donating compounds.

Neutral Complexes

The great majority of known complexes with organic compounds involve $TiCl_4$, although the tetrabromide has received a fair amount of attention. Complexes of TiI_4 are few, and it seems that no complex of ZrI_4 or HfI_4 is known. The metal may be in five, six, seven or eight coordinate, but most complexes are six-coordinate monomers of the type $TiX_4.2L$ or $TiX_4.B$, where L = monodentate and B = bidentate neutral ligands. They are crystalline solids often soluble in organic solvents so that their spectroscopic and other properties have been well studied,[77,86,87,88] and are invariably extremely sensitive to moisture and air. Nitrogen donor ligands which form addition compounds with the metal halides include those formed with amides, imides, amines, imines, cyanides and nitro compounds; and those with oxygen donor ligands include esters, ethers and carbonyl compounds. Addition complexes of the metal halides with arsenic and phosphorus compounds are also known.[77,87] The reactions of amines with the metal halides, however, are more complicated than those of oxygen and other donor ligands, because, in addition to the formation of adducts, either reduction to Ti(III) or substitution reaction may occur. In general, tertiary or heterocyclic amines simply form adducts. Primary or secondary amines are believed to coordinate initially to the metal atom, followed by a base-catalysed elimination of hydrogen halide.[77,86,87] Finally, it should be mentioned that several ligands containing replacable protons react with the halides with elimination of HX to form chelated compounds.

Anionic Complexes

Hexahalo salts of titanium, zirconium and hafnium of the type R_2MX_6 (R = alkali metal or uni-positive organic cation; X = F, Cl or Br) can be prepared by a variety of methods.[77, 81, 87] The salts become progressively more difficult to prepare on passing from the fluoride to iodide, and in fact there is no evidence for MI_6^{-2} ion in the solid state, free iodine being liberated in all attempts to prepare such species. Salts of organic cations are usually prepared by mixing dichloromethane solutions of appropriate reactants.

III. 5. Experimental

a) General

Titanium, zirconium and hafnium halide complexes are extremely sensitive to air and moisture. In order to avoid contact of the compounds with the atmosphere all experiments reported were carried out under an atmosphere of dry nitrogen and at ambient temperature (20°C). Isolation of products and all reactions were carried out in a nitrogen-filled glove box. Volume reduction and sample drying were in vacuo. The detailed experimental conditions are given in Table 3.1.

b) Materials

The metals titanium (foil, 0.67 mm thick, m2N7), zirconium (foil, 0.25 mm thick, M3N), and hafnium (wire, 1 mm diameter, m3N7) were used as supplied (Alfa Inorganics). Acetonitrile, methanol and ethylenediamine were dried over molecular sieves, benzene was dried over freshly pressed sodium, and were distilled under nitrogen before use. Tetraalkylammoniumhalides were dried in the oven (~ 80°C) for a few hours before they were used. Thionyl chloride, 2,2′-bipyridine, bromine liquid and chlorine gas were used as supplied.

c) Analysis

Halogen analysis was by the Volhard method (Chapter II). Titanium was determined by titration against ethylenediaminetetraacetic acid (EDTA, disodium salt).[89] The samples (~ 25 mg) were dissolved in nitric acid and oxidized with 2 cm^3 of 30% hydrogen peroxide; after addition of excess EDTA and neutralization with ammonia solution, sufficient glacial acetic acid is added to make the solution acidic once more and the solution titrated with standard bismuth (III) nitrate, using xylenol orange as indicator to the orange to red end point.

A similar method was used for zirconium and hafnium. Solutions prepared by dissolving the sample in sulphuric acid and sodium sulphate were boiled, then cooled and titrated with standard EDTA using Xylenol orange indicator to the red to yellow transition.[89]

d) Physical Measurements

Infrared spectra were recorded with a Beckman IR-12 spectrophotometer with a range of 4,000 - 200 cm^{-1} as nujol-mulls using KBr windows. The IR spectra served to identify the presence of neutral ligands or quaternaryammonium cations in the solids prepared.

e) Preparative Electrochemistry

The electrochemical method used for the preparation of the compounds was described in Chapter II. Ti, Zr and Hf metals formed the anode of the cell in all cases. The detailed experimental conditions are given in Table 3.1. The electrolysis, and all subsequent operations, were carried out under a stream of nitrogen, or in a dry-box. Excess chlorine or bromine was removed from the solution with a stream of nitrogen before any further treatment of the electrolysis solutions.

3

Table 3.1. Experimental conditions for electrochemical preparation of Ti, Zr and Hf complexes

Elements	Solution phase composition (volumes in cm^3)	R_4NX added (g)	Initial		Time of electrolysis (h)	Weight metal dissolved (g)
			Voltage (V)	Current (mA)		
			Neutral Complexes			
Ti/Cl	MeCN 50;$Cl_{2(g)}$	0	20	150	8.0	0.53
Zr/Cl	MeCN 50;$Cl_{2(g)}$	0	10	100	6.0	e
Hf/Cl	MeCN 50;$Cl_{2(g)}$	0	20	150	8.0	0.71
Ti/Br	MeCN 50;Br_2 2	0	10	200	4.5	1.34
Zr/Br	MeCN 50;Br_2 2	0	10	170	4.5	e
Hf/Br	MeCN 50; Br_2 2	0	15	200	3.0	1.21
			Anionic Complexes			
Ti/Cl	$SOCl_2$ 50;$Cl_{2(g)}$	0.5^c	30	150	6.0	0.63
Zr/Cl	$SOCl_2$ 50;$Cl_{2(g)}$	1.0^c	30	150	10.0	0.54
Hf/Cl	$SOCl_2$ 50;$Cl_{2(g)}$	1.0^c	50	25	8.0	0.72
Ti/Br^{a,b}	C_6H_6 60;Br_2 2	1.0^d	30	130	0.5	0.21
Ti/Br^b	C_6H_6 15;Br_2 3	1.0^d	15	400	3.0	e
Zr/Br^{a,b}	C_6H_6 20;Br_2 2	1.0^d	15	350	3.0	0.07
Hf/Br^{a,b}	C_6H_6 15;Br_2 2	1.0^d	15	150	4.0	0.15

[a] Two phases; reaction apparently occurs only in lower, conducting layer.

[b] See Text for details

[c] R = n-pr

[d] R = Et

[e] Not recorded

Electrochemical Preparation of $TiCl_4.2MeCN$

The solution resulting from electrolysing titanium in acetonitrile and chlorine (Table 3.1.) was reduced in volume about 30%, and then stored over night in a sealed vessel in the refrigerator. The yellow powder so obtained was filtered under nitrogen, then sublimed at $\sim 80^{\circ}C$. The yellow solid is soluble in methanol, acetonitrile, water but insoluble in benzene, diethyl ether, and very slightly soluble in chlorform and carbon tetrachloride.

Electrochemical Preparation of $ZrCl_4.2MeCN$ and $HfCl_4.2MeCN$

The same procedure as for $TiCl_4.2MeCN$ was followed, but in this case colourless solids were obtained. The solubilities of both $ZrCl_4.2MeCN$ and $HfCl_4.2MeCN$ are similar to those of $TiCl_4.2MeCN$.

Electrochemical Preparation of $TiBr_4.2MeCN$

The red solid obtained directly from the electrolysis of titanium in acetonitrile and bromine was filtered under nitrogen, then dried in vacuo for abour 3 h. The compound is extremely hydroscopic and fumes strongly in moist air. It is very soluble in methanol giving a colourless solution, and in acetonitrile, giving a yellow solution, but insoluble in benzene or CCl_4 and slightly soluble in $CHCl_3$. The compound changes colour from red to yellow at about 120°C, but did not melt even over 300°C.

Electrochemical Preparation of $ZrBr_4.2MeCN$

In this case no solid formed directly in the electrolysis cell. The solution was reduced about 50% in volume, and left over-night in the refrigerator in a sealed vessel. The resultant orange solid was filtered under nitrogen, collected, and dried in vacuo for about 4 h. The compound is similar to $TiBr_4.2MeCN$, being very hygroscopic and fuming strongly in air. The solubility also resembles that of $TiBr_4.2MeCN$, except that a yellow solution was obtained with methanol and gas evolution was observed.

Electrochemical Preparation of $HfBr_4.2MeCN$

The same procedure as with $ZrBr_4.2MeCN$ was followed, but in this case the volume was reduced by ~ 30%.

Electrochemical Preparation of $(Pr_4N)TiCl_5$

The electrolysis solution was treated dropwise with diethyl ether until a yellow solid was precipitated. This solid was filtered and washed a few times with the same solvent.

Electrochemical Preparation of $(Pr_4N)ZrCl_5$ and $(Pr_4N)HfCl_5$

The colourless solid obtained from electrolysis was filtered and washed a few times with diethyl ether.

Electrochemical Preparation of $(Et_4N)_2TiBr_6$

The red solid obtained from electrolysis was filtered and washed with diethyl ether. It should be mentioned here that tetraethyl ammonium bromide is insoluble in benzene, so that in order to prepare the mixture (Table 3.1.) for electrolysis bromine was first added to benzene, followed by the salt. In this way two phases were formed, but only the lower phase had any significant conductivity, and the cell was arranged so that both electrodes were immersed in this layer.

Electrochemical Preparation of $(Et_4N)TiBr_4$

When the bromine content was increased in the benzene-Br_2-Et_4NBr system (see above) the two phases eventually coalesced; in the present case, this occurred when the benzene-bromine ratio was approximately 5:1 (v/v). The blue-black solid obtained by electrolytic oxidation of titanium in this solution was filtered, and dried in vacuo for 3 h. The solid is extremely hygroscopic and like $(Et_4N)_2TiBr_6$ fumes strongly in air, and eventually changes colour to yellow. It is very soluble in methanol, insoluble in ethers, benzene, carbon tetrachloride and chloroform, and very slightly soluble in acetone. It melts with decomposition at 283^{0}C.

Electrochemical Preparation of $(Et_4N)_2ZrBr_6$ and $(Et_4N)HfBr_6$

The procedure used for $(Et_4N)_2TiBr_6$ was followed.

Electrochemical Preparation of $TiBr_4$.en, $ZrBr_4$.en and $HfBr_4$.en

Titanium metal was electrolysed in a mixture of 60 cm^3 benzene, 20 cm^3 methanol and 2 cm^3 Br_2 for 3 h under 30 V potential and 200 mA current. Under these conditions, 0.47 g metal dissolved. After excess Br_2 was removed by a stream of N_2, 5 cm^3 of the electrolysis solution was diluted with 15 cm^3 methanol and 2 cm^3 of ethylenediamine in 15 cm^3 of the same solvent was added dropwise until a colourless solid started to appear. This was left in contact with the solution for about 10 minutes and then filtered and washed with methanol several times. The solid was collected and dried in vacuo for about 3 h.

Electrochemical Preparation of $TiBr_4$.2en

~50 mg $TiBr_4$.2MeCN prepared as before was dissolved in 10 cm^3 MeCN and 3 cm^3 en in 15 cm^3 of same solvent was added dropwise. The faint yellow solid obtained was filtered, collected and dried in vacuo.

Electrochemical Preparation of $TiBr_4$.2bipy

The same procedure as $TiBr_4$.2en, except in this case

3 cm^3 en was replaced by 50 mg bipyridine.

III. 6. Results and Discussion

Table 3.2. shows the analytical results for the neutral and anionic complexes of titanium, zirconium and hafnium prepared by the electrochemical method. The table also contains the addition compounds prepared using $TiBr_4.2MeCN$ as a starting point.

Neutral Halides

The experimental conditions detailed in Table 3.1. allowed us to produce gram quantities of $MX_4.2MeCN$ (M = Ti, Zr, Hf; X = Cl, Br) within a few hours. The presence of two cis-acetonitrile ligands was confirmed by doublet absorptions in the ν(C$\equiv$N) region of the infrared spectrum, Table 3.3.

Table 3.2. Analytical results for neutral and anionic complexes of Ti, Zr and Hf.

		Found(%)		Calculated(%)	
Compound	Colour	Metal	Halogen	Metal	Halogen
		Electrochemical Syntheses			
$TiCl_4 \cdot 2MeCN$	Yellow	17.7	52.2	17.7	52.2
$ZrCl_4 \cdot 2MeCN$	Colourless	28.8	45.1	28.9	45.1
$HfCl_4 \cdot 2MeCN$	Colourless	44.2	35.1	44.4	35.3
$TiBr_4 \cdot 2MeCN$	Red	10.8	71.1	10.7	71.1
$ZrBr_4 \cdot 2MeCN$	Orange	18.4	64.8	18.5	64.9
$HfBr_4 \cdot 2MeCN$	Orange	30.1	54.8	30.8	55.1
$(Pr_4N)TiCl_5$	Yellow	11.7	43.1	11.7	43.1
$(Pr_4N)ZrCl_5$	Colourless	20.4	38.9	20.2	38.8
$(Pr_4N)HfCl_5$	Colourless	32.5	32.6	32.8	32.8
Et_4NTiBr_4	Blue-black	9.4	63.7	9.5	63.2
$(Et_4N)_2TiBr_6$	Red	6.0	60.3	6.1	60.9
$(Et_4N)_2ZrBr_6$	Pale yellow	10.6	56.7	10.7	56.7
$(Et_4N)_2HfBr_6$	Pale yellow	19.1	51.0	19.0	51.4
		Neutral addition compounds			
$TiBr_4 \cdot en$	Colourless	11.2	74.0	11.2	74.4
$TiBr_4 \cdot 2en$	Pale yellow	9.6	65.1	9.8	65.5
$TiBr_4 \cdot 2bipy$	Yellow	7.2	46.8	7.1	47.0
$ZrBr_4 \cdot en$	Colourless	19.2	67.3	19.3	67.9
$HfBr_4 \cdot en$	Colourless	30.5	57.4	31.9	57.4

Table 3.3. Infrared absorptions of $MX_4.2CH_3CN$ adducts (M = Ti, Zr, Hf; X = Cl, Br)[a]

Compound	$\nu(C\equiv N)$
$TiCl_4.2MeCN$	2286, 2310
$TiBr_4.2MeCN$	2280, 2305
$ZrCl_4.2MeCN$	2284, 2306
$ZrBr_4.2MeCN$	2260, 2285
$HfCl_4.2MeCN$	2275, 2303
$HfBr_4.2MeCN$	2280, broad

[a] Frequencies in cm^{-1}; samples run as Nujol mulls between potassium bromide plates and prepared under nitrogen.

The frequencies are in good agreement with those previously reported[90] for these compounds, confirming the formulation based on the analytical results. Thus the first conclusion from this work is that these complexes of the three chemically inert metals are now readily available in high yield by a room temperature synthetic route which uses the metals as the accessible source of high purity element.

We were not able to prepare any of the tetraiodo complexes of these elements (nor any anionic iodo complexes), despite the fact that iodides of a number of other transition metals have been obtained by electrochemical synthesis.[63, 64, 65] A range of experimental conditions was investigated, varying such factors as voltage, current, composition, metal surface pre-treatment (titanium was boiled with oxalic acid), and the use of Br_2-I_2 mixtures, all without success, in that in no case were we able to isolate MI_4, or $MI_4.L_2$ species. By monitoring the weight of the anode, it was found that appreciable quantities (0.05 - 0.5 g) of titanium or zirconium dissolved, and in some cases solids of indeterminate composition were obtained. For example, electrolysis of titanium (anode) with a solution of iodine in acetonitrile yielded a product containing 7.4% Ti, 32.5% I, and having no $\nu(C\equiv N)$ absorption in the infrared. In another case zirconium was electrolytically dissolved (0.38 g) into a benzene-methanol solution of iodine and n-Pr_4NI; the final solid contained

36.7% Zr, 26.5% I. It is known that TiI_4 is a weak Lewis acid and very few adducts have been reported.[91]

Adducts of MX_4

The literature on the adducts of tetrachlorides and tetrabromides of Group IVA is very extensive.[86,87] Our experiments have revealed one aspect of the chemistry of these compounds not apparently reported, namely that bidentate ligands such as ethylenediamine and 2,2'-bipyridine may form both 1:1 and 1:2 adducts with $TiBr_4$. The existing literature on the preparation of the adducts of such ligands[92,93] refers to experiments carried out in benzene solution, from which compounds such as $TiBr_4$.bipy precipitate. Our earliest preparations used electrochemically prepared solutions of MBr_4 in benzene-methanol (3:1); excess bromine was removed from the solution with a stream of nitrogen, and ethylenediamine also in benzene-methanol added dropwise until precipitation occurred. The resultant solids were shown to be the 1:1 adduct MBr_4.en (M = Ti, Br, Hf: see Table 3.3) Later experiments used $TiBr_4$.2MeCN as the starting material, and acetonitrile as the reaction medium. Typical conditions would involve 50 - 100 mg of $TiBr_4.2CH_3CN$ in 10 cm^3 acetonitrile; a solution of 50 mg of 2,2'-bipyridine in 15 cm^3 of the same solvent was added dropwise until yellow precipitation occurred. The product was collected and dried in vacuo. Under such conditions, we obtained the compounds $TiBr_4.2en$ and $TiBr_4.2bipy$, of which the latter does not appear to have been reported previously. Solvent dielectric constant may be the critical factor in these preparations; benzene may favour the neutral six-coordinate MX_4L_2, while in acetonitrile an ionic species $(MX_2B_2)X_2$ could be formed.

Anionic Complexes

Although benzene-methanol proved to be a satisfactory reaction medium for the electrochemical preparation of a number of transition metal anionic bromo-complexes,[67] we were not able to use it for the preparation of anionic complexes of Group IVA metals. For the chlorides, thionylchloride proved very useful, and electrochemical oxidation of titanium, zirconium, or hafnium in the presence of chlorine in this solvent (Table 3.1-) containing tetra-n-propylammonium chloride leads to the formation of the salt $n\text{-}Pr_4N(MCl_5)$ in each case. With the two heavier metals, the compound precipitated from the solution as the electrolysis proceeded; for titanium, addition of diethylether to the final reaction solution resulted in precipitation of the salt. In cells containing benzene, bromine, and tetraethylammoniumbromide, two different experimental conditions applied. For relatively low bromine concentrations (those marked ^{a} in Table 3.1.), two phases are present; only the lower of these had any significant conductivity, and the cell was arranged so that both electrodes were immersed in this layer. As the electrolysis proceeded, precipitation of the $(Et_4N)_2$ (MBr_6) salts occurred, with the reaction visibly taking place in the lower phase.

The MCl_5^- and MBr_6^{2-} salts (or their analogues with other cations) have been reported previously[77,81,87,94] with one exception. The salt (Et_4N) $(TiCl_5)$ results from the reaction of Et_4NCl and $TiCl_4$ in dichloromethane[95] and a solvated salt (Et_4N) $(ZrCl_5)CH_3CN$ has been reported by Feltz.[96] The vibrational spectral analyses of $TiCl_5^-$ and $TiBr_5^-$ have been investigated by Creaser and Creighton.[94] The hexabromo complexes of the Group IVA metals were prepared by Clark and co-workers,[97] who also analysed the vibrational spectra. Thus only the salt $(n\text{-}Pr_4N)$ $(HfCl_5)$ represents a new complex, and one which completes a group of lighter analogues. In view of the extensive literature on the structure and vibrational spectra of these anions, we have not carried out any further investigation of the compounds prepared.

If the bromine content is increased in the benzene-Br_2-

Et_4NBr system, prepared by adding Et_4NBr to a solution of bromine in benzene (as explained above). Electrolytic oxidation of titanium in this solution, produced not titanium (IV), but the known titanium (III) salt[98] $(Et_4N)(TiBr_4)$. A possible explanation of the anomaly that an increase in the concentration of the apparent oxidizing agent in solution (i.e. Br_2) results in a decrease in the oxidation state of titanium in the final product is discussed below. Two relevant precedents for this synthesis can be noted immediately. Firstly, the electrochemical oxidation of titanium in the presence of β-diketonates and similar ligands results in the formation of titanium (III) TiL_3 complexes, which can be subsequently oxidized to $TiOL_2$. Zirconium and hafnium form only ML_4 species under such conditions.[61] Secondly, the electrochemical oxidation of other top row transition metals to form anhydrous bromides under conditions similar to those used in the present work yields low oxidation state compounds, including vanadium (II)[64] and copper (I).[64] The formation of the $TiBr_4^-$ anion is therefore part of this pattern; we were not able to produce the M (III) states of either zicronium or hafnium, again in keeping with the result of diketonates.

We conclude that the electrochemical method of these various complexes represents a rapid and convenient synthesis which avoids the synthesis and isolation of the MX_4 intermediates.

Reaction Mechanism

In an earlier discussion of the electrochemical synthesis of other transition metal halides,[64] it was pointed out that measurement of the current efficiency gives a good indication of the possible reaction mechanism. In the present work, we have carried out such experiments over short periods of time (1-2 h) at constant current (40-50 mA) for the M-Br_2 in benzene system. The measured current efficiencies were 1.1 mol TiF^{-1}, 2.7 mol ZrF^{-1}, and 1.25 mol HfF^{-1}, in terms of weight of metal dissolved. These values are some what lower than the range of 2-10 mol F^{-1} reported,[64] but higher than can be accounted for by a primary process $M \longrightarrow M^{4+} + 4e^-$, for which the current efficiency should be 0.25 mol F^{-1}.

The proposed mechanism envisages the first step as being the formation of Cl_2^- or Br_2^-

$$Br_2 + e^- \longrightarrow Br_2^- \qquad (1)$$

and the anode process is believed to be

$$Br_2^- + M \longrightarrow MBr + Br + e^- \qquad (2)$$

with subsequent reactions

$$MBr + Br \longrightarrow MBr_2 \qquad (3)$$

$$MBr + Br_2 \longrightarrow MBr_3 \qquad (4)$$

$$MBr_2 + Br_2 \longrightarrow MBr_4 \qquad (5)$$

other reactions are also possible, the main point of (3), (4) and (5) is to show that different oxidation states of a given metal may be produced in such systems. Reactions such as the sequence

$$MBr + Br_2 \longrightarrow MBr_2 + Br \tag{6}$$

$$M + Br \longrightarrow MBr \tag{7}$$

can be invoked to explain current efficiences higher than 1 mole metal dissolved per Faraday. In all but one case, the oxidation sequence obviously produces compounds in which the M(IV) oxidation state is stabilized. The exception is the oxidation of titanium in the presence of high concentrations of Br_2 and Br^- (and hence Br_3^-). This may point to the importance of (4) under such conditions. Certainly the stability of the M(III) state is significantly higher in titanium than in the heavier metals, and this, coupled with the observed precipitation of a salt that is insoluble and therefore resistant to oxidation, serves to rationalize the experimental result. The situation may be more complicated than it has been described, the information of an intermediate oxidation state does support a mechanism involving stepwise oxidation of the metal in these electrochemical experiments.

CHAPTER IV

NEUTRAL ORGANO-TITANIUM, ZIRCONIUM AND HAFNIUM HALIDE COMPLEXES

IV. 1. Introduction

The general chemistry of Group IVA was discussed in Chapter III. This Chapter will deal with the organometallic chemistry of these elements.

The interest in the organometallic chemistry of titanium dates back to the second half of the last century. During that period of time alkylation of some transition metals was attempted by using zinc dialkyls. The preparation of ethyltitanium compounds from $TiCl_4$ and $ZnEt_2$ was attempted in 1861 by Cahours.[99] Grignard reagents and organolithium compounds were used later, but at the time the sensitivity of the expected compounds to air and moisture was not sufficiently appreciated and the low thermal stability of the products resulted in decomposition. Only when techniques were developed for working under an inert atmosphere and at low temperatures was it possible to isolate organometallic compounds of Ti, Zr and Hf. The isolation of the first organometallic compound phenyltitaniumtriisopropoxide did not occur until 1952 by Herman and Nelson,[100, 101] since that time considerable development in the field has occurred.

The interest in the organo-compounds of these elements is due to the activity of the derivatives of these metals as catalysts in polymerizations and in the chemical fixation of nitrogen, especially compounds of tri- and bi-valent metals.

Several books have recently appeared on the organometallic chemistry of Ti, Zr and Hf.[76, 99, 102, 103] Brief mention of organotitanium compounds has been made in the books by Feld and Cowe in 1965,[87] and by Clark in 1968[86] and organic complexes of lower valent titanium were reviewed by Coutts and Wailes.[104] An annual survey covering the year 1975[105] and two reviews in the specialist periodical report[106, 107] have also appeared recently. A comprehensive review on σ-alkyl and aryl complexes of the group IV - VII transition metals has been published by Shrock and Parshall.[108]

Recently significant advances have been made in the organometallic chemistry of Ti, Zr, and Hf since these bear direct relevance to the work in this dissertation, it would be appropriate to present a brief resume of some of the current literature.

IV. 2. Binary Alkyl Complexes

Pure binary compounds of these elements have been until recently, a rarity. Transition metal compounds bearing only σ-alkyls have been scarce and little studied, giving the impression that binary metal alkyls are inherently unstable. In general, the binary metal alkyls are very unstable to air and moisture and have only modest thermal stability. The majority of the organometallic compounds of Ti, Zr and Hf are cyclopentadienyl derivatives. The stabilizing influence of this ligand has allowed the isolation of many metal-carbon bonded compounds. Compounds with other alkyl or aryl group are also known.

Methyl Compounds

$TiMe_4$ was first prepared in 1959 by Clauss and Beerman[109] from methyllithium or a methyl Grignard reagent and $TiCl_4$ in diethyl ether at -78°; $ZrMe_4$ was similarly prepared.[110] After the first report of the preparation of $TiMeCl_3$ from $TiCl_4$ and $AlMe_2Cl$,[111] a few other methods of preparations were reported.[112] The most stable parent alkyl compounds $TiMeX_3$ (X = Cl, Br) are best prepared by using $ZnMe_2$ as the alkylating agent. $TiMeCl_3$ prepared by this method[112] has been described as a deep violet solid which is stable at room temperature and melts at 28-29° to give a yellow oil. It gives a yellow solution in saturated or aromatic hydrocarbons and is monomeric in benzene. The red solution in ether has been taken to show the presence of $TiMeCl_3(ether)_x$. Further alkylation of $TiMeCl_3$ with $ZnMe_2$ gives black $TiMe_2Cl_2$,[114] which is less atable than $TiMeCl_3$ and decomposes at -10° to $TiCl_2$. Addition of dioxane to a yellow hexane solution of $TiMe_2Cl_2$ gives a yellow dioxane adduct[114], which is stable for several days at room temperature. $TiMeCl_3$ also acts as a Lewis acid and, reacts with both monodentate and bidentate ligands.[113,115]

$TiMeBr_3$ has properties analogous to those of $TiMeCl_3$, but is less stable, a general observation for many halide-alkyl complexes.[116]

$TiMe_3I$ was mentioned briefly by Ber[illegible]ld and Groh but no further details have appeared.[117] In toluene at -10° to 0°, brick red solutions of $ZrMeX_3$ (X = Cl, Br) result. Addition of diethyl ether gives stable, isolable etherates, $ZrMeX_3(ether)_2$. In pyridine at 0° alkylation proceeds further to give brown solutions which are believed to contain the adducts $ZrR_2X_2.2py$. These could not be isolated but the addition of 2,2'-bipyridine gave isolable $ZrR_2X_2(bipy)$.[116]

Phenyl Compounds

$TiPh_4$[118] and $ZrPh_4$[119] were prepared by the reaction of MCl_4 with LiPh in diethyl ether at -40° under an argon atmosphere.

These compounds were not isolated in the crystalline state, but were characterized by reaction with $HgCl_2$ to give PhHgCl. A number of $TiPh_4$ adducts were prepared for spectroscopic purposes, but only $TiPh_4$(bipy) which is stable at 0°, was isolated, although adducts with TMPDA, py, TMEDA and TMMDA were observed in solution.[120]

Tetrakis (pentafluorophenyl) titanium and tetrakis (pentafluorophenyl) zirconium[121] have also been prepared from the reaction of MCl_4 with C_6F_5MgCl or C_6F_5Li in ethereal solution at -15°. $Ti(C_6F_5)_4$ and $Zr(C_6F_5)_4$ have a number of properties which distinguish them from their phenyl analogs, particularly their enhanced thermal stability.

Phenyl titanium halides are prepared by arylation of TiX_4 with $ZnPh_2$.[114] In this method $TiPhCl_3$ or $TiPhBr_3$ can be obtained either in the pure state or in the form of complexes. In such reactions, it is important that the molar ratios of the reactants are strictly observed because an excess of $ZnPh_2$ could lead to the formation of $TiPh_2X_2$.[116] $TiPhCl_3$ has properties analogous to $TiMeCl_3$, but is less thermally stable.

Coordination with aromatic nitrogen bases affords $TiPhCl_3$ adducts with a higher thermal stability than the parent compound. The pyridine adduct $TiPhCl_3 \cdot 2py$, for example, can be handled at room temperature, but should be stored at 0^o, and the 2,2′-bipyridine adduct is thermally stable up to 130^o.[122] Prolonged reaction of $ZrPhCl_3.3THF$ in neat MeCN afforded $ZrPhCl_3.2MeCN$ which in turn gave $ZrPhCl_3.L$, where L is a bidentate ligand such as 2,2′-bipy, 4,4′-bipy or diphos.[122]

Benzyl Compounds

MBZ_4 (M = Ti, Zr or Hf) are prepared from MCl_4 and BzMgX (X = Cl or Br) in diethyl ether.[123,124,125] $TiBz_4$ was also obtained by the reaction between $TiMe_4$ and BBz_3 in diethyl ether.[126] The red crystalline $TiBz_4$ melts at 70-71^o [123] and is the most thermally stable of the tetraalkyl or tetraaryl compounds. Despite the poor Lewis acceptor properties of MBz_4 compared with MCl_4, the tetrabenzyl derivatives of the three metals form a series of adducts with oxygen and nitrogen containing ligands, which have higher thermal stabilities than the parent compounds.[122,126,127,128]

Some Ti and Zr benzyl halides have been derived from MBz_4.[124] Thus the reaction of $ZrBz_4$ with stoichiometric amounts of iodine gave benzyl zirconium iodides as slightly soluble solids whose thermal stabilities could be improved by complexation with 2,2′-bipyridine.[128]

Other Alkyls

Complexes containing alkyl groups other than methyl are less stable. The $TiRCl_3$ species have been prepared where R = Et,[111,114] , pr,[114] Bu^i [111] and n-pent[114] employing alkyl aluminium or zinc reagents, but are only stable at low temperature. The 2,2′-bipyridine adducts $TiRCl_3$(bipy) were isolated in low yields.[114]

The Present Work

In this chapter we report the preparation of some organo-titanium, zirconium and hafnium halide complexes by direct electrochemical oxidation reactions of the three metals in presence of alkyl or aryl halides, organic solvent(s) and a ligand. Generally compounds of the type $R_2MX_2.L$ (L = bipy or 2 MeCN) are obtained. However, there are some notable variations, especially when MeI is used as the organic halide. The complexes are investigated by standard techniques such as analysis, infrared and nmr spectroscopy. The results are discussed on the basis that redistribution reactions play a significant role with these metals, or alternatively that the final product depends on the ultimate fate of the unstable primary species $RM^{II}X$.

IV. 3. Experimental

a) General. Titanium, zirconium and hafnium organometallic compounds are air and water sensitive. In order to restrict contact of the compounds with the atmosphere, electrolysis and all other subsequent operations were carried out under a stream of nitrogen or in a nitrogen filled glove box. Volume reduction and sample drying were in vacuo. The detailed experimental conditions of the electrochemical preparation of organo Group IVA halide complexes are given in Table 4.1.

b) Materials. Titanium, zirconium and hafnium metals MeCN, MeOH, C_6H_6, Et_4NX and 2,2'-bipyridine were treated in the manner specified in Chapter III. BzCl and BzBr were dried over $MgSO_4$; PhCl, PhBr, PhI and MeI were dried over $CaCl_2$. EtBr was dried with a sodium wire, then distilled. BzI was used as supplied (ICN).

c) Analysis. Halogen and metal analyses were performed as before (Chapter III). The analytical results are given in Table 4.2.

d) Physical Measurements

Infrared Spectra were recorded with a Beckman IR-12 spectrophotometer with a range of 4,000 - 200 cm^{-1} as nujol-mulls using KBr windows. The IR spectra served to identify the presence of neutral ligand and/or ν(M-C) frequencies.

Mass spectra were obtained with a Varian MAT CH_5 Double focusing spectrometer at an electron energy of 70 eV.

Proton Nuclear Magnetic Resonance Spectra were recorded on a Varian EM-360 instrument operating at 60 MHZ. The resonance frequencies are based on external TMS.

Current Efficiency Measurements were measured as before (see Chapter II and III).

e) Preparative Electrochemistry

The electrochemical method used was described in Chapter II. In all experiments reported metal of group IVA formed the anode of the cell and platinum wire was the cathode.

Electrochemical Preparation of Bz_2TiCl_2.bipy

The faint yellow colour of the mixture of BzCl, MeCN, bipyridine and Et_4NBr (Table 4.1.) changed progressively to dark brown as electrolysis proceded. At the end of the electrolysis (5.5 h), a dark brown solid covered the anode and deposited in the cell. This was filtered, washed several times with MeCN, then dried in vacuo for about 2 h. The solid is soluble in MeOH and DMSO, and very hygroscopic.

Electrochemical Preparations of Bz_2ZrCl_2.bipy and Bz_2HfCl_2.bipy

The same procedure as for Bz_2TiCl_2.bipy was followed, but in this case pink-red solids are obtained. The solids are soluble in MeOH and DMSO but insoluble in C_6H_6, MeCN, CH_2Cl_2, CCl_4, $CHCl_3$ and acetone.

Electrochemical Preparation of $BzTiBr_2$.bipy

The green solid formed as the mixture was electrolysed, (Table 4.1.) was filtered off, washed with MeCN, and dried in vacuo. The solid is soluble in MeOH but insoluble in MeCN, Et_2O, CH_2Cl_2, $CHCl_3$, CCl_4, and C_6H_6. The green solid changes colour to yellow when exposed to air.

Electrochemical Preparations of Bz_2ZrBr_2.bipy and Bz_2HfBr_2.bipy

The same procedure as for $BzTiBr_2$.bipy was followed, but in this case pink-red crystalline solids were obtained. The pink solids were forming around the anodes as beautiful needles extending from Zr or Hf metals. The solubilities of the solids are similar to those of the chlorides analogues.

Electrochemical Preparation of Bz_2TiI_2.bipy, Bz_2ZrI_2.bipy and Bz_2HfI_2.bipy

The faint yellow solutions progressively became brown as electrolysis proceeded and dark brown solids precipitated at the bottom of the cells and around the anodes. The solids were filtered, washed with ether, and dried in vacuo. More solid was obtained when the filtrates were treated with ether, or when the volume was reduced in vacuo. Those dark brown solids are extremely insoluble in organic solvents and water. Halide analyses were performed by the Oakdale-Thompson method (Chapter II).

Electrolysis of Ti, Zr or Hf under similar conditions, but in absence of 2,2'-bipyridine, afforded solid products of indeterminate composition, showing $\nu(C\equiv N)$ frequencies in their IR spectra.

Electrochemical Preparations of $Ph_2TiCl_2.2MeCN$, $Ph_2ZrCl_2.2MeCN$ and $Ph_2HfCl_2.bipy$

After electrolysis, the colorless solution had changed to a pale yellow colour and pale yellow (Ti) or colorless (Zr or Hf) solid deposited in the bottom of the cell. The solid was filtered in the glove-box, then dried in vacuo. If the volume of the filtrate was reduced in vacuo, an additional quantity of solid was obtained.

Electrochemical Preparation of Ph_2TiBr_2

A pink coloration appeared around the cathode during electrolysis, changing to brown away from the electrode surface, and the colorless solution changed to a progressively deeper brown colour as electrolysis continued. A brown solid was deposited at the bottom of the cell during electrolysis although on filtering, the amount of the product was found to be too small to permit characterization.

The volume of the filterate was then reduced in vacuo, when a brown solid settled in the container. This was filtered under nitrogen and then dried in vacuo.

Electrochemical Preparation of Ph_2ZrBr_2

The procedure used for Ph_2TiBr_2 was followed, except in this case addition of benzene to the filtrate precipitated the colorless solid; a violet coloration was observed around the cathode in electrolysing the mixture under the specified conditions.

Electrolysis of Hf in PhBr

When hafnium was electrolysed in a mixture of 20 cm^3, 20 cm^3 MeCN, 2 cm^3 MeOH and 20 mg Et_4NBr under conditions similar to those specified for Ti and Zr, a very insoluble, colorless solid was obtained which analysed as 4.8% Br, 54.4% Hf, 2.98% C and 2.11% H. On the basis of this analyses, and solubility difficulties, the compound was not characterised any further.

Electrolysis of Zr in PhCl, MeCN and bipy

In an attempt to prepare the compound Ph_2ZrCl_2.bipy, zirconium formed the anode of a cell which contained 20 cm^3 PhCl, 20 cm^3 MeCN, 0.5 g 2,2′-bipyridine and 20 mg Et_4NBr, and electrolysed for 15 h at a current of 20 mA (50V). The violet colour observed around the cathode changed to a faint yellow, away from the cathode surface. At the same time a pink solid was deposited at the anode, and adhered to the surface. This caused the current to drop gradually to zero and no more metal was dissolved. This cycle was repeated after cleaning the anode, and at the end of the electrolysis only 21 mg of Zr had dissolved. The amount of product recovered was too small to permit characterization.

Electrochemical Preparations of Ph_3TiI and Ph_3ZrI

A deep brown colour developed as the electrolysis progressed and a brown solid deposited around the cathode and in the bottom of the cell. The electrode was cleaned whenever the current dropped by pulling it up then down again in the rubber stopper. At the end of the electrolysis the sticky precipitate was filtered, washed a few times with ether, then dried in vacuo. The solids are slightly soluble in MeOH, MeCN and C_5H_5N, but insoluble in CCl_4, $CHCl_3$ and MeCOOH.

Electrolysis of Hf in the same manner as for Ti and Zr, gave a brown solid of indeterminate composition.

Electrolysis of Zr in PhI and bipy

When zirconium was electrolysed in a mixture of 10 cm^3 PhI, 10 cm^3 MeCN, 0.5 gm of bipy and 20 mg of Et_4NBr, similar difficulties to those discussed above were encountered, in that the metal dissolved but the brown solid obtained was in too small a quantity to permit complete characterization. The NMR and IR spectra of the compound confirmed the presence of both phenyl and bipyridyl groups.

Electrochemical Preparations of $Me_3TiI.bipy$, $Me_3ZrI.bipy$ and $Me_3HfI.bipy$

After a few minutes of electrolysis a yellow colour appeared in the cell and was changing progressively to brown in each case. With hafnium, the compound precipitated from the solution as the electrolysis proceeded; for zirconium, addition of MeCN to the final reaction solution resulted in precipitation of the compound; and for titanium addition of MeCN followed by dropwise addition of diethyl ether precipitated the compound.

Electrochemical Preparations of $Et_2ZrBr_2.2MeCN$ and $Et_2HfBr_2.2MeCN$

This electrochemical reaction is one of the fastest reactions investigated in this study. Thus, once the electrolysis was started a colorless crystalline solid deposited on the anode surface, then settles on the bottom of the cell. The white solid formed as electrolysis progressed was filtered off and dried in vacuo.

Electrochemical ~~Preparations~~ of $Et_2TiBr_2.2MeCN$ and $EtTiBr_2.3MeCN$

When titanium metal was electrolysed in a solution consisting of 10 cm^3 EtBr, 20 cm^3 MeCN and 30 mg Et_4NBr, at a constant current of 30 mA (25V), we observed that two products were obviously forming. After a few minutes of electrolysis a yellow colour began to appear around the anode and the colour of the solution progressively changed to brown. After ~ 45 minutes a green solid started to deposit in the cell, and was filtered off, collected and dried in vacuo. This green solid was characterized as $EtTiBr_2.3MeCN$. The filtrate was then treated with diethyl ether and a brown solid precipitated which was identified as $Et_2TiBr_2.2MeCN$. A 77.2 mg sample of this compound decomposed with glacial acetic acid evolved 7.5 cm^3 of gas at STP; required 9.94 cm^3.

Electrochemical Preparations of $Et_2ZrBr_2.bipy$ and $Et_2HfBr_2.bipy$

A pink colour began to appear around the anode, but was apparent for only short time. A yellow solid subsequently began to deposit on the anode surface and in the bottom of the cell, and the colour of the solution progressively changed to yellow. At the end of the electrolysis the yellow solid was filtered off, collected and dried in vacuo.

Electochemical Preparations of Et_2TiBr_2.bipy and $EtTiBr_2$.2bipy

Titanium was similarly electrolysed as above. Again, in this case two different compounds were seem to form, one green and the other brown. The brown compound was filtered off, collected and identified as Et_2TiBr_2.bipy. Gas analysis on 86.8 mg sample of this compound evolved 7.3 cm^3 of gas at STP, required 9.2 cm^3. The green material was precipitated by adding diethyl ether to the filtrate and analysed as $EtTiBr_2$.2bipy.

IV. 4. Results

Mass Spectrometric Studies.

The adducts Et_2ZrBr_2 with acetonitrile, $BzTiBr_2$ and MeHfI with bipyridine were investigated by mass spectrometric techniques, although no parent peaks could be obtained, the mass spectra of the three compounds show identifiable peaks, (Table 4.3. 4.4. and 4.5.) The main feature of the mass spectra of these complexes is a strong peak due to the nitrogen-donor ligand, m/e = 41 for MeCN and 156 for 2.2$'$-bipyridine with relative intensity of 100% in $Et_2ZrBr_2.2MeCN$, 62% in $BzTiBr_2.bipy$ and 38% in $Me_3HfI.bipy$.

The high temperature required to achieve sufficient vapour pressure for the halide species clearly causes profound molecular decomposition and ligand redistribution before ionization, since no $\overline{RM}$ species were detected in any spectrum. The R^+ ion was detected with high relative intensity, in agreement with the low thermal stability of the C-M bond in these species.

Vibrational Spectroscopy

The infrared spectra of all the compounds investigated are generally characterized by a broad and strong band in the region Ca 500 cm^{-1}. This region of the spectrum has been assigned in a variety of papers on similar compounds to the C-M stretching frequency (M = Ti, Zr).[112,113,122] The infrared absorptions of the complexes studied in this region of the spectrum are shown in Table 4.6. and are assigned as ν(C-M). The presence of two cis-acetonitrile ligands was confirmed by doublet absorptions in the $\nu(C\equiv N)$ region of the spectrum of the acetonitrile complexes investigated. (Table 4.7). The 2,2'-bipyridyl complexes showed some frequency shifts confirming complexation of the ligand with the metal. The absorption of the free ligand at

752 cm^{-1}, corresponding to out of plane C-H bending and the absorptions in the region 1400 - 1600 cm^{-1} corresponding to ν(c=c) are shifted to higher frequencies. All the bipyridyl complexes show similar shifts; Table 4.8 gives the IR spectra of the 2,2'-bipyridyl adducts of Et_2MBr_2 (M = Ti, Zr and Hf) as representative examples.

Proton Nuclear Magnetic Resonance Studies

The ^1H NMR spectra of some neutral organo Group IVA halide adducts are shown in Table 4.9. Unfortunately the complexes are generally insoluble in non-donor solvents and the limited solubility in donor solvents prevented resolution of the splitting patterns. Some chemical shift data were obtained and the results are generally in agreement with those of similar Group IVA compounds.[115, 124, 127]

Table 4.1.

Electrolysis of Ti, Zr and Hf in presence of alkyl and aryl halides

System	Metal	Solution phase composition vols. in cm^3	R_4NX (mg)	2,2′-bipy (g)	Initial		Time of electrolysis (h)	Weight of metal dissolve(mg)
					Voltage (V)	Current (mA)		
BzCl/bipy	Ti	BzCl 20;MeCN 20	20	0.5	50	40	5.5	59
	Zr	BzCl 20;MeCN 20	20	0.5	50	40	2.5	132
	Hf	BzCl 20;MeCN 20	20	0.5	50	25	5.5	196
BzBr/bipy	Ti	BzBr 20;MeCN 20	20	0.5	50	50	3.0	97
	Br	BzBr 20;MeCN 20	20	0.5	50	20	14.5	69
	Hf	BzBr 20;MeCN 20	20	0.5	50	25	3.0	129
BzI/bipy	Ti	BzI 0.7g;MeCN 40	20	0.5	50	25	3.0	20
	Zr	BzI 0.7g;MeCN 40	20	0.5	50	50	5.5	a
	Hf	BzI 0.7g;MeCN 40	20	0.5	50	25	3.0	24
PhCl/MeCN	Ti	PhCl 20;MeCN 20	20	0	50	10	40	40
	Zr	PhCl 20;MeCN 20	20	0	50	15	14	145
	Hf	PhCl 20;MeCN 20	20	0	50	10	16	143
PhBr/MeCN	Ti	PhBr 20;MeCN 20; MeOH 2	20	0	50	15	14	37
	Zr	PhBr 20;MeCN 20; MeOH 2	20	0	50	80	5.0	258
	Hf(b)	PhBr 20;MeCN 20; MeOH 2	10	0	50	40	4.0	211

Table 4.1. (cont'd)

PhI/MeCN	Ti	PhI 15;MeCN 15; MeOH 2	10	0	50	20	48	30
	Zr	PhI 15;MeCN 15; MeOH 2	20	0	50	10	13	45
	Hf(b)	PhI 15;MeCN 15; MeOH 2	20	0	50	10	6	67
MeI/bipy	Ti	MeI 20;MeOH 2	20	0.5	50	10	4.0	51
	Zr	MeI 20;MeOH 2	20	0.5	50	40	10	180
	Hf	MeI 15;MeOH 2	10	0.25	30	30	12	55
EtBr/MeCN	Ti	EtBr 10;MeCN 20	30	0	25	30	5	102
	Zr	EtBr 20;MeCN 20	20	0	50	25	3	103
	Hf	EtBr 20;MeCN 20	20	0	50	15	2	94
EtBr/bipy	Ti	EtBr 20;MeCN 20	20	0.5	50	30	1.5	25
	Zr	EtBr 20;MeCN 20	20	0.5	50	50	1.5	104
	Hf	EtBr 20;MeCN 20	20	0.5	50	20	8.5	114

(a) not recorded

(b) an identifiable compound was not isolated from this system; see text

Table 4.2.

Analytical results for neutral organo Group IVA halide complexes

Compound	Found(%)		Found (%)	
	Metal	Halogen	Metal	Halogen
Bz_2TiCl_2.bipy	10.7	15.4	10.5	15.3
Bz_2ZrCl_2.bipy	18.9	14.1	18.2	14.0
Bz_2HfCl_2.bipy	30.1	11.9	30.4	12.0
$BzTiBr_2$.bipy	10.0	35.9	10.5	35.2
Bz_2ZrBr_2.bipy	15.5	27.8	15.4	27.2
$BzHfBr_2$.bipy	27.4	24.4	26.3	23.7
Bz_2TiI_2.bipy(a)	6.2	37.8	7.5	39.7
Bz_2ZrI_2.bipy	13.0	37.2	13.3	37.1
Bz_2HfI_2.bipy	22.1	32.5	23.1	33.0
Ph_2TiCl_2.2MeCN	13.6	19.8	13.6	19.8
Ph_2ZrCl_2.2MeCN	23.0	17.1	23.0	17.6
Ph_2HfCl_2.2MeCN	36.5	14.4	36.8	14.5
Ph_2TiBr_2	13.5	44.5	13.3	44.2
Ph_2ZrBr_2	22.0	39.2	22.5	39.5
Ph_3TiI	11.0	30.9	11.8	31.3
Ph_3ZrI	20.0	27.8	20.3	28.3
Me_3TiI.bipy	12.7	34.1	12.8	33.8
Me_3ZrI.bipy	21.8	30.3	21.7	30.3

Table 4.2. (cont'd)

Me_3HfI. bipy	35.6	25.1	35.2	25.0
Et_2TiBr_2. 2MeCN(b)	13.6	46.0	13.8	46.0
$EtTiBr_2$. 3MeCN(b)	13.1	44.0	13.3	44.5
Et_2ZrBr_2. 2MeCN	23.8	40.6	23.3	40.9
Et_2TiBr_2. bipy(b)	11.5	37.1	11.4	37.9
$EtTiBr_2$. 2bipy(b)	8.6	28.9	8.7	29.1
Et_2ZrBr_2. bipy	19.6	34.6	19.6	34.4
Et_2HfBr_2. bipy	32.0	29.2	32.2	29.0

(a) Poor analysis because of solubility; see text for details.

(b) Two compounds were isolated from the same reaction; see text for details.

Table 4.3.

EI Mass Spectrum of $Et_2ZrBr_2 \cdot 2MeCN$

m/e	Intensity	Assignment
30	14	$C_2H_6^+$
31	8	
41	100	$MeCN^+$
42	6	
44	47	$C_3H_8^+$
45	7	
58	3	$C_4H_{10}^+$
59	1	
79	4	Br^+
81	4.5	
91	4	Zr^+
92	1.4	
94	0.71	
96	0.96	
109	1.6	$C_2H_5Br^+$
111	0.5	
169	6	$ZrBr^+$
170	4.7	
171	0.8	
173	0.5	
175	3.7	
250	3.4	$ZrBr_2^+$
251	1.6	

Table 4.4.

FI Mass Spectrum of $BzTiBr_2$.bipy

m/e	Intensity	Assignment
78	17	
79	13	$C_6H_6^+$ or Br^+
80	23	
91	100	$C_7H_7^+$
92	8	
128	20	
129	16	$TiBr^+$
130	8	
156	76	$C_{10}H_8N_2^+$
157	9	
170	11	$C_7H_7Br^+$
172	6	
182	3	$C_{14}H_{14}^+$
204	13	
205	8	$TiBr_2^+$
203	3	

Table 4.5.

FI Mass Spectrum of $Me_3HfI.bipy$

m/e	Intensity	Assignment
142	3	MeI^+
156	38	$C_{10}H_8N_2^+$
157	11	
303	51	
306	34	HfI^+
307	100	

Table 4.6.

Infrared absorptions of neutral organo Group IVA halide adducts

Compound (a)	(M-C)
Bz_2TiCl_2.bipy	480 w
Bz_2ZrCl_2.bipy	465 s, br
Bz_2HfCl_2.bipy	465 s, br
$BzTiBr_2$.bipy	470 m, br
Bz_2ZrBr_2.bipy	465 s, br
Bz_2HfBr_2.bipy	465 s, br
Bz_2TiI_2.bipy	~ 550 vw
Bz_2ZrI_2.bipy	470 w, vbr
Bz_2HfI_2.bipy	465 m, br
Ph_2TiCl_2.2MeCN	490 w
Ph_2ZrCl_2.2MeCN	490 m, br
Ph_2HfCl_2.2MeCN	480 br
Ph_2TiBr_2	460 w
Ph_2ZrBr_2	470 br
Ph_3TiI	495 m, br
Ph_3ZrI	470 m, br
Et_2TiBr_2.2MeCN	~ 500 w, br
Et_2ZrBr_2.2MeCN	510 w, br
Et_2HfBr_2.2MeCN	490 m, br
Et_2TiBr_2.bipy	530 w, br
Et_2ZrBr_2.bipy	493 w
Et_2HfBr_2.bipy	475 m, br
Me_3TiI.bipy	535 m, br
Me_3ZrI.bipy	495 s, br
Me_3HfI.bipy	470 m, br

(a) Frequencies in cm^{-1}, samples run as nujol-mull between potassium bromide plates.

Table 4.7.

Infrered absorptions of neutral organo Group IVA halide adducts

Compound (a)	(C N)
$Ph_2TiCl_2.2MeCN$	2280. 2310
$Ph_2ZrCl_2.2MeCN$	2300 (b)
$Ph_2HfCl_2.2MeCN$	2280, 2305
$Et_2TiBr_2.2MeCN$	2300, 2351
$Et_2ZrBr_2.2MeCN$	2295, 2312
$Et_2HfBr_2.2MeCN$	2290, 2305

(a) Frequencies in cm^{-1}; samples run as Nujol-mulls between potassium bromide plates.

(b) Broad band, not resolved

Table 4.8. I.R. Spectra of 2,2'bipyridine adducts of Et_2MBr_2 (M = Ti, Zr and Hf)

bipy[a]	Et_2TiBr_2.bipy[b]	Et_2ZrBr_2.bipy[b]	Et_2HfBr_2.bipy[b]
404 s	418 m	420 m	418 m
429 w	530 m, br	493 w	475 m, br
618 s	640 m	640 m	640 w
652 s	660 m	655 s	660 m
740 m	670 sh	670 sh	738 m
752 s	680 w	680 w	772 s
892 m	740 s	735 s	1000 w
992 s	770 vs	765 vs	1030 s
1039 m	830 s	1028 vs	1075 w
1062 m	1022 sh	1045 w	1105 w
1083 m	1035 s	1075 m	1161 s
1139 m	1065 m	1105 m	1250 w
1249 m	1105 m	1155 s	1265 w
1312 s	1160 s	1250 m	1285 w
1418 s	1250 w	1285 m	1323 m
1552 s	1320 s	1322 s	1381 s
1575 s	1380 vs	1380 vs	1445 s
	1445 s	1440 vs	1460 vs
	1470 s	1495 m	1500 w
	1495 m	1530 m	1530 m
	1530 w	1585 w	1590 w
	1580 w	1605 vs	1605 vs
	1610 s		

a - Ref. 129

b - Frequencies in cm^{-1}, samples run as Nujol mulls between potassium bromide plates

Table 4.9.

Proton nmr spectra of neutral organo Group IVA halide complexes in perdeuteromethanol (in ppm, from TMS)

Compound	R	Assignment	Neutal ligand	Assignment
$BzTiCl_2.bipy$	1.25	CH_2-Ti	7.75-9.5 (a)	$C_{10}H_8N_2$-Ti
$BzZrCl_2.bipy$	1.25 1.45(b)	CH_2-Zr	7.4-9.0 (a) 7.9-9.1 (a)	$C_{10}H_8N_2$-Zr
$BzHfCl_2.bipy$	1.1 1.5(b)	CH_2-Hf	7.4-9.0 (a) 8.0-9.25 (a)	$C_{10}H_8N_2$-Hf
$BzTiBr_2.bipy$	1.9	CH_2-Ti	7.0-9.0 (a)	$C_{10}H_8N_2$-Ti
$BzZrBr_2.bipy$	2.0	CH_2-Zr	7.25-9.0 (a)	$C_{10}H_8N_2$-Zr
$BzHfBr_2.bipy$	2.0	CH_2-Hf	7.3-9.0 (a)	$C_{10}H_8N_2$-Hf
$PhTiCl_2.2MeCN$	7.4	C_6H_5-Ti		
$PhZrCl_2.2MeCN$	7.25	C_6H_5-Zr	2.0	MeCN-Zr
$PhHfCl_2.2MeCN$	7.35	C_6H_5-Hf	2.0	MeCN-Hf
Ph_2TiBr_2	7.3	C_6H_5-Ti		
Ph_2ZrBr_2	7.3	C_6H_5-Zr		
Ph_3TiI	7.2-7.9	C_6H_5-Ti		
Ph_3ZrI	6.6-7.6	C_6H_5-Zr		
$Me_3TiI.bipy$	3.2	Me-Ti	7.6-9.0	$C_{10}H_8N_2$-Ti
$Me_3ZrI.bipy$	3.3	Me-Zr	7.2-9.0	$C_{10}H_8N_2$-Zr
$Me_3HfI.bipy$	3.4	Me-Hf	7.6-9.2	$C_{10}H_8N_2$-Hf

(a) No attempt made to distinguish the overlapping benzyl and 2,2′-bipyridine resonances in this region.

(b) Spectrum in d_6-dimethylsulphoxide

IV. 5. Discussion

Traditional preparative routes using aluminium alkyls or Grignard or lithium reagents for the synthesis of organohalides of group IVA are generally complicated or accompanied by side reactions.[112, 116] As explained in previous chapters, a number of electrochemical syntheses of organometallics have been devised recently. In pursuing applications of the direct electrochemical oxidation of metals in non-aqueous media, we have now found that the oxidation of anodic titanium, zirconium and hafnium in alkyl or aryl halides, and in the presence of a stabilizing ligand, represents a simple synthetic route to these important compounds (Table 4.1 and 4.2). Because of the fact that the stability of the organometallic halides of those metals can be improved considerably by complexation, the products were most easily obtained as adducts with stabilising ligands such as 2,2′bipyridine. In this respect, a detailed investigation of the complexes of methyl titaniumtrihalides was made by Clark and McAllees:[130] for example, $MeTiCl_3$, which in its pure form decomposes above 40°C, can be stabilized considerably by 2,2′-bipyridine, and the adduct only decomposes above 180°C.[116] Another system where the difference in the decomposition temperature between the adduct and the parent compound is pronounced involves $PhTiCl_3$, which decomposes above -5°C, whereas the bipyridyl adduct decomposes above 130°C. More examples of this stabilizing effect are to be found in ref. 116.

The IR, ^{1}H NMR and mass spectra data, together with the elemental analysis of the compounds prepared confirm the production of these adducts. The thrust of this discussion is therefore to establish the advantage of the direct electrochemical method and to attempt to identify a plausible mechanism for the electrochemical oxidation reactions of those metals from the experimental evidence.

In general, compounds of the type $R_2MX_2 \cdot L$ where L = 2,2′-bipy or 2 MeCN were produced by these experiments. There are, however, some notable exceptions, especially with organic iodides, but those will be discussed later, and the formation of the diorganometallic dihalides will be considered first. The general reaction under study in the present work, as in related studies with cadmium,[56,57] nickel[60] and tin[59] has a stoichiometry which corresponds to the oxidative insertion reaction

$$\underline{n}RX + M \longrightarrow R_{\underline{n}}MX_{\underline{n}}$$

(M = Cd or Ni, n = 1; M = Sn, Ti, Zr or Hf, n = 2)
The anode is consumed during the electrolysis and the current efficiences of experiments reported in Table 4.1. were between

0.3 and 0.4 mol/F^{-1}, based on weight of metal dissolved. These values are lower than those reported for the electrochemical preparation of organotin compounds[59] and for neutral and anionic chloro- and bromo-complexes of Ti, Zr and Hf (see Chapter III). If the reaction were truly electrochemical, i.e. followed Faraday's laws, the current efficiency would be 0.25 mol/F^{-1} to account for the primary process $M \longrightarrow M^{4+} + 4e^-$. However the experimental values are not very reliable, since insoluble compounds adhered to the surface of the anode (see experimental section) through electrolysis, thus suppressing the dissolution of the electrode.

The formation of radicals at the cathode in organic solvent electrolysis has been successfully postulated in earlier studies of electrochemical synthesis of organometallic compounds (see Chapter I). The following sequence of reactions is postulated to account for the formation of R_2MX_2 species.

At cathode:

Alkyl halide reduction takes place at the cathode of the cell as

$$RX + e^- \longrightarrow R^{\bullet} + X^- \qquad (1)$$

and the formation of R_2 may proceed either by

$$2R^{\bullet} \longrightarrow R_2 \qquad (2)$$

or

$$R^{\bullet} + RX \longrightarrow R_2 + X^{\bullet} \qquad (3)$$

At anode:

$$X^{-} \longrightarrow X^{\bullet} + e^{-} \qquad (4)$$

$$X^{\bullet} + M \longrightarrow MX \qquad (5)$$

$$MX + RX \longrightarrow RMX + X^{\bullet} \qquad (6)$$

The essential features of the anode reactions are, first, the oxidation of X^{-} to atomic X and second, the attack of X on the anode to give the monohalide of the metal. Reactions (4) - (6) explain the relatively high current efficiences in many such systems, since $X^{\bullet}$ acts as a chain carrier whose existence can be terminated by

$$X^{\bullet} + RX \longrightarrow X_2 + R^{\bullet} \qquad (7)$$

or

$$X^{\bullet} + MX \longrightarrow MX_2 \qquad (8)$$

The overall mechanism for the formation of RMX is similar to that established by Mottus and Ort[52] in work on the electrochemical dissolution of aluminium in dichloromethane, and by Tuck and Habeeb[59] on the electrochemical preparation of organotin compounds.

Organotitanium(II), Zirconium(II) and hafnium(II) species are unstable, and can react by the oxidative-addition reaction.[131]

$$RMX + RX \longrightarrow R_2MX_2 \qquad (9)$$

thus explaining the formation of R_2MX_2 species which will be stabilized in the presence of a ligand. However, some exceptions to the general production of R_2MX_2 species from these electrochemical reactions are encountered (Table 4.2). Firstly, while the electrochemical oxidation of zirconium and hafnium produce species only in +4 oxidation state, titanium under similar conditions gives species either in the +4 (most of the reported compounds), in +3 oxidation state ($BzTiBr_2$.bipy), or both oxidation states from the same reaction (Et_2TiBr_2 and $EtTiBr_2$ as bipy or MeCN adducts). The generation of titanium compounds in lower oxidation states in the electrochemical oxidation reactions seems to be a part of a pattern which other top row transition metals follow including vanadium(II)[64] and copper(I).[67]

It should also be noted that polarographic studies on Cp_2TiX_2 (X = F, Cl, Br, I), show clear cathodic waves corresponding to two one-electron steps.[132,133] The value of the half-wave potential for each step is highly dependent on solvent and supporting electrolyte. It is possible therefore to reduce a dihalide to a lower valent form.

In any case, whether the generation of Ti(III) species is a result of a cathodic reduction process, or the consequence of the stepwise anodic oxidation of the metal, does not affect the usefulness of the preparative method. It is not surprising that any such +3 products are more readily with titanium than zirconium or hafnium, given the established chemistry of these elements.

Secondly, as noted above, R_3MI species were the final products when methyl or phenyliodide was used in the reactions. Again, relevant precedents for this synthesis can be noted. while the compounds $MeMX_3$[112, 116] and Me_2MX_2[114, 116] (M = Ti, Zr, X = Cl, Br) are known, it seems that only Me_3TiI has been prepared.[117] Gray and coworkers[134] maintain that in the presence of excess $AlMe_3$, the formation of the transient Me_3TiCl species from $TiCl_4$ can be detected. Now the electrochemical oxidation of tin in the presence of MeI and similar alkyl halides results in the formation of R_2SnI_2 complexes,[59] provided that freshly prepared compound is used. However, redistribution products such as Me_3SnI, etc. were detected in solutions of Me_2SnI_2 in $CDCl_3$ or CD_3OD, especially if the solution were allowed to stand for some hours at room temperature. Similar results were obtained with Et_2SnI_2. Furthermore, it was found that the product obtained in relatively short experiments is pure R_2SnI_2, but that longer electrolyses lead to a mixture of R_4Sn, R_3SnI, etc. These results were explained in two ways, a) R_2SnI_2 in solution undergoes a series of slow redistribution reactions to

R_4Sn, etc., or b) R_2SnI_2 in solution reacts with the tin anode by the following process

$$2R_2SnI_2 + Sn \longrightarrow R_4Sn + SnI_4 + Sn \qquad (10)$$

followed by exchange reactions between R_4Sn and SnI_4.

Thus, the formation of Me_3MI (M = Ti, Zr or Hf), prepared by using methods similar to those for tin probably follows a similar pattern, in which case the present results would indicate that redistribution reactions occur more readily than in the case of tin.

Alternatively, or additionally, an exchange reaction like

$$R_2MX_2 + RX \longrightarrow R_3MX + X_2 \qquad (11)$$

may account for the formation of R_3MI and I_2 species. The fact that this is only observed for X = I may be related to the stability of the iodide complexes. For example the Me_nTiX_{4-n} (n = 1, 2, 3, 4) series is the only one in which at least one species has been isolated for each value of n,[108] and in this series the thermal stability of the pure compounds decreases in the order $n > 1 > 2 > 3 > 4$ and X = $Cl > Br > I$. According to this order, species like R_2MI_2 would be expected to be less stable than R_2MCl_2 or R_2MBr_2. Furthermore, it has been shown that phenyl-titanium(IV) and zirconium(IV) derivatives decompose and being reduced to bivalent metal complexes.[119] Thus, reaction (11) is more likely to be observed in the iodide compounds than elsewhere. The iodine produced in the electrolysis of zirconium in phI was analysed quantitatively by using standard ~~Na~~$_2S_2O_3$ solution and found that 3.5×10^{-4} mole of iodine generated in this reaction, which is approximately equal to the number of moles of metal dissolved (3.7×10^{-4}). This experimental result can be taken as an evidence for reaction (11), in which one mole of metal dissolves to produce one mole of R_2MX_2, which then exchanges with RX to give one mole of X_2.

The situation may be even more complicated than the above discussion suggests. It must be emphasized, however, that complete identification of all the possible intermediates in any of these reactions has not been made. This is an extremely difficult task because at least some of the intermediates are very reactive and unstable, and exist only in low concentrations. Although this mechanism is believed valid in terms of the present experimental information, and is compatible with a mechanism involving stepwise oxidation of the metal in these electrochemical experiments, there are variations possible and some of these may be observed as more cases are investigated.

In general, these electrochemical preparations of the organohalide complexes of Group IVA appear to have some advantages over existing methods, in particular in the ability to work at room temperature, the ready availability of easily handled starting materials, and the simplicity of the apparatus. In addition, one has the opportunity of forming adducts in situ, which allows one to stabilise compounds which would otherwise decompose before complexation could be achieved.

CHAPTER V

NEUTRAL COMPLEXES OF INDIUM TRIHALIDES

V.1. Introduction

Indium, the fourth member of group IIIA of the periodic table is a silvery white soft metallic element with a brilliant lustre, melting at 157° and boiling at about 2,700°. The element was discovered in 1863 by Reich and Richter from the intense indigo blue line in its emission spectra, from which property it derives its name.[129] The electronic configuration of indium in its ground state is (Kr) $4d^{10}5s^{2}5p^{1}$ and it is possible for indium to lose one, two or three electrons to form compounds in the +1, +2 and +3 oxidation states. Although a large amount of energy is required to remove three electrons from the atom (27.9 eV), the tripositive state dominates the chemistry of the element. Because this chapter deals with the electrochemical preparation of some neutral In(III) complexes, this section will be confined to this oxidation state and mainly on neutral complexes of In(III) with uncharged ligands.

All four halides have been prepared. Anhydrous $InCl_3$ and $InBr_3$ are prepared by passing the halogen over heated indium metal in an atmosphere of nitrogen, while InI_3 is prepared by heating stoichiometric amounts of indium metal and iodine in an evacuated sealed tube at 250° for 4 h.[135, 136] All the halides are deliquescent and may be purified by sublimation under vacuum, preparation of the hydrated trihalides is accomplished by dissolving indium metal in the appropriate aqueous acid and then evaporating the solvent.

The solubility of the halides in organic solvents, particularly polar solvents is quite high and increases in the sequence $InCl_3 < InBr_3 < InI_3$. Such solutions are a convenient source of InX_3 for complexation. Indium(III) halides react as Lewis acids and are thus able to form complexes with a variety of donors of many different structural types. Neutral species having the stoichiometry InX_3L_3, InX_3L_2, $InX_3L_{1.5}$ and InX_3L have been prepared. The coordination chemistry of In(III) has been reviewed in a variety of papers.[137, 138] The stoichiometry InX_3L_3 is by far the most common and well characterized for a variety of monodentate ligands such as pyridine, 4-cyanopyridine,[139] dimethylsulphoxide,[135, 139] diphenylsulphoxide,[140] aniline[141] and morpholine.[139]

Conductivity measurements in nitromethane or nitrobenzene show that these species have nonionic 6-coordinate structures,[135, 139, 142, 143] but ionic dimer formulations such as $(InX_2(py)_4)(InX_4(py)_2)$ or $(In(py)_6)InX_6$ are not entirely eliminated. Complexes of the type InX_3L_2 are less frequently encountered than their tris counterparts.

They can apparently be prepared by careful thermal decomposition of InX_3L_3 (X=Cl, Br; L=py, β-pic),[142] although the structural consequences of such decomposition are rarely understood. In a few cases,[139] the InX_3L_2 stoichiometry can be achieved by washing the tris adduct with solvent. Among the monodentate ligands which directly form complexes of formula InX_3L_2 and Ph_3P, Ph_3PO, certain amines and dimethylsulphoxide.[144, 145] The structural possibilities are 5-coordinate indium (D_{3h} or C_{4v}), a polymeric species or an ionic one. Infrared measurements on the series $InX_3(Ph_3P)_2$ (X=Cl, Br, I) were consistent with the presence of monomeric 5-coordinate trigonal bipyramidal units,[146] a result confirmed by an X-ray structural analysis of $InCl_3(Ph_3P)_2$[147]

Complexes having the somewhat unusual stoichiometry $InX_3L_{1.5}$ (X=Cl, Br, I; L=2,2'-bipyridine, 1, 10-Phenanthroline) are precipitated from acetonitrile or ethanol solutions of indium salts and the nitrogen chelates.[135, 138, 140] The structure of these complexes is in question, for conductivities are intermediate between a non-electrolyte and a 1:1 electrolyte. The structure could be ionic or a neutral dimeric species, and although no X-ray studies have been reported there is infrared evidence[138, 143] that these species have the ionic structure $(InX_2L_2)(InX_4L)$. The possible structures of such complexes have been thoroughly discussed in a review by Carty and Tuck.[138]

Complexes of the type InX_3L (L = oxgyen or amine-type ligands) are uncommon and in fact there are relatively few examples of chloride complexes of this type. There is evidence that InI_3 forms mono adducts with nitrogen bases more readily than do the other halides.[142] The formation of mono rather than bis or tris adducts has been attributed to the lower Lewis acidity of the triiodide.[138, 148] The pyridine adducts of indium tribromide and trichloride of this stoichiometry have been reported.[142] Also, complexes of InX_3 and phosphine ligands are known,[135, 144] and X-ray evidence shows $InI_3(Ph_3P)$ to be monomeric.

The Present Work

This chapter reports the direct electrochemical preparation of InX_3.nMeCN and related complexes (X = Cl or Br, n = 3; X = I, n = 2). $InBr_3$.3MeCN is found to undergo further reactions to form other neutral adducts. The complexes prepared were investigated by elemental analysis, infrared and Raman spectra and conductivity measurements. The infrared spectra of the acetonitrile adducts show that the iodide is both structurally and stoichiometrically different from its lighter congeners.

V. 2. Experimental

a) Materials. Indium shot (Alfa Inorganics, m4 N) was beaten into a sheet normally 1 x 1 cm^2 and supported onto a platinum wire to form the anode of the cells used. A stout Pt. wire formed the cathode. Acetonitrile, benzene, diethylether and pet. ether were purified as before. Ethylacetate, nitromethane and pyridine were dried over Linde molecular sieves. Chlorine gas, bromine liquid, iodine, triphenyl phosphine and 2,2′-bipyridine were used as supplied.

b) Analysis. Indium analysis was by atomic absorption spectrophotometry, and halide analysis by the Volhard method. The analytical results are given in Table 5.2.

c) Physical Measurements. The infrared spectra between 50-4000 cm^{-1} were recorded with Beckman IR-12 and/or perkin-Elmer 180 instruments, using nujol mulls between KBr or polyethylene windows. The Raman spectra were recorded on a Beckman 700 laser Raman (argon ion, 488.0 nm excitation) instrument.

A conductivity bridge philips PR 9501 and a cell 3403 having a cell constant 1 cm^{-1} (Yellow Springs Instrument Co. Inc.) were used to measure the conductivity of mM solutions in $MeNO_2$.

Electrochemical Preparations.

The electrochemical method was essentially described in terms of the preparation of neutral chloro- and bromo complexes of Group IVA (Chapter III). All operations were done under nitrogen. Table 5.1. shows the detailed experimental conditions.

Electrochemical Preparation of $InCl_3.3MeCN$

The cell was flushed with dry nitrogen, and a mixture of chlorine and nitrogen then passed through the solution. The cell was cooled in an ice-bath throughout the experiment, to dissipate the appreciable quantities of heat evolved. After 45 minutes the gas flow was terminated and the power supply disconnected, after which the cell was flushed with nitrogen to expell excess chlorine. The resulting solution was filtered and the solvent removed by pumping in vacuo at room temperature. The resultant hygroscopic off-white solid was collected and dried in vacuo. It is soluble in MeCN, MeOH, Et_2O but insoluble in CCl_4 and C_6H_6.

Electrochemical Preparation of $InBr_3.3MeCN$

The preparation is essentially identical to that described for $InCl_3.3MeCN$, except that 2 cm^3 of bromine liquid was added to the solution phase instead of a stream of chlorine gas. The collection and subsequent treatment of the product were as for $InCl_3.3MeCN$.

Electrochemical Preparation of $InI_3.2MeCN$

The same procedure as that of $InCl_3.3MeCN$ and $InBr_3.3MeCN$ was followed, except in this case 2 g of iodine was used instead of

Cl_2 gas or Br_2 liquid. Stirring the solution continuously was apparently important in this system, since otherwise the current dropped to the point at which reaction ceased.

We also noted that if electrolysis was continued beyond the point at which the solution was completely decolorised, deposition of indium(I) iodide occurs at the cathode (Found In 47.3, I 52.3% req'd. for InI; In 47.6, I 52.4%,), clearly indicating reduction of indium(III) species in solution.

Electrochemical Preparation of $InBr_3$.1.5 bipy

The brown solid precipitated during electrolysis, was collected and dried in vacuo.

Electrochemical Preparation of $InBr_3$.$2Ph_3P$

With triphenyl phosphine, it was necessary to add ethylacetate followed by pet. ether to precipitate an oil which subsequently crystallised on trituration. This was collected, washed with pet. ether and dried in vacuo.

Electrochemical Preparation of $InBr_3$.2py and InBr3.3py

Two different adducts of pyridine and $InBr_3$ could be obtained from an electrochemically-prepared solution of $InBr_3$ in acetonitrile.

a) The addition of 2 cm^3 of pyridine to 5 cm^3 of the acetonitrile solution gave a yellow oil, which was decanted and treated with benzene; the resultant yellow powder was dried in vacuo, and shown to be $InBr_3.2py$.

b) The acetonitrile solution (5 cm^3) was diluted with 15 cm^3 acetonitrile, and 5 cm^3 pyridine added, followed by 15 cm^3 pet. ether. Stirring produced a white crystalline precipitate of $InBr_3.3py$, which was collected and dried in vacuo.

The electrochemical oxidation of indium in the presence of MeCN + py + Br_2 yielded a dark brown hygroscopic solid. Analysis gave Br 40.2, In 9.1%, but we were not able to characterise this material. It seems probable that species formed by the electrolysis and/or bromination of pyridine play an important part in this system, which was not investigated further.

V.3. Results and Discussion

The methods described permit the synthesis of a number of different adducts of indium trihalides, and there is no doubt that similar techniques could be developed for compounds with other neutral ligands. The yields are good, and gram quantities of product can be synthesised directly from the metal in a few hours with simple apparatus.

In Chapter III, as well as in other papers[59, 65, 149] the importance of the current efficiency (E_F) in identifying the mechanism of an electrochemical oxidation process has been emphasised. For the In/X_2/MeCN systems, E_F was measured at constant current for periods of 1-2 h. The values obtained were

X = Cl, E_F = 23.4 mol F^{-1}

Br E_F = 7.9 " "

I E_F = 4.9 " "

These values are generally higher than those found for transition metals,[65, 149] but are in keeping with the mechanism previously suggested, whereby the anode reactions are

$$X_2^{-} + M \longrightarrow MX + X^{\bullet} + e^{-} \qquad (1)$$

$$X^{\bullet} + M \longrightarrow MX \qquad (2)$$

$$MX + X_2 \longrightarrow MX_2 + X \qquad (3)$$

$$MX + X_2 \longrightarrow MX_3 \qquad (4)$$

Reactions (2) and (3) clearly form a sequence of chain processes (see Chapter III), and (4) which must compete with (3), accounts for the formation of the trihalides. The formation of indium(I) species by anodic oxidation of the metal has been reported previously,[66] and clearly the outcome of the competition between reactions (3) and (4) must depend in part on the halogen involved and on the nature of the other stablilising species (ligands) present in the solution phase.

Structural Consideration

The structural characterisation of the addition compounds of indium trihalides has been the substance of a number of studies.[139, 150] It is not necessary to review these earlier studies (see Introduction) but there are some important structural conclusions which arise from the present work.

The structure of the pyridine compounds $InCl_3.3py$ has been the subject of some debate.[139, 142, 143, 146] A mononuclear six-coordinate species is generally favoured. The solution properties of such adducts have been discussed earlier,[135] particularly in terms of equilibria such as

$$InX_3L_3 \rightleftharpoons InX_3L_2 + L \qquad (5)$$

and

$$InX_3L_3 \rightleftharpoons InX_2L_3^+ + X^- \qquad (6)$$

The present work confirms that for X = Br and L = py, eqn. (5) is valid, since different preparative treatments of the same mother liquor yield compounds with 2 or 3 pyridine ligands respectively (see the experimental section). The main conclusion to be drawn from these and many similar observations[138] is that the case in which equilibria such as (5) are disturbed renders any extrapolation of structural information from solution to solid phases an unreliable procedure. The acetonitrile adducts of the indium(III) halides have not been studied in detail previously, and indeed the preparation of these compounds have been surprisingly difficult. It was at one time suggested[139] that $InCl_3$ does not form a complex with MeCN, but a more recent paper reports that $InCl_3.2MeCN$ is obtained by refluxing indium metal in acetonitrile in the presence of chlorine.[151]

The ease with which the acetonitrile adducts of indium(III) halides has been prepared electrochemically made it possible for the first time to investigate the structures of the complete series of the three compounds $InCl_3.3MeCN$, $InBr_3.3MeCN$ and $InI_3.2MeCN$. The infrared spectra of these complexes (Table 5.3.) show that the iodide is both structurally and stoichiometrically different from its lighter congeners. For the chloride and bromide, a six-coordinate neutral monomer could have either fac (C_{2v}) or mer (C_{3v}) stereochemistry. The presence of two strong $\nu(C\equiv N)$ vibrations of equal intensity in the infrared spectrum implies the presence of the fac-isomer, and in keeping with this there are two readily identifiable $\nu(In-X)$ bands in the far IR, at 328 and 292(Cl), and 225 and 200 (Br) cm^{-1}. The $\nu(In-N)$ vibrations are then assigned to broad bands at 270 and 235 (Cl) and 274 and 245 (Br) cm^{-1}.

The iodide compound, in contrast, has a complex set of

ν(C$\equiv$N) vibrations, (see Table 5.3.), suggesting a cis $(InI_2(MeCN)_4)^+$ cation, for which analogy with ν(CO) of a cis-$M(CO)_4L_2$ compound[152] requires 4 IR-active vibrations $(2a_1 + b_1 + b_2)$, of relative intensity w, ms, w, m (in order of decreasing energy). The results in Table 5.3. are indeed in this order. The structure of the compound is then that of ionic dimer $(InI_2(MeCN)_4)(InI_4)$, and the far infrared has a strong absorption at 184 cm^{-1}, assigned as ν_3 of InI_4^- (cf. ref. 153). We therefore conclude that the ionic formulation is correct, and that the structure is very similar to that[154] of $(InI_2(dmso)_4)InI_4$. In this series of acetonitrile adducts then, as in other indium(III) systems[63] the stability of the InI_4^- anion produces a structure different from those of the chloride and bromide analogues. The ν(In-N) vibrations are assigned to a broad band at 240 m and a sharper band at 206 s cm^{-1}.

Solution Properties

A complete analysis of the vibrational spectra of the acetonitrile adducts was not possible since the Raman spectra of the solids were dominated by extensive random scattering. The Raman spectra of solution in acetonitrile (Cl, Br) or methanol (I) are only capable of analysis in the ν(In-X) region, and in each case the dominant feature was ν_1 of InX_4^- (X = Cl), ν_1 = 328 m; Br, ν_1 = 197 m; I, ν_1 = 138 vs cm^{-1}), other bands were also present in the ν(In-X) regions, but were not unambiguously identified.

The molar conductivities of the three acetonitrile adducts were measured for mM solutions in nitromethane. The experimental results were

$InCl_3.3MeCN$	54 ohm^{-1}	cm^2	mol^{-1}
$InBr_3.3MeCN$	76 "	"	"
$InI_3.2MeCN$	64 "	"	"

These results, as in previous work, are best interpreted by hindsight, rather than giving primary structural information. The value for $InI_3.2MeCN$ when doubled to account for the proposed ionic dimer structure is close to that normally found for 1:1 electrolytes in nitromethane.[155] The values for the remaining compounds are best seen as the result of equilibria such as (6); in addition, the Raman spectra imply that rearrangement reactions in solution can also extend to the formation of InX_4^- species for X = Cl and Br. In the absence of more detailed information, any identification of all the solution species is not possible at present.

Table 5.1. Experimental conditions for the electrochemical preparation of adducts of indium(III) halides

System (a)	Solution phase Composition (vol. in cm^3)			Initial voltage (V)	Initial current (mA)	Time of electrolysis (min)	Metal dissolved (g)
	MeCN	Other	Ligands				
$MeCN/Cl_2$	50	-	$Cl_2 + N_2$	2	30	45	2.26
$MeCN/Br_2$	50	-	2g Br_2	7	40	60	1.36
$MeCN/I_2$	50	-	2g I_2	17	20	85	0.60
bipy/Br_2	15	40 C_6H_6 30 mg Et_4NBr	2g Br_2, 2g bipy	30	30	75	0.41
Ph_3P/Br_2	15	30 C_6H_6 30 mg Et_4NBr	2g Br_2, 2g Ph_3P	4	50	105	1.70
py/Br_2 (c)	10	30 mg Et_4NBr	15 g Br_2	15	40	180	0.28
dmso/Cl_2 (b)	-	50 C_6H_6	50 dmso; $Cl_2 + N_2$	15	100	120	0.75
dmso/Br (b)	-	50 C_6H_6	50 dmso; 2g Br_2	15	100	120	0.89

(a) bipy = 2,2 -bipyridine; py = pyridine; dmso = dimethylsulphoxide

(b) values from ref. (63)

(c) no identifiable compound obtained from this system

Table 5.2. Analytical results for indium(III) halide adducts prepared electrochemically

Compound (a)	Found (%)		Calculated (%)	
	Halogen	In	Halogen	In
$InCl_3.3MeCN$	31.2	33.3	30.6	33.5
$InBr_3.3MeCN$	49.8	24.5	50.2	24.1
$InI_3.2MeCN$	65.5	19.7	65.9	19.9
$InBr_3.1.5$ bipy	40.5	19.1	40.7	19.5
$InBr_3.2Ph_3P$	36.0	17.0	36.2	17.3
$InBr_3.3py$	40.2	19.2	40.5	19.4
$InBr_3.2py$	46.3	22.1	46.8	22.4

(a) The presence of the appropriate neutral ligand was demonstrated in each case by established infrared spectral criteria.

Table 5.3. Vibrational spectra of acetonitrile adducts of indium trihalides (cm^{-1})

Compound (a)	ν(C$\equiv$N) (IR)	ν(In-X)	ν(In-N)
$InCl_3 \cdot 3MeCN$	2320 vs, 2291 vs	328 s, 292 sh	270 br, 235 br
$InBr_3 \cdot 3MeCN$	2295 vs, 2260 vs	225 s, 200 m	274 br, 245 br
$InI_3 \cdot 2MeCN$	2365 m, 2325 s, 2290 s, 2265 m	183 vs	240 m br, 206 s

(a) Samples run as Nujol mulls between KBr or polyethylene plates.

CHAPTER VI

NEUTRAL AND ANIONIC ORGANOINDIUMHALIDES

VI. I. Introduction

Organic derivatives of indium have not been extensively studied, but an increasing amount of attention has recently been given to this field. Indium, like gallium in the +3 oxidation state forms compounds R_3M, R_2MX and RMX_2, and coordination complexes of these species. The +3 oxidation state compounds of indium are intermediate in properties between their aluminium and thallium counterparts; they have less tendency to associate through electron deficient MCM bridges than have organoaluminium compounds, and their metal - carbon bonds are less readily cleaved by protic reagents or unsaturated compounds.[156] Some recent reviews of the organometallic chemistry of indium are to be found in references 157-159.

Indium alkyl compounds have been prepared for a variety of lower alkyls, such as Me_3In,[160] Et_3In[161] and $(i\text{-}Bu)_3In$,[162] and indium aryls such as Ph_3In[163] and Cp_3In[164] are also known. They can be prepared by the following methods a) exchange between indium metal and mercury alkyls or aryls, b) alkylation or arylation of indium trihalides by Grignard reagents, organolithium or organoaluminium compounds, or c) the reaction between alkyl bromide and Mg/In alloy.[129]

Halide derivatives of Me_3In,[160,165] Et_3In[166] and Ph_3In[167,168,169,170,171] of the type $RInX_2$ or R_2InX (X = Cl, Br or I) have also been prepared. Those derivatives can be prepared by the reaction of Grignard reagents with $InCl_3$,[167] by titrating Ph_3In with stoichiometric quantities of either Br_2 or I_2 in benzene,[168] or by oxidative insertion of In(I)I into C-I bond.[172,173,174] Diaryl indium iodides were also prepared by the reaction of aryl iodides with activated indium powder, prepared by reducing $InCl_3$ with fresh potassium metal in dry xylene.[169]

The vibrational, ^1H NMR and mass spectra of the compounds, $RInX_2$ (X = Br, I; R = Me, Et) result from the reaction of InBr or InI with alkyl halides, were recorded.[175] For $EtInBr_2$ evidence is presented in support of polymeric structure in both solid and vapour phases, but for $MeInI_2$ an ionic formulation, $(Me_2In)^+(InI_4)^-$ is proposed. The compounds $PhInX_2$ (X = Cl or Br) also adopt a polymeric lattice, but results on $PhInI_2$ are most consistent with an ionic formulation, $(Ph_2In)^+(InI_4)^-$, similar to the description given for $MeInI_2$.[170]

The Lewis acidity of the R_3In, R_2InX and $RInX_2$ species allow complexation with Lewis bases, so that dimethylindium halides, like trimethyl indium, react with donor molecules such as py, Ph_3P, Ph_3PO, 2,2′-bipy, 1,10-Phen and en to yield a series of 4- and 5- coordinate complexes.[164, 165] The adducts $C_6F_5InCl_2.L$ (L = 2,2′-bipy, 1,10-phen, terpy and diphos) have been prepared by reaction of $C_6F_5InCl_2$.diox with the appropriate ligands, but reaction with the monodentate ligands, py, DMSO and Ph_3p causes quantative rearrangement into the corresponding $InCl_3$ and $(C_6F_5)_3In$ complexes.[176]

Adducts $R_3In.XH$ with a hydrogen atom attached to the donor atom may lose hydrocarbon RH when heated, forming R_2MX (X = NR_2, PR_2, AsR_2, OR, SR etc.).[156, 177] A few anionic organo-complexes of indium have been reported by Clark and Pickard,[165] Lithiumtetramethylindate(III), $Li(Me_4In)$, was synthesized by condensing Me_3In onto MeLi in ether. $(Et_4N)(Me_2InCl_2)$ and $(Ph_4As)(Me_2InCl_2)$ were similarly prepared from the reaction of Me_2InCl and the tetraalkyl salt respectively. The anionic complexes $(Me_4Sb)(MeInCl_3)$ and $(Me_4As)(MeInCl_3)$ were obtained by methylating Me_3SbCl_2 and Me_3AsCl_2 respectively with Me_2InCl and their vibrational spectra were discussed.[178]

The Present Work

In this chapter we report the preparation of some neutral and anionic organoindiumhalide complexes by direct electrochemical oxidation of indium metal in cells consisting of alkyl or aryl halide, organic solvent(s) and a neutral ligand. The complexes prepared were studied by standard methods such as elemental analysis; IR, NMR and mass spectra; conductivity and current efficiency measurements. We propose a mechanism based on the anodic formation of InX, which reacts with RX to give $RInX_2$, which is then stabilized as an adduct or the anionic complex.

VI. 2. Experimental

a) Material. Indium metal was used as before (Chapter V). All solvents used were dried either over activated molecular sieves or over freshly pressed sodium wire.

b) Analytical Measurements. Indium and halide analyses were carried out by the procedures described in the previous chapter. Carbon, hydrogen and nitrogen analyses were performed by Gygli microanalytical laboratories in Toronto. The analytical data are given in Tables 6.1 and 6.2 for the neutral and anionic complexes.

c) Physical Measurements. Infrared spectra were recorded with Beckman IR-12, NMR spectra with a Varian EM-360 spectrometer operating at 60 MHZ and mass spectra were obtained using a Varian MAT CH_5 double focusing spectrometer at an electron energy of 70 eV. Current efficiency and conductivity measurements were performed as before.

d) Electrochemical Preparations. Indium metal was used as the anode of the cell in all experiments, except one (see below). Electrolysis and all subsequent operations were carried out under nitrogen. The detailed experimental conditions for the electrochemical preparations are given in Table 6.3.

Electrochemical Preparation of $EtInBr_2$.bipy

The solution resulted from electrolysis of indium (connected as anode, see Table 6.3) was treated with diethyl ether until a light yellow solid precipitated. This solid which was filtered off under nitrogen and dried in vacuo was characterized as $EtInBr_2$.bipy, which is slightly soluble in MeCN or MeOH and insoluble in aromatic solvents. In another experiment indium metal was used as cathode of the cell; electrolysis under similar conditions as above (see Table 6.3) produced the same compound. No special differences were observed between the two cases and the details of the isolation were the same.

Electrochemical Preparation of Me_2InI.bipy and $MeInI_2$.bipy

A dark brown colour in the solution phase developed as the electrolysis progressed and a small amount of a light yellow solid deposited on both electrodes. The polarities were reversed for short periods to remove from the cathode the material adhering to the surface. After 3.5 h the solution was filtered, but the amount of yellow solid recovered was in too small quantity to permit characterization. The filtrate was then evaporated in vacuo and the fluffy orange solid resulted was thoroughly washed with benzene in order to remove excess 2,2'-bipyridine. The orange powder which was collected and dried in vacuo analysed as $Me_2InI.bipy$, which is very soluble in MeCN.

In another experiment indium was electrolysed in a mixture of 40 cm^3 MeCN, 5 cm^3 MeI, 0.7 g bipy. and 30 mg Et_4NBr for 20 h, (not included in Table 6.3); 0.57 g indium dissolved. In this experiment the large quantity of a yellow solid which deposited in the cell was collected and dried in vacuo, and identified as $MeInI_2.bipy$. When the filtrate was treated with petroleum ether, then concentrated and triturated, a yellow-orange solid precipitated. This solid was recrystallized from MeCN, collected, dried in vacuo, and identified as $Me_2InI.bipy$.

Electrochemical Preparation of $BzInCl_2.bipy$

The faint yellow colour of the solution changed progressively to bright yellow as electrolysis progressed. The volume of the solution resulted from electrolysis was reduced in vacuo by 50%

to yield a bright yellow crystalline solid. This was collected by filtration, washed with benzene, and dried in vacuo. It is slightly soluble in BzCl, but insoluble in C_6H_6.

Electrolysis of indium under similar conditions but in absence of 2,2'-bipyridine gave a very unstable yellow solid which decomposed to a grey material when electrolysis was contained for more than 45 min. With shorter electrolyses, the yellow solid obtained was in too small a quantity to permit characterization.

Electrochemical Preparation of $BzInBr_2$.bipy.

The same procedure used for $BzInCl_2$.bipy was followed, except in this case volume reduction did not precipitate the compound. Dropwise addition of diethyl ether to the electrolyte phase until the solution became turbid, followed by cooling in the refrigerator, afforded a crystalline solid which was recrystallised from MeCN, filtered and dried in vacuo.

Electrochemical Preparation of $BzInI_2$.bipy

The same procedure as for $BzInCl_2$.bipy and $BzInBr_2$.bipy was followed except in this case a violet coloration was observed around the cathode during electrolysis; the solution changed to a progressively yellow colour as electrolysis continued and a yellow fluffy solid deposited in the cell. The solid was collected and dried in vacuo. When the volume of the filtrate was reduced, or the solution treated with diethyl ether, an additional quantity of solid was obtained.

Electrochemical Preparation of $PhInCl_2$.bipy, $PhInBr_2$.bipy and $PhInI_2$.bipy

A similar procedure was used to prepare these three compounds. The brown $PhInI_2$.bipy deposited in the cell during electrolysis but a subsequent addition of diethyl ether was required to precipitate the off white $PhInCl_2$.bipy or $PhInBr_2$.bipy. A dark violet coloration around the cathode was again observed during $PhInCl_2$.bipy preparation. It was also observed that if $PhInCl_2$.bipy was left for some time (even under nitrogen) it changes colour to grey and the indium content increases gradually.

Electrochemical Preparation of $(Et_4N)(MeInI_3)$

After a few minutes of electrolysis the anode of the cell was covered with a red-violet solid ($In^{I}I$). At the end of the electrolysis (20 h) the colorless solution was filtered and the solvent was then removed in vacuo. When the resulting colorless solid was thoroughly washed with chloroform, some of the crude material dissolved. The residue which remained was characterized as Et_4NI; the filtrate was evaporated to dryness to yield the anionic compound $(Et_4N)(MeInI_3)$.

Electrochemical Preparation of $(Bu_4N)(Me_2InI_2)$

The colorless solid precipitated when the solution resulted from electrolysis was treated with diethyl ether, was characterized as Bu_4NI. This starting salt was filtered off and the filtrate was evaporated to dryness to obtain the anionic compound $(Bu_4N)(Me_2InI_2)$.

Electrochemical Preparation of $(Et_4N)(EtInBr_3)$

The colorless solution resulted from electrolysis was treated with diethyl ether. A solid precipitated and was washed thoroughly with chloroform to dissolve excess Et_4NBr. The colorless solid which is insoluble in chloroform was characterized as $(Et_4N)(EtInBr_3)$. It is slightly soluble in MeCN, soluble in MeOH, but insoluble in acetone or benzene.

Electrochemical Preparation of $(Et_4N)(PhInCl_3)$ and $(Et_4N)(PhInBr_3)$

A brown coloration was observed around the cathode and a very small quantity of a brown solid deposited in the cell, but the solution colour was pale yellow at the end of the electrolysis. The solution was filtered and the details of the isolation is the same as for $(Et_4N)(EtInBr_3)$.

Electrochemical Preparation of $(Et_4N)(PhInI_3)$

A dark brown coloration appeared around the cathode and changed to yellow away from the electrode and a small quantity of a brown solid deposited in the cell. At the end of electrolysis (20 h) the solution was filtered and diethyl ether added to the filtrate. The solid produced was collected, thoroughly washed with chloroform, filtered again and the residue rejected. The two filtrates were combined and again treated with diethyl ether; no solids were obtained at this point, but when the volume was reduced in vacuo, a brown solid settled in the container. This was collected and dried in vacuo.

Electrochemical Preparation of $(Bu_4N)(PhInI_3)$

A dark brown colour developed around the cathode, and the solution colour progressively changed to brown. The solution resulted from electrolysis was treated with diethyl ether and the colorless precipitate characterized as Bu_4NI. This was filtered off and the filtrate again treated with ether and the volume reduced in vacuo, when a yellow solid precipitated. The solid which was collected and dried in vacuo was characterised as $(Bu_4N)(PhInI_3)$.

Electrochemical Preparation of $(Et_4N)(BzInI_3)$

A small quantity of a colorless solid deposited in the cell, together with a finely divided disintegrated indium metal. The solution was filtered and the filtrate treated with diethyl ether, when a colorless solid precipitated. The solid was collected and washed thoroughly with chloroform to dissolve excess Et_4NCl, The colorless residue was characterized as $(Et_4N)(BzInCl_3)$, which is extremely insoluble in MeCN, MeOH, C_6H_6 and C_5H_5N but sparingly soluble in BzCl.

VI. 3. Results

Mass Spectra

Mass spectra were obtained for a number of the compounds prepared, with the results summerized in Tables 6.4 - 6.7. In general, the modes of decomposition are those to be expected for indium(III) compounds. The highest intensity peaks for the compound $PhInBr_2.bipy$ are $InBr_2(bipy)^+$, $PhInBr(bipy)^+$ and $PhInBr_3(bipy)^+$. With this compound, as with others,[172, 175] it seems that the most important species in the mass spectra of neutral indium(III) halides is always InX_2^+ with or without complexation. The highest intensity peak for the anionic $(Et_4N)(BzInCl_3)$ at m/e = 130 is assigned for the Et_4N^+ cation.

Vibrational Spectra

The vibrational spectra of the neutral and anionic organoindiumhalide complexes, prepared electrochemically, in the ν(In-C), ν(In-X) and ν(In-N) regions are shown in Tables 6.8 and 6.9. In general the frequencies in these regions agree with those reported in the literature for similar compounds,[160, 165, 172, 174] and confirm the formation of the complexes. The complete medium infrared spectra of the two compounds $BzInBr_2$.bipy and $(Et_4N)(MeInI_3)$ are given in Table 6.10 as representative examples.

Proton Magnetic Resonance Spectra

The proton NMR spectra of some neutral and anionic complexes of organoindiumhalides at ambient temperature are shown in Tables 6.11 and 6.12. In the case of 2,2'-bipyridine adducts, limited solubility prevented resolution of the splitting patterns, but some chemical shift data were obtained and the results are in agreement with those for similar indium compounds.[164, 175] Anionic complexes are soluble in some organic solvents and especially in acetonitrile, chloroform and methanol, and the ^1H NMR spectra were therefore recorded in CD_3CN, CD_3OD or $CDCl_3$ and generally good resolution was obtained (Table 6.12).

Table 6.1

Analytical results for neutral organoindiumhalide complexes

Compound	Colour	Found					Calculated				
		%C	%H	%N	%Halide	%In	%C	%H	%N	%Halide	%In
$EtInBr_2$.bipy (In^-, pt^+)	light yellow	30.8	2.4	5.7	34.7	-	31.3	2.8	6.0	34.8	-
$EtInBr_2$.bipy (In^+, pt^-)	light yellow	-	-	-	35.0	24.8	-	-	-	34.8	25.0
$BzInCl_2$.bipy	yellow	46.8	3.7	5.5	16.0	26.2	47.1	3.5	6.5	16.2	26.6
$BzInBr_2$.bipy	yellow	-	-	-	30.5	22.1	-	-	-	30.6	22.0
$BzInI_2$.bipy	yellow	-	-	-	40.9	18.2	-	-	-	41.2	18.6
$PhInCl_2$.bipy	off white	-	-	-	16.5	27.9	-	-	-	16.7	27.5
$PhInBr_2$.bipy	off white	-	-	-	31.7	23.0	-	-	-	31.5	22.6
$PhInI_2$.bipy	brown	31.3	2.9	4.0	42.0	20.0	31.9	2.2	4.7	42.2	19.1
Me_2InI.bipy	orange	-	-	-	29.2	27.1	-	-	-	29.7	26.9
$MeInI_2$bipy	yellow	-	-	-	46.9	21.8	-	-	-	47.0	21.3

Table 6.2

Analytical results for anionic organoindiumhalide complexes

Compound	Colour	Found		Calculated	
		%Halide	%In	%Halide	%In
$(Et_4N)(MeInI_3)$[a]	faint yellow	59.6	17.4	59.5	17.9
$(Bu_4N)(Me_2InI_2)$	colourless	39.5	18.5	39.6	18.0
$(Et_4N)(EtInBr_3)$	colourless	46.3	23.0	46.7	22.4
$(Et_4N)(PhInI_3)$	brown	54.7	15.9	54.2	16.4
$(Bu_4N)(PhInI_3)$	yellow	46.3	14.3	46.7	14.1
$(Et_4N)(PhInBr_3)$	yellow	42.7	21.1	42.7	20.5
$(Et_4N)(PhInCl_3)$	colourless	25.1	27.7	24.6	26.9
$(Et_4N)(BzInCl_3)$	colourless	23.2	27.0	23.8	26.1

(a)

	%C	%H	%N
Found	17.6	3.8	2.3
Calculated	16.9	3.6	2.2

Table 6.3

Experimental conditions for electrochemical preparation of organoindiumhalide complexes

System	Solution phase composition vol. in cm^3	2,2'bipyridine added (g)	R_4NX added (mg)	Initial Voltage (V)	Initial Current (mA)	Time of electrolysis (h)	Weight metal dissolved (g)
Neutral							
In/EtBr (In$^-$,Pt$^+$)	20MeCN; 20EtBr	0.5	30	25	25	3.5	0.2
In/EtBr (In$^+$,Pt$^-$)	20MeCN; 15 EtBr	1.0	30	30	30	14	0.15
In/BzCl	10MeCN;15C_6H_6;15BzCl	0.5	30	30	10	9	0.19
In/BzBr	40MeCN; 5BzBr	1.0	30	25	30	5	0.72
In/BzI	40MeCN; 0.7g BzI	1.0	30	25	35	4	0.29
In/PhCl	40MeCN; 10PhCl	1.0	30	25	20	12	0.35
In/PhBr	40MeCN; 10PhBr	1.0	30	25	20	8.5	0.37
In/PhI	15MeCN; 15C_6H_6; 15PhI	0.5	40	30	7	9	0.10
In/MeI	10MeCN; 15C_6H_6; 15MeI	0.5	30	30	10	3.5	0.06

Table 6.3 (continued)

Experimental conditions for electrochemical preparation of organoindiumhalide complexes

Anionic							
In/MeI/Et_4NI	50MeCN; 5MeI	-	1.0	15	70	20	0.36
In/MeI/Bu_4NI	30MeCN; 10C_6H_6; 5MeI	-	3.0	10	60	21.5	0.69
In/EtBr/Et_4NBr	50MeCN; 10EtBr	-	2.0	5	80	20	1.62
In/PhI/Et_4NI	50MeCN; 5PhI	-	1.0	5	20	20	0.26
In/PhI/Bu_4NI	40MeCN; 10C_6H_6; 10PhI	-	2.0	5	40	18	0.19
In/PhBr/Et_4NBr	40MeCN; 10PhBr	-	2.0	5	80	6	0.50
In/PhCl/Et_4NCl	40MeCN; 10PhCl	-	2.0	5	90	10	0.70
In/BzCl/Et_4NCl	40MeCN; 5BzCl	-	2.0	20	60	16	0.50

Table 6.4

EI Mass spectrum of $BzInCl_2 \cdot bipy$

Source Temperature = 70°C

m/e	Intensity	Assignment
78	20	$C_6H_6^+$
79	1	
91	46	$C_7H_7^+$
92	5	
126	15	$C_7H_7Cl^+$
128	8	
127	2	CH_2In^+
129	9	
156	100	$C_{10}H_8N_2^+$
157	14	

Table 6.5

FD Mass spectrum of phInBr$_2$.bipy

Source Temperature = 52°C

m/e	Intensity	Assignment
115	9	In$^+$
156	27	$C_{10}H_8N_2^+$
157	3	
427	5	$C_{16}H_{13}N_2InBr^+$ or $C_{10}H_8N_2InBr_2^+$
429	41	
430	12	
431	100	
433	60	
434	5	
583	2	$C_{16}H_{13}N_2InBr_3^+$
584	2	
585	100	
586	41	
587	75	
589	17	
590	15	

Table 6.6

FD Mass spectrum of $BzInBr_2$.bipy

Source Temperature = 51°C

m/e	Intensity	Assignment
156	4	$C_{10}H_8N_2^+$
247	100	
248	11	$C_7H_7^+ + C_{10}H_8N_2^+$
249	1	
429	2	
431	4	$C_{10}H_8N_2InBr_2$
433	1	

Table 6.7

EI Mass spectrum of $(Et_4N)(BzInCl_3)$

Source Temperature = 64°C

m/e	Intensity	Assignment
91	3	$C_7H_7^+$
92	1	
113	1	In^+
115	23	
126	100	$C_7H_7Cl^+$
127	5	
128	34	
130	100	$C_8H_{20}N^+$
131	9	
150	18	$InCl^+$
152	5	
185	5	$InCl_2^+$
187	3	

* A constant excitation voltage of 3000 V was used in all mass spectra reported.

Table 6.8

Infrared absorptions of neutral organoindiumhalide complexes

Compound	(In-C)[(a)]	(In-X)[(b)]	(In-N)[(b)]
$EtInBr_2.bipy$	462 w, br		
$BzInCl_2.bipy$	474 m		
$BzInBr_2.bipy$	459 s	212 s 208 s 197 sh	235 vs
$PhInCl_2.bipy$	473 w, br		
$PhInBr_2.bipy$	460 w		
$PhInI_2.bipy$	474 w, br		
$MeInI_2.bipy$	490 w	182 s 182 s	252 m 232 s
$Me_2InI.bipy$	495 s	185 m 179 s	235 s 228 s

(a) Samples run as nujol mulls between KBr plates

(b) Samples run as nujol mulls between polyethylene plates.

Table 6.9

Infrared absorptions of anionic organoindiumhalide complexes

Compound	(In-C)[(a)]	(In-X)[(b)] and others
$(Et_4N)(MeInI_3)$	509 vs	152 sh 165 vs, vb 182 m 200 sh
$(Bu_4N)(Me_2InI_2)$	503 s	
$(Et_4N)(EtInBr_3)$	468 w	
$(Et_4N)(PhInI_3)$	477 m	
$(Et_4N)(PhInBr_3)$	472 w	
$(Et_4N)(BzInCl_3)$	452 vs, vbr	273 sh 283 vs, vb 320 vw

(a) Frequencies in cm^{-1}, samples run as nujol mulls between KBr plates

(b) Samples run as nujol mulls between polyethylene plates

Table 6.10

Infrared spectra of $(Et_4N)(MeInI_3)$
and $BzInBr_2$.bipy

$BzInBr_2$.bipy	$(Et_4N)(MeInI_3)$
459 s ν(In-C)	509 vs ν(In-C)
550 w	722 s ν(In-Me)
615 w	783 s
645 w	1012 s
660 m	1065 m
705 m	1078 w
733 s	1148 sh
772 s	1178 s
809 m	1392 s
870 m	1480 s
1025 sh	
1035 s	
1055 w	
1072 m	
1105 m	
1258 m	
1328 s	
1385 s	
1450 s	
1470 s	
1495 m	
1471 m	
1582 w	
1598 s	
1608 w	

Table 6.11

^1H NMR data of some neutral organoindiumhalide complexes

Chemical shifts are in ppm down field from external TMS

Neutral compounds	Solvent	Bipyridine	R[b]	Assignment
$EtInBr_2.bipy$[a] (In^-, Pt^+)	CD_3CN	7.2-8.9	1.2 3.5	CH_3 CH_2 - In
$EtInBr_2.bipy$[a] (In^+, Pt^-)	CD_3CN	7.5-8.9	1.25 3.45	CH_3 CH_2 - In
Me_2InI .bipy	CD_3CN	7.6-8.7	0.52	CH_3 - In

(a) see text for details

(b) R is organic group attached on In

Table 6.12

^{1}H NMR data of some anionic organoindiumhalide complexes

Chemical shifts are in ppm down field from external TMS

Anionic compounds	Solvent	R_4N^+	$R'^{(b)}$	Assignment
$(Et_4N)(MeInI_3)$	$CDCl_3$	3.35 1.4	0.7	Me - In
$(Bu_4N)(MeInI_2)$	CD_3CN	2.9 1.3 0.72	0.43	Me - In
$(Et_4N)(EtInBr_3)^{(a)}$	CD_3OD	1.0 2.9	-	-
$(Et_4N)(PhInI_3)$	$CDCl_3$	1.4 3.2	7.2 7.1 6.7	Aromatic C-H, Ph - In
$(Bu_4N)(PhInI_3)$	$CDCl_3$	3.1 1.7 1.1	7.6 7.3 7.1	Aromatic C-H Ph - In
$(Et_4N)(PhInBr_3)$	CD_3OD	1.0 3.0	7.3	Aromatic C-H Ph - In

(a) No attempt made to distinguish the overlapping R_4N and R' resonances in this region.

(b) R' is the organic moiety attached on In.

VI. 4 Discussion

The methods described allowed us to prepare electrochemically a number of neutral and anionic organoindiumhalide complexes. The yield is generally good, ranging between 90 and 95%, based on the weight of metal dissolved. The infrared, mass and proton nuclear magnetic resonance spectra together with elemental analysis confirm the formation of these complexes. The electrochemical methods, as elsewhere in this dissertation, are characterized by their simplicity, with the reactions being carried out at room temperature for relatively short periods of time, thereby offering considerable advantages over existing methods for the preparations of organoindiumhalide compounds.

Neutral Adducts

Generally cells of the type

$\mathrm{Pt}_{(-)}/\mathrm{RX}$ + organic solvent(s) + 2,2'-bipyridine $/\mathrm{In}_{(+)}$

were used to prepare the neutral adducts. The compounds precipitated from the solution as electrolysis proceeded in most systems, but in other cases the addition of diethylether to the final reaction solution resulted in precipitation. Acetonitrile mixed with alkyl or aryl halide proved to be a satisfactory reaction medium. In some cases it was found that under these conditions indium may disintegrate physically causing some difficulties in recovering a pure product. To overcome this difficulty, a solution phase of benzene plus MeCN and RX was used and proved to be a considerable improvement (Table 6.3)

The products are the compounds $RInX_2.bipy$, except that with RX = MeI, the products are $MeInI_2.bipy$ and/or Me_2InI. $RInX_2.bipy$ and $R_2InX.bipy$ species (or their analogues with other ligands) have been prepared previously, by other routes (see Introduction) with one exception. The benzyl derivatives of indium are not easy to prepare by conventional methods,[172] but a recent report by Gynane et al[179] described the preparation of $BzInBr_2$ and $BzInI_2$ from the reaction of In(I)X and BzX; no description was given for $BzInCl_2$. Thus $BzInCl_2.bipy$ represents a new complex which completes the group, and the electrochemical method provides a facile route for the preparation of all three complexes. The molar conductivity of a mM solution of $BzInCl_2.bipy$ in $MeNO_2$ gave 17.4 $ohm^{-1}\ cm^2\ mol^{-1}$ which indicates the non-ionic nature of the compound. The insolubility in common organic solvents may indicate that the compound may be polymeric in the solid state.

Anionic Complexes

Cells similar to those used for the neutral adducts were employed, except that in this case 2,2′-bipyridine was replaced by the appropriate tetraalkylammonium salt.

$$Pt_{(-)}/RX + \text{organic solvent(s)} + R_4NX/In_{(+)}$$

Addition of benzene to the solution phase was found, again, to suppress the disintegration of indium during electrolysis. In contrast to neutral adducts, the isolation of product required some manipulation to separate it from the excess tetraalkylammonium salt present. As was explained in the experimental section, the difference in solubility between product, say $(Et_4N)(BzInCl_3)$ and the salt Et_4NCl in chloroform proved to be very efficient in separating the two compounds. Other solvents could be used depending on the solubilities of the two compounds concerned (see experimental section).

It was noted in the Introduction that the number and the range of anionic organoindium complexes which have been prepared is quite limited. The ease and speed with which these complexes can be prepared electrochemically is very promising, and such methods should receive more attention in future.

Analytical results for the complexes prepared electrochemically (Table 6.2), together with the ^1H NMR data (Table 6.12) and the infrared spectra confirm the formation of the complexes. Molar conductivity measurements of some complexes in MeCN gave the following results

$(Et_4N)(PhInCl_3)$	117.4 ohm^{-1}	cm^2	mol^{-1}
$(Et_4N)(EtInBr_3)$	138.0 "	"	"
$(Bu_4N)(Me_2InI_2)$	148.0 "	"	"

These values are in good agreement with other values reported for 1:1 electrolyte type compounds, which fall in the range 120-160 ohm^{-1} cm^2 mol^{-1} at mM solutions in acetonitrile.[155]

Reaction Mechanism

A mechanism similar to that, postulated for the formation of organogroup IVA halide complexes by direct electrochemical oxidation of the metal (see Chapter IV), is extended here to the formation of organoindiumhalide complexes. The mechanism is based in principle on the anodic formation of In(I)X. Formation of In(I)I was indeed observed on the anode surface when organic iodides were used in the reaction mixture, and especially in the preparation of the compound $(Et_4N)(MeInI_3)$ (see experimental section). The reaction sequence proposed is as follow.

At cathode

$$RX + e^- \longrightarrow R^\cdot + X^- \qquad (1)$$

The fate of $R^\cdot$ may be represented (as before) by

$$2R^\cdot \longrightarrow R_2 \qquad (2)$$

or $R^{\cdot} + RX \longrightarrow R_2 + X^{\cdot}$ (3)

At anode

$$X^- \longrightarrow X^{\cdot} + e^- \quad (4)$$

followed by

$$X^{\cdot} + In \longrightarrow InX \quad (5)$$

Thus, the important feature of the anode reaction is the attack by $X^{\cdot}$ to form InX. Now, InX may react with RX as follow

$$InX + RX \longrightarrow RInX_2 \quad (6)$$

and $RInX_2$ can then complex with 2,2′-bipyridine

$$RInX_2 + bipy \longrightarrow RInX_2.bipy \quad (7)$$

or halide ion from R_4NX

$$RInX_2 + X^- \rightleftharpoons RInX_3^- \quad (8)$$

Most of the neutral and anionic compounds prepared have the stoichiometry given in equations (7) or (8) consequently: a plausible explanation for the anomaly observed when RX = MeI will be discussed later.

Reaction (6) may be described as an oxidative insertion of InX into RX. Such reaction has been reported in a number of papers,[172, 173, 174, 180] and in fact (as noted earlier) constitutes an important synthetic route for the preparation of organoindium(III) halide species.

In all but one of the reactions we carried out, indium was used as the anode of the cell, for which the mechanism proposed is valid. It was noted earlier (Chapter I) that in essence electrochemical methods can utilize either sacrificial cathodes or anodes for direct preparations and the underlying principles must have a common base, irrespective of the charge of the electrode which undergoes dissolution. In this respect we have investigated the electrolysis of ethyl bromide in acetonitrile in the presence of 2,2′-bipyridine at an indium cathode. Interestingly the same product ($EtInBr_2.bipy$) was obtained as in the sacrificial anode case. To account for this result, the following sequence of reaction is proposed:

At cathode (indium metal), RX is reduced (as in eq. (1)) to give $R^{\bullet}$ and X^{-}, followed by

$$R^{\bullet} + In \longrightarrow RIn \qquad (9)$$

In this case the cathodic reaction is characterized by the direct attack of $R^{\bullet}$ on the indium cathode; RIn may then react by

$$RIn + RX \rightleftharpoons RInX + R^{\bullet} \qquad (10)$$

and

$$RInX + RX \rightleftharpoons RInX_2 + R^{\bullet} \qquad (11)$$

$$2R^{\bullet} \longrightarrow R_2 \qquad (12)$$

$RInX_2$ can then complex with 2,2′-bipyridine as in eq. 7.

At anode

$$X^- \longrightarrow X^{\cdot} + e^- \qquad (13)$$

$$2X^{\cdot} \longrightarrow X_2 \qquad (14)$$

This mechanism seems to explain successfully the formation of $EtInBr_2$ (as 2,2′-bipyridine adduct). However, there are other possibilities for reactions (10) and (11) which still can explain the formation of the final product. For example the reaction

$$RIn + X_2 \longrightarrow RInX_2 \qquad (15)$$

which is less probable because of the very low concentration of X_2 relative to RX. There are only two organoindium(I) compounds known, namely cyclopentadienylindium(I)[181] and the anologue with methylcyclopentadiene.[164] The properties of these were not studied in detail, but it is known that they are readily oxidized to indium(III) species,[164] in which case reactions (10) and (11) are justified.

In the present work, as before, we have measured the current efficiency for a few systems over short periods of time (1-2 h) at constant current (20-30 mA). The following values were obtained

System	E_F mol (In) F^{-1}
$In_{(+)}$/MeCN + EtBr/$Pt_{(-)}$	1.7
$In_{(-)}$/MeCN+ EtBr/$Pt_{(+)}$	0.8
$In_{(+)}$/MeCN+MeI+Bu_4NI/$Pt_{(-)}$	1.3

These values are interpreted as before, being higher than required by Faraday's law. The reactions (1) through (8) require that $E_F \simeq 1$, since 1 g atom of the indium anode is consumed per Faraday. The values 1.7 and 1.3 for the two systems given above for anodic indium are higher than can be counted by equation (1) - (8). For this reason the following sequence of reactions is proposed

$$InX + RX \xrightarrow{\circ} RInX + X^{\cdot} \qquad (16)$$

$$X^{\cdot} + In \longrightarrow InX \qquad (17)$$

followed by reactions(11) to give the final product. Equations (16) and (17) require that E_F to be $>$ 1, because more than 1 g atom of indium is consumed per Faraday. The scheme proposed for the system where indium was used as the cathode of the cell (equations 9-14) requires $E_F = 1$, which is close to the experimental value obtained (0.8).

Now, we turn to the anomaly observed when RX = MeI. We speculate that these results can be explained by considering the species RInX produced by reaction (16) and the following scheme

$$RInX + RX \begin{array}{l} \xrightarrow{a} R_2InX + X^{\cdot} \\ \xrightarrow[b]{} RInX_2 + R^{\cdot} \end{array} \qquad (18)$$

The choice between these routes must then depend on factors which have yet to be elucidated. The present results indicate that, when

RX = MeI both routes are important, since $MeInI_2$ and Me_2InI (as 2,2'-bipyridine) were isolated from the same reaction. It appears that such reactions will always be important for metals whose stable oxidation state in organometallic halides is +3. Preliminary results show that gallium and thallium behave in the same way as does aluminium,[41,51] and in keeping with this workers in USSR prepared Me_2InI by electrolysing MeI in aqueous solution of K_2HPO_4 or in a MeCN solution of $NaClO_4$.[20]

Additionally or alternatively the following equilibrium

$$RInX_2 + RX \rightleftharpoons R_2InX + X_2 \qquad (19)$$

may be invoked to explain the formation of two neutral methyl derivatives of indium from the same reaction where this solution equilibrium and the precipitation process are in competition.

Similarly, equilibria like

$$RInX_2 + X^- \rightleftharpoons RInX_3^- \qquad (8)$$

and

$$R_2InX + X^- \rightleftharpoons R_2InX_2^- \qquad (20)$$

may be invoked to explain the formation of two different anionic complexes. The isolation of different salts with different cations suggests that solution equilibria and solubility are both important. The fact that the formation of two different compounds was only observed for RX = MeI, may be related to the structure of

$MeInI_2$, which is unstable as the monomer. Two related equilibria were proposed for dimerization.[172]

$$\mathrm{MeInI_2}\quad\begin{array}{l}\overset{a}{\rightleftharpoons}\ (\mathrm{Me_2In})(\mathrm{InI_4})\\ \qquad\qquad\quad \Big\downarrow\!\Big\uparrow c\\ \underset{b}{\rightleftharpoons}\ \mathrm{Me_2InI + InI_3}\end{array}\qquad (21)$$

For RX = EtBr, PhBr, BzBr ..... etc, the equilibria are presumably also established, but the solid state species, precipitated during electrolysis, is now the stable neutral dimer.[175]

Thus, it is to be concluded that these results obtained are within the known pattern of the established chemistry of this element. The potential of these electrochemical methods for the preparation of organoindiumhalides is of interest, and further routes are opened by this direct electrochemical technique.

CHAPTER VII

CATIONIC COMPLEXES OF METAL IONS

VII. 1 Introduction

In the preceding chapters, we have described methods for the preparation of some inorganic and organometallic compounds by a direct electrochemical method for a number of transition and main group elements. Both neutral and anionic complexes were obtained in such experiments. In this chapter we will describe methods for the preparation of some cationic complexes of a number of transition and main group elements. The metals are oxidized electrochemically in cells containing HBF_4 in DMSO; the direct products are the $[M(dmso)_6]^{n+}$ salts with BF_4^- but products such as $[M(bipy)_3]^{n+}$, $[M(en)_3]^{n+}$ and $[M(diphos)_m]^{n+}$ can be obtained by subsequent reaction ($m \neq n = 2, 3$).

In an early publication from this laboratory,[66] it was noted that the electrochemical oxidation of indium in the cell

$$Pt_{(-)} / HClO_4 + MeOH + dmso / In_{(+)}$$

gave rise to the known compound $[In(dmso)_6](ClO_4)_3$. We now report the development of this approach into a general method for the synthesis of cationic complexes. The use of a mixed aqueous/organic solution of tetrafluoroboric acid allows the complexes to be recovered as the tetrafluoroborate salts, which removes the hazards implicit both in the use of perchloric acid in organic solvents, and in the handling of perchlorate salts of complexes with organic ligands.

Many studies of cationic complexes have involved salts with perchlorate or tetrafluoroborate anions and it has generally been found that these do not coordinate to the metal ions.[182, 183] However, a few papers have described complexes in which an interaction between these anions (and especially with ClO_4^-) and metal ions are found.[184, 185, 186]

VII. 2 Experimental

a) General. The electrochemical procedure is essentially the same as was described before except in this case a plastic beaker was used. The solution phase is typically prepared by mixing equal volumes (40 cm^3) of 48% HBF_4 solution (Alfa Inorganics) or $HBF_4.OEt_2$ solution (Aldrich) with purified dmso at 0°C. Electrolytic oxidation of a number of transition and main group metals (see below) were achieved with voltages in the 0.5-3.0 V range, which gave currents of 100-300 mA. Over a period of 10-20 h at room temperature, typically 1-2 g of metal dissolved, giving Ca 5 g quantities of product. In some cases, the products precipitated, but were more frequently obtained on reducing the volume of the solution in vacuo or on a hot plate. The electrolysis was carried out under nitrogen.

b) Analytical Measurements. Metal analyses including boron were by atomic absorption spectrophotometry. Carbon, hydrogen, nitrogen, and sulfur of some samples were carried out by Spang Microanalytical Lab. in Michigan.

c) Physical Measurements. Infrared spectra were recorded with Beckman IR-12 to demonstrate the presence of dmso, BF_4^- anion and the absence of water. Current efficiency measurements were carried out by the procedure described before. In the systems examined, the dissolution of the metal obeys Faraday's Law, except in the case of manganese, which undergoes a spontaneous chemical reaction when immersed in the solution.

d) Electrochemical Preparative Chemistry. The experimental conditions for electrochemical preparation of the dmso cationic complexes are given in Table 7.1.

Electrochemical Preparation of $[V(dmso)_6](BF_4)_2$

The blue-green precipitate which formed during electrolysis was filtered off, washed with acetone and then dried in vacuo.

Analysis

Found: V, 7.3

Required: 7.4

Electrochemical Preparation of [$Cr(dmso)_6$] $(BF_4)_3$

A portion (~ 10 cm^3) of the dark green solution resulted from electrolysis was heated on a hot plate with continuous stirring to about 50°C. After ~ 30 min. a thick, dark green solid precipitated which was filtered off, and washed thoroughly with diethyl ether. The lighter green fine powder resulted was collected and dried in vacuo. 17.8 g product was recovered, 91.3% yield.

Analysis

	B	Cr	C	H	S
Found:	4.1;	6.6;	18.4;	4,5;	24.4
Required:	4.2;	6.6;	18.4;	4.6;	24.6

The same compound was obtained when aqueous HBF_4 was replaced with $HBF_4.OEt_2$. The details of isolation is the same in both cases.

Electrochemical Preparation of [$Cr(bipy)_3$] $(BF_4)_3$

0.4 g bipyrodine was dissolved in 15 cm^3 MeOH, and 5 cm^3 of the electrolysis solution (cr/dmso), prepared before, was stirred with the bipyridine solution. No solid was precipitated at this point, but when the mixture was stirred and heated (~ 60°C) on a hot plate, a green solid deposited which was filtered off, washed with a mixture of diethyl ether and methanol. The solid was collected and dried in vacuo.

Analysis

Found: Cr, 7.6

Required: 7.5

Electrochemical Preparation of $[Mn(dmso)_6](BF_4)_2$

The reaction in this case was spontaneous, i.e. no electrolysis was necessary. Once the metal was immersed in a mixture of 30 cm^3 dmso and 30 cm^3 HBF_4 the reaction started and the colorless solution changed progressively to pink. At the end of the reaction (10 h), 5.2 g Mn had dissolved. 10 cm^3 of the resulting solution was heated to 50°C with continuous stirring; the pink oil settled in the container and was decanted and then treated with diethyl ether to give a fine pink powder which was filtered, washed thoroughly with ether, collected, and dried in vacuo.

Analysis

Found: Mn, 8.0; B, 3.3

Required: 7.9; 3.2

Electrochemical Preparation of $[Mn(bipy)_3](BF_4)_2$ and $[Mn(Phen)_3](BF_4)_2$

0.3 g 2,2'-bipyridine or 0.2 g 1,10-phenanthroline was dissolved in 10 cm^3 MeOH and mixed with 3 cm^3 of the (Mn/dmso) pink solution prepared before. The resulting yellow solution was heated (50°C) and stirred to yield a yellow solid. This solid was filtered, washed with ether, then recrystallized from MeOH, collected and dried in vacuo.

Analysis

	bipy complex	Phen complex
Found:	Mn, 8.0	Mn, 7.3
Required:	7.9	7.2

Electrochemical Preparation of $[Fe(dmso)_6](BF_4)_3$

The volume of the resulting yellow-green solution was reduced in vacuo (left over night on the vacuum line), a lime green solid deposited in the container. The solid was filtered, washed thoroughly with diethyl ether, collected and dried in-vacuo. 24.5 g was recovered, 92.1% yield.

Analysis

Found:	Fe, 7.0;	B, 4.1
Required:	7.1;	4.2

The same compound was obtained when aqueous HBF_4 was replaced with $HBF_4.OEt_2$ (see Table 7.1). The consequences of isolation is the same in both cases.

Electrochemical Preparation of $[Fe(Phen)_3](BF_4)_3$

5 cm^3 of the yellow-green electrolysis solution (Fe/dmso) was mixed and stirred with 0.3 g 1, 10-phenanthroline. The colour

immediately changed to dark red and a solid with the same colour precipitated in the container. The solid was filtered off, washed with benzene, collected and dried in vacuo.

Analysis

Found:	Fe,	6.6
Required:		6.5

Electrochemical Preparation of [$Fe(en)_3$] $(BF_4)_3$

Ethylene diamine was added dropwise to a 5 cm^3 of the original (Fe/dmso) solution. The yellow-brown solid precipitated was filtered off and dried in vacuo.

Analysis

Found:	Fe,	11.2
Required:		11.3

Electrochemical Preparation of [$Co(dmso)_6$] $(BF_4)_3$

The volume of the resulting red-pink solution was reduced in vacuo. The pink solid precipitated was filtered off, collected and dried in vacuo.

Analysis

Found:	Co,	7.4
Required:		7.5

Electrochemical Preparation of $[Co(diphos)_2](BF_4)_2$

0.3 g diphos was stirred with a portion of the original pink (Co/dmso) solution. The yellow solid precipitated was filtered off, washed with diethyl ether, collected and dried in vacuo.

Analysis

Found: Co, 5.4

Required: 5.4

Electrochemical Preparation of $[Ni(dmso)_6](BF_4)_2$

The light green solid deposited in the cell was filtered off, washed with diethyl ether and acetone, collected and dried in vacuo. Another quantity of the solid is obtained if the filtrate volume is reduced.

Analysis

Found: Ni, 8.4

Required: 8.4

Electrochemical Preparation of $[Ni(bipy)_3](BF_4)_2$ and $[Ni(diphos)_3](BF_4)_2$

0.5 g bipy or 0.35 g diphos was stirred with portion of original (Ni/dmso) electrolysis solution. The solid precipitated was filtered off, washed with diethyl ether, collected and dried in vacuo.

Analysis

	bipy complex	diphos complex
Found:	Ni, 8.4	4.2
Required:	8.4	4.1

Electrochemical Preparation of $[Cu(Phen)_3](BF_4)_2$

The blue solution resulting from electrolysis of Cu in dmso and HBF_4 (Table 7.1) failed to give any solid. When the solution was heated to 80°C in vacuo, a colorless solid sublimed but was found to contain a negligible amount of Cu. 0.4 g of 1,10-phenanthroline was dissolved in 15 cm^3 benzene and stirred with 5 cm^3 of the electrolysis solution. The oil produced was decanted and stirred with 10 cm^3 diethyl ether to produce a greenish-blue solid. This was filtered, washed with diethyl ether and benzene, collected and then recrystallized from MeOH.

Analysis

Found:	Cu,	8.1
Required:		8.2

Electrochemical Preparation of $[Zn(dmso)_6](BF_4)_2$

The white solid deposited in the cell was filtered off and recrystallized from acetone. It was dissolved in acetone then diethyl ether was added until precipitation occurred. The solid was filtered off, washed with ether, collected and dried in vacuo.

Analysis

Found: Zn, 9.2

Required: 9.2

Electrochemical Preparations of [$Cd(dmso)_6$]$(BF_4)_2$

10 cm^3 of the colorless solution resulted from electrolysis was heated (60°C) and stirred with 15 cm^3 of diethyl ether. The oil produced was decanted and treated with more ether to produce a fine colorless powder which was filtered, collected and dried in vacuo.

Analysis

Found: Cd, 14.8

Required: 14.9

Electrochemical Preparation of [$Cd(phen)_3$] $(BF_4)_2$

3 cm^3 of electrolysis solution (Cd/dmso) was mixed with a solution of 0.2 g 1,10-phenanthroline in 15 cm^3 chloroform. The light pink solid resulted was filtered, washed thoroughly with chloroform and dried in vacuo.

Analysis

Found: Cd, 13.5

Required: 13.6

Electrochemical Preparation of [In(dmso)$_6$](BF$_4$)$_3$

The white thick solid deposited in the cell was filtered, washed with ether and methanol, collected and dried in vacuo.

Analysis

	In	B
Found:	13,6;	3.8
Required:	13.6;	3.9

Electrochemical Preparation of [In(bipy)$_3$](BF$_4$)$_3$

0.1 g of [In(dmso)$_6$](BF$_4$)$_3$ was stirred with a solution of 0.3 g bipyridine in 1 : 4 diethyl ether : methanol. The white solid which dissolved in stirring and then deposited was filtered, washed with ether and dried in vacuo.

Analysis

	In
Found:	13.6
Required:	13.6

Electrochemical of [Ti(MeCN)$_6$](BF$_4$)$_3$

The reaction is spontaneous, i.e. no electrolysis was necessary. The colorless solution progressively changed to light violet and a solid of this same colour deposited in the container. At the end of the reaction (20 h), 1.23 g Ti dissolved, the solid was filtered and dried in vacuo.

?

Analysis

Found: Ti, 8.9

Required: 8.6

Electrochemical Preparation of $[In(MeCN)_6](BF_4)_3$

The colorless solution resulting from electrolysis was evaporated in vacuo. The white solid obtained was washed with pet. ether, collected and dried in vacuo.

Analysis

Found: In, 18.8

Required: 18.2

Electrochemical Preparation of $[Cr(MeCN)_6](BF_4)_2$

The blue solution resulting from electrolysis was evaporated in vacuo. The navy blue solid obtained was washed with diethyl ether, collected and dried in vacuo.

Analysis

Found: Cr, 12.4

Required: 12.4

Electrochemical Preparation of $[Cr(MeCN)_4](BF_4)_2$

1 gm bipyridine was dissolved in 40 cm^3 MeCN but when 5 cm^3 $HBF_4.OEt_2$ was added to the solution an insoluble colorless solid started to deposit, (bipy H^+ BF_4^- ?) Electrolysis of Cr was

carried out under these conditions (see Table 7.1). The colorless solution progressively changed to pink. At the end of electrolysis (12 h) the solution was filtered (to separate the undissolved solid) and the filtrate volume was reduced in vacuo; the pink solid deposited was filtered off and dried in vacuo and characterized as $[Cr(MeCN)_4](BF_4)_2$.

Analysis

Found: Cr, 13.0; C, 24.3; H, 3.1; N, 13.5

Required: 13.3; 24.6; 3.1; 14.3

The pink solid dissolves in MeCN and changes colour to blue-green, and slightly dissolves in MeOH with the same colour change.

VII. 3 Results and Discussion

The metal tetrafluoroborates and perchlorates are usually prepared by treating an excess of metal carbonate with tetrafluoroboric or perchloric acids, filtering off excess of carbonate, and concentrating the filtrate on a steam-bath to effect crystallization.[182] The metal salt is then dissolved in a solvent and a slight excess of the desired ligand added. We found that this cycle of operations can be circumvented by a direct electrochemical process, in which the metal acts as the anode of the cell. Tables 7.1 and 7.2 show the experimental conditions for electrochemical preparation of some dmso and MeCN cationic complexes prepared by this method. Thus the first conclusion from this work is that these complexes are readily available in high yield by a room temperature synthetic route which uses the metals as the accessible source of high purity element.

Dimethylsulfoxide Complexes

Several years ago Cotton et al[187] commenced an investigation of the ability of the sulfur-oxygen grouping in sulfoxides (RR'SO) to function as an electron donor, and a large number of cationic complexes containing dimethylsulfoxide and analogous compounds with other sulfoxides were prepared. The majority of the complexes prepared are with salts of transition metals, and it is complexes of this class which have been most extensively studied. Compounds of the type $[M(dmso)_{4\text{ or }6}]^{+n}(ClO_4)_{2\text{ or }3}$ or $[M(dmso)_{4\text{ or }6}](BF_4)_{2\text{ or }3}$ which stand in direct stiochiometric analogy to the corresponding aquo compounds, are known to contain the $[M(dmso)_6]^{+n}$ and $[M(dmso)_4]^{+n}$ cations indicated.[182, 187, 188, 189]

In many cases the materials obtained by adding the appropriate metal salt to dmso are oily in appearance and contain excess dmso,[187] so that analytically pure compounds are obtained by heating, which frequently results in decomposition.[183] One advantage of the method employed here is that most complexes are readily obtained in crystalline form. In only one case, namely copper in dmso and HBF_4, did electrolysis fail to give any solids, with consequent heating resulting in decomposition.

In some cases concentrated aqueous solutions of the metal salts can be used to prepare dmso complexes, but this is of uncertain reliability; often the compounds obtained contain water as well as dmso.[187] Apparently water and dmso compete fairly evenly for sites in the coordination sphere.

We have carried out two types of experiments. Our earliest preparations used 48% HBF_4 solution (in water) and purified dmso. Electrolytic oxidation of the metals (see Table 7.1), were achieved with voltages in the 0.5-3.0 V range, which gave currents of 100-200 mA. These voltages are appreciably lower than those found necessary in our previous work, and this is no doubt due to the presence of substantial amounts of water originating in the HBF_4 solution. The resulting compounds have been characterised analytically, and the presence of dmso and BF_4^-, and the absence of water, demonstrated by infrared spectroscopy (see below).

Later experiments with Cr or Fe (see Table 7.1) used $HBF_4 \cdot OEt_2$ as a non-aqueous solution. The resulting products have been again characterised as the same as the compounds obtained with 48% HBF_4 solution. It is thus to be concluded that there are no substantial synthetic differences between the two cases, except that in the presence of water higher currents are obtained.

The cations which we have prepared by this method are the six-coordinate dmso complexes of the metals outlined in Table 7.1. The production of compounds of low oxidation (V^{II}, Cr^{III}, Mn^{II}) by oxidation of the metal is a characteristic of the electrochemical method here, as elsewhere.[65] Titanium dissolves in the cell, but we were unable to recover a pure product, presumably because the Ti^{III} cation first produced undergoes further reaction with dmso. (c.f. ref. 190).

A further advantage of the method is that the solution obtained by electrolysis can be used as a source of other cationic complexes. Thus, the addition of a solution of 2,2'-bipyridine after electrolysis has given rise to the cations $[Mn(bipy)_3]^{2+}$, $[In(bipy)_3]^{3+}$ ... etc., all as BF_4^- salts. Similar experiments also yielded $[Mn(Phen)_3]^{2+}$, $[Cu(Phen)_3]^{2+}$, $[Fe(en)_3]^{3+}$ (see experimental section).

Vibrational Spectroscopy

The sulfoxides are pyramidal molecules with unshared pairs of electrons on both sulfur and oxygen, and one classical point of importance in considering the structures of the adducts of sulfoxides has been the identification of the donor atom.[187, 188, 189] Although oxygen has been counted as the donor atom in the majority of the studies, mainly because of steric consideration, the possibility of the sulfur being the donor cannot be discounted. In many cases the infrared spectra have been of value in deducing the structures of the compounds, and in considering the spectra the main interest has been in the behaviour of the SO stretching frequency, since this should be most informative with respect to the nature of the metal-ligand bonding. The reason for this follows from the bond structure of the sulfoxide group and the shift difference observed in the spectra of this group in the complexes relative to that in the free dmso. The S-O stretching frequency for uncoordinated dmso has been assigned at 1050 cm^{-1} (in $MeNO_2$ solution).[188, 189] Unfortunately the BF_4^- anion also absorbs in this important region of the spectrum with a very strong broad band at 1030-1160 cm^{-1} in the uncoordinated anion.[182] As a matter of fact all the spectra we recorded for the dmso complexes have a very strong broad band in the region Ca. 1000-1200 cm^{-1}, but because of this interference, which makes the assignment of S-O stretching frequency an impossible task. In Table 7.3 the IR spectrum of $[Cr(dmso)_6](BF_4)_3$ is shown as a representative example of this class of compounds, along with the dmso and BF_4^- infrared spectra. The spectra of other complexes have been recorded, and are all very similar.

The tetrafluoroborate ion has T_d symmetry. The effects of coordination on the IR activity of the various vibrations of this ion has been discussed by Hathaway and Underhill[191] and by Brown et al.[182] The vibrations of BF_4^- are given in Table 7.3 and compared with those of $[Cr(dmso)_6](BF_4)_3$. Because of the distinct similarity in frequency of the free ion and that of the complex, it is to be concluded that this complex, and others, contain ionic tetrafluoroborate.

Acetonitrile Complexes

Electrochemical oxidation of the metal in a cell containing HBF_4 in MeCN produced the salts $[M(MeCN)_6]^{+n}$ of BF_4^-, and the compounds prepared by this method are given in Table 7.2. The contrast between this system, in which a Cr(II) species is produced, and that involving dmso, where a Cr(III) complex was obtained, may be due to the oxidation $Cr^{II} \longrightarrow Cr^{III}$ by dmso. In(III) is the only metal for which the same oxidation state was produced in both cases, clearly because In(II) is very unstable and generation of the metal in this oxidation state is very unlikely. Two different Cr(II) complexes were prepared. One of them is the blue six-coordinate $[Cr(MeCN)_6](BF_4)_2$ complex, which was simply prepared by electrolysing chromium in a mixture of MeCN and HBF_4.

The other one is the pink, apparently four-coordinate MeCN complex which was prepared by electrolysing the metal in a similar mixture in the presence of 2,2'-bipyridine. As a matter of fact, 2,2'-bipyridine was added to the reaction mixture in an attempt to prepare the 2,2'-bipyridyl complex of chromium directly, but as explained in the experimental section the bipyridinum salt ($bipyH^+BF_4^-$) precipitated in the reaction mixture. Electrolysis in the presence of bipyridinium salt resulted in the pink solid $[Cr(MeCN)_4](BF_4)_2$. The presence of acetonitrile and the absence of 2,2'-bipyridine was demonstrated by both IR and ^1H NMR spectra. Obviously more work is needed on this topic in order to identify the reason for the two different reactions.

The current efficiency was measured for two systems over a short periods of time (1-2 h) at constant current. The following values were obtained.

System	Current Efficiency Mol(M)F^{-1}
$Cd_{(+)}$/ DMSO + HBF_4 /$Pt_{(-)}$	0.52
$Cr_{(+)}$/ MeCN + HBF_4 /$Pt_{(-)}$	0.51

In contrast to other systems investigated previously for electrochemical preparations, the dissolution of the metal in these systems obeys Faraday's law. In the case of manganese and titanium, a spontaneous chemical reaction occurs when the metal is immersed in the solution.

Table 7.1

Experimental conditions for electrochemical preparations of some transition and main group cationic dmso complexes

Elements	Products	Solution phase composition (vols. in cm^3)	Initial		Time of electrolysis (h)	Weight metal dissolves (g)
			voltage (V)	current (mA)		
V	$[V(dmso)_6](BF_4)_2$	DMSO50; $HBF_4$50	2	100	16	0.4
Cr	$[Cr(dmso)_6](BF_4)_2$ (a)	DMSO30; $HBF_4$30	3.5	100	20	1.3
		or DMSO20; $HBF_4 \cdot OEt_2$5	6	50	7	0.7
Mn	$[Mn(dmso)_6](BF_4)_2$ (b)	DMSO30; $HBF_4$30	-	-	-	-
Fe	$[Fe(dmso)_6](BF_4)_3$ (a)	DMSO30; $HBF_4$30	2	210	22	1.9
		or DMSO20; $HBF_4 \cdot OEt_2$5	4	40	7.5	0.6
Co	$[Co(dmso)_6](BF_4)_3$	DMSO50; $HBF_4$50	2	100	16	1.1
Ni	$[Ni(dmso)_6](BF_4)_2$	DMSO40; $HBF_4$40	2	100	16	1.6
Cu	(c)	DMSO30; $HBF_4$30	2	200	23.5	2.4
Zn	$[Zn(dmso)_6](BF_4)_2$	DMSO40; $HBF_4$40	2	100	56	3.0
Cd	$[Cd(dmso)_6](BF_4)_2$	DMSO30; $HBF_4$30	1	80	22	3.0
In	$[In(dmso)_6](BF_4)_2$	DMSO40; $HBF_4$40	1	50	62	0.9

(a) The same product in both cases

(b) Reaction spontaneous, no electrolysis was necessary

(c) No identifiable compound was isolated.

Table 7.2

Experimental conditions for electrochemical preparations of some transition and main group MeCN complexes

Elements	Products	Solution phase Composition (vols. in cm^3)	Initial		Time of electrolysis (h)	Weight metal dissolved (g)
			voltage (V)	current (mA)		
Ti(a)	$[Ti(MeCN)_6](BF_4)_3$	MeCN20; $HBF_4$20	-	-	-	-
Cr	$[Cr(MeCN)_6](BF_4)_2$	MeCN20; $HBF_4$20	3	100	24	2.6
Cr	$[Cr(MeCN)_4](BF_4)_2$	MeCN40; $HBF_4.OEt_2$ 20; 1 g bipy	2	50	12	0.5
In	$[In(MeCN)_6](BF_4)_3$	MeCN20; $HBF_4$20	1	100	17	2.4

(a) Reaction spontaneous

Table 7.3

IR spectra (cm^{-1}) of [Cr(dmso)$_6$](BF$_4$)$_2$, dmso and BF$_4^-$

dmso[a]	[Cr(dmso)$_6$] (BF$_4$)$_3$[b]	BF$_4^-$ [c]
	530 s	525 ν_4
669 mw, sym. C-S, str.	672 w	
700 s, asym. C-S, str.	728 ms	
	775 w	773 ν_1
931 m Me rocks 954 s	965 s	
	1000 ms	
1040 vs S-O, str.	1000-1200 ms	1030-1160 ν_3
1310 m sym. Me def.	1320 m	
1409 ms asym. Me def.	1342 m	
1438 s	1388 s	

(a) Neat, Ref. 129

(b) Nujol mull, KBr plates

(c) Ref. 182

CHAPTER VIII

OLEFIN POLYMERIZATION

VIII. 1. Introduction

Ziegler-Natta type catalysts are, in general, composed of a transition metal compound and an organometallic reducing agent containing a Group I-III metal. The transition metal derivative is usually a halide, but it may sometimes be an alkoxide or β-diketonate of titanium, vanadium, zirconium, cobalt or chromium. The base metal compound is normally a trialkylaluminium or alkylaluminiumhalide, although organolithium, organomagnesium, and organozinc compounds have found some use. The role of the base metal alkyl is alkylation of the transition metal, and possibly to complex with it. Not all combinations of these two components have the required activity and it is necessary to choose the catalyst to suit the monomer to be polymerized.[99] Most commonly the catalyst used in industry is based on $TiCl_3$ and Et_2AlCl. Titanium alkylation occurs and polymerization is thought to be initiated at alkyltitanium sites.[192,193] Organotitanium compounds without added alkylaluminium, but in combination with titanium halides, also polymerize olefins; examples include $MeTiCl_3$[194] and Cp_2TiMe_2,[99] each in combination with $TiCl_3$. Recently, benzyl derivatives of Ti and

Zr have been shown to polymerize ethylene, propylene, 4-methyl-1-pentene, and butadiene.[195,196] In the presence of tribenzylaluminium[196] the activity of the benzyltitanium and zirconium catalysts is considerably increased.

It was pointed out in Chapter IV that some of the interest in the organo-compounds of Group IVA stems from their activity as catalysts in polymerization. We have briefly investigated the possibility of using the direct electrochemical technique to generate an organotitanium catalyst in a cell where the olefin under investigation forms one constituent of the solution phase. Consequently, with such a system polymerization could be directly initiated without isolating the organometallic catalyst produced in the reaction. Some of the experiments which have been conducted are described below. It is important to emphasize that considerable more work is required, and that the material presented here is only a preliminary report. Unfortunately, because of instrumentation restrictions the polymers obtained were not studied, but the promising results obtained suggest that this field would be an interesting subject for future studies.

Electrochemical Polymerization of Styrene

Titanium metal was electrolysed in a mixture of 20 cm^3 styrene, 20 cm^3 PhCl, 5 cm^3 MeCN, 10 cm^3 MeOH and 30 mg

Et_4NBr under 50 V and 100 mA. The colorless solution progressively became yellow, but no solid was deposited. At the end of the electrolysis (24 h), 26 mg Ti dissolved. The solution was treated with methanol to give a white sticky material which gradually solidified after the solvent had been decanted off. The proton NMR of this solid in methylethylketone showed in addition to the phenyl signal a distorted aliphatic multiplet at approximately 3.5 ppm. The NMR spectrum was almost identical to that of a sample of polystyrene in methylethylketone. Dr. K.G. Rutherford is thanked for providing this material.

No solid product was obtained when a similar mixture was electrolysed between two platinum electrodes under similar conditions, which demonstrates the importance of the titanium anode in the process.

Electrochemical Polymerization of Vinylacetate

Titanium was electrolysed in 10 cm^3 vinylacetate, 10 cm^3 MeOH, 10 cm^3 benzyl chloride, 0.7 g hexamethyleneamine and 30 mg Et_4NBr under 50 V and 60 mA. The green colour of the solution was progressively decolorized. After ~ 1 h the current suddenly jumped to 150 mA and the colour of the solution started to change to red. The electrolysis was terminated after 2.5 h and the solution left overnight under nitrogen. The next morning the whole solution phase had been converted to a red gum mass. This material was soluble in MeOH; addition of acetone converted it to a yellow powder. A sample of this material was dried in the oven for 2 h and then analysed for titanium and chloride (Found, 7.5% Ti, 15.8% Cl). Although it has been previously mentioned that no further study was conducted on these compounds, the appearance of the gummy material was taken to indicate the presence of polymeric species.

It appears that an organotitanium compound, which is most likely in a low oxidation state is produced in these electrochemical reactions (as shown in previous chapters). This species, in turn, initiates the polymerization. The two olefins used in this work demonstrate the possibility of using the direct electrochemical method for polymerization, and there seems to be considerable scope for further work in this field.

REFERENCES

1. B.L. Laube and C.D. Schmulbach, Prog. Inorg. Chem., 14, 65 (1971) and references cited therein.

2. H. Lehmkuhl, in 'Organic Electrochemistry', M.M. Baizer (ed), Marcel Dekker, New York, 1973, pp. 621-678.

3. W.J. Settineri and L.D. McKeever, in 'Technique of Electro-organic Synthesis', N.L. Weinberg (ed), Wiley-Interscience, New York, 1975, Part II, pp. 397, 558.

4. R. Schulten and B. Bergmann, Chem. Inorg. Tech. No. 4, 238 (1972).

5. G.A. Tedoradze, J. Organometal. Chem., 88, 1-36 (1975) and references cited therein.

6. J. Tafel and K. Schmitz, Z. Electrochem., 8 287 (1902).

7. J. Grimshaw and E. Rea, J. Chem., Soc., C, 2628 (1967).

8. T. Arai and T. Orgura, Bull. Chem. Soc. Jap., 33 1018 (1966).

9. L. Holleck and D. Marguarding, Naturswiss, 49, 468 (1962).

10. L.V. Kaabak and A.P. Tomilov, Zh. Obshch. Khim, 33, 2808 (1963).

11. S. Manahan, Inorg. Chem., 5, 2063 (1966).

12. H. Lehmkuhl, Synthesis, 377 (1973).

13. H. Lehmkuhl, W. Leuchte and E. Janssen, J. Organometal. Chem., 30, 407 (1971).

14. J. Grimshaw and J.S. Ramsey, J. Chem. Soc., (B), 60 (1968).

15. N. Hush and K.B. Oldham, J. Electroanal. Chem., 6, 34 (1963).

16. A. Kirmann and M. Kleine-peter, Bull. Soc. Chim., France, 894 (1957).

17. C.K. Mann, J.L. Webb and H.M. Walborsky, Tetrahedron Lett., 2249 (1966).

18. J.L. Webb, C.K. Mann and H.M. Walborsky, J.A.C.S., 92, 2042 (1970).

19. A.P. Tomilov, Yu.D. Smirnov and S.C. Varshavskii, Zh. Obshch. Khim., 35, 391, (1965).

20. I.N. Chernykh and A.P. Tomilov, Electrokhimiya, 10(6), 971 (1974) C.A. 81 (1974) 85209V.

21. D.G. Tuck, 6th Int. Conf. on non-aqueous solvents, (Waterloo, August 1978), to be published.

22. E.F. Silversmith and W.J. Sloan, U.S. Patent 3 197 392 (1965).

23. H.J. Ulery, J. Electrochem. Soc., 119, 1474 (1972).

24. H.J. Ulery, J. Electrochem. Soc., 120, 1493 (1973).

25. O.R. Brown, E.R. Gonzalez and A.R. Wright, Electrochem. Acta, 18, 369 (1973).

26. R. Galli, Chim. Ind. (Milan), 50, 977 (1968).

27. R. Galli, J. Electroanal. Chem. Interfacial Electrochem., 22, 75 (1969).

28. R. Galli and F. Olivani, J. Electroanal. Chem. Interfacial Electrochem., 25, 331 (1970).

29. J.A. Azoo, F.G. Coll and J. Grimshaw, J. Chem. Soc., (C) 2521 (1969).

30. R.E. Dessy, R. King and M. Waldrop, J.A.C.S., 88, 5112 (1966).

31. T. Psarras and R.E. Dessy, J.A.C.S. 88, 5132 (1966).

32. R.E. Dessy, W. Kitching and T. Chivers, J.A.C.S., 88, 453 (1966).

33. L.D. Gavrilova and S.I. Zhdanov, Coll. Czech. Chem. Commun., 32, 453 (1966).

34. R.E. Dessy, F.E. Stary, R.B. King and M. Waldrop, J.A.C.S., 88, 471 (1966).

35. W.A. Waters, 'The Chemistry of Free Radicals', Oxford, Clarendon Press, 1946.

36. Ch. Walling, 'Free Radicals in Solution', New York, Wiley, London, Chapman and Hall, 1957.

37. R. Benesch and R.E. Benesch, J.A.C.S., 73, 3391 (1951).

38. L.B. Rogers and A.I. Diefenderfer, J. Electrochem. Soc., 114, 942 (1967).

39. A.B. Ershler, A.I. Kashin, K.P. Butin and I.P. Beletskaya, Electrokhimiya, 7, 953 (1971).

40. H. Ulery, J. Electrochem. Soc., 116, 1201 (1969).

41. S. French and M. Drane, J.A.C.S., 56, 654 (1934).

42. W. Evans and F. Lee, J.A.C.S., 56, 654 (1934).

43. W. Evans and R. Pearson, J.A.C.S., 64, 2865 (1942).

44. F. Hein and F.A. Segitz, Z. Anorg. Allg. Chem., 158, 153, 159 (1926).

45. K. Ziegler and H.G. Gellert, Z. Anorg. Allg. Chem., 283, 414 (1956).

46. K. Ziegler, Brennst. Chemie, 40, 209 (1959).

47. R.C. Pinkerton, U.S. Patent 30 28 325 (1962) C.A., 57, 11234 d.

48. J.W. Ryznar and J.C. Premo, U.S. Patent 3 100 181 (1963); C.A., 57, 11234 d.

49. W.P. Hettinger, U.S. Patent 3 079 311 (1963); C.A. 57, 2859 f.

50. D.G. Braithwaite, U.S. Patent 3 079 57 (1961); C.A., 56, 3280 f.

51. J. Chadwick and E. Kinsella, J. Organometal. Chem., 4, 335 (1965).

52. E. Mottes and M. Ort, J. Electrochem. Soc., 117, 885 (1970).

53. S. Valcher and E. Alunni, Ric. Sci., 38, 527 (1968).

54. H. Lehmkuhl, W. Leuchte and W. Eisenbach, Ann. Chem., 692 (1973).

55. H. Lehmkuhl and W. Leuchte, J. Organometal. Chem. 23, C30 (1970).

56. J.J. Habeeb, A. Osman and D.G. Tuck, Chem. Commun., 696 (1976).

57. J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 146, 213 (1978).

58. J.J. Habeeb, A. Osman and D.G. Tuck, Unpublished results.

59. J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 134, 363 (1977).

60. J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 139, C17 (1977).

61. J.J. Habeeb, D.G. Tuck and F.H. Walters, J. Coord. Chem., 8, 27 (1978).

62. H. Lehmkuhl and W. Eisenbach, Justus. Liebig Ann. Chem., 672 (1975).

63. J.J. Habeeb and D.G. Tuck, Inorg. Syntheses, 19, 257 (1979).

64. J.J. Habeeb, L. Neilson and D.G. Tuck, Can. J. Chem., 55, 2631 (1977), and unpublished results.

65. J.J. Habeeb and D.G. Tuck, Inorg. Chem., 17, 306 (1978).

66. J.J. Habeeb and D.G. Tuck, Chem. Commun., 808 (1975).

67. J.J. Habeeb, L. Neilson and D.G. Tuck, Synth. Reac. Inorg. Metl. Org. Chem., 6, 105 (1976).

68. W. Evans, F. Lee and C. Lee, J.A.C.S., 57, 489 (1955).

69. K. Ziegler, H. Lehmkuhl and E. Lindner, Chem. Ber., 92, 2320, (1959).

70. L. Foster and G. Hooper, J.A.C.S., 57, 76 (1935).

71. V.O. Oakdale and J.J. Thompson, J.A.C.S., 52, 1195 (1931).

72. A.E. Van Arkel and J.H. de Boer, Z. Anorg. Und Allgem. Chem., 148, 345 (1925).

73. G. Von Hevesy, Chem. Rev. 2, 1 (1925).

74. G. Brauer, Handbook of Preparative Inorganic Chemistry, 2nd ed., Academic Press, New York (1965).

75. R.T. Allsop, Educ. Chem., 10, 222 (1973).

76. R.J.H. Clark, 'The Chemistry of Ti, Zr and Hf', D.C. Bradley and P. Thornton, (Pergamon Press, N.Y.) 1975.

77. R.J.H. Clark, In Comprehensive Inorganic Chemistry, Vol. 3, Pergamon Press, Oxford, England 1973.

78. J.C. Olsen and E.P. Ryan, J.A.C.S. 54, 2215 (1932).

79. R.F. Rolsten and H.H. Sisler, J.A.C.S. 79, 5891 (1957).

80. P.M. Druce, M.F. Lappert and P.N.K. Riley, Chem. Commun. 486 (1967).

81. J.H. Canterford and R. Colton, 'Halides of the Second and Third Row Transition Metals,' Wiley, London, 1968.

82. Y. Morino and H. Uehara, J. Chem. Phys., 45, 4543 (1966).

83. M. Lister and L.E. Sutton, Trans. Faraday Soc., 37, 393 (1941).

84. B. Krebs, Z. Anorg. Chem., 378, 263 (1970).

85. R.J.H. Clark and C.J. Willis, Inorg. Chem., 10, 1118 (1971).

86. R.J.H. Clark, 'The Chemistry of Titanium and Vanadium', Elsevier, Amsterdam (1968).

87. R. Feld and P. Cowe, 'In the Organic Chemistry of Titanium', London, Butterworths (1965).

88. C.E. Michelson, D.S. Dyer and R.O. Ragsdale, J. Chem. Soc., A, 2296 (1970).

89. T.S. West, 'Complexometry with EDTA and related reagents', BDH Chemicals Ltd., Poole, U.K., (1969).

90. Y. Kawano, Y. Hase and O. Sala, J. Mol. Struct., 30, 45 (1976) and references cited therein.

91. H.J. Emeleus and G.S. Rao, J. Chem. Soc., 4245 (1958).

92. R.J.H. Clark, J. Chem. Soc., 1377 (1963).

93. G.W.A. Fowles and R.A. Walton, J. Less Common Metals, 5, 510 (1963).

94. C.S. Creaser and J.A. Creighton, J.C.S. Dalton 1402 (1975).

95. J.A. Greighton and J.H.S. Green, J. Chem. Soc., A, 808 (1968).

96. A. Feltz, Z. Anorg. Chem., 21, 358 (1968).

97. W. Van Bronswyk, R.J.H. Clark and L. Maresca, Inorg. Chem., 8, 1395 (1969).

98. G.W.A. Fowles and B.J. Russ, J. Chem. Soc., A, 517 (1967).

99. P.C. Wailes, R.S.P. Coutts and H. Weigold, 'Organometallic Chemistry of Ti, Zr and Hf', Academic Press, N.Y., (1974) and references cited therein.

100. D.F. Herman and W.K. Nelson, J.A.C.S., 74, 2693 (1952).

101. D.F. Herman and W.K. Nelson, J.A.C.S., 75, 3877 (1953).

102. D.L. Kepert, 'The Early Transition Metals', Academic Press, N.Y., (1972).

103. 'Organozirconium Compounds' and 'Organohafnium Compounds' in Gmelin's hand book of Inorganic Chemistry, Verlag Chemie, Weinheim, (1974).

104. R.S.P. Coutt and P.C. Wailes, Adv. Organometal., Chem., 9, 135 (1970).

105. P.C. Wailes, J. Organometal. Chem., 126, 361 (1977).

106. F.L. Bowden, 'The Early Transition Metals, Part 1, Ti, Zr, Hf, V, Nb and Ta' Inorg. Chem. Trans. Chem., 4, 1, (1976).

107. F.L. Bowden, K. Grundy and B.E. Reichert, 'The Early Transition Metals, Part 1, Ti, Zr, Hf, V, Nb and Ta', Inorg. Chem. Trans. Chem., 5, 1 (1977).

108. R.R. Shrock and G.W. Parshall, Chem. Reviews, 76, No. 2 (1976).

109. K. Clauss and C. Beermann, Angew. Chem., 71, 627 (1959).

110. H.J. Berthold and G. Groh, Angew. Chem., 78, 495 (1966).

111. C. Beerman and H. Bestian, Angew. Chem., 71, 618 (1959).

112. R.J.H. Clark and M.A. Coles, Inorg. Synth., 16, 120 (1976).

113. R.J.H. Clark and A.J. McAlees, Inorg. Chem., 11, 342 (1972).

114. K.H. Thiele, P. Zdunneck and D. Baumgart, Z. Anorg. Allg. Chem., 62, 378 (1970).

115. G.W.A. Fowles, D.A. Rice and J.D. Wilkins, J. Chem. Soc., A, 1920 (1971).

116. K.H. Thiele, Pure Appl. Chem., 30., 575 (1972).

117. H.J. Berthold and G. Groh, Z. Anorg. Allg. Chem., 319, 230 (1963).

118. V.N. Latyaeva, G.A. Razuvaev, A.V. Molysheva and G.A. Kiyakova, J. Organometal. Chem., 2, 388 (1964).

119. G.A. Razuvaev, V.N. Latyaeva, L.I. Vishinskaya and A.M. Rabinovitch, J. Organometal. Chem., 49, 441 (1973).

120. R. Tabacchi and A. Jacot. Guillarmod, Chimica, 24, 271 (1970).

121. V.N. Latyaeva, A.N. Lineva, E.N. Shatalin and G.A. Razuvaev, Zh. Obshch. Khim, 46(4), 931 (1976).

122. J.F. Clarke, G.W.A. Fowles and D.A. Rice, J. Organometal. Chem., 76, 349 (1974).

123. U. Giannini and U. Zucchini, Chem. Commun., 940 (1968).

124. U. Zucchini, E. Albizzati and U. Giannini, J. Organometal. Chem., 26, 357 (1971).

125. J.J. Felten and W.P. Anderson, J. Organometal. Chem. 82, 375 (1974).

126. A. Adunneck and K.H. Thiele, J. Organometal. Chem., 22, 659 (1970).

127. J. F. Clarke, G.W.A. Fowles and D.A. Rice, J. Organometal. Chem., 74, 417 (1974).

128. K.H. Thiele, E. Kohlier and B. Alder, J. Organometal, Chem., 50, 153 (1973).

129. A.F. Berniaz, Ph.D. Dissertation, Simon Fraser University (1973).

130. R.J.H. Clark and A.J. McAllees, J. Chem. Soc. (A), 2026 (1970).

131. C. Floriani and G. Fachinetti, J. Chem. Soc., Chem. Commun., 790 (1972).

132. T. Chivers and F.D. Ibrahim, Can. J. Chem. 51, 815 (1973).

133. S.P. Gubin and S.A. Smirnova, J. Organomet. Chem., 20, 229 (1969); ibid 20, 241 (1969).

134. A.P. Gray, A.B. Callear and F.H.C. Edgecombe, Can. J. Chem., 41, 1502 (1963).

135. A.J. Carty and D.G. Tuck, J. Chem. Soc., (A), 1081 (1966).

136. N.N. Greenwood, D.J. Prince and B.P. Straughan, J. Chem. Soc., (A), 1694 (1968).

137. A.J. Carty, Coord. Chem. Rev., 4, 29 (1969).

138. A.J. Carty and D.G. Tuck, Prog. Inorg. Chem., 19, 245 (1975).

139. B.F.G. Johnson and R.A. Walton, Inorg. Chem., 5, 49 (1966).

140. T.N. Srivastava and G. Mohan, J. Inorg. Nucl. Chem., 32, 2808 (1970).

141. O.A. Osipov and I.M. Semenova, Zh. Obschch. Khim., 34, 2702 (1964).

142. D.H. Brown and D.J. Stewart, J. Inorg. Nucl. Chem., 32, 3751 (1970).

143. R.A. Walton, J. Chem. Soc., (A), 61 (1969).

144. A.J. Carty, T. Hinsberger and P.M. Boorman, Can. J. Chem., 48, 1959 (1970).

145. I.R. Beattie, T. Gilson and G.A. Ozin, J. Chem. Soc., (A), 1092 (1968).

146. D.M. Adams, A.J. Carty, P. Carty and D.G. Tuck, J. Chem. Soc., (A), 162 (1968).

147. M.V. Veidis and G.J. Palenik, Chem. Commun., 586 (1969).

148. N.N. Greenwood and D.J. Prince, J. Chem. Soc., (A), 2876 (1969).

149. J.J. Habeeb, F.F. Said and D.G. Tuck, Can. J. Chem., 55, 3883 (1977).

150. A. Pidcock, M.T.P. Int. Rev. of Science, Vol. I (M.F. Lappert ed) series 2, 1974, p. 281.

151. J. Reedijk and W.L. Groenveld, Rec. Trav. Chim., 87, 552 (1968).

152. D.M. Adams, Metal-Ligand and Related Vibrations, Arnold, London, 1967, p. 100.

153. J. Gislason, M.H. Lloyd and D.G. Tuck, Inorg. Chem., 10, 1907 (1971).

154. F.W.B. Einstein and D.G. Tuck, Chem. Commun., 1182 (1970).

155. W.J. Geary, Coord. Chem. Revs., 7, 81 (1971).

156. K. Wade and A.J. Banister, in Comprehensive Inorganic Chemistry. Vol. I Pergamon Press, Oxford, England 1973.

157. T. Tanaka, J. Organometal. Chem., 147, 183 (1978).

158. T. Tanaka, J. Organometal. Chem., 130, 345 (1977).

159. R. Okawara, J. Organometal. Chem., 98, 445 (1975).

160. H.C. Clark and A.L. Pickard, J. Organometal. Chem., 8, 427 (1967).

161. E. Todt and R. Dotzer, Z. Anorg. Chem., 321, 120 (1963).

162. J.J. Eisch. J.A.C.S., 84, 3605 (1962).

163. H. Gilman and R. Jones, J.A.C.S., 62, 2353 (1940).

164. J.S. Poland and D.G. Tuck, J. Organometal. Chem., 42, 307 (1972).

165. H.C. Clark and A.L. Pickard, J. Organometal. Chem., 13, 61 (1968).

166. K. Yasuda and R. Okawara, Inorg. Nucl. Chem. Lett., 3, 135 (1967).

167. A. Victorova, Dokl. Akad. Nauk., SSR., 177, 103 (1967).

168. W. Schumb and H. Crane, J.A.C.S., 60, 306 (1938).

169. L. Chao and R.D. Rieke, Synth. Reac. Inorg. Met. - Org. Chem., 5, 165 (1975).

170. S.B. Miller, B.L. Jelus and T.B. Brill, J. Organometal. Chem., 96, 1 (1975).

171. J. Pohlmann and F. Brinkmann, Z. Naturforsch., 5, 206 (1965).

172. J.S. Poland and D.G. Tuck, J. Organometal. Chem., 42, 315, (1972).

173. L. Waterworth and I.J. Worrall, Chem. Commun., 569 (1971).

174. M.J.S. Gynane, L.J. Waterworth and I.J. Worrall, J. Organometal. Chem., 40, C9 (1972).

175. M.J.S. Gynane, L.G. Waterworth and I.J. Worrall, J. Organometal. Chem., 43, 357 (1972).

176. G.B. Deacon and J.C. Parrott, Aust. J. Chem., 27, 2547 (1974).

177. J.B. Farmer and K. Wade, Intern. Rev. Sci., Inorg. Chem. Series, 1, 4, 105 (1972).

178. H.J. Wilder, H.D. Hausen and J. Weidlein, Z. Naturforsch., 30B, 645 (1975).

179. M.J.S. Gynane, L.G. Waterworth and I.J. Worrall, Inorg. Nucl. Chem. Lett., 9, 543 (1973).

180. L.G. Waterworth and I.J. Worrall, J. Organometal. Chem., 81, 23 (1974).

181. E.O. Fischer and H.P. Hofmann, Angew. Chem., 69, 639 (1957).

182. D.H. Brown, R.H. Nuttall, J. Meavoy and D.W.A. Sharp, J. Chem. Soc. (A), 892 (1966).

183. D.S. Brown, J.D. Lee and B.G.A. Melsom Chem. Commun., 852 (1968).

184. N.T. Barker, C.M. Harris and E.D. McKenzie, Proc. Chem. Soc. 335 (1961).

185. S. Buffagni, L.M. Vallarino and J.V. Quagliano, Inorg. Chem., 3, 671 (1964); ibid. 4, 1598 (1965).

186. D.S. Brown, J.D. Lee and B.G.A. Melsom, Acta Cryst., B24, 730 (1968).

187. F.A. Cotton and R. Francis, J.A.C.S., 82, 2986 (1960).

188. F.A. Cotton, R. Francis and W.D. Horrocks, J. Phys. Chem., 64, 1534 (1960).

189. R.S. Drago and D. Meck, J. Phys. Chem., 65, 1446 (1961).

190. O. Christofis, J.J. Habeeb, R.S. Steevensz and D.G. Tuck, Can. J. Chem., 56, 2269 (1978).

191. B.J. Hathaway and A.E. Underhill, J. Chem. Soc., 3091 (1961).

192. J. Boor, Macromol. Rev., 2, 115 (1967).

193. J.C.W. Chein, J. Catal. 23, 71 (1971).

194. E.H. Adema, J. Polym. Sci., Part C16, 3643 (1968).

195. L G. Cannell, J.A.C.S., 94, 6867 (1972).

196. U. Giannini, U. Zucchini and E. Albizzati, J. Polym. Sci., Part B8, 405 (1970).

VITA AUCTORIS

Born: September 16, 1944, Nables, West Bank of Jordan.

University Education:

1963-1967: Baghdad University, Baghdad, Iraq.

1967: Received B.Sc. in chemistry.

1969-1970: University of Newcastle Upon Tyne, England.

1970: Received M.Sc. in Radiation Chemistry.

Awards and Scholarships:

1969: The British Council Scholarship.

1975-1976: University of Windsor Scholarship.

1977-1978: The Indium Coorporation of America Research Assistantship.

Publications:

Pulse Radiolysis of Some Gaseous Systems, M.Sc. Thesis, University of Newcastle Upon Tyne 1970.

Direct Electrochemical Synthesis of Neutral and Anionic Chloro- and Bromo-Complexes of Titanium, Zirconium and Hafnium, Can. J. Chem., 55, 3882 (1977).

The Direct Electrochemical Synthesis of Cationic Complexes of Metal Ions, Inorg. Nucl. Chem. Lett., 15, 113 (1979).

Neutral Complexes of Indium Trihalides, submitted for publication.

Neutral and Anionic Organoindiumhalide Complexes. In preparation for submission.

Neutral Organo-Titanium, Zirconium and Hafnium Halide Complexes, in preparation for submission.

Marital Status: Wife, Layla Najib Khasrou.