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Electrochemical synthesis in non-aqueous media.

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NL-339 (3/77)

ELECTROCHEMICAL SYNTHESIS IN NON-AQUEOUS MEDIA

by

Samuel Zhandire

A Thesis
submitted to the Faculty of Graduate Studies
through the Department of
Chemistry in Partial Fulfillment
of the requirements for the Degree
of Master of Science at
The University of Windsor

Windsor, Ontario, Canada

1978

DEDICATION

To Makaibe and Lynn

ABSTRACT

A review of electrochemical syntheses involving both sacrificial and inert electrodes is presented. In particular, the electrochemical syntheses of alkyl metal compounds of both main group and transition metals in non-aqueous solution is discussed. Some of the more established methods for the synthesis of heteronuclear metal carbonyls are also reviewed.

In the present work, the direct electrochemical synthesis of polynuclear metal carbonyls of the type $LM[M'(CO)_n]_m$ $[M' = Co$ (n = 4), $M' = Mn$ (n = 5), M = Zn or Cd (m = 2) and M = In (m = 3) L = 2,2'-bipyridyl (bipy) or N,N,N',N'-tetramethylethylenediamine (TMED) has been achieved by the electrolysis of the carbonyls $Mn_2(CO_{10}$ and $Co_2(CO)_8$ in benzene/methanol solution in the presence of small amounts of Et_4NClO_4. The sacrificial anode was made of the appropriate metal M, the cathode was platinum and all reactions were carried out in a nitrogen atmosphere. The experiments involving the use of a tin anode did not yield the expected products.

Current efficiency measurements were made for a few of the systems studied and a mechanism has been proposed for the formation of the complexes prepared.

Field ionisation (FI) and field desorption (FD) mass spectral studies have been carried out for the compounds synthesized. The advantages of these two techniques over the more widely used electron impact (EI) technique are also discussed. Molecular ion peaks are observed for a majority of the compounds at considerably higher relative abundances than in the corresponding EI studies.

The advantages of the electrochemical methods in the synthesis of heteronuclear polymetallic carbonyls are presented.

Attempts to effect the coupling of 2-and 3-bromopyridines electro-

chemically were unsuccessful. However, coupling occurs with 4-bromo and 4-chloropyridine hydrochloride to form the 4,4-bipyridyl dihydrohalides.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge with thanks the guidance and encouragement given by my adviser, Dr. D.G. Tuck and all the members of his research group.

I would also like to thank Mr. R. Charleton for the technical assistance in running the mass spectra, Miss Anne Matthewman for typing the first draft and Miss Cavelle Walwyn for typing the final draft.

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LIST OF ABBREVIATIONS

acac	Acetylacetonate
bipy	2,2'-bipyridyl
nBu	n butyl
tBu	t butyl
CDT	1,5,9-cyclodecatriene
COD	1,5-cyclooctadiene
COT	cyclooctatetraene
DGDB	diethyleneglycol dibutyl ether
DMF	dimethylformamide
DMSO	dimethylsulphoxide
e.g.	for example
Et	ethyl
m/e	mass to charge ratio
Me	methyl
mA	milli Ampere
OAc	acetate
Phen	1,10-phenanthroline
Ph	phenyl
γ-pic	picoline
nPr	n propyl
py	pyridine
%RA	percent relative abundance
THF	tetrahydrofuran
TMED	N,N,N,N-tetramethylethylenediamine
V	volts

CHAPTER I

A LITERATURE SURVEY: ELECTROCHEMICAL OXIDATION REACTIONS IN SYNTHESIS

1.1. General Remarks:

Electrolytic techniques have been used for the synthesis and analysis of aqueous and nonaqueous organic and inorganic systems for many years.

Electron transfer between reactant A and substrate F or G are reductions or oxidations:

$$A + F \longrightarrow A^{+} + F^{-}$$

OR

$$A + G \longrightarrow A^{-} + G^{+}$$

The oxidation of a substrate signifies the reduction of the reactant and oxidation of the reactant signifies the reduction of the latter. Kinetic restraints resulting from high activation energies sometimes make it impossible for the direct reaction of components to form the products. However, electrochemically induced, the reactions may occur quite readily.

A complete electrochemical system generally consists of a voltage source, a cathode, an anode and the electrolyte solution. The anode and cathode can be of the inert type or the active type. In the latter type the anode or cathode is dissolved by passage of a current. This review will concentrate mainly on the work involving active anodes and inert cathodes and a nonaqueous solution phase.

The efficient operation of any electrochemical system places certain demands on the solvent and electrolyte combination to be employed in the synthesis. Thus the combination(s) selected must meet the following requirements: the solvent -electrolyte combination must be sufficiently inert towards starting and end products; be more resistant to reduction (or oxidation) than the starting reagents, be so selected that the separation of products is possible after electrolysis, and form systems of sufficient electrical conductivity.

In keeping with the above restrictions, the following solvents and electrolytes have found very wide applications: acetonitrile, methanol, ethyleneglycol dibutyl ether, tetrahydrofuran (THF), pyridine, ethanol dichloromethane and R_4NX (R = alkyl and X = Cl, Br, I, ClO_4, PF_6 or BF_4)or MX (M = Li, K or Na; X = Cl, Br, I or ClO_4,) as supporting electrolytes.

1.2 Electrochemical Synthesis of Main Group Compounds:

The electrolytic preparation of tetraalkyllead compound has been a subject of considerable interest in the past two decades due to the economic importance of these compounds as fuel anti-knock additives. In 1930, work done by French and Drane[1] has shown that anodes of aluminium, zinc, and cadmium could be dissolved by electrolysis in ether solutions of isopentyl magnesium chloride to yield the alkylmetal compounds of the respective anode metals. The use of Grignard reagents in the preparation of alkylmetals showed that they were electroactive at both sacrificial and inert electrodes in nonaqueous soloution. A direct result of this was the use of Grignard reagents in the synthesis of tetraalkyllead compounds involving the use of a sacrificial lead anode and an inert cathode in ether solutions.

The overall reaction is now believed to involve the following steps:[2]

Pb anode

$$4R^- + Pb \longrightarrow R_4Pb + 4e^-$$

Steel cathode:

$$4MgX^+ + 4\ 3 \longrightarrow 2Mg + 2MgX_2$$

Overall:

$$4R^- + Pb + 4MgX^+ \longrightarrow R_4Pb + 2Mg + 2MgX_2$$

(X = Cl or Br and R is alkyl or aryl radical).

The Nalco Chemical Company, and others in a series of investigations[3-16] has varied conditions like cell design, proper concentration ratios of Grignard reagent and excess alkyl halide, temperature, pressure and electrolyte flow rate to evolve a system capable of yields of alkyllead compounds up to 96%. Solvents generally used are mixtures of ethers, tetrahydrofuran, diethyleneglycol and butyl ether. Braithwaite et al have also found that replacing the lead anode with lanthanum, thallium and bismuth[5] and zinc, cadmium and aluminium[17] yields the alkyls of these metals. In another series of investigations,[18-19] the same author has reported that excess alkyl halide is not necessary for the synthesis of tetraalkyllead compounds although the magnesium metal deposited at the cathode must then be recovered by alternative method. Mixed tetraalkyllead compounds have also been prepared electrochemically from Grignard reagents in the presence of an excess alkyl (aryl) halide whose alkyl (aryl) group differed from that of the original reagent.[17,20,21]. For example, $Et_2Pb(Me)_2$ and $tBuPbMe_3$ were obtained by electrolysing

RX and RMgX in THF and diethyleneglycol dibutyl ether (DGDB) using a lead anode. Triaklyaluminium and trialkylborons are suitable substitutes for the alkyl halides in these syntheses.[22] Mixtures of trimethylvinyllead, dimethyldivinyllead and tetramethyllead as well as methyltrivinyllead have been synthesized by the electrolysis of vinyl magnesium chloride, trimethylboron and trimethylaluminium in THF-elthyeneglycol monoether. Similar results were obtained with dimethylmethoxyaluminium, triphenylaluminnim and triphenoxyaluminium employing a steel cathode and a lead anode.

Schuler and Kegelmann[23] have prepared R_4Pb compounds by electrolysing RX (R = Et, Me, iPr, tBu and X = Br) in acetonitrile and water. Falling yields of R_4Pb in going from R = Me to tBu are reported. Species of the type Pb_2Et_6 were the major products when ethyl bromide was used.

Using a lead anode and a platinum cathode, Giraitis [24] has reported the synthesis of tetraalkyllead by the electrolysis of metal alkyls, eg. Et_2Sn and Et_3Al in ether. In a solution phase consisting of acetonitrile and sodium tetramethylaluminate, electrolysis yields $(Me)_4Pb$ when a lead anode and a mercury cathode are employed.[25] The synthesis of terraethyllead in triethylaluminium at lead electrodes requires no supporting electrolyte.[26]

Tin, antimony, mercury and lead alkyls have been prepared by the electrolysis of mixed alkali alkylalkoxyborates or alkali alkoxyaluminates in THF at a mercury cathode and anode of the metal whose alkyl is sought,[27] with yields ranging from 90% for Et_4Pb to 10% for Et_4Sn.

Yields of dibutyltin[28] dibromide of up to 100% have been attained in a system consisting of butyl bromide, bromine or $ZnBr_2$ in butyl acetate and employing a sacrificial tin anode and magnesium cathode. If the solvent was changed to methanol, butyl alcohol, ethyl acetate or i-butyl acetate and mixtures thereof, the only tin compound isolated was tributyltin bromide. Other reports[29] suggest that some alkyltin halides are formed in these esters and their alcohol mixtures by anodic oxidation of tin in the presence of an alkyl halide, zinc bromide or bromine.

Armenskaya[30] <u>et al</u> have synthesized a variety of alkyltin compounds by the electrolysis of alkyl halide, tin salt, zinc bromide or bromine using a zinc anode and a magnesium cathode. More recently, Tuck and Habeeb[31] have reported the direct electrochemical synthesis of compounds of the type R_2SnX_2, R_4Sn, R_6Sn_2, $R_2SnX_2 2L$ and R_2SnX_2L (R = Et, Me, Ph or ^{n}Bu and X = I, Br, or Cl and L = CH_3CN or DMSO and L = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) or 1,2-bis(diphenylphosphino)ethane. The preparation of R_2SnX_2 was achieved by electrolysis of a mixture of the alkyl halide, methanol/benzene and small amounts of tetraethylammonium perchlorate using a platinum cathode and a tin anode. The adducts were prepared by addition of the appropriate ligand to the electrolyte mixture. By alternately connecting the tin and cadmium electrodes the electrolysis resulted in the formation of R_4Sn.

$$4CH_3I + Sn + 2Cd \longrightarrow Sn(CH_3)_4 + 2CdI_2$$

The same product was obtained when R_2SnX_2 was electrolysed in methanol/benzene mixture, ie:

$$2R_2SnI_2 + 2Cd \longrightarrow SnR_4 + 2CdI_2 + Sn$$

Hexaphenyl and hexamethylditinwere synthesized by halogen abstraction from the compounds Ph_3SnBr and Me_3SnCl respectively by cadmium in benzene/acetone mixture. One mechanism of the formation of the R_2SnX_2 compound is believed to involve the steps:

Cathode:

$$RX + e^- \longrightarrow R^\bullet + X^-$$

Anode:

$$X^- \longrightarrow X^\bullet + e^-$$

$$X^\bullet + Sn \longrightarrow SnX$$

$$SnX + RX \longrightarrow RSnX + X^\bullet$$

$$\text{and } RSnX + RX \longrightarrow R_2SnX_2$$

The current efficiencies measured can only be explained in terms of an electrochemical-chemical process as above.

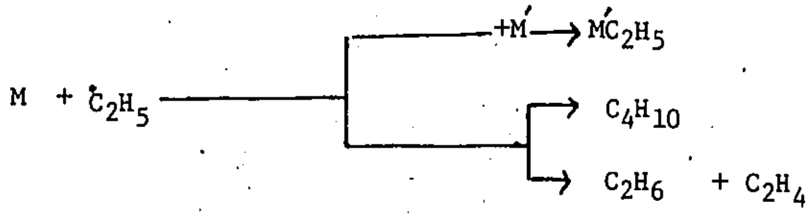
Compounds of the type RMX (R = alkyl or aryl, M = Cd, Zn or Hg and X = I, Br or Cl) are unstable. Tuck <u>et al</u> [32] have been able to prepare these compounds and stabilize them with neutral ligands. Electrolysis of mixtures of alkyl halides RX ligands, eg. bipy, phen, and dioxane in acetonitrile/benzene in the presence of small amounts of tetraetylammonium perchlorate have yielded reasonably stable compounds of the type RCdX L (R = Me, Ph, Et, n bu and L = dioxan, bipy or phen) and RZnX bipy[33] (R = Et, C_6F_5, CF_3, C_6H_5 or $C_6H_5CH_2$ and X = Br, I or Cl). If an equivalent amount of nPr_4NX is added to the reaction mixture, compounds of the type $[nPr_4N][RMX_2]$ [32-33] (X = Br or I and R = Me or Et for M = Cd, and X = I or Br and R = Et, C_6H_5, CF_3 or CH_2= CH_2 for M = Zn) are obtained. The N,N,N′,N′-tetramethylethylenediamine adducts of the compounds $(C_6H_5)_3SnMCl$[33] have also been prepared by electrolysis of $(C_6H_5)_3SnCl$ in acetonitrile/benzene mixtures using Et_4NClO_4 as the supporting electrolyte, cadmium or zinc anodes, and a platinum cathode. Thus:

$$(C_6H_5)_3SnCl + M + TMED \longrightarrow (C_6H_5)_3SnMCl(TMED)$$

(M = Zn or Cd)

The anodic oxidation of metal complexes containing carbanions is a widely used method for the preparation of organometallic compounds. The technique is based on observations that solutions of alkali metals and dialkylzinc or trialkylaluminium produce alkyl radicals on anodic oxidation. These radicals dissolve the metal anode in the form of its alkylmetal compound. With metals which do not form stable alkyl compounds, disproportionation or dimerisation of products occurs, eg:

$$M{-}C_2H_5 \xrightarrow{e^-} M^+ + \dot{C}_2H_5$$



(M = Na, Li(K) 1/3 Al, 1/2 Mg and M′ = 1/2 Zn, 1/2 Cd, 1/2 Hg, 1/3 Ga, 1/3 Al, 1/3 In, 1/4 Sn, 1/4 Pb, 1/3 Sb, 1/3 Bi)

Dimerisation of the organometallic radicals generated electrochemically can lead to metal-metal bond formation. Thus:

$$2R_nMX + 2e^- \longrightarrow 2R_nM \longrightarrow R_nM{-}MR_n$$

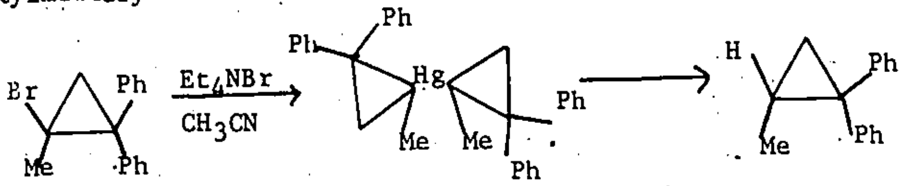
(M = Pb, R = C_2H_5, n = 3 and X = OH)
(M = As, R = C_6H_5, n = 2 and X = Br)
(M = Sn, R = alkyl or aryl, n = 3 and X = halogen)

The electrolysis of 3-iodopropionitrile in 0.5M H_2SO_4 or aqueous sodium sulphate with a tin, lead or mercury anode leads to reactions of the type:

$$I{-}CH_2CH_2{-}CN + e^- + M \xrightarrow[-I]{} M{-}CH_2CH_2CN$$[36]

(M = 1/4 Sn, 1/4 Pb or 1/2 Hg)

1-methyl-2,2-diphenylcyclopropane has been synthesized by electrolysing 1-bromo-1-methyl-2,2-diphenylcyclopropane in acetonitrile with Et_4NBr as supporting electrolyte between mercury electrodes. The dialkylmercury is the intermediate and not the alkylmercury halide.[37] Thus:



The mechanism proposed for this reaction goes through the steps:

$$R—Br + e^- \longrightarrow [R^\bullet—Br]^-$$
$$[R^\bullet—Br]^- \longrightarrow R^\bullet + Br^-$$
$$R^\bullet + e^- \longrightarrow R^-$$
$$R^\bullet + Hg \longrightarrow RHg_n^\bullet$$
$$RHg_n + e^- \longrightarrow R^- + Hg_n$$
$$RHg_n^\bullet + RHg_n^\bullet \longrightarrow RHg_nR \longrightarrow Hg_{n-1} + RHgR$$
$$R_2Hg + e^- \longrightarrow R^- \; Hg \xrightarrow[Hg]{} RHg_n^\bullet$$
$$R^- + Et_4NBr \longrightarrow RH + CH_2=CH_2 + Et_3N + Br^-$$

Hush and Oldham[38] have studied the electrolysis of alkyl halides in Et_4NI and have reported that hydrocarbons are formed in these reactions. However, they suggest that the proton needed to form the hydrocarbon is removed from the solvent (water-alcohol). Both processes[37-38] were shown to involve two electrons per molecule reacted from the current integration.

Methylenebis-(aluminiumdichloride) has been synthesized electrochemically[39] although the reaction is not a straightforward electrochemical but electrochemical-chemical. The reaction takes place on electrolysing a dichloromethane solution containing $AlCl_3$ or

Et_4NCl as supporting electrolyte. The aluminium anode is consumed during the electrolysis. 1 mole of Al anode is consumed per Faraday - a clear indication that the reaction is not purely electrochemical. The mechanism proposed involves the following sequence:

Cathode:

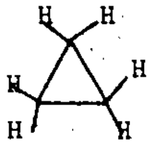
$$CH_2Cl_2 + e^- \longrightarrow Cl^- + ClCH_2^{\bullet}$$

$$CH_2Cl_2 + 2e^- \longrightarrow 2Cl^- + CH_2{:}$$

The first equation however is improbable since dimerisation to form Cl CH_2CH_2Cl would be expected.

$$2CH_2{:} \longrightarrow CH_2{=}CH_2$$

$$CH_2{=}CH_2 + CH_2{:} \longrightarrow$$



$$CH_2{:} + CH_2Cl_2 \longrightarrow ClCH_2CH_2Cl$$

Anode:

$$Cl^- \longrightarrow e^- + Cl^{\bullet}$$

$$Al + Cl^{\bullet} \longrightarrow AlCl$$

$$Al + CH_2Cl_2 \longrightarrow Cl_2AlCH_2Cl$$

$$AlCl + Cl_2AlCH_2Cl \longrightarrow Cl_2AlCH_2Cl$$

$$AlCl + Cl_2AlCH_2Cl \longrightarrow Cl_2AlCH_2AlCl_2$$

Anionic and neutral organoindium compounds [40] have been prepared by the electrolysis of alkyl or aryl halides in acetonitrile. The neutral complexes $RInX_2$ bipy (R = Et, Ph or benzyl, X= I, Br or Cl) were prepared in the presence of small amounts of R_4NX and in at least one case, the reaction gives the same products whether indium is the anode or cathode. The anionic complexes $[R_4N][RInX_3]$, $[Bu_4N][Me_2InI_2]$

(R = Et, iBu, R = Me, Et or Ph and X = I, Br or Cl) have been synthesized under essentially the same conditions as for the neutral species except in this case excess R_4NX is present in the electrolysis mixture.

1.3 Electrochemical Synthesis of Transition-metal Compounds

Organometallic compounds of the transition-metals are of great technical and preparative interest because of their ever-increasing use as active catalysts for the conversion of unsaturated organic compounds by hydrogenation, isomerisation, dimerisation, oligomerisation, polymerisation and hydroformylation. Some of these compounds have the ability to complex hydrogen, oxygen or nitrogen and thus bring these into an active form. This may have a special significance in nitrogen fixation. Applying an electrochemical method, Manahan[41] synthesized the metal-olefin complex bis(1,5-cyclooctadiene)-copper(I) perchlorate: Thus:

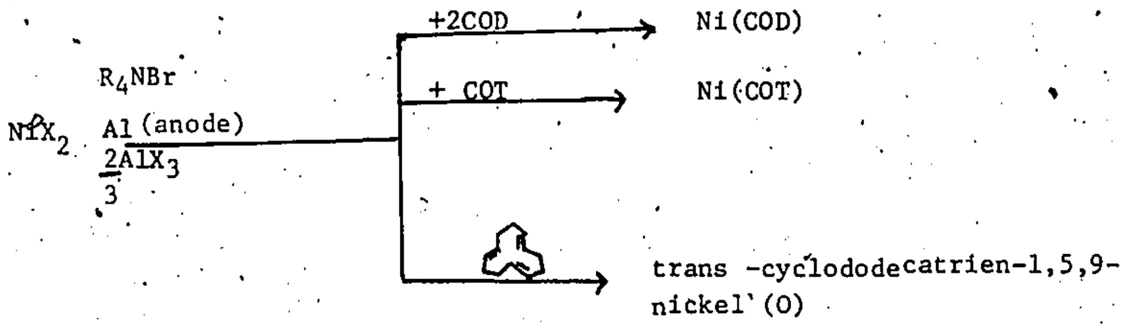
$$\mathrm{COD} + \mathrm{Cu(ClO_4)_2} \xrightarrow[\mathrm{Cu}_-]{\mathrm{Cu}_+} \text{bis (1,5-cyclooctadiene)-copper(I) perchlorate}$$

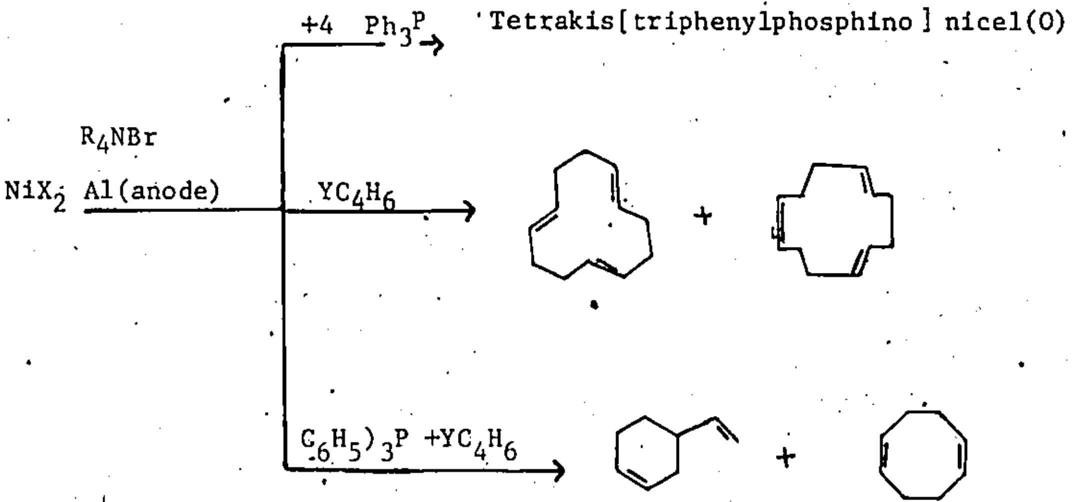
Most syntheses of organotransition-metal compounds have used a modification of this basic procedure.[42]

In general then, the anode material is the metal of the desired organometallic product and the solution phase contains the cycloolefins. Thus:

$$\mathrm{M(anode)} + \mathrm{L} \xrightarrow{\text{electrolysis}} \mathrm{M{-}L}$$

Some of the compounds prepared by Lehmkuhl[42] are shown in the following diagrams:





The synthesis of Ni(COT) by electrolysis of cyclooctatetraene-(COT) in dimethylformamide (DMF) or pyridine /THF at a nickel anode has also been reported.[43] The synthesis of Ni(COD) can be represented as follows if Ni anode is used:

$$Ni(acac)_2 + 2\bar{e} \longrightarrow Ni + 2(acac)^-$$

$$\begin{tikzcd} & \text{Ni(Lattice) deposited at cathode} \\ \text{Ni(0)} \arrow[ur] \arrow[r, "2COD"] & \text{Ni(COD)}_2 \end{tikzcd}$$

COD = 1,5cyclooctadiene, (acac) = acetylacetonate

If the organometallic complexes formed by cathodic reduction are more readily oxidizable than the metal itself then the reaction may be reversed by anodic oxidation. In cases like this diaphrams have been used to prevent mixing of the products. Alternatively one could use a more electropositive metal as an auxilliary anode, eg:

$$3Ni(acac)_2 + 6COD + 2Al(anode) \longrightarrow 3Ni(COD)_2 + Al(acac)_3$$

$$3Ni(acac)_2 + 3CDT + Al(anode) \longrightarrow 3Ni(CDT) + Al(acac)_3$$

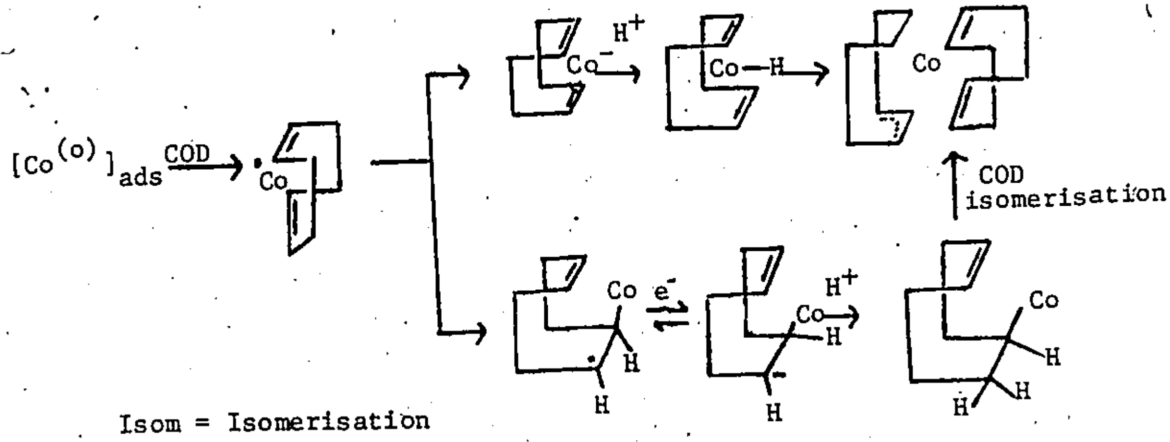
and

$$Fe(acac) + 2COT + Al(anode) \longrightarrow Fe(COT)_2 + Al(acac)_3$$

(CDT = 1,5,9 -cyclododecatriene)

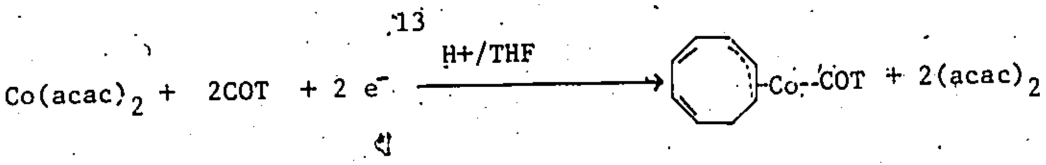
Earlier attempts to prepare π-cycloctenylcobaltcyclooctadiene electrochemically failed because the compound was readily oxidised at the aluminium anode in the presence of 1,5-cyclooctadiene. This has been overcome with the use of proton donor solvents, eg. methanol and ethanol, which stabilize the cobalt anions shown below:

$$Co(acac)_2 \xrightarrow{2e^-,\text{Cathode}} [Co^{(o)}]ads + 2(acac)^-$$

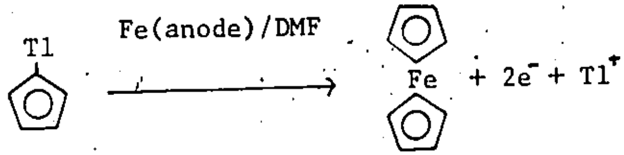


Isom = Isomerisation

π -cyclooctatrienylcobaltcyclooctateraene can also be synthesized in a similar manner. Thus:



Ferrocene has been synthesized by the electrolysis of cyclopentadienylthallium in DMF at an iron anode:



In general, cyclopentadienyl compounds of alkali metals can be electrolysed to form the cyclopentadienyl-transition-metal complexes.[46]

Organometallic catalysts have been prepared <u>in situ</u> for the polymerisation of ethylene to form polyethylene, butadiene to form polybutadiene,[47] 1,3,7-octatriene,[48] 1,5-cyclooctadiene,[42] alkynes to form polyalkynes[49] and a host of other reactions. The commonest solvents for these electrochemical syntheses include methanol, acetonitrile, ethanol, pyridine and THF. The supporting electrolytes are usually the tetraalkylammonium halides.

Organometallic nickel and palladium complexes[50] of the type RNiX.2L ($R = C_6F_5$, $L = Et_3P$, diphos or pyridine) have been prepared electrochemically in 1:1 mixtures of ethanol/pentafluorobromobenzene or RCN and Et_4NBr.

The electrochemical oxidation of the metals titanium, zirconium, and hafnium has been successfully applied in the synthesis of the transition-metal halides and their adducts.[51] With a platinum cathode and an anode of the appropriate metal M the halides MX_4L_2 (M = Ti, Hf or Zr, X = Br or Cl and L_2 = bipy or phen) have been synthesized. In the presence of tetraalkylammonium salts, the salts R_4NMCl_5, $(R_4N)_2MBr_6$ and R_4NTiBr_4 (R = Et and M = Ti, Hf or Zr) could also be prepared.

The solution phase consisted of acetonitrile and the halogen for neutral complexes or SO_2Cl_2:Cl_2 for anionic chlorine complexes or benzene/Br_2 for the bromine complexes.

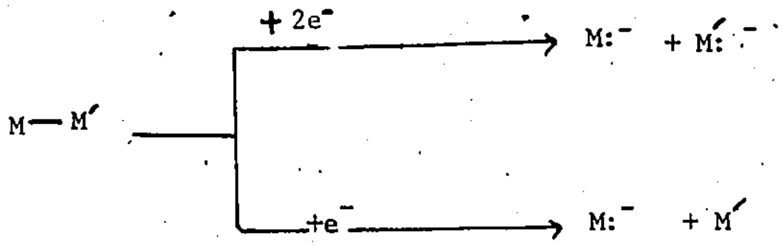
In another extension of their work on electrochemical oxidation of metals, Tuck and Said have synthesized the complexes R_2MX_2.bipy[52] (R = benzyl or ethyl, X = Cl or Br and M = Ti, Hf or Zr) and $R_2MX_2 2CH_3CN$[52] (R = Ph or Et and X = Cl or Br) by carrying out the electrolyses in the presence of the alkyl or aryl halide RX.

Steevensz and Tuck[53] have used an electrochemical method to generate Ti(III) species which then reduce sulfoxides to sulphides, oximes to ketones, maleic acid to succinic acid; fumaric acid to succinic acid and nitrobenzene to aniline.

Substituted cyclopentadienylmaganese tricarbonyl compounds have been prepared by the electrolysis of a solution of a Mn(II) salt, a cyclopentadiene hydrocarbon and a transition-metal carbonyl in such solvents as DMF, diethyleneglycol dibutyl ether or hexamethylphosphoramide under a pressure of carbon monoxide.[54-55] Thus, by applying a potential of 25-30V across manganese electrodes, methylcyclopentadienylmanganese tricarbonyl and fluorenylmanganese tricarbonyl were synthesized.

Electrolysis of the sodium alkyl (aryl) cyclopentadienide and excess alkyl (aryl) cyclopentadiene in THF - or pyridine/diethyleneglycol dimethyl ether at a manganese anode and a copper cathode under a nitrogen atmosphere yields the manganese alkyl (aryl) cyclopentadienides[40] in 25% yields. Manganesemethylcyclopentadienide and cyclopentadienylmanganese tricarbonyl were prepared this way.

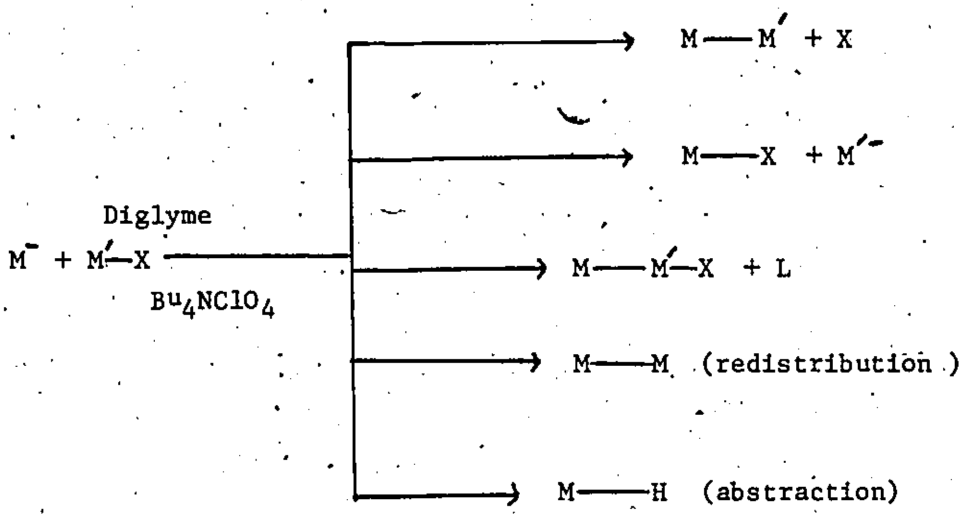
Dessy[56] et al have investigated the polarographic behaviour of a large number of metal carbonyl systems and have determined the number of electrons involved in various electrochemical systems, and other polarographic parameters. Stable radical anions and perhaps dianions generally could be expected from bridged bimetallic species having a metal-metal bond, while radical cations may be formed from those not having metal-metal bonding. The electrochemical scission of metal-metal bonds may proceed by two different pathways in glyme/tetrabutylammonium perchlorate:[56]



A general conclusion from the studies illustrates that homodimetallics accept two electrons per molecule and form two anions while heterodimetallic compounds may do the same or accept only one electron per molecule and form a radical and an anion.

In systems involving compounds of the type $(CO)_5M - M(CO)_5$ (M = Re or Mn), $[CpM(CO)_2]_2$ (M = Fe, Mo or W), $CpM(CO)_2I$ (M = Fe, W or Mo and Cp = cyclopentadienyl), compounds of the type $[M(CO)5]_2Hg$, $[CpM(CO)_2]_2Hg$ and $[CpM(CO)_2]_2Hg$ were characterized. A mercury cathode was used in these reactions.

Depending on the nucleophilicity of the anion and the respective bond strenths of the bonds that may be formed, electrochemically generated anions will react with organometallic halides in one of the following ways:[56]



Thus, [π-C_5H_5) Fe$(CO)_2$]$^-$ ion forms the diiron compound with (π-C_5H_5) Fe$(CO)_2$I, but the [Mn$(CO)_5$]$^-$ ion does not react with $(CO)_5$MnCl to form $Mn_2(CO)_{10}$ because of the low nucleophilicity of the [Mn$(CO)_5$]$^-$ ion. Addition of triphenyltin chloride to the [Mn$(CO)_5$]$^-$ ion yielded a mixture of dimanganese, ditin and manganese-tin compounds in approximately equal proportions.[56]

Clearly, various synthetic routes employing electrochemically generated anions are possible. The anion can be reacted with a polymetallic compound to form a new polymetallic atomic compound and the least nucleophilic or most stable anion.[56] The redistribution reaction has been used to prepare $(C_6H_5)_3$SnFe$(CO)_2$ (π-C_5H_5) from $(C_6H_5)_3Sn^-$ and [π-C_5H_5)Fe$(CO)_2]_2$, [(C_5H_5Fe$(CO)_2)_2$ and [Mn$(CO)_5$]$^-$ from [(π-C_5H_5)Fe$(CO)_2$]$^-$ and $Mn_2(CO)_{10}$. From a knowledge of the nucleophilicities and bond strengths, a qualitative prediction of the products of these reactions can be made.

CHAPTER II

NON-ELECTROCHEMICAL SYNTHESIS AND REACTIONS OF METAL CARBONYLS: A LITERATURE SURVEY

2.1 Synthesis of $M[M'(CO)_n]_m$ and $L_xM[M'(CO)_n]_m$ Complexes:

The synthesis of metal-metal bonded carbonyls of the type $M\,M'(CO)_{n\ m}$ and $L_xM[M'(CO)_n]_m$ has been a subject of considerable interest in the last decade. In these compounds, L can be a bidentate ligand (eg. 1,10-phenanthroline (phen), 2,2'-bipyridyl (bipy) and N,N,N',N'-tetramethylethylenediamine (TMED) in which case x = 1 or a monodentate ligand eg. pyridine (py), in which case X = 2.

One of the earlier preparations to be reported was that of $M[Co(CO)_4]_2$ (M = Cd or Zn) by Hieber and Teller.[57] Their method involved the reaction of the metals cadmium and zinc with dicobalt octacarbonyl at high carbon momoxide pressure and high temperature.

Using a very similar procedure but under milder conditions, compounds $M[Mn(CO)_5]_2$ (M = Zn or Cd) have been prepared[58] *via* the reaction of the finely powdered main group metal with dimanganese decacarbonyl in diglyme at 120°C in an argon atmosphere. Reasonable yields were obtained for the Cd and Zn complexes by subliming the compounds at 130°/0.001mm and 120°/0.001mm respectively. Carey and Noltes[59] have reported the synthesis of the complexes of zinc and cadmium with dimanganese decacarbonyl. In general, their scheme involves the reaction of the manganese pentacarbonyl hydride with the dialkylzinc or dialkylcadmium to form the compounds $Zn[Mn(CO)_5]_2$ and $Cd[Mn(CO)_2]_2$ respectively. Thus:

$$2Mn(CO)_5H + R_2M \longrightarrow M[Mn(CO)_5]_2 + 2RH.$$

(R = Et or Me)

The adducts $LM[Mn(CO)_5]_2$ (L = bipy) have also been reported.[59] Thus by the reaction of bipyridyl derivatives of R_2M for zinc and cadmium with the manganese pentacarbonylhydride in THF media, the nitrogen donor adducts can be prepared in satisfactory yields under nitrogen.

Complexes in which group IIB metals are inserted into the Re-Re bond have been reported.[60] Following the procedure of Carey and Noltes,[59] Hsieh and Mays[60] have synthesized the complexes $M[Re(CO)_5]_2$ (M = Zn or Cd) from pentacarbonylrhenium hydride and the dialkylzinc or dialkylcadmium. Using an entirely different procedure, the authors[60] have reported the synthesis of $Hg[Re(CO)_5]_2$ from the reaction of mercuric cyanide and the sodium salt of rhenium pentacarbonyl. Thus:

$$Hg(CN)_2(aq) + 2NaRe(CO)_5 \longrightarrow Hg[Re(CO)_5]_2 + 2NaCN$$

The corresponding zinc and cadmium compounds can also be obtained by metal exchange reactions between the Hg complex or direct reaction of $Re_2(CO)_{10}$ with the metals in refluxing bis-(2-methoxyethyl) ether:

$$M + Hg[Re(CO)_5]_2 \longrightarrow M[Re(CO)_5]_2 + Hg$$

Oxygen and nitrogen donor adducts of these compounds can then be obtained by direct reaction of the complex and the ligand.

The substitution of some of the carbon monoxide ligands in any metal carbonyl by non-π-acceptor ligands such as tertiary phosphines, π - bonded aryl rings and cyclopentadienyl makes it considerably more difficult to remove the remaining CO ligands.[61] Since these derivatives are usually quite stable, it is not difficult to see why they have been used so extensively in the synthesis of compounds of the type $[(\pi\text{-}C_5H_5)M'(CO)_n]_m M$, $[(\pi\text{-}C_5H_5)M'(CO)_n]_m ML'$ and $[(\pi\text{-}C_5H_5)M'(CO)_n]_m ML_2$ (L = unidentate amines, L' = bidentate amines, M = Cd, Hg or Sn (L = halogen or alkyl group) and M' = Fe, Ni, W or Mo).

Bonati and Wilkinson[62] have reported the synthesis of complexes of the type $[(\pi\text{-}C_5H_5)M'(CO)_nSnCl_2$ (M' =Fe, Mo or W) by the reaction of the tin(II) chloride and carbonyl-π-cyclopentadienyl complexes of iron and molybdenum. Thus

$$[(\pi\text{-}C_5H_5)M'(CO)_n]_2 + SnCl_2 \longrightarrow [(\pi\text{-}C_5H_5)M'(CO)_n]_2SnCl_2$$

(M' = Fe, n = 2, M' = Mo and n = 3)

Similar systems have been used for the insertion of Sn into the Ni-Ni bond in $[(\pi\text{-}C_5H_5)Ni(CO)_2]_2$ and insertion of indium into the Fe-Fe bond in $[(\pi\text{-}C_5H_5)Ni(CO)_2]_2$ to form $BrIn[\pi\text{-}C_5H_5)Fe(CO)_2]_2$ Tin(II) chloride reacts in a similar manner with $Co_2(CO)_8$[63] and $Mn_2(CO)_{10}$, although severe conditions 180-190°C in a sealed tube for 22 hours) are required for $Mn_2(CO)_{10}$. Hsieh and Mays[66] have since shown that oxidative insertion of Sn and In into the metal-metal bond takes place readily in refluxing dioxane (b.p 100-102°C) for $Mn_2(CO)_{10}$, $[(\pi\text{-}C_5H_5)M'(CO)_3]_2$ (M' = W or Mo) using the halides $SnCl_2$ and InBr.

Mays and Robb[67] reported the cadmium compounds of the type $[(\pi\text{-}C_5H_5)M(CO)_3]_2Cd$ and the amine adducts from cadmium cyanide and the appropriate sodium salt of the cyclopentadienyl metal carbonyl. Thus

$$Cd(CN)_2(aq) + 2(\pi\text{-}C_5H_5)M'(CO)_3Na \longrightarrow [\pi\text{-}C_5H_5M'(CO)_3]_2Cd + 2NaCN$$

Using unidentate ligands, they were also able to prepare the adducts $[(\pi\text{-}C_5H_5)M'(CO)_3]_2CdL_2$ or $[(\pi\text{-}C_5H_5)M'(CO)_3]_2CdL'$ (M' = W or Mo, L = unidentate amine and L = bidentate amine.) Although a metal exchange reaction is possible for the preparation of $Cd[Co(CO)_4]_2$ from $Hg[Co(CO)_4]_2$, the workers[67] found that the same reaction does not occur for the $[(\pi\text{-}C_5H_5)M'(CO)_3]_2Hg$ complex which is quite unreactive towards cadmium. In fact, Hg replaces Cd in the complex $[(\pi\text{-}C_5H_5)M'(CO)_3]_2Cd$.

Cornwell _et al_[68] have reported the synthesis of the tin-cobalt bonded complex $Sn[Co(CO)_4]_4$ from bis-(methylcyclopentadiene)tin and dicobalt octacarbonyl in cyclohexane and they suggest a mechanism of the type:

$$\begin{tikzcd}
(MeC_5H_4)_2Sn + Co_2(CO)_8 \arrow[r] & (MeC_5H_4)_2Sn[Co(CO)_4]_2 \arrow[d, "\substack{-MeC_5H_4 \\ +Co(CO)_4^-}"'] \\
Sn[Co(CO)_4]_4 & (MeC_5H_4)Sn[Co(CO)_4]_3 \arrow[l, "-MeC_5H_4" above, "+Co(CO)_4^-" below]
\end{tikzcd}$$

Using $(C_5H_5)_2Sn$ and $(\pi\text{-}C_5H_5)W(CO)_3H$, the same workers were able to prepare the divalent tin derivative $Sn[W(CO)_3(C_5H_5)]_2$. More recently, both $Sn[Co(CO)_4]_4$ and $Pb[Co(CO)_4]_4$ have been prepared[69] by the reaction of the metals with dicobaltoctacarbonyl in ether.

Other complexes involving group IV metals and Mn and Re have also been reported.[70] Thus, treatment of $Br_3SnRe(CO)_5$ with $NaRe(CO)_5$ yields the ditin compound $\{[Re(CO)_5]_3Sn\}_2$ and the reaction of diphenyltin dibromide and $NaRe(CO)_5$ yields the compound $Br_2Sn[Re(CO)_5]_2$

$$5Re(CO)_5^- + Br_3SnRe(CO)_5 \longrightarrow \{Sn[Re(CO)_5]_3\}_2 + 3Br^-$$

and

$$2\,NaRe(CO)_5 + Ph_2SnBr_2 \longrightarrow Ph_2Sn[Re(CO)_5]_2 + 2\,NaBr$$

The Mn analogues of $BrSn[Re(CO)_5]_2$ have recently been reported.[71] Their preparation involves reaction of SnX_2 and $Mn_2(CO)_{10}$ in a bomb tube. The synthesis of cobalt carbonyl complexes of In, Tl, Zn, Cd and Sn by a method involving the use of cobalt, $CoBr_2$, carbon monoxide and the metal (M = In, Tl, Zn, Cd or Sn) has been reported.[72] Thus, the complexes $In[Co(CO)_4]_3$, $Zn[Co(CO)_4]_2$, $Cd[Co(CO)_4]_2$, $Tl[Co(CO)_4]$ or $Tl[Co(CO)_4]_3$ and $Sn[Co(CO)_4]_2$ have been prepared at elevated temperatures and high carbon monoxide pressures.

Hieber and Schropp[73] have synthesized the complex $Hg[Mn(CO)_5]_2$ using the alkylmercuryhydroxide and the sodium salt of $Mn_2(CO)_{10}$:

$$2Mn(CO)_5 + 2\ RHgOH \longrightarrow 2OH^- + Hg[Mn(CO)_5]_2 + R_2Hg$$

in which the unstable intermediate $RHgMn(CO)_5$ is believed to be formed.

Carbon monoxide and nitric oxide are known to behave in a similar manner when bonded to transition metals. Indeed, metal complexes in which NO replaces some carbon monoxide groups are known, and these behave in a manner very similar to the unsubstituted CO complexes. The synthesis of the mixed CO - NO complexes has been carried out by Hieber and Beutner.[72] Thus, the reaction of $[Fe(CO)_3NO]^-$ and ammonium hexachlorostannate (IV) in methanol yields $Sn[Fe(CO)_3]_4$ ie:

$$4Fe(CO)_3NO]^- + [SnCl_6]^{2-} \xrightarrow[MeOH]{} Sn[Fe(CO)_3NO]_4 + 6Cl^-$$

The reactions:

$$3[Fe(CO)_3NO]^- + Sn\ (II)\ or\ Sn\ (IV) \longrightarrow ClSn[Fe(CO)_3NO]_3$$

and

$$[Fe(CO)_3NO]^- + Hg(CN)_2 \longrightarrow Hg[Fe(CO)_3NO]_2 + 2CN^-$$

have been carried out, giving good yields of the products indicated.

2.2 Properties of Polynuclear Metal Complexes:

The compounds of the type $M[Co(CO)_4]_2$ (M = Hg, Zn or Cd) are usually yellow, air sensitive crystalline compounds which are easily oxidised in air over short periods of time. The $Mn_2(CO)_{10}$ derivatives are usually red to bronze and are also air sensitive.

(i) Reactions with Lewis Bases:

For most compounds of general formula $M[M'(CO)_n]_2$ nitrogen donor and oxygen donor adducts have been reported.[74] Hsieh and Mays were able to isolate the 1,10-phenanthroline, 2,2'-bipyridyl, pyridine and γ-picoline adducts of $M[Mn(CO)_5]_2$ (M = Zn or Cd but not Hg.) Thus:

$$M[Mn(CO)_5]_2 + L_2 \longrightarrow M[Mn(CO)_5]_2L$$

(L = phen, bipy, 2 py or 2 γ- pic)

Not only is it possible to form 1:1 adducts with N-donor ligands, but oxygen-donor ligands eg. diglyme have also been found to form complexes of the same type for Cd but not Zn. The colour changes observed in the case of zinc however do suggest adduct formation although none has been isolated. These adducts are formed by reaction of the $M[Mn(CO)_5]_2$ in methanol or ethanol and a solution of the ligand in acetone, THF or alcohol. If the reaction is carried out in diglyme however, there is initial formation of the diglyme adducts which is then replaced by the N-donor ligand. This behaviour is typical for Cd complexes.

The Hg complex on prolonged heating under reflux in THF solution gives the substitution product. Thus:

$$Hg[Mn(CO)_5]_2 + L \longrightarrow Hg + Mn_2(CO)_8L$$

(L = phen or bipy)

If a 3 fold excess of N-donor is reacted with $Zn[Mn(CO)_5$, the extremely air sensitive, red-orange adduct$(L_3)Zn[Mn(CO)_5]_2$ is formed (L_2 = bipy, phen or terpyridine).

The bidentate ligands phen and bipy replace the unidentate ligands py, γ-pic in $L_2Cd[Mn(CO)_5]_2$ to yield free base and the phen or bipy adduct. $Cd[Co(CO)_4]_2$ and $Zn[Co(CO)_4]_2$ [75] form adducts with pyridine, phen or NH_3. Thus:

$$M[Co(CO)_4]_2 + \underset{\text{or } L'}{L} \longrightarrow \underset{\text{or} M[Co(CO)_4]_2L'}{M[Co(CO)_4]_2L_2}$$

(L = py or NH_3, L' = phen and M = Cd or Zn)

The corresponding mercury adducts have not been reported. $Hg[Co(CO)_4]_2$ will disproportionate in basic media and thus it is difficult to study the acceptor properties of this complex.

Mays and Robb [76] have reported that the complexes $[(\pi\text{-}C_5H_5M'(CO)_3]_2M$ do not disproportionate in basic media. Thus adducts of the type $[\pi\text{-}C_5H_5)M'(CO)_3]_2ML_2$ or $[(\pi\text{-}C_5H_5)M'(CO)_3]_2ML'$ (M = Cd and M' = Mo or W) are formed by direct reaction of the unidentate amine L or bidentate amine L' with the complexes $[\pi\text{-}C_5H_5)M'(CO)_3]_2M$. The reaction with L' = ethylenediamine is unique as the reaction is of the type:

$$[(\pi\text{-}C_5H_5)M'(CO)_3]_2Cd + 3en \longrightarrow [Cden_3]\ [(\pi\text{-}C_5H_5)M'(CO)_3]_2$$

Unlike the case of $Hg[Co(CO)_4]_2$, the $[\pi\text{-}C_5H_5)M'(CO)_3]_3Hg$ complexes do form adducts with bidentate ligands bipy and phen. These adducts however disproportionate completely on attempting to recrystallize them from ethanol. From these observations it is clear that the Hg complexes of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, $[(\pi\text{-}C_5H_5)W(CO)\ ]_2$ and $Co_2(CO)_8$ are weaker Lewis acids than the corresponding Cd and Zn complexes.

With trialkyl phosphite and pyridine, $Hg[Co(CO)_4]_2$ reacts to form free mercury, carbon monoxide and the cobalt complex. Thus:

$$3Hg[Co(CO)_4]_2 + 12py \longrightarrow 3Hg + 2[Co(Py_6)][Co(CO)_4] + 8CO$$

and

$$Hg[Co(CO)_4[_2 + P(OCH_3)_3 \longrightarrow Hg + 2CO + [Co(CO)_3P(OCH_3)_3]_2$$

(ii) <u>Reactions involving Carbon Monoxide Substitution:</u>

Although it may be expected that tertiary phosphines, arsines, stibines and phosphites will react in a manner similar to the N-donor ligands, a completely different type of behaviour is observed. It turns out that these ligands will in general not form the 2:1 adducts but rather the complexes $M[M'(CO)_{n-1}L]$ and $[\pi\text{-}C_5H_5M'(CO)_{n-1}L]M$. Thus the reaction of $Hg[(Co(CO)_4]_2$ with trialkyl phosphine has been reported[75] to occur at room temperature according to the equation:

$$Hg[Co(CO)_4]_2 + R_3P \longrightarrow Hg[Co(CO)_3(PR_3)\ ]_2 + 2CO$$

(R = phenyl, cyclohexyl or ethyl)

The Cd, Zn and Sn derivatives of $M[Co(CO)_4]_n$ react similarly to form $M[Co(CO)_3Ph_3P]_2$. In a typical reaction,[75] triphenylphosphine reacts with $R_2Sn[Co(CO)_4]_2$ to form the product $R_2Sn[Co(CO)_3Ph_3P]_2$. Thus:

$$R\ Sn[Co(CO)_4]_2 + Ph_3P \longrightarrow R_3Sn[Co(CO)_3Ph_3P\ \ 2CO$$

(R = methyl or n-butyl)

Hieber and Schropp[75] reported a very similar reaction for

Thus:

$$Hg[Mn(CO)_5]_2 + R_3P \longrightarrow Hg[Mn(CO)_4R_3P]_2 + 2CO.$$

(R = alkyl or aryl)

The reactions of Ph_3P, $(PhO)_3P$ and $(MeO)_3P$ with the π-cyclopentadienyl complexes $[\pi\text{-}C_5H_5)M'(CO)_3]_2Hg$ have been reported[77] and these behave in an analogous manner to those previously discussed, eg:

$$[\pi\text{-}C_5H_5)M(CO)_3]_2Hg + PR_3 \longrightarrow [(\pi\text{-}C_5H_5)M'(CO)_2PR_3]_2Hg + CO$$

(M′ = Mo, Cr or W) The Cr complexes are less stable than their Mo and W analogues.

(111) <u>Reactions with Halogens, Hydrogen Halides, Aryl Chlorides, Acid Anhydrides, Alkyl Halides and Tetraalkylammonium Salts:</u>

Hsieh and Mays[74] have carried out the reactions between $M[Mn(CO)_5]_2$ and HX (X = Br, Cl or I), MeI, RCOCl and $(CH_3CO)_2O$ for the Zn and Cd complexes. The $M[Mn(CO)_5]_2$ complexes are cleaved by hydrogen halides in CCl_4 solution at room temperature:

$$M[Mn(CO)_5]_2 + HX \longrightarrow MX_2 + XMn(CO)_5 \quad ^{73}$$

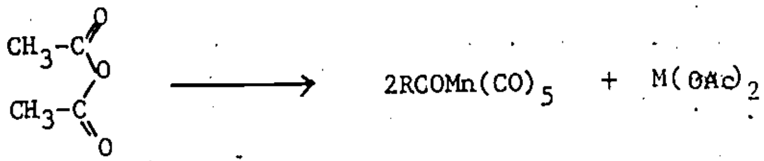
The other reactions studied can be summarized as:

$$M[Mn(CO)_5]_2 + HX \xrightarrow[\text{(15 min.)}]{\text{room temp.}} MX_2 + HMn(CO)_5$$

$$M[Mn(CO)_5]_2 + MeI \xrightarrow{THF} MeMn(CO)_5 + MX_2$$

$$M[Mn(CO)_5]_2 + 2CH_3C{\overset{\displaystyle /\!\!/O}{\underset{\displaystyle \diagdown Cl}{}}} \longrightarrow 2RCOMn(CO)_5 + MX_2$$

or



$$(CH_3CO)_2O \longrightarrow 2RCOMn(CO)_5 + M(OAc)_2$$

The reaction with methyl iodide is observed for Zn, Cd and Hg, although the mercury reaction is very slow.

In a reaction employing $Cd[(\pi-C_5H_5)M'(CO)_3]_2$[67] (M' = W or Mo) tetramethylammonium iodide forms the 1:1 adduct formulated as $(Me_4N)_2(\pi-C_5H_5)M'(CO)_3]_2CdI_2)$.

The effect of halogens on the complexes $M[(\pi-C_5H_5M'(CO)_3]_2$ (M = Hg, Cd or Zn, and M' = W, Mo or Cr) has been studied.[76] Bromine and iodine react to form the compounds $(\pi-C_5H_5)M'(CO)_3X$ (X = Br or I) and HgX_2. Chlorine reacts vigorously with $[\pi-C_5H_5)Cr(CO)_3]_2Hg$ to form a product which shows no C—O stretch.

(iv) Exchange reactions:

Mays and Robb[67,76] have investigated the reactions of various complexes with HgX_2 and CdX_2 (X = Br, Cl or I). These reactions are equilibria which favour the exchange products. Thus in

$$[(\pi-C_5H_5)M'(CO)_3]_2M + MX_2 \rightleftharpoons 2(\pi-C_5H_5)M'(CO)_3MX$$

(M' = Mo or W), M = Cd or Hg)

The equilibria favours the right-hand side of the equation in methanol solution at room temperature. The same type of reaction has been observed for cases in which M' = Fe or Cr and X = Br, Cl, I or SCN in acetone solution at room temperature.

Employing the methylmercury iodide for reaction with $[(\pi-C_5H_5)M'(CO)_3]_2Hg$, the equilibrium

$$2MeHgI + [(\pi-C_5H_5Mo(CO)_3]_2Hg \rightleftharpoons (CH_3)_2Hg + 2(\pi-C_5H_5)Mo(CO)_3HgI$$

is established. $Hg[Co(CO)_4]_2$ reacts with Cd and Zn metal to form the metal exchange product $M[Co(CO)_4]_2$ (M = Zn or Cd.) $[(\pi-C_5H_5)M'(CO)_3]_2Hg$ will readily displace Cd in $[(\pi-C_5H_5)M'(CO)_3]_2Cd$ (M' = W, Mo or Fe.) $Cd[Mn(CO)_5]_2$ complexes will react with cadmium halides in a manner entirely analogous to the cobalt carbonyl complexes.[18]

CHAPTER III

EXPERIMENTAL METHODS , RESULTS AND DISCUSSION

3.1 Objective of Work:

In principle, the electrochemical technique represents the simplest and most direct method of carrying out oxidation or reduction reactions, since the removal or addition of electrons can be achieved without the complications otherwise associated with the addition of redox reagents. Other work[56] has concentrated on the determination of fundamental parameters like E_o, number of electrons involved in a reduction or oxidation and the current/voltage relationships. The present investigations do not concern these fundamental variables, rather they set out to show that the general applicability of anodic oxidation of metal M (M = Zn, Cd, In or Sn) in the presence of dinuclear metal carbonyls in nonaqueous solution can lead to the formation of species of the type $M[M(CO)_n]_n$.

Although the number of systems studied is relatively small, it is conceivable that the method can be of general applicability for a wide variety of main group metals M and metal carbonyls $M_2(CO)_{2n}$.

For a few of the systems studied, measurements of current efficiencies (E_F) have been made and they provide considerable information on the nature of the mechanism of the process

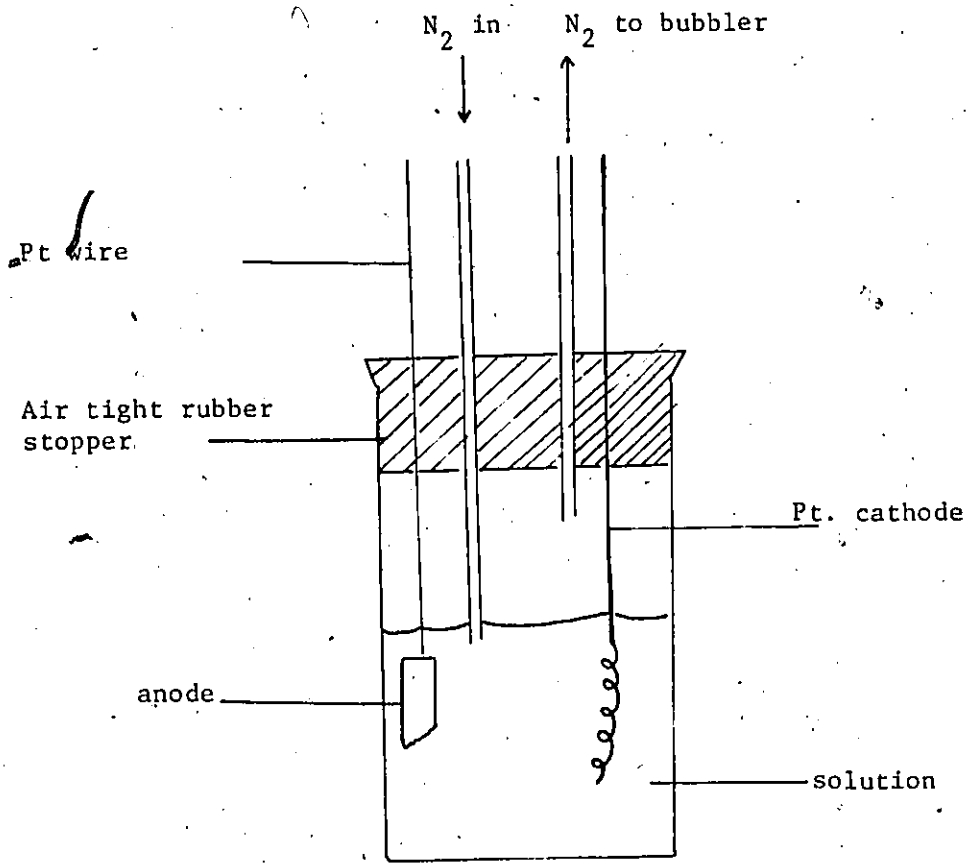


Figure 1: Electrochemical Cell.

3.2 Experimental:

General:

The general experimental set-up is shown in the diagram (Figure 1.)

Cadmium (Alfa Inorganics) and zinc were used in the form of rods (10cm long and 1cm diameter). The part immersed in the solution was flattened out to increase the surface area of the electrode. Tin metal (Alfa Inorganics) was used in the form of a sheet (5cm by 5cm by 0.127mm) supported by a platinum wire lead. Indium electrode was made from In Shot (Alfa Inorganics) by hammering it into a thin sheet (2cm x 2cm). The purities of the zinc, cadmium and tin metal used were M_4N+ and M5N respectively. Platinum wire (10cm long and 1mm diameter) was used as the cathode in all experiments. It was sometimes essential to spiral the lower end of the wire for greater electrode surface area.

The applied voltage was 20 -50V, as dictated by the solution conditions, given that a current 20-50 mA produced a reasonable rate of reaction without overheating the solution. A Coutant 50/50 power supply was used in all experiments but one could use any source of D.C. power.

The temperature was ambient ($\sim 20^\circ$ C) and all experiments reported were carried out under an atmosphere of dry nitrogen. Isolation of products was carried out in glove box.

Solution compositions and analytical data for the experiments are given in Tables 1 and 2, respectively. In all experiments, Et_4NClO_4 or Et_4NBr ($\sim$10-15 mg) were used to enhance the conductivity of the solution. In cases in which more methanol than benzene was used, it was found that sufficient current could flow without any tetraethylammonium salt in solution. Because of possible side reactions that can occur with Et_4NBr, Et_4NClO_4 is a better electrolyte. 2,2′-bipyridyl was used without further purification and N,N,N′,N′-tetramethylethylenediamine (TMED) was dried in KOH and then distilled in nitrogen atmosphere. Methanol (Analytical grade) was dried over Linde molecular sieves. Benzene, diethyl ether and petroleum ether (36-55°C b.p.) were dried over sodium strips. Dicobalt octacarbonyl and dimanganese decacarbonyl were used without further purification and were supplied by Alfa.

Infra-red spectra were recorded with Beckman IR -12, and NMR spectra with a Varian EM - 360 operating at 60MHZ. Mass spectra were obtained on a Varian CH-5 spectrometer. Metal analyses were done by atomic absorption spectrophotometry.

(i) Electrochemical Preparation of $Cd(Co(CO)_4]_2$

A cadmium rod was made the anode of the cell and a platinum wire (~1mm diam.) was the cathode. The composition of the solution is given in Table 1. Using an initial voltage of 8 volts and a current of 40mA, a solution of 0.4g $Co_2(CO)_8$ in 50 mls of methanol was electrolysed for 6 hours. After the period of 6 hours, the brown solution had changed to a pale yellow colour and some pink material was deposited on the cathode. The mixture was filtered under dry nitrogen. The resulting filtrate was evaporated to dryness <u>in vacuo</u> and the pale yellow crystals were obtained. This crude product was sublimed at 80°C <u>in vacuo</u> yielding 0.35g of product (65% yeild on the basis of Cd dissolved.) 0.3g of Cd were dissolved from the anode.

The pink residue obtained was found to contain 25.2% cobalt and 6.92% cadmium. It was not possible to establish the identity of this compound because of its insolubility in organic solvents. The i.r. data for the C—O stretching frequencies are given in Table 3 and the mass spectral and analytical data in Tables 4-10 and 2 respectively.

(ii) Electrochemical Preparation of (TMED)Cd[Co(CO$_4$]$_2$

A mixture consisting of 20mg Et_4NClO_4, 30mls of methanol, 30mls of benzene, 0.3g of TMED and 0.6g of $Co_2(CO)_8$ was electrolysed for 13 hours using a current of 25mA and an initial voltage of 10 volts. The other parameters of the cell were exactly the same as in (i) above. The voltage was raised as appropriate to maintain a current of 25mA.

At the end of the period of time, 0.25g of cadmium had been dissolved from the anode. The mixture of products was then filtered. The pink residue (0.3g) was dried and on analysis found to contain 52.1% cobalt. Insolubility of this product made characterisation impossible. The resulting orange-yellow filtrate was reduced in volume <u>in vacuo</u> at ambient temperature. Yellow crystals were filtered off and dried <u>in vacuo</u> for 3 hours. The total yield of the yellow product was 1.0g (74% based on Cd dissolved).

(iii) Electrochemical Preparation of BipyCd[Co(CO)$_4$]$_2$

A mixture consisting of 0.56 bipyridyl, 1.2g $Co_2(CO)_8$, 20mg Et_4NClO_4 60mls methanol and 20mls benzene was electrolysed for 6 hours using an initial voltage of 3 volts and a current of 50mA.

The reaction mixture was then filtered, leaving a brown residue and an orange-yellow filtrate. The filtrate was then reduced in volume and the precipitate formed filtered off under nitrogen. This process was repeated until most of the liquid had been removed. The colour of precipitate collected in these stages ranged from orange to pale yellow. All the fractions were then dissolved in benzene and any residue resulting was filtered off (brown-orange). The filtrate was then evaporated to dryness and the yellow crystals dried and analysed.

The orange-brown residue (0.3g) was found to contain 2.5% Cd and 23.5% cobalt. This was probably the unreacted $Co_2(CO)_8$. The yield of product (yellow crystals) was 1.4g (64% based on Cd dissolved).

(iv) Electrochemical Preparation of $BipyCd[Mn(CO)_5]_2$

0.9g $Mn_2(CO)_{10}$, 0.4g 2,2-bipyridyl and 30mg of tetraethylammonium bromide were dissolved in a mixture of 40mls benzene and 30mls methanol and electrolysed for 12 hours using a voltage of 30 - 50 volts and maintaining a current of 20mA.

The yellow solution changed to a progressively deeper orange-red colour as electrolysis was continued. The reaction mixture was then filtered and the filtrate evaporated to dryness. The orange-red solid was then sublimed. On raising the temperature to 150°C, yellow crystals were deposited on the "cold finger" of the sublimer. These yellow crystals were removed and the temperature raised further to 180°C at which point orange-red crystals started to sublime. The yield of sublimate was 1g (61% based on Cd dissolved).

(v) Electrochemical Synthesis of $BipyZn[Co(CO)_4]_2$

A mixture consisting of 0.25g bipyridyl, 20mg Et_4NClO_4, 0.6g $Co_2(CO)_8$, 40mls methanol and 25mls benzene was electrolysed for 9 hours using an initial voltage of 6V and 30mA current.

The solution gradually changed colour from brown to a pale yellow as electrolysis was continued. The mixture of products was then filtered and the filtrate reduced in volume in vacuo. A yellow precipitate which formed as the volume was reduced was then filtered off and dried in vacuo.

0.25g of zinc metal had been dissolved at the end of the reaction and the yield of product was 0.6g (33% based on Zn dissolved).

(vi) Electrochemical Preparation of $BipyZn[Mn(CO)_5]_2$

1g $Mn_2(CO)_{10}$, 0.5g bipyridyl and 20mg of Et_4NClO_4 were dissolved in a mixture of 40mls benzene and 30mls methanol. The mixture was then electrolysed for 26 hours at 20 -50 volts and a current of 25mA.

The yellow solution progressively became red-orange as electrolysis proceeded and a solid precipitated at the bottom of the cell. On filtering the cell contents and reducing the volume of the filtrate, large orange-red crystals were obtained. These were then filtered off and a total yield of 1g was obtained (55% on basis of Zn dissolved). The yellow-white residue from the first filtration did not contain any zinc.

(vii) Electrochemical Preparation of $In[Co(CO)_4]_3$

A mixture consisting of 0.7g of $Co_2(CO)_8$, 20mg Et_4NClO_4, 30mls of methanol and 10mls of benzene was electrolysed between a platinum cathode and an indium anode. The solution turned from brown to a deep red as the electrolysis progressed. A yellow 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 enable characterization.

The filtrate was then treated with a mixture of petroleum ether (b.p. 35 - 65°C) and benzene. A small amount of the yellow product precipitated and the mixture was then filtered. The red filtrate was then evaporated to dryness and the red solid analysed for In and Co. The yellow product was discarded because the quantities were too small for characterization.

0.67g of product (82% on basis of $Co_2(CO)_8$ was isolated.)

(viii) Electrochemical Preparation of $BipyIn[Co(CO)_4]_3$

A mixture consisting of 1g $Co_2(CO)_8$, 20mg Et_4NClO_4, 0.17g bipyridyl, 40mls methanol and 10mls benzene was electrolysed using a current of 60mA (5V) for 4 hours. After this period of time, the reaction mixture was filtered off to remove metallic indium which was deposited in the cell. The red filtrate was treated with pet. ether/benzene and the small amount of yellow precipitate filtered off.

The filtrate was then evaporated to dryness *in vacuo* and the resulting red solid washed thoroughly with pet ether/benzene mixture to remove any unreacted bipyridyl. The yield of product was 1.0g (66% yield on basis of $Co_2(CO)_8$.)

(ix) Electrochemical Preparation of $BipyIn[Mn(CO)_5]_3$

A solution containing 0.9g $Mn_2(CO)_{10}$, 0.24g bipyridyl and 20mg

Et_4NClO_4, was electrolysed for 16 hours. An initial current of 30mA (40 volts) was employed.

The yellow solution gradually turned violet as electrolysis was continued. On filtering the mixture, a violet filtrate was obtained. The volume of the solution was then reduced and some $Mn_2(CO)_{10}$ which formed in the flask also removed. The remainder of the filtrate was then evaporated to dryness and the violet solid washed thoroughly with petroleum ether and pentane. The product (0.7g) was dried in vacuo for 2 hours and then analysed for Mn and In.

(x) Electrolysis of $Mn_2(CO)_{10}$/Sn/Bipyridyl

A solution of 0.5g $Mn_2(CO)_{10}$ and 0.3g bipy in 30mls methanol and 35 mls benzene was electrolysed for 15 hours at a current of 30mA (30 volts).

A deep red colour developed as the electrolysis progressed. The contents of the cell were then filtered and the volume of the filtrate reduced in vacuo. n-Pentane was then added to the solution and the brown-yellow precipitate filtered off. The red filtrate was then evaporated to dryness and the solid dissolved in THF/pet. ether mixture and the whole left in the freezer for 2 days. Large red crystals were obtained on filtering.

The yield of residue from n-pentate precipitate was 0.3g and that from pet. ether was 0.3g 0.14g of tin was dissolved from the anode. Metal analyses were 30.9% Sn and 14.4% Mn for brown-yellow solid and 30.2% Sn and 10.85% Mn for the red crystals.

(xi) Electrolysis of $Sn/Mn_2(CO)_{10}$

0.5g $Mn_2(CO)_{10}$ was dissolved in 40mls benzene and 10 mls methanol and the mixture electrolysed for 16 hours. An orange-red colour developed as the electrolysis progressed. The mixture was then filtered and the filtrate treated with n-pentane. A dark red oil which formed at the bottom of the reaction vessel was removed and evaporated to dryness. The remainder of the solution was yellow and on evaporation showed only $Mn_2(CO)_{10}$ was present. The solid from the oil (0.4g) was analysed for Sn and Mn. 0.6% of product was isolated. 23.6% Sn and 26.2% Mn were present in the sample.

(xii) Electrolysis of $Sn/Co_2(CO)_8$/bipyridyl

A solution containing 0.5g $Co_2(CO)_8$ and 0.24g bipyridyl in 50mls of methanol was electrolysed for 8 hours at a current of 30mA (6 volts). An orange-red solid was formed as the mixture was electrolysed.

The solid was then filtered off and treated with THF, n-pentane, benzene and cyclohexane in an attempt to recrystallize it. The solid was found to be insoluble in all these solvents. The filtrate contained a very small amount of solid after evaporation to dryness *in vacuo*.

The yield of product was 0.5g and 0.4g of tin dissolved. The tin and cobalt analyses gave 33.9% and 11.8% respectively.

(xiii) Electrolysis of $Sn/Co_2(CO)_8$

0.3g $Co_2(CO)_8$ was dissolved in 30mls methanol and 15mls benzene and the solution electrolysed for 8 hours. The deep orange coloured mixture was then filtered and the filtrate treated with the same solvents as for (xii) above. No precipitate was formed with any of the solvents. The product was evaporated to dryness in vacuo. A black solid was deposited in the flask. 0.3g of product was isolated and 0.1g of tin dissolved. The product was found to contain 38.4% Co and 10.1% Sn.

Measurement of Current Efficiencies:

Using exactly the same conditions as in the actual experiment in which the products were isolated and characterised, readings of current and time were taken for periods of time ranging from 1 hour to 3 hours. The amount of time depended upon the possibility of maintaining a constant current without going over the maximum output voltage of the power supply.

From a knowledge of the amount of metal dissolved, the current and the time, one can calculate the total electric charge that flowed through the solution:

$Q = It$ (I = current in Amperes, t = time in seconds, Q = charge in Coulombs)

$$\frac{Q}{F} = \frac{It}{96500}$$

Number of moles of metal dissolved $= \frac{m}{M}$

Current efficiency $= \frac{m.96500}{M.\ It}$ moles/Faraday $= E_F$

m = mass of metal dissolved in time (t)

M = atomic weight of the metal

3.3 Results

Table 1: Solution Phase Compositions

Compound	Colour	Time (hrs)	Vol of MeOH (ml)	Vol of C_6H_6 (ml)	Initial voltage (V)	Initial current (mA)	Mass of metal dissolved in (g)	%Yield of product on basis of metal dissolved
$Cd[Co(CO)_4]_2$	pale yellow	6	50	0	8	40	0.30	65
$TMEDCd[Co(CO)_4]_2$	pale yellow	13	30	30	10	25	0.25	74
$BipyCd[Co(CO)_4]_2$	yellow	8	60	20	3	50	0.40	64
$BipyCd[Mn(CO)_5]_2$	orange-red	12	30	40	30	20	0.50	61
$In[Co(CO)_4]_3$	red	41/2	30	10	8	50	-	82(a)
$BipyIn[Co(CO)_4]_3$	red	4	40	10	5	60	-	66(a)
$BipyIn[Mn(CO)_5]_3$	violet	16	30	20	40	30	-	80 (a)
$BipyZn[Co(CO)_4]_2$	yellow	9	40	25	6	30	0.25	33
$BipyZn[Co(CO)_5]_2$	orange-red	26	30	40	20	25	0.20	55

(a) Wt of metal dissolved not measured because metallic indium was deposited at the bottom of the cell. % Yield based on $Mn_2(CO)_{10}$ or $Co_2(CO)_8$.

Table 2: Analytical Data

Compound	%Zn/In/Cd	%Mn/Co	%C	%H	%N
$Cd[Co(CO)_4]_2$	25.3 (24.95)	25.9 (26.20)	-	-	-
$BipyCd[Co(CO)_4]_2$	18.4 (18.42)	18.9 (19.31)	35.62 (35.41)	1.24 (1.31)	4.49 (4.59)
$(TMED)Cd[Co(CO)_4]_2$	19.8 (19.71)	20.8 (20.68)	28.97 (29.50)	2.84 (2.81)	5.30 (4.91)
$BipyCd[Mn(CO)_5]_2$	17.1 (17.07)	- -	37.65 (36.47)	1.55 (1.22)	4.43 (4.25)
$BipyZn[Co(CO)_4]_2$	11.5 (11.67)	21.2 (21.04)	39.18 (39.03)	1.41 (1.45)	4.98 (5.06)
$BipyZn[Mn(CO)_5]_2$	10.4 (10.69)	18.3 (17.97)	39.44 (39.28)	1.26 (1.32)	4.39 (4.58)
$In[Co(CO)_4]_3$	18.1 (18.00)	27.8 (28.18)	- -	- -	- -
$BipyIn[Co(CO)_4]_3$	14.0 (14.67)	23.2 (22.58)	- -	- -	- -
$BipyIn[Mn(CO)_5]_3$	13.6 (13.40)	19.0 (19.20)	- -	- -	- -

Figures in parenthesis are the calculated values.

Table 3: Infrared Data

Compound	Solvent	ν C - O (cm^{-1})
$Cd[Co(CO)_4]_2$	$CHCl_3$ pentane	1966(sh), 1970(b), 2020(sh), 2054(vs), 2067(sh) 1910(sh), 1970(m), 2020(sh), 2060(m), 2073(vs
$BipyCd[Co(CO)_4]_2$	$CHCl_3$	1965(s), 1983(sh), 2049(vs), 2060(s)
$(TMED)Cd[Co(CO)_4]_2$	$CHCl_3$	1940(sh), 1950(m), 1970(sh), 1990(s), 2050(vs), 2067(vs)
$BipyCd[Mn(CO)_5]_2$	Nujol mull	1925(s), 1943(s), 1961(s), 1973(sh), 1992(m) 2043(s), 2065(s)
$BipyZn[Co(CO)_4]_2$	$CHCl_3$ Nujol	1970(vs), 1980(sh), 2055(s), 2065(s) 2043(s), 1957(s), 1972(m), 2055(vs, 2065(vs)
$BipyZn[Mn(CO)_5]_2$	Nujol	1924(s), 1941(vs), 1960(s), 1970(sh) 1990(m), 2040(vs) 2060(s)
$In[Co(CO)_4]_3$	Nujol	2003(vs), 2080(vs), 2090(sh)

s - strong, b - broad, m - medium, v - very, sh - shoulder.

Table 4 Mass Spectrum: $\mathrm{Cd[Co(CO)_4]_2}$

Peak no.	m/e	%RA	Assignment
1	59.15	12.00	Co^+
2	142.87	5.82	$\mathrm{Co((CO)_3}^+$
3	170.87	6.68	$\mathrm{Co(CO)_4^+}$
4	280.93	0.41	$^{110}\mathrm{CdCo(CO)_4^+}$
5	281.99	0.80	$^{111}\mathrm{CdCo(CO)_4^+}$
6	282.81	0.60	$^{112}\mathrm{CdCo(CO)_4^+}$
7	283.87	0.96	$^{113}\mathrm{CdCo(CO)_4^+}$
8	284.87	1.89	$^{114}\mathrm{CdCo(CO)_4^+}$
9	447.96	2.33	$^{106}\mathrm{Cd[Co(CO)_4]_2^+}$
10	449.90	3.39	$^{108}\mathrm{CdCo[Co(CO)_4]_2^+}$
11	451.96	40.63	$^{110}\mathrm{Cd[Co(CO)_4]_2^+}$
12	452.99	45.60	$^{111}\mathrm{Cd[Co(CO)_4]_2^+}$
13	453.99	84.06	$^{112}\mathrm{Cd[Co(CO)_4]_2^+}$
14	455.03	52.07	$^{113}\mathrm{Cd[Co(CO)_4]_2^+}$
15	455.99	100.00	$^{114}\mathrm{Cd[Co(CO)_4]_2^+}$
16	456.99	8.18	$\mathrm{M+_1}$ $\mathrm{Cd[Co(CO)_4]_2^+}$
17	458.03	25.52	$^{116}\mathrm{Cd[Co(CO)_4]_2^+}$

Table 5: Mass Spectral Data: BipyCd[Co(CO)$_4$]$_2$

Peak no.	m/e	%RA	Assignment
1	156.09	41.77	Bipy$^+$
2	170.95	27.85	Co(CO)$_4^+$
3	173.00	9.68	Cd-Co$^+$
4	433.00	2.53	Bipy ^{106}CdCo(CO)$_4^+$
5	436.97	27.85	Bipy ^{110}CdCo(CO)$_4^+$
6	437.94	53.16	Bipy ^{111}CdCo(CO)$_4^+$
7	438.94	100.00	Bipy ^{112}CdCo(CO)$_4^+$
8	439.87	51.90	Bipy ^{113}CdCo(CO)$_4^+$
9	440.91	93.67	Bipy ^{114}CdCo(CO)$_4^+$
10	441.91	13.92	BipyCd $^{m+n}$Co(CO)$_4^+$
11	442.94	26.58	Bipy ^{116}CdCo(CO)$_4^+$
12	443.97	7.59	BipyCd $^{m+n}$Co(CO)$_4^+$
13	444.94	2.53	BipyCd $^{m+n}$Co(CO)$_4^+$
14	452.69	2.53	^{111}Cd[Co(CO)$_4$]$_2^+$
15	453.75	10.13	^{112}Cd[Co(CO)$_4$]$_2^+$
16	455.79	22.78	^{114}Cd[Co(CO)$_4$]$_2^+$
17	457.78	10.13	^{116}Cd[Co(CO)$_4$]$_2^+$

Table 6: Mass Spectral Data: $\mathrm{(TMED)Cd[Co(CO)_4]_2}$

Peak no.	m/e	%RA	Assignment
1	58.04	10.83	Co^+
2	116.16	50.83	TMED^+
3	117.12	4.17	$\mathrm{Co\text{-}Co}^+$
4	142.82	8.33	$\mathrm{Co(CO)_3}^+$
5	170.92	44.17	$\mathrm{Co(CO)_4}^+$
6	174.08	6.67	$\mathrm{Cd\text{-}Co}^+$
7	397.00	46.67	$\mathrm{TMED}\,{}^{110}\mathrm{CdCo(CO)_4^+}$
8	397.97	28.33	$\mathrm{TMED}\,{}^{111}\mathrm{CdCo(CO)_4^+}$
9	398.97	65.83	$\mathrm{TMED}\,{}^{112}\mathrm{CdCo(CO)_4^+}$
10	399.97	65.83	$\mathrm{TMED}\,{}^{113}\mathrm{CdCo(CO)_4^+}$
11	401.00	100.00	$\mathrm{TMED}\,{}^{114}\mathrm{CdCo(CO)_4^+}$
12	402.00	16.67	$\mathrm{TMED}\,{}^{116}\mathrm{CdCo(CO)_4^+}$
13	403.03	20.00	$\mathrm{TMED}\,{}^{116}\mathrm{CdCo(CO)_4^+}$
14	404.94	2.50	$\mathrm{TMED}\,{}^{116+1}\mathrm{CdCo(CO)_4^+}$
15	451.75	12.50	${}^{110}\mathrm{Cd[Co(CO)_4]_2^+}$
16	452.87	14.17	${}^{111}\mathrm{Cd[Co(CO)_4]_2^+}$
17	453.78	16.67	${}^{112}\mathrm{Cd[Co(CO)_4]_2^+}$
18	454.69	9.17	${}^{113}\mathrm{Cd[Co(CO)_4]_2^+}$
19	455.78	35.00	${}^{114}\mathrm{Cd[Co(CO)_4]_2^+}$
20	457.84	2.50	${}^{114+1}\mathrm{Cd[Co(CO)_4]_2^+}$

Table 7: Mass Spectral Data: $\mathrm{BipyZn[Co(CO)_4]_2}$

Peak no.	m/e	%RA	Assignment
1	58.07	55.56	$\mathrm{Co^+}$ or $\mathrm{(CO)_2^+}$
2	170.92	10.00	$\mathrm{Co(CO)_4^+}$
3	377.72	66.67	$\mathrm{(CO)_2Co\text{-}Zn\text{-}Co(CO)_4^+}$
4	390.69	100.00	$\mathrm{BipyZn^{64}Co(CO)_4^+}$
5	392.56	22.22	$\mathrm{BipyZn^{66}Co(CO)_4^+}$
6	394.59	33.33	$\mathrm{BipyZn^{66}Co(CO)4^+}$
7	396.66	33.33	$\mathrm{BipyZn^{70}Co(CO)_4^+}$
8	520.25	5.00	$\mathrm{Bipy(CO)_2CoC^+\ Zn^{64}Co(CO)_4}$

Table 8: Mass Spectral Data: $\mathrm{BipyCd[Mn(CO)_5]_2}$

Peak no.	m/e	%RA	Assignment
1	155.84	12.02	Bipy^+
2	194.65	3.88	$\mathrm{Mn(CO)}_5^+$
3	308.46	1.55	$\mathrm{Cd}^{114}\mathrm{Mn(CO)}_5^+$
4	391.31	4.26	$\mathrm{(CO)Mn\text{-}Cd\text{-}Mn(CO)}_5^+$
5	421.21	1.94	$\mathrm{Bipy}^{114}\mathrm{CdMn(CO)_3C}^+$
6	422.28	3.10	$\mathrm{Bipy}^{116}\mathrm{CdMn(CO)_3C}^+$
7	440.40	2.71	$\mathrm{BipyCdMn(CO)}_4{}^+$
8	460.68	20.54	$\mathrm{Bipy}^{110}\mathrm{Cd\text{-}Mn(CO)}_5^+$
9	461.68	29.46	$\mathrm{Bipy}^{111}\mathrm{Cd\text{-}Mn(CO)}_5^+$
10	462.68	65,50	$\mathrm{Bipy}^{112}\mathrm{CdMn(CO)}_5{}^+$
11	463.71	46.90	$\mathrm{Bipy}^{113}\mathrm{CdMn(CO)}_5{}^+$
12	464.71	74.03	$\mathrm{Bipy}^{114}\mathrm{CdMn(CO)}_5{}^+$
13	465.78	3.49	$\mathrm{Bipy}^{m+n}\mathrm{Mn(CO)}_5{}^+$
14	466.68	22.48	$\mathrm{Bipy}^{116}\mathrm{CdMn(CO)}_5{}^+$
15	467.84	2.33	$\mathrm{BipyCd}^{m+n}\mathrm{Mn(CO)}_5{}^+$
16	468.75	1.55	$\mathrm{BipyCd}^{m+n}\mathrm{Mn(CO)}_5{}^+$
17	499.49	3.49	$^{110}\mathrm{Cd[Mn(CO)_4]_2}^+$
18	500.53	5.81	$^{111}\mathrm{Cd[Mn(CO)_5]_2^+}$
19	501.49	17.05	$^{112}\mathrm{Cd[Mn(CO)_5]_2}^+$
20	503.56	20.54	$^{113}\mathrm{Cd[Mn(CO)_5]_2^+}$
21	503.56	12.44	$^{114}\mathrm{Cd[Mn(CO)_5]_2^+}$
22	651.65	3.49	$\mathrm{Bipy}^{110}\mathrm{Cd[Mn(CO)_5]_2^+}$
23	656.28	74.42	$\mathrm{Bipy}^{111}\mathrm{Cd[Mn(CO)_5]_2}^+$
24	657.62	79.07	$\mathrm{Bipy}^{112}\mathrm{Cd[Mn(CO)_5]_2}^+$

Table 8 con't

Peak no.	m/e	%RA	Assignment
25	658.71	90.31	Bipy ^{113}Cd$[Mn(CO)_5]_2^+$
26	659.71	100.00	Bipy ^{114}Cd$[Mn(CO)_5]_2^+$
27	661.31	13.18	Bipy^{114+1}Cd$[Mn(CO)_5]_2^+$
28	662.78	10.08	Bipy^{116}Cd$[Mn(CO)_5]_2^+$

Table 9: Mass Spectral Data:Bipy$Zn[Mn(CO)_5]_2$

Peak no.	m/e	%RA	Assignment
1	58.12	1.09	$(CO)_2^+$
2	156.14	28.23	$Bipy^+$
3	170.98	2.55	
4	194.94	13.66	$Mn(CO)_5^+$
5	295.12	5.83	$^{66}ZnMn(CO)_6^+$
6	414.87	100.00	$Bipy\,^{64+1}ZnMn(CO)_5^+$
7	415.87	10.20	$Bipy\,^{66}ZnMn(CO)_5^+$
8	416.87	43.35	$Bipy\,^{67}ZnMn(CO)_5^+$
9	417.84	10.56	$Bipy\,^{68}ZnMn(CO)_5^+$
10	418.87	32.60	$Bipy\,^{67}ZnMn(CO)_5^+$
11	419.91	5.46	$Bipy\,^{68+1}ZnMn(CO)_5^+$
12	420.91	5.10	$Bipy\,^{70}ZnMn(CO)_5^+$
13	453.69	37.70	$^{64}Zn[Mn(CO)_5]_2^+$
14	455.69	19.85	$^{66}Zn[Mn(CO)_5]_2^+$
15	456.72	5.10	$^{68}Zn[Mn(CO)_5]_2^+$
16	457.69	17.49	$^{68}Zn\ Mn(CO)_5]_2^+$

Table 10: Mass Spectral Data: $In[Co(CO)_4]_3$

Peak no.	m/e	%RA	Assignment
1	114.91	0.03	In^+
2	170.97	5.77	$[Co(CO)_4]_2^+$
3	456.69	14.23	$In^{113}_{115}[Co(CO)_4]_2^+$
4	457.69	0.73	$In\ [Co(CO)_4]_2^+$
5	625.31	4.52	$In^{113}[Co(CO)_4]_3^+$
6	627.31	100.00	$In[Co(CO)_4]_3^+$
7	628.31	13.38	$In[Co(CO)_4]_3+$
8	629.31	2.56	$In[Co(CO)_4]_3+$

Table 11: Current Efficiencies

System	Current efficiencies (moles F^{-1})
$Sn/Mn_2(CO)_{10}/bipy$	0.5
$Cd/Mn_2(CO)_{10}/bipy$	0.5
$Zn/Mn_2(CO)_{10}/bipy$	0.5

3.4 Discussion

The variety of experimental systems successfully investigated and the range of products obtained in the direct electrochemical synthesis described suggests that such methods have definite advantages over the other methods described earlier.

Although the amounts used are suitable for normal laboratory working, the scale of production can no doubt be increased if necessary to the 10-100g scale.

Characterisation of the products were established by elemental analyses, infra-red and mass spectroscopy.

It is quite clear from the results that compounds of the type $M[M'(CO)_n]_m$ and the adducts of bidentate ligands TMED and bipyridyl (m = Cd, Zn or In and M' = Mn or Co) can effectively be prepared in satisfactory quantities by a direct electrochemical method. The system involving tin and both metal carbonyls fail to give the expected products $Sn[Co(CO)_4]_4$ or $Sn[Mn(CO)_4]_4$ for reasons which are not clear at this point. Measurements of current efficiency (0.5 mol F^{-1}) for the $Sn/Mn_2(CO)_{10}$/bipy system suggest, as in the other systems investigated, that the initial formation of divalent tin species presumably would then react with two more units of $Mn(CO)_5$. Thus

$$Sn \longrightarrow Sn^{2+} + 2e^-$$

$$(CO)_5Mn - Mn(CO)_5 + 2e \longrightarrow 2Mn(CO)_5^-$$

$$Sn^2 + 2Mn(CO)_5 \longrightarrow Sn[Mn(CO)_5]_2 \xrightarrow{Mn_2(CO)_{10}} Sn[Mn(CO)_5]_4$$

The elemental analyses for the $Sn/Mn_2(CO)_{10}$/bipy system indicate a ratio of (1: 1.2) for Sn: Mn while the $Co_2(CO)_8$/Sn bipy system consistently gives a (1: 1.6) ratio for Co: Sn. It is possible that the products consists of mixtures of divalent and tetravalent tin complexes.

(i) Vibrational Spectra:

The vibrational spectra of polynuclear metal carbonyls in the carbonyl stretching region (2150-1800cm^{-1}) have been studied and are well documented.

In view of this, it will suffice to state that the stretching frequencies agree closely with those in the literature except for bipyZn[Mn(CO)$_5$]$_2$. Both bipyZn[Mn(CO)$_5$]$_2$ and bipyCd[Mn(CO)$_5$]$_2$ would, on the basis of group theory considerations, be expected to have the same number (seven) of i.r active bands. Hsieh and Mays[74] however found only three bands in nujol for the zinc complex, although they did observe seven bands for the cadmium complex. In this work seven bands are observed for both complexes as is indeed expected.

(ii) Mass Spectra:

In studying inorganic or organometallic systems, mass spectrometry is a useful tool in three main areas. Molecular weight can be determined and from the isotopic patterns, the detailed composition of the molecule can be established. Mass spectral data can also help in the determination of structure if a careful analysis of the fragmentation pattern is made. The third and equally important aspect of mass spectroscopy is the determination of appearance and ionisation potentials and the relative bond energies of similar molecules. Three main techniques have been developed, namely electron impact (EI) mass spectrometry, field ionisation (FI), mass spectrometry and field desorption (FD) mass spectrometry. With an electron impact source, fragmentation of the molecules under investigation occurs only if the ionising electrons have energy in excess of ionisation potential of the molecules.

The resulting mass spectra are complicated. This however, is not the case with the two "softer" techniques which will normally exhibit a strong parent ion peak.

If a very high electric field acts on a molecule, the potential energy of the molecule is changed in such a way that an electron in the ground state of the molecule is removed. During this type of ionisation process, the molecules do not acquire sufficient energy to lead to extensive fragmentation. The results are therefore simple to interpret and more information can be compiled. For molecules which are so unstable that the major part is decomposed thermally during the sample evaporation prior to ionisation process both FI and EI are virtually useless. FD on the other hand has the advantage that the molecules in question are not decomposed by the dissolved process. A further advantage is the part that FD requires much smaller amounts of sample.

Important as mass spectrometry is, any results obtained must emphasize some of the main dangers that may be encountered in mass spectral studies of inorganic and organometallic systems. In the determination of molecular weight data, it is generally true that the highest m/e peak is the parent ion in FD and FI studies although this is hardly the case in electron impact studies. As pointed out earlier, a careful correlation of the various fragments will give a reasonable estimate of the molecular weight of the compound in question in the event that the parent peak is missing. The probe temperature may rise to 300°C and most inorganic or organometallic molecules start to decompose thermally or polymerise at such temperatures.

A look at the tables of mass spectral data will show that the molecular ion peak (M^+) was observed for the compounds bipyCd[Mn(CO)$_5$]$_2$,

$Cd[Co(CO)_4]_2$ and In $[Co(CO)_4]_3$. It is significant in all three cases that these are also the base peaks. $BipyZn[Mn'(CO)_5]_2$, $bipyZn[Co(CO)_4]_2$, $bipyCd[CO)_4]_2$ and $TMEDZn[Co(CO)_4]_2$ on the other hand have the fragments $[bipyZnMn(CO)_5]^+$, $[bipyCdCo(CO)_4]^+$ and $[TMEDZnCo(CO_4]^+$ corresponding to the loss of a $Co(CO)_4$ or $Mn(CO)_5$ group as the base peaks. This could be an indication of the greater bond strength between Cd - Mn as compared to Zn - Co or Zn - Mn. This observation is in complete agreement with the fact that M - M' is stronger the larger the metal atoms, eg. Re - Re bond is stronger than Mn - Mn bond in $(OC)_5M-M(CO)_5$.

Other common fragments of high relative abundance are $M[M'(CO)_n]^+_m$ $M'(CO)^+_n$, and $bipy(CO)_4ZnCo(CO)_2C^+$. The presence of fragments like $bipyM-M(CO)^+_n$, $M[M'(CO)_n]^+_m$, and $M'-M^+$ clearly shows that a M -M' bound is present in these compounds. Ions of the type $[M'(CO)_{n+1}]^+$ or $[M'(CO)_n)]^+$ are conspicuous by their absence. This suggests that even in the high energy conditions operative in the mass spectrometer, no tendency to bond M' to carbon monoxide through the oxygen atom occurs and that rearrangements caused by migration of carbon monoxide groups to $[M'(CO)_{n+1}]^+$ do not occur.

Lewis and Johnson[78] and Hsieh and Mays[60] have reported that the relative abundance of the ions $M'_2(CO)_xC^+$ (M' = Mn or Re and n = 0 to 8 or 9) for the compounds $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$ (for M = Zn or Cd) increases as x decreases. They also report successive loss of CO groups from the compounds. Although this work does not show this trend or for that matter the successive loss of CO groups, the solution probably lies in the fact that electron impact and not field ionisation or field desorption was used in their studies.

(iii) Current Efficiencies In Electrochemical Synthesis

It has been suggested that a knowledge of the number of electrons involved in the electrochemical process can give some insight into the mechanism of the electrochemical reaction. Thus in the electrochemical oxidation of a metal M to M^{n+}, according to Faraday's Laws, n Faradays of electricity would oxidise 1 mole of the metal if the process was a purely electrochemical one.

Dessy[56] et al have showed that in the reduction of metal-metal bonded dimetallics, the electrochemical process could either be a two electron transfer process or a one electron transfer process. From the results of a wide range of homodimetallics it has been found that homodimetallics tend to prefer the former pathway.

The current efficiencies measured in this work (page 50) show that for reactions involving Zn, Cd or Sn, two electrons are involved. The reactions could thus be envisaged to go through the steps -

Cathode:

$$(OC)_nM'\text{-}M'(CO)_n \quad 2e^- \longrightarrow 2[M'(CO)_n]^-$$

Anode:

$$2[M'(CO)_n]^- + M \longrightarrow M[M'(CO)_n]_2 \quad + 2e^-$$

Overall:

$$(OC)_nM\ M(CO)_n \quad + \quad M \longrightarrow M[M(CO)_n]_2$$

The reactions can be summarized as follows

$$M + Mn_2(CO)_{10} \quad + \text{bipy} \xrightarrow[Et_4NClO_4]{CH_3OH/C_6H_6} M[Mn(CO)_5]_3\text{bipy}$$

(M = Zn or Cd)

$$M + Co_2(CO)_8 \quad + L_2 \xrightarrow[Et_4NClO_4]{MeOH/C_6H_6} M[Co(CO)_4]_2L_2$$

(M = Zn or Cd and L_2 = TMED or bipy)

$$2In + 3Mn_2(CO)_{10} + bipy \xrightarrow[Et_4NClO_4]{C_6H_6/CH_3OH} 2In[Mn(CO)_5]_3bipy$$

(iv). Advantages of the Electrochemical Method.

The methods hitherto applied in the synthesis of the complexes of the type $M[M'(CO)_n]_m$, $M[M'(CO)_n]_mL$ and $M[C_5H_5M'(CO)_n]_m$ involve the use of metal carbonyl hydrides, sodium salts of the dimeric species (synthesized from the dimeric species), the dimeric metal carbonyls and some alkylmetal species. Further, the methods discussed earlier require severe conditions (high temperatures and pressure, low temperatures) and sometimes long periods for work up.

In general, the final product is synthesized in more than one step and even then, the separation of reactants from products can become quite intricate in cases where the solubility properties of the products are the same as those of the reactants. The severe conditions of reaction employed in the other methods usually dictate the use of reasonably sophisticated apparatus.

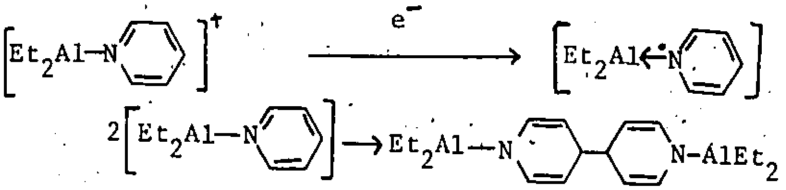
Electrochemical synthesis of metal-metal bonded polynuclear carbonyls elimates most of the above problems. One employs simple apparatus, readily available, starting materials which require only minimal care in handling (cf use of R_2M in synthesis of Mn carbonyls), and the reactions are one step processes carried out at room temperature and atmospheric pressure. It is conceivable that if larger reaction cells and larger surface area electrodes were used the process could indeed find a wider application than is presently apparent.

CHAPTER IV

Electrochemical Reactions of Halopyridines and Halopyridinium Salts:

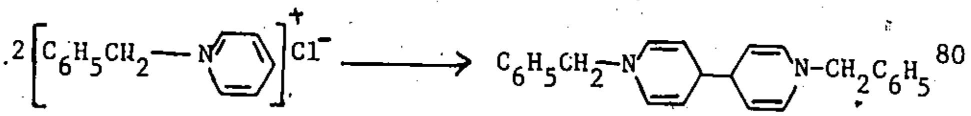
4.1 Introduction:

A relatively large amount of work has been done on the electrochemical reactions of alkyl and aryl halides. In comparison, the electrochemical reactions of unsubstituted and substituted aromatic heterocyclic compounds such as pyridine, substituted pyridines, and pyridinium salts has received little attention. In some of the earlier work the cathodic reduction of the pyridine complex of diethylaluminium cation [R-M-X = $Et_2AlPyr]^+$ give rise to organoaluminium radicals which dimerised to tetrahydropyridyl derivatives.[79]



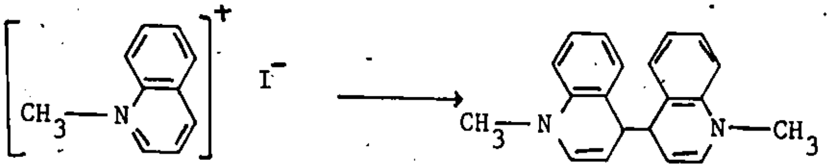
The beryllium analogues behave in a similar manner.

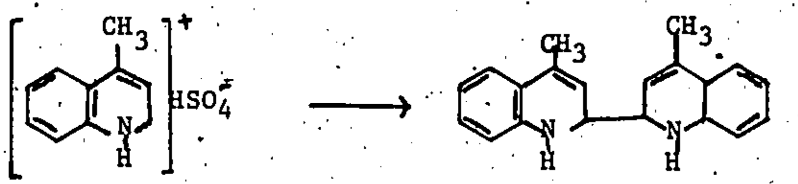
The electrolyses of pyridinium and quinolinium salts have been carried out, producing dihydropyridines and quinolines.[80,81] In these reactions two ions accept two electrons at the cathode to form radicals which then couple. The reaction can be summarised as follows



80

50%





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Tuck and Habeeb[82,83] have shown that anodic cadmium is an effective halogen abstracting reagent and that n-PrBr and n-BuBr will undergo a reaction involving electrochemical halide abstraction to form the coupling products n-C_6H_{14} and n-C_8H_{18} respectively.[32] The same authors have also reported the synthesis of cadmium compounds of the type RCdX (R = Me or Et; X = I or Br.The present work was intended to investigate the reaction of bromopyridines and pyridinium salts under conditions very similar to those in which coupling is observed for alkyl halides and aryl halides.

3.2 Experimental

General: The experimental arrangement is shown in Figure 1. Cadmium metal, methanol and benzene were treated in the manner specified in Chapter II.

2- and 3-Bromopyridine (Aldrich) were dried over Linde Molecular sieves. 4-bromopyridine hydrochloride and 4-chloropyridine hydrochloride (Aldrich) were dried for 3 hours at 100°C. All reactions were carried out at ambient temperature and in nitrogen atmosphere.

Current efficiencies were determined in the same manner as in the previous chapter. Halogen analyses were done by the Volhard method[84] and an adaptation of the Oakdale-Thompson method.[85] Cadmium analysis were done both by atomic absorption and by EDTA titration using solochrome black T indicator in alk[illegible]dium.[86]

(i) Electrolysis of 4-bromopyridine hydrochloride in methanol and benzene

1.0g of 4-bromopyridine hydrochloride was dissolved in 20mls of methanol and 15mls benzene added to the solution. The mixture was electrolysed for 3 hours using an initial current of 50mA. The colour of the solution changed progressively from colourless to yellow and then brown. Filtration of the cell contents left a light brown solid(I).

The filtrate was then pumped off and light yellow crystals were left behind. The yellow product (II) was then recrystallized from methanol and 0.54g of the product isolated (93% on the basis of 0.15g cadmium anode dissolved)- later shown to be 4,4′-bipyridyl dihydrobromide (II).

(ib) Electrolysis of 4-Chloropyridine hydrochloride in Methanol and Benzene

1.0g of 4-chloropyridine hydrochloride was dissolved in 10mls of methanol and 30mls benzene and the mixture electrolysed for 3 hours employing an initial current of 60mA. An off white solid was formed in the cell as the electrolysis was continued.

The mixture was filtered off and the solid washed with ether/methanol mixture. 0.2g of this product (III) was isolated (79% on the basis of Cd dissolved). The compound was later shown to be 4,4′-bipyridyl dihydrochloride (III). 0.13g of Cd was dissolved from the anode.

The filtrate was reduced in volume and then kept at 0°C for 2 days after which 0.3g of a light yellow solid(IV) was isolated. This contained 20.0% chloride and 26.72% Cd.

(iii) Electrolysis of 2-bromopyridine in methanol and benzene

A solution consisting of 2g bromopyridine, 20mg Et_4NClO_4, 15mls methanol and 10mls benzene was electrolysed for 3 hours. The initial current was 50mA.

The white solid formed as the electrolysis progressed was filtered off and washed thoroughly with methanol and benzene. 0.2g of this solid (V) was isolated. The solid was not suluble in methanol, benzene, acetone, acetonitrile, pet. ether, diethyl ether or THF. After stirring the residue with 2,2′-bipyridyl in Et_2O or pet. ether the starting material was found to be unchanged.

A small amount of the residue was dissolved in concentrated HNO_3/CF_3COOD mixture and a NMR spectrum obtained.

An aliquot of the filtrate was then taken and run on a S.E. 30 column to determine the composition of the filtrate. However the only peaks observed were for 2-bromopyridine and the solvents.

In a separate electrochemical experiment employing 100mg Et_4NBr as the supporting electrolyte the precipitate was found to contain 27.9% Cd and 39.)% Br.

(iv) Electrolysis of 2-bromopyridine in Acetonitrile and Benzene

A solution of 15mg Et_4NClO_4 and 2mls of 2-bromopyridine in 20mls acetonitrile and 10mls benzene was electrolysed at a current of 50mA for 4 hours. After a few minutes a brown colour began to form in the cell and a brown solid was deposited at the bottom of the cell. 0.1g of Cd was dissolved.

The mixture was then filtered leaving a brown solid behind. Washing with pet. ether and then with benzene gave an off-white solid (VII). 0.18g of the product was isolated.

The filtrate was pumped off and the remaining oil was found to contain unreacted 2-bromopyridine by gas chromatography and small amounts of benzene and acetonitrile.

(V) Electrolysis of 3-bromopyridine in Acetonitrile and Benzene

2mls of 3-bromopyridine were added to a mixture of 10mls benzene and 20mls acetonitrile. 15mg Et_4NClO_4 was then dissolved in the solution. The solution was electrolysed for 6 hours employing an initial current of 50mA. The white solid that was formed during the electrolysis was filtered off and washed with methanol/benzene mixture and then with pet. ether. 0.1g of product (VIII) was isolated; 0.056g of cadmium dissolved.

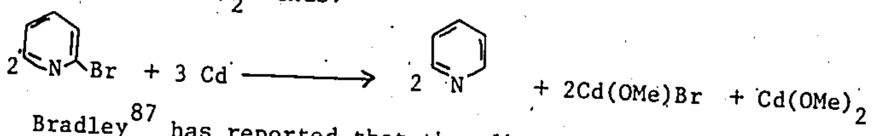
The filtrate was reduced in volume and a sample run on an S.E. 30 chromatographic column. The only peaks formed were those belonging to unreacted 3-bromopyridine and the solvents.

3.3. Results and Discussion

The electrolysis of 4-chloropyridine hydrochloride and 4-bromopyridine hydrochloride yields the expected products 4,4'-bipyridyl dihydrobromide respectively. These products were identified by comparison of the NMR and IR data with authentic samples and elemental analyses. (Table 12)

The reactions of 2-and 3-bromopyridine in acetonitrile/benzene did not give the coupling products 2,2' bipyridyl and 3,3'-bipyridyl as had been expected. Although it is not possible to characterise the products with the information available, one can draw a few conclusions from the i.r, NMR and mass spectra of these compounds.

The product (V) from the electrolysis of 2-bromopyridine in methanol/benzene has the empirical formula $Cd_2Br_2C_4H_{12}O_4$. The i.r spectrum (Table 13) of this compound shows strong bands at $1045cm^{-1}$, $1105cm^{-1}$, $1385cm^{-1}$, $1450cm^{-1}$, and $2930cm^{-1}$. (See Table 13). This is evidence that there is no pyridine type unit in the compound. When the product is dissolved in HNO_3/CF_3COOD the NMR spectrum exhibits two peaks at $\delta = 3.3$. and $\delta = 4.1$ which is in agreement with the NMR peaks of authentic methanol. The data therefore suggests the presence of a methoxy group. Thus the product can be envisaged as a mixture of Cd(OMe)Br and Cd(OMe)$_2$ thus:



Bradley[87] has reported that the alkoxides of low valence metals are generally insoluble in organic solvents. The reason advanced for this is that they tend to form polymers. Another feature of metal alkoxides is that they form very few coordination compounds with donor molecules. That the reaction of the product in this case did not react with 2,2′-bipyridyl is therefore not surprising.

The compound (VI) has an i.r spectrum that indicates the presence of a pyridine nucleus. It is insoluble in methanol, acetone, acetonitrile, benzene, THF and dichloromethane.

Although the compounds from the electrolysis of 2-and 3-bromopyridine in acetonitrile/benzene have not been characterised, it is obvious as in the case of 2-bromopyridine in MeOH/C_6H_6 that scission of the C—Br bond occurs. The mass spectra of both products show the presence of a base peak at m/e = 79. The product (VIII) from the 3-bromo isomer exhibits peaks of much lower relative abundance at m/e = 80(%RA = 10.98%), m/e = 15.6 (%RA = 4.02), m/e = 157 (%RA = 2.57), m/e = 158 (%RA = 3.64) and m/e = 159 (%RA = 2.38). Since the probe temperature was set at 205°C, it is possible that the peaks at m/3 = 156, 157, 158, and 159 are a result of recombination of pyridine radicals.

The presence of a pyridine skeleton in compounds VI and VIII and the ratio of atoms suggests that insertion compounds of the type RCdBr (R = Pyridine) may be formed in these reactions. The existence of mixtures of these compounds with $CdBr_2$ is not unlikely.

The reactivity of the 2-and 4-sites is very similar although the 4-position is slightly more reactive towards nucleophiles. It would therefore be expected that if coupling occurs in the case of the 4-bromopyridinium hydrohalide, the same reaction would occur for the 2-bromopyridinium hydrohalide. In the light of the present results it would be worthwhile to investigate these reactions further, employing the pyridinium salts instead of the halopyridines.

Table 12 Analytical Data

Compound	%Cd	%X	% C	%H	%N	Probable Product
II	0.3(0.0)	50.7(50.3)	-	-	-	4,4'-bipyridyl dihydrobromide
III	0.5(0.0)	30.7(30.9)	-	-	-	4,4'-bipyridyl dihydrochloride
V	53.8	26.2	7.76	1.99	-	$Cd_2Br_2C_4H_{12}O_4$
VI	27.9	39.0	-	-	-	$CdBr_2(C_5H_5N)_2$
VII	35.0	51.9	15.50	1.68	2.36	$Cd_{1.8}Br_{1.8}C_{7.6}H_{9.9}N_{1.0}$
VIII	32.4	43.5	17.21	1.83	2.79	$Cd_{1.5}Br_{2.7}C_{7.2}H_{9.2}N_{1.0}$

Numbers in parenthesis are the calculated values.

X = Br or Cl

Table 13: I.R. DATA

Compound	Frequencies (cm^{-1})
V	635(sb; 1045(m), 1105(s); 1385(sb) 1450(sb); 2930(s); 3580(vs)
VI	663(w); 690)s); 780(s); 1000(vs); 1033(s) 1365(s); 1400(vs); 1390(vs); 1455(vs), 1465(sh)14808); 1602(s); 29750); 3080(w)
VII	640(s); 695(vs); 750(s); 900(vs); 1012(s); 1040(vs) 1070(S); 1160(s); 1220(vs); 1445(vs); 1485(m); 1505(w); 1602(vs); 2920(vw); 3140(w)
VIII	638(vs); 696(vs); 710(s); 730(w); 800(vs); 948(m); 992(m); 1030(vs); 1042(s sh); 1088(s); 1100(vs) 1118(s); 1322(s); 1420(vs); 1468(vs); 1560(s); 1590(vs); 3090(s)

b - broad, s - strong, sh - shoulder, v - very, m - medium, w - weak

REFERENCES

1. H.E. French and M. Drane , J. Amer.Chem. Soc. 52, 4904 (1930)
2. S. Wawzonek, Science 155, 39(1967)
3. F. Guccione, Chem. Eng. (N.Y.) 72 (13) 102 (1965)
4. D.G Braithwaite, U.S. Pat. 3,007857 (1957); C.A. 56, 3280f (1962)
5. National Aluminate Corp, Brit. Pat. 829172 (1960); C.A. 54, 24036i
6. D.G. Braithwaite, U.S. Pat. 3,007,858 (1959); C.A. 56,4526h (1962
7. D.G. Braithwaite et al, U.S. Pat. 3,141,841 (1964); C.A. 61,10323g (1964)
8. F.G. Pearce et al, U.S. Pat. 3,180810 (1965); C.A. 63, 3902h(1965)
9. D.G. Braithwaite et al, Ger. Pat. 1,216,303(1966; C.A. 65,8962c (1966)
10. D.G. Braithwaite, U.S. Pat. 3,312, 605(1967) C.A. 67, 11589h (1967)
11. D.G Braithwaite et al, Belg. Pat. 671,841 (1966); C.A. 66, 76157q (1967)
12. D.G. Braithwaite, Ger. Pat. 1,202, 790 (1965); C.A. 64, 30646 (1966)
13. D.G. Braithwaite, U.S. Pat. 3,256,161 (1966); C.A. 65, 6751d (1966)
14. Nalco Chem. Co., Neth. Pat. Appl. 6,514,238 (1966) C.A. 65, 6751f (1966)
15. D.G. Braithwaite, Ger. Pat. 1,226,100 (1966), C.A. 65, 14690g (1966)
16. A.V. Walke, U.S. Pat. 3,372,098 (1968), C.A. 68, 83834C (1968)
17. D.G. Braithwaite, U.S. Pat. 3,391066 (1968), C.A. 69, 67537y (1968)
18. D.G. Braithwaite, Ger. Pat. 1,231,242 (1967), C.A. 66, 95196t (1967)
19. D.G. Braithwaite et al, U.S. Pat. 3,380,899 (1968); C.A. 69, 1541n (1968)
20. D.G. Braithwaite, Ger. Pat. 1,231,700 (1967), C.A. 66, 76155n (1967)
21. D.G. Braithwaite, U.S. Pat. 3391,067 (1968), C.A. 69, 64148m (1968)
22. P. Kobetz & W.H. Thomas, U.S. Patent 3,344,048 (1967) C.A. 68, 45633d (1968)
23. M. Schuler and M. Kegelmann, J. Electrochem. Soc. 116,1201 (1969)
24. A.P. Giraitis, Ger. Pat. 1,046,617 (1958), C.A. 55, 383c (1961)
25. H. Lehmkuhl et al, Chem Ing - Tech. 36, 612(1964)
26. Ethyl Corp., Brit. Pat. 842,090 (1960), C.A. 55, 5199e (1961)
27. H. Lehmkuhl & Ziegler, Ger. Pat. 1,212,085 (1966), C.A. 64, 19675a (1966)

28. L.V. Armenskaya et al, Khim. Prom. (Moscow) 44, 665 (1968); C.A. 69, 102461e (1968)

29. K.N. Korotaevskii et al, Zh. Obshch. Khim., 36, 167(1966), C.A. 64, 13751b (1966).

30. L.V. Armenskaya et al, U.S.S.R. Pat. 184,853 (1966); C.A. 66, 71949q (1967)

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

32. J.J. Habeeb, A. Osman, D.G. Tuck, Chem. Comm. 379 (1976)

33. A. Osman & D.G. Tuck, Unpublished results.

34. W.V. Evans et al, J. Amer. Chem. Soc. 56, 6540934), 58, 720 (1936), 58, 2284 (1935) and 61, 898 (1939)

35. R.E. Dessy, T. Chivers and W. Kitching, J. Amer. Chem. Soc. 88, 467 (1966)

36. A.P. Tomilov, D. Smirnow and S.L. Varshavsku, Zhur. Obshch. Khim. 35, 391 (1965); C.A. 63, 5238 (1965).

37. C.K. Mann and J.L. Webb, Tetrahedron Letters 2249 (1966)

38. E.H Mottus & M.R. Ort, J. Electrochem. Soc. 117 885 (1970)

40. F.Said and D.G. Tuck, Unpublished results.

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

42. H.Lehmkuhl et al, J. Organometal. Chem. 23, C 30 (1970; 25, C44 (1959); 20, 229 (1967)

43. H.Lehmkuhl, Synthesis 377 (1973); W. Leuchte, Dissertation Universitat Bochum (1971).

44. G.Wilke and C. Grard, Chem, and Chemical Industry (Japan) 20, 1308 (1967).

45. S. Valcher and E. Alunni, Ricerca Scientific 38, 527 (1968)

46. A.P. Giraitis, T.H. Pearson and R.C. Pinkerton, U.S. Patent 2960450 (1959) Ethyl Corp., C.A. 55, 8430 (1961). T.H. Pearson, U.S. Pat. 2915440 (1959), Ethyl Corp; C.A. 54, 17415 (1960)

47. M.R. Ort and E.H. Mottus et al, U.S. Pat. 3546083 (1967) Monsanto.

48. T. Ohta, K. Ebina and N. Yamazaki, Bull. Chem. Soc Japan 44, 1321 (1971)

49. W.A. Kornicker, U.S. Pat. 3474012 (1964), Monsanto; C.A. 72, 22145 (1970).

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

51. F. Said, J.J. Habeeb and D.G. Tuck, Can J. Chem. 55,3832 (1977)

52. F.Said, J.J. Habeeb and D.G. Tuck, Unpublished results

53. R.S. Stevensz and D.G. Tuck, Unpublished results

54. T.H. Pearson, U.S. Pat. 2,915,440 (1959), C.A. 54, 17415g (1960)

55. Ethyl Corp., Brit. Pat. 845,074, (1960), C.A., 55, 4205g (1961)

56. R.Dessy et al, J. Amer. Chem Soc. 88, 453, 460, 467, 471, 5112 (1966)

57. W. Hieber & U. Teller, Z. anaorg. Chem. 43, 249 (1942)

58. J.M. Burlitch, Chem. Comm. 887, (1968)

59. N.A.D. Carey and J.G. Noltes, Chem. Comm. 147 (1968)

60. A.T.T. Hsieh & M.J. Mays, J. Chem.Soc. (A) 2648 (1971)

61. R.B. King, Advances in Organometallic Chem. 2, 176 (1964)

62. F. Bonati & G. Wilkinson, J. Chem.Soc. 179 (1964)

63. H.R.H. Patil & W.A.G. Graham, Inorg. Chem. 5,1401 (1966)

64. A.T.T. Hsieh and M.J. Mays, J. Organometal. Chem. 37, 9 (1972)

65. J. Hoyano, D.J. Patmore and W.A.G. Graham, Inorg. Nuclear Chem. Letters, 4, 20. (1968)

66. A.T.T. Hsieh & M.J. Mays, Inorg. Nuclear Chem. Letters, 7, 223 (1971)

67. J.D. Robb & M.J. Mays, J. Chem Soc. (A) 561 (1968)

68. A.B. Cornwell, P.G. Harrison & J.A. Richards, J. Organometal. Chem. 108, 47 (1976)

69. Gunter Schmid & Gunter Etzrodt, J. Organometal. Chem. 131(3) 477 (1977) C.A. 87, 1977, 15294k

70. B.R. King, Ann. Rev. Organometal. Chem. 202 (1964); C.A. 58, 9870c

71. Von H. J. Haupt & R.Hoffmann, Z.anorg. allg. Chem. 429, 162 (1977) C.A. 86, (25) 19917u (1977)

72. R.B. King, Advances in Organometal. Chem., 2, 156 (1964)
W.Hieber & H. Beutner, Z. anorg. allgem Chem 320, 101 (1963)

73. W. Hieber & W. Schropp, Jr., Chem. Ber 93, 455 (1960)

74. M.J. Mays and A.T.T. Hsieh, J. Chem. Soc. (A), 729 (k871)

75. W.Hieber & R. Breu, Chem. Ber. 90, 1259 (1957)

76. M.J. Mays & J.D. Robb, J. Chem. Soc (A) 329 (1968)

77. A.R. Manning and D.J. Thornhill, J. Chem. Soc. (A) 637 (1971)

78. J. Lewis & B.F.G. Johnson, Acc. Chem. Res. 1, 245 (1968)

79. H. Lehmkuhl & G.Fuchs & R. Koster, Tetrahedron Lett. 2511 (1965)

80. B. Emmert, Ber. 42,1997 (1909); S. Swann Jr., Technique of Organic Chem. Vol. II, p. 519

81. V. Levchenko and A. Zats, J. Gen. Chem. U.S.S.R. 22, 1301 (1952)

82. J.J. Habeeb & D.G. Tuck, J. Organometal. Chem. 146,213 (1978)

83. J.J. Habeeb & D.G. Tuck, Chem. Comm. 696 (1976)

84. D.A. Skoog and D.M. West, Fundamentals of Analytical Chemistry, Holt, Rinehart and Winston (N.Y.), page 262 (1963)

85. A.F. Berniaz, Ph.D. Dissertation, Simon Fraser University 1973.

86. T.S. West, Complexometry with EDTA and related reagents, 3rd ed. B.D.H. Chemicals Poole Ltd. page 176 (1969)

87. D.C. Bradley, Prog. Inorg. Chem. 2, 303 (1960)

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