

DIRECT ELECTROCHEMICAL SYNTHESIS OF INORGANIC AND ORGANOMETALLIC COMPOUNDS

Dennis G. Tuck

Department of Chemistry, University of Windsor, Windsor, Ontario, Canada
N9B 3P4

Abstract - Although the electrochemical properties of inorganic and organometallic compounds have been widely studied, there has been comparatively little attempt to apply the results of such work in preparative chemistry. Recent experiments have shown that the sacrificial dissolution of either anodic or cathodic metals in non-aqueous media yields a number of different types of inorganic and organometallic complexes; examples of such syntheses are reviewed. The possible mechanisms of these reactions, and the advantages of electrochemical preparative methods, are also discussed.

I PREPARATIVE ELECTROCHEMISTRY

The electrochemical technique represents one of the simplest and most direct methods of carrying out oxidation or reduction reactions, since the removal or addition of electrons can be achieved without the attendant complications otherwise involved in the addition of redox reagents. The applications of this principle in inorganic and organometallic chemistry are well-documented in the extensive literature describing the oxidation or reduction of solute species at inert electrodes to yield either direct products, or intermediate species which subsequently decompose to the required substance. Despite the inherent simplicity, and despite the amount of information available from polarographic studies and other physical measurements, preparative inorganic and organometallic chemists have not taken advantage of electrochemical methods to the extent which might have been expected. The reasons for this are beyond the scope of this review, but one obvious factor which is especially relevant to the theme of the present Conference is that experiments in aqueous media impose restrictions which it is often impossible to overcome, especially with organometallic compounds.

Electrochemistry in non-aqueous solvents is now a mature subject in its own right, as the papers presented in Section IV of this Conference demonstrate, and I shall concentrate in the present discussion only on those aspects which are relevant to preparative chemistry. With non-aqueous solution electrochemistry, as with aqueous systems, some thorough reviews (1-3) suggest that more effort has been devoted to the study of phenomena such as current-voltage relationships than to the preparative applications of the processes involved. One of the purposes of this paper will be to demonstrate that an ignorance of the detailed electrochemistry, and even of such fundamental parameters as E_0 , need be no bar to the use of electrochemical methods in non-aqueous solvents in preparative chemistry.

As noted above, large areas of electrochemistry involve inert electrodes which effectively act as the source of, or sink for, electrons in the reduction or oxidation of solute species. We shall be concerned in the present context only with those electrochemical systems in which one or both of the electrodes serves not only in this sense, but in addition, undergoes reaction with species present in the solution, or generated in solution as electrolysis proceeds. Such reactions are said to involve sacrificial electrodes, and under appropriate conditions offer the chance of using the metal electrode as the starting point of a synthesis.

II METALS AS REAGENTS

Relatively few of the synthetic methods used in inorganic or organometallic chemistry use a metal as the starting point, although in fact some compounds of crucial importance can be synthesised directly from the element. Grignard reagents, and Frankland's synthesis of organozinc halides, are salutary examples of the ability of metals to cleave strong chemical bonds. In recent years, the use of metals has increased through the development of vapour phase synthesis, in which vaporisation of the metal is followed by low temperature reactions in a condensed phase. In consequence, a considerable literature now describes the use of direct synthetic methods and the technique has been reviewed by a number of authors (4-6). The applications of such direct vapour phase syntheses will surely continue to increase as more sophisticated apparatus becomes available. In general, the requirements for such experiments include an efficient high vacuum system of appreciable pumping capacity, some means of evaporating gram quantities of metals, and a cold trap for the collection of the product, or for the spectroscopic examination of the species produced.

With electrochemical reactions, in contrast, one normally works at, or near, room temperature, with all the advantages of producing compounds by the oxidation or reduction of electrode metals under ambient conditions using relatively unsophisticated apparatus. Such methods then constitute direct electrochemical syntheses, and have many attractions which should recommend them in inorganic and organometallic chemistry. The syntheses can obviously involve either cathode or anode, and it will be convenient to discuss these two situations separately, although the underlying principles must have some common base, irrespective of the charge of the electrode, and some comprehension of the principles involved is clearly important in planning future synthetic work.

III DIRECT SYNTHESIS AT SACRIFICIAL CATHODES

III (a) Reactions involving organohalides

The irreversible electrochemical reduction of an organic halide RX has been studied in detail, frequently with mercury pool cathodes. The prime process is still a matter of debate (2,3,7), but for the present purposes the following scheme will suffice

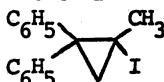


The ultimate fate of the radical R^\cdot may include the formation of the dimer R_2 , a process which has found a number of synthetic applications. More importantly in the present context, the reaction



which may well occur in consecutive steps, gives rise to a series of important metal alkyl compounds. Table 1 lists some typical examples of such syntheses in non-aqueous solution; a number of similar preparations in aqueous or mixed aqueous/organic media have also been reported, but are outside the scope of this review (see refs. 2,3).

TABLE 1. Formation of metal alkyls from sacrificial cathodes in non-aqueous media

Substrate	Cathode, supporting electrolyte, solvent	Product	Reference
$\text{RC}_6\text{H}_4\text{CH}_2\text{Br}$	Hg, LiBr, CH_3OH	$\text{Hg}(\text{CH}_2\text{C}_6\text{H}_4\text{R})_2$	8
	Hg, $(\text{CH}_3)_4\text{NBr}$, CH_3CN	HgR_2	9,10
$\text{C}_2\text{H}_5\text{Br}$	Sn, $(\text{C}_2\text{H}_5)_4\text{NBr}$, CH_3CN	$\text{Sn}(\text{C}_2\text{H}_5)_4$	11
RX	Sn, various, CH_3OH or CH_3CN	SnR_4	12,13,14
$\text{C}_2\text{H}_5\text{Br}$	Pb, $(\text{C}_2\text{H}_5)_4\text{NBr}$, propylene carbonate	$\text{Pb}(\text{C}_2\text{H}_5)_4$	15,16
$\text{C}_2\text{H}_5\text{Br}$	Pb, various salts, propylene carbonate	$\text{Pb}(\text{C}_2\text{H}_5)_4$	17
$\text{C}_2\text{H}_5\text{Br}$	Pb, $(\text{C}_2\text{H}_5)_4\text{NBr}$, various solvents	$\text{Pb}(\text{C}_2\text{H}_5)_4$	15
$\text{C}_2\text{H}_5\text{Br}$	Pb, LiBr, various solvents	$\text{Pb}(\text{C}_2\text{H}_5)_4$	11
CH_3Cl , Br, I $\text{C}_2\text{H}_5\text{Cl}$, I	Pb , $(\text{C}_2\text{H}_5)_4\text{NBr}$, CH_3CN	PbR_4	11

One interesting conclusion to be drawn from Table 1 is the small number of metallic elements which have been used in such work, since the results refer only to mercury, lead and tin. Special emphasis has been placed on lead alkyls, and particularly $\text{Pb}(\text{C}_2\text{H}_5)_4$, because of the industrial importance of these compounds.

Instead of, or as well as the formation of metal alkyls, the reduction of RX may give rise to R_3SnSnR_3 (18), $RHgX$ (19), or R_2TlX (18), although these products were in fact obtained from electrolysis in aqueous solution. Electrolysis of ethyl bromide at an indium cathode in acetonitrile in the presence of 2,2'-bipyridyl gave $C_2H_5InBr_2 \cdot bipy$, which is interestingly the same product as obtained when indium is the anode (20). The significance of this finding is discussed later. (See section IV.1.(f)).

III (b) Reduction of carbonyl compounds

The electrochemical reduction of ketones, and some aldehydes, at a sacrificial mercury cathode gives rise eventually to organomercurials (21). Most, if not all, of these reactions have been carried out in aqueous acid, and the overall stoichiometry is



The species initially generated is presumed to be the radical $R_2COH\cdot$ (7). Other cathodes (3) utilized again include lead, and $Pb(C_2H_5)_4$ has been obtained in this way through electrochemical reactions in non-aqueous solution (11).

III (c) Some miscellaneous reactions at sacrificial cathodes

The fate of the species produced in the electrochemical reduction of various organometallic compounds has been reviewed by Lehmkuhl (2), following a scheme proposed by Dessy (22,23). The examples of such reactions given in Table 2 represent simple synthetic routes to a number of useful compounds. Some of these processes are in fact transmetalation reactions, and we shall see other similar examples later, then involving metal anodes. (See section IV.3(b)). Other reactions result in the insertion of mercury into the metal-metal bond of a dinuclear metal carbonyl, and again this process can be achieved with anodic metals (Section IV.3(c)).

TABLE 2. Other reactions involving sacrificial cathodes

	Reference
$RHgBr + Hg_{(-)} \longrightarrow R_2Hg + HgBr_2$	10
$Ph_2PbCl_2 + 3Hg_{(-)} \longrightarrow Ph_2Hg + Pb + Hg_2Cl_2$	24
$2Ph_3PbCl + 5Hg_{(-)} \longrightarrow 3Ph_2Hg + 2Pb + Hg_2Cl_2$	24
$Ph_2Pb(OAc)_2 + Hg_{(-)} \longrightarrow Ph_2Hg + Pb + 2OAc$	24
$2C_5H_5Tl + Hg_{(-)} \longrightarrow (C_5H_5)_2Hg + 2Tl$	25
$Mn_2(CO)_{10} + Hg_{(-)} \longrightarrow Hg[Mn(CO)_5]_2$	26
$Re_2(CO)_{10} + Hg_{(-)} \longrightarrow Hg[Re(CO)_5]_2$	26

IV DIRECT SYNTHESIS AT METAL ANODES

IV.1 Reactions involving organohalides

Much of the work which we have done recently at Windsor has been concerned with cells in which the reduction of an organic halide at an inert cathode, usually platinum, is accompanied by oxidation of a metal anode. The alkyl or aryl halide may be either neat, or diluted with acetonitrile, or methanol/benzene, and the latter mixture has been especially useful in allowing neutral or anionic donors (halide) to be added to the solution before electrolysis. The observed reaction corresponds to an oxidative insertion reaction to form the appropriate organometallic halides

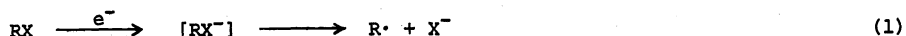


or



depending on the element involved, although some variations on these simple reactions are noted below. This new route then allows the direct synthesis of compounds which are not only interesting in their own right, but which are also useful starting materials for other syntheses (e.g., $R-M-R'$).

Two important parameters can be measured for such reactions - the chemical yield, and the current efficiency, or electrical yield. We define chemical yield as 10^2 (moles product)/(moles metal dissolved), and have generally obtained yields of the order of 70-95% in the experiments described below. The current efficiency (E_F) is defined as moles metal dissolved per Faraday of electricity passed through the cell; this measurement is made at a controlled constant current. For a variety of organometallic halide preparations, E_F is found to be typically non-integral, and in the range 1-10 mol F^{-1} , from which the following simple reaction mechanism has been proposed. The initial step is that established by earlier workers (2,3), namely



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



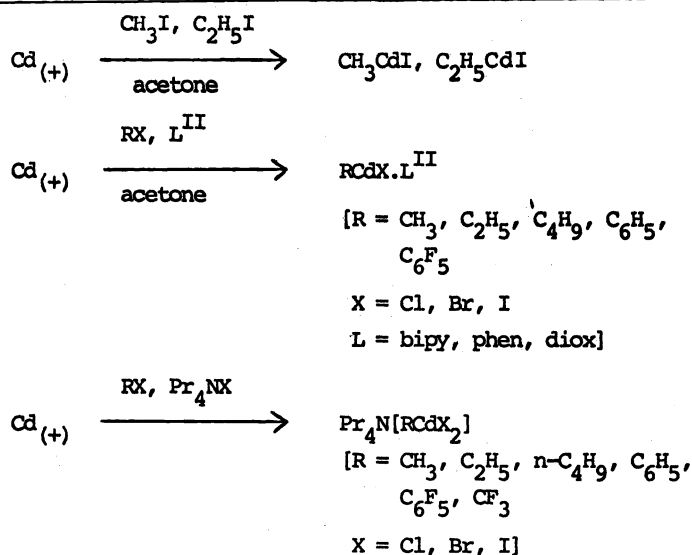
in which reactions (7) and (8) obviously constitute a chain process, thereby explaining the high current efficiencies observed.

We shall now briefly review the work in terms of the metals involved, emphasising the advantages of these preparative methods.

(a) Cadmium. Organocadmium halides cannot be prepared by direct catalytic or photochemical reaction of the metal and organic halide; mixtures of R_2Cd and CdX_2 yield RCdX via a Schlenk equilibrium, but separation of the three components poses an intractable problem (27,28). The electrochemical route yields CH_3CdI and $\text{C}_2\text{H}_5\text{CdI}$, which are very reactive, but these and other compounds are readily stabilised as adducts with 2,2'-bipyridyl, etc., present in the electrolysis solution (29,30). (See Table 3).

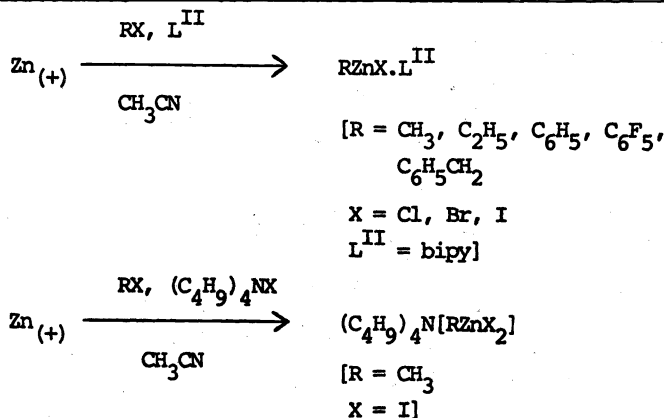
Alternatively, the reactive RCdX species can be stabilised as the RCdX_2^- anion, by adding excess $\text{R}'_4\text{NX}$ to the electrolysis solution. In these experiments, direct electrochemical synthesis gives rise to a series of previously unknown anionic organocadmium halides (29,31).

TABLE 3. Formation of organocadmium halide complexes



(b) Zinc

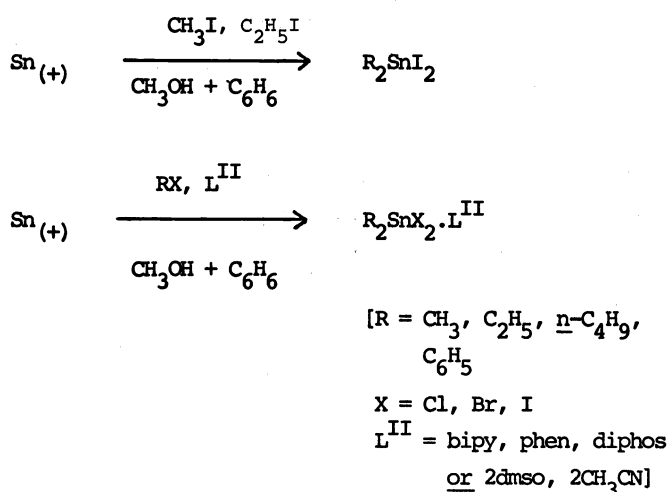
TABLE 4. Formation of organozinc halide complexes



Zinc metal is more reactive towards alkyl halides than is cadmium, and alkylzinc halides can be readily prepared by direct reaction between RX and the metal, or zinc/copper couple (32). This route is not available for aryl compounds, but we have recently shown that the electrochemical oxidation yields $RZnX$ ($R = \text{aryl}$; $X = \text{Cl, Br, I}$), again handled most conveniently as adducts with neutral bidentate ligands, or as the anionic $RZnX_2^-$ species (32).

(c) Tin. The preparation of R_2SnX_2 compounds may be achieved by the catalysed reaction of tin with RX (typically 100–180°C, for 1–50 h). Redistribution reactions provide the other main synthetic route to these compounds, but unfortunately both methods, and others which have been used, give a mixture of mono-, di- and tri-halides, so that separation procedures are of considerable importance (33). Electrochemical methods for the preparation of $(C_4H_9)_2SnCl_2$ have been described by workers in the U.S.S.R. and we have shown that this approach is a general one, which does not apparently require the rather complex organic solvent mixture described by these workers (34). As Table 5 shows, electrochemical oxidation of anodic tin yields R_2SnX_2 compounds directly and these can be isolated in the pure state or stabilised with bidentate ligands (35).

TABLE 5. Formation of diorganotin dihalides



Spectrochemical examination established that the products were indeed the pure R_2SnX_2 species, uncontaminated by R_3SnX , $RSnX$, etc., provided that the product was removed from the solution as soon as possible after electrolysis. We believe that the relative insolubility of the products, and especially of the adducts, in the solvent(s) used, plays an important role in the retardation of the redistribution reactions which would otherwise give rise to $RSnX_3$, etc. This point is again considered below. (Section IV.1.(f)).

(d) Nickel and Palladium

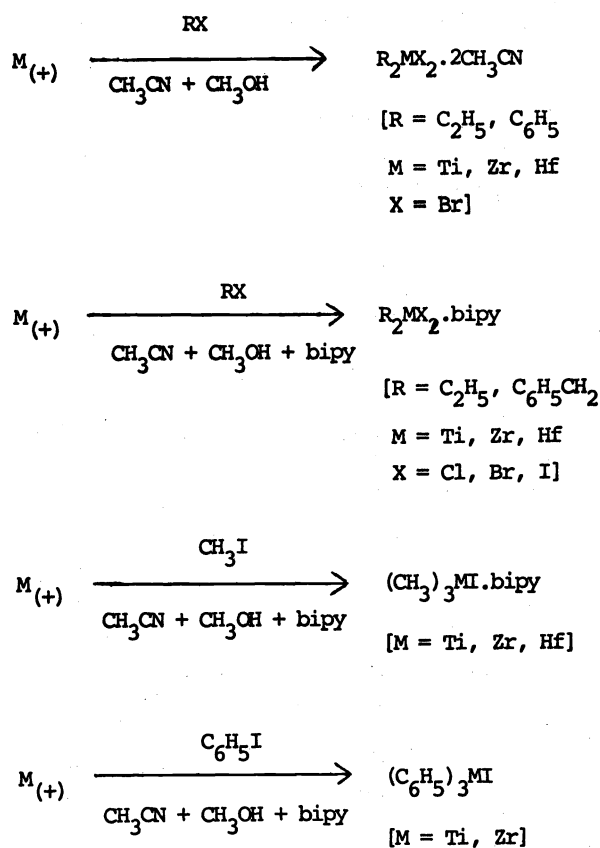
TABLE 6. Organo-nickel and -palladium halide complexes prepared electrochemically

C_6F_5NiBr	
$C_6F_5NiBr \cdot 2Et_3P$	$C_6F_5PdBr \cdot 2Et_3P$
	$C_6F_5PdBr \cdot \text{diphos}$
	$C_6F_5PdBr \cdot 2py$ (unstable)
$CH_3NiCN \cdot 2CH_3CN$	
$CH_3NiCN \cdot 2Et_3P$	
$C_2H_5NiCN \cdot 2Et_3P$	
$C_6F_5NiCN \cdot 2Et_3P$	
$C_6H_5NiCN \cdot 2Et_3P$	
$C_6H_5CH_2NiCN \cdot Et_3P$	
$C_6H_5CH_2NiCl$ (unstable)	

The compounds RMX.L_2 ($\text{M} = \text{Ni, Pd, Pt}$) were prepared some years ago by the reaction of the appropriate LiR or RMgX compound with MX_2 (36). In the light of the introductory remarks about the uses of metal vapour phase synthesis, it is worth noting Klabunde and others have prepared these compounds by reaction of M and RX for $\text{M} = \text{Ni, Pd, or Pt}$ (6,37). We have shown that these compounds can also be obtained by direct electrochemical synthesis (38); the products are most readily handled as adducts with Et_3P , added to the electrolysis solution. The preparation is efficient for Ni but less so for Pd , and does not apparently proceed at all for Pt . Further work on these, and other transition metal systems, is proceeding.

(e) Titanium, Zirconium and Hafnium. Electrochemical oxidation reaction of these metals, using methods similar to those for tin, gave in general compounds of the type $\text{R}_2\text{MX}_2 \cdot 2\text{CH}_3\text{CN}$ or $\text{R}_2\text{MX}_2 \cdot \text{bipy}$ (20). There are, however, some notable differences, especially when CH_3I or $\text{C}_6\text{H}_5\text{I}$ are the organic halides, since in these cases the product is R_3MI (Table 7).

TABLE 7. Electrochemical preparation of organometallic halide complexes of titanium, zirconium and hafnium



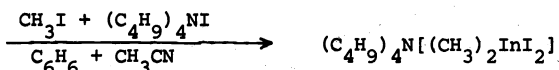
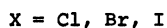
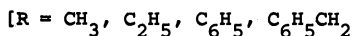
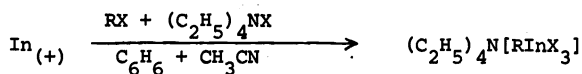
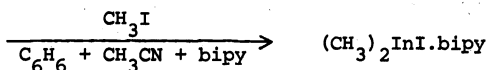
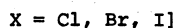
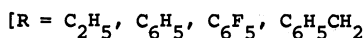
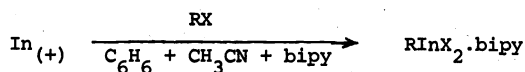
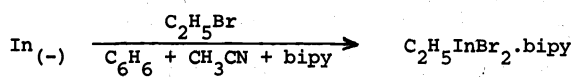
The results suggest that with these elements the redistribution reactions occur more readily than in the case of tin, or alternatively that the reactions of the primary $\text{RM}^{\text{II}}\text{X}$ product follow a different route from those of $\text{RSn}^{\text{II}}\text{X}$, possibly because R_2MX , a M^{III} species, is now of significant stability. Work on inorganic halides and neutral complexes (see below) certainly demonstrates the importance of titanium(III) compounds in electrochemical oxidation. Further work on this matter is clearly needed.

(f) Indium. Again with this element, we find reactions over and above the primary electrochemical reaction, since either R_2InX or RInX_2 compounds are obtained (as the adducts with bipy) depending on the organic halide used (20). (See Table 8). Anionic complexes of the type $\text{R}_4\text{N}[\text{R}_2\text{InX}_2]$ can be prepared by addition of R_4NX to the solution in the standard way.

We believe that these results can be explained by the fact that the product of the insertion reaction at either electrode is the indium(II) species RInX , which is highly unstable, reacting by either of the routes

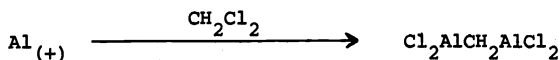
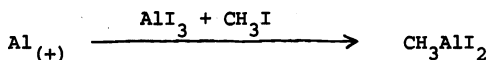


TABLE 8. Electrochemical preparation of organo-indium halide complexes



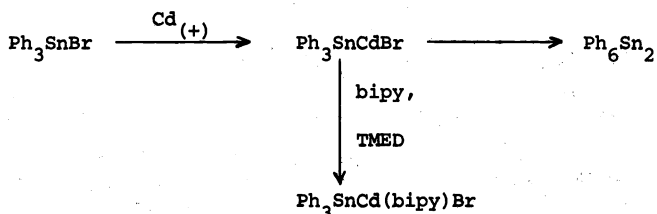
The choice between these must depend on factors which have yet to be elucidated, but it does appear that such reactions will always be important for metals whose most stable oxidation state in organometallic halides is +3. Preliminary results show that gallium and thallium behave in the same way, as does aluminium (39-41) (Table 9).

TABLE 9. Electrochemical synthesis of organo-aluminium halides



(g) Triphenyltin chloride. It is interesting that the type of reaction just described is not necessarily restricted to organic halides, since electrochemical reduction can lead to the rupture of bonds from halogen to elements other than carbon. Dessy and his co-workers have shown that for Ph_3SnX , this process yields $\text{Ph}_3\text{Sn}\cdot$ and X^- (24). In view of the foregoing discussion, it is therefore not surprising that with a sacrificial cadmium anode the electrochemical product is Ph_3SnCdBr . This can be stabilised as $\text{Ph}_3\text{SnCd}(\text{bipy})\text{Br}$, without which decomposition to Ph_6Sn_2 occurs (31) (Table 10). These Sn-Cd bonded compounds have previously been prepared by more conventional routes by Noltes and his colleagues (42,43).

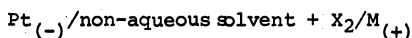
TABLE 10. Electrochemical insertion of cadmium into tin-bromine bond



IV.2 Preparation of anhydrous halides and derivatives

(a) Anhydrous halides, and neutral adducts. The availability of anhydrous halides of main group and transition metals is often the first requirement in the synthesis of neutral or anionic complexes, and of organometallic derivatives. Of the methods presently available, thermal dehydration of the readily available hydrated halides is only rarely useful, since decomposition often predominates over dehydration. The use of reactions with compounds such as thionyl chloride has been advocated, since water is removed as volatiles ($\text{SO}_2 + \text{HCl}$), but the reactions are not always straightforward, and in any case the products may not be suitable as starting materials (44). Methods for the preparation of the anhydrous halides in a pure state normally begin with either the metal or metal oxide. The former can be halogenated directly, with sealed tube or flow techniques; high temperatures, typically in the 200-800°C range, are necessary, and the products are generally the halides of the high oxidation state of the element, especially in the case of chlorination. Many metal oxides can be made to react with elemental halogen, or reduced with reagents such as CCl_4 , AlCl_3 or SOCl_2 , but here again high temperatures are required. The lower halides are not normally obtained in such reactions, and are prepared either by reduction of the higher halides with the metal itself, aluminum, HX , etc., or in some cases by thermal decomposition.

During recent years, we have been successful at Windsor in developing electrochemical methods by which a metal can be halogenated directly at room temperature. In its simplest form, the cell can be represented as



For bromine and iodine, the halogen is added prior to electrolysis; for chlorine, the diluted gas is bubbled through the solution. The solvent has generally been acetonitrile, or a benzene-methanol (3:1) mixture, so that the metal halide is recovered either as the anhydrous compound, or as an acetonitrile or methanol adduct which can be thermally decomposed to the anhydrous compound (45). It has been suggested that in many cases the acetonitrile adducts would be as useful as synthetic starting materials as the halides themselves. Table 11 shows the compounds which we have prepared in this way (including halides of all the top row transition metals). In our earliest work (46,47), adducts of InX_3 with dmsO were prepared by adding the ligand to the solution before electrolysis, and this is apparently a general route to adducts, since compounds of Ti, Zr and Hf are conveniently prepared in the same way (48). Some of these adducts are also shown in Table 11.

TABLE 11. Electrochemical preparation of anhydrous metal halides, and some adducts

$\text{TiCl}_4, \text{TiBr}_4$	(also Zr, HfX_4)
$\text{VCl}_2, \text{VBr}_2, \text{VI}_2$	
CrBr_3	
MnBr_2	
$\text{FeCl}_2, \text{FeBr}_2, \text{FeI}_2$	
CoBr_2	
$\text{NiCl}_2, \text{NiBr}_2, \text{NiI}_2$	
$\text{CuBr}, \text{CuBr}_2$	
ZnBr_2	
$\text{InI}, \text{InCl}_3, \text{InBr}_3, \text{InI}_3$	
$\text{In} \xrightarrow[\text{C}_6\text{H}_6 + \text{CH}_3\text{OH}]{\text{X}_2, \text{L}} \text{InX}_3 \cdot 3\text{dmsO}$	
[X = Cl, Br]	
$\text{InX}_3 \cdot 3\text{CH}_3\text{CN}, \text{InI}_3 \cdot 2\text{CH}_3\text{CN}$	
[X = Cl, Br]	
$\text{Ti, Zr, Hf} \xrightarrow[\text{CH}_3\text{CN}]{\text{X}_2} \text{MX}_4 \cdot 2\text{CH}_3\text{CN}$	
[X = Cl, Br]	

The case of CrBr_3 is especially instructive in demonstrating the advantage of the electrochemical method (49). The recommended route to CrBr_3 is via $\text{Cr} + \text{Br}_2$ at 850°C. The present route not only avoids the high temperature method, but also yields a reactive product from which complexes of the type $[\text{CrL}_6]\text{Br}_3$ are easily and quickly obtained, so that such preparations avoid the difficulties which otherwise arise from the kinetic stability of Cr^{III} complexes. The vanadium(II) halides are also useful synthetic materials for obtaining some rare

TABLE 12. Some reactions of electrochemically prepared VX_2 and $CrBr_3$

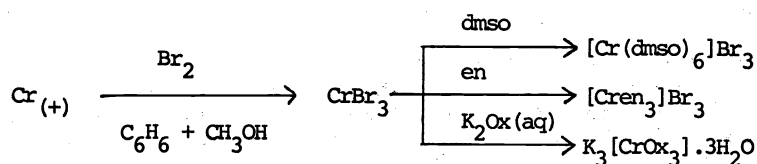
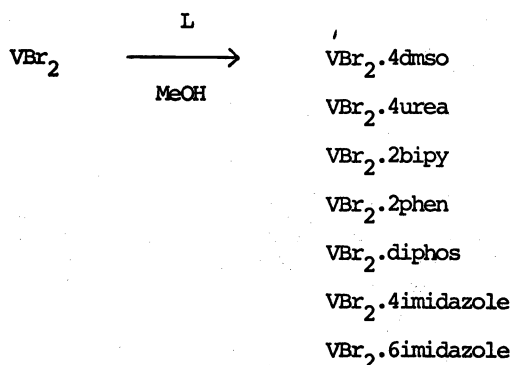
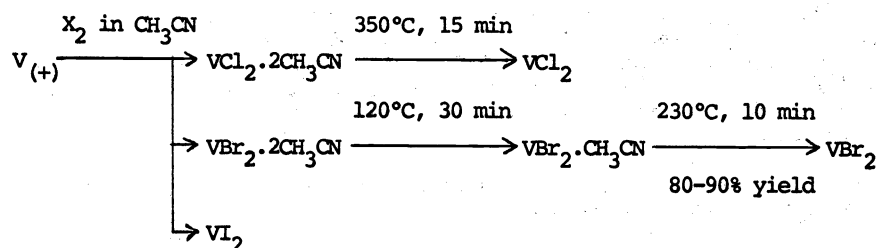
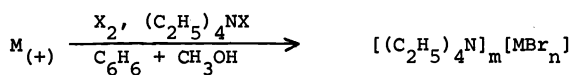


TABLE 13. Electrochemical synthesis of anionic halogeno complexes



anions: TiCl_6^{2-} , TiBr_4^-
 ZrCl_6^{2-} , ZrBr_6^{2-}
 HfCl_6^{2-} , HfBr_6^{2-}
 FeBr_4^-
 CoBr_4^{2-}
 NiBr_4^{2-}
 AuBr_4^-
 CdBr_3^-
 InCl_5^{2-} , InBr_5^{2-} , InI_2^-
 SnBr_6^{2-}

(c) Reaction mechanism. A satisfactory mechanism for these reactions must explain a number of experimental points. Firstly, the products generally contain the metals in low oxidation states (i.e., VII, CrIII, MnII), which is especially striking given that the compounds are formed in the presence of free halogen. Secondly, in one case where a comparison is possible, the electrochemical route yields a different product from the thermal solution phase reaction, in that VX_2 , not VX_3 is obtained (53). Thirdly, in three cases complexes of two different oxidation states of the same metal have been obtained depending upon the detailed conditions (In^I and In^{III} ; Ti^{III} and Ti^{IV} ; Cu^I and Cu^{II}). Fourthly, the current efficiencies are typically 1-20 and non-integral, suggesting that some chain reaction follows the initial electrochemical step.

We believe that these are readily explained by cathodic reduction of $X_2 \longrightarrow X_2^-$, which migrates to the anode where the reactions are



followed by



in which the chain process is clearly (13) + (14). The nature of the final product MX_n must depend on the specific interactions of M with the halide in question, and may be influenced by stabilising factors such as adduct formation, lattice energy for anionic complexes, etc. A detailed justification of this mechanism and its implications has been given elsewhere (45); whatever its shortcomings, it offers a very useful basis on which to plan further experimental work.

IV.3 Syntheses involving inorganic or organic anions

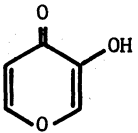
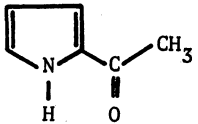
This section brings together a number of apparently different electrochemical syntheses which in fact have a unifying theme, namely that in each case inorganic or organic anions undergo reaction on discharging at a sacrificial anode. These anions may be added to or generated in the solution, and the metal complexes formed may be neutral or cationic as the coordination chemistry dictates.

(a) Chelating ligands. The synthesis of neutral compounds of chelating ligands normally begins with an aqueous solution of a salt of the metal in question, and addition of the chelating agent is followed by extraction, precipitation, crystallisation, etc., as appropriate. Since the parent neutral compounds are weak acids, the direct reaction



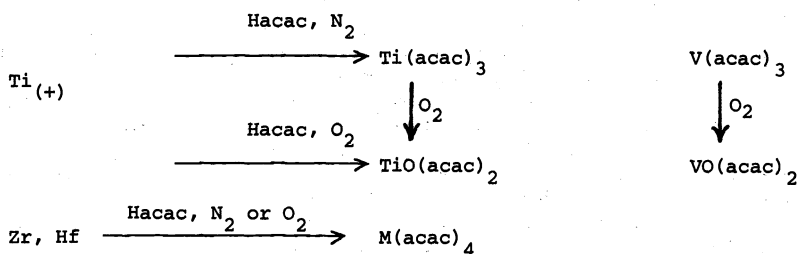
is rarely possible, but we have shown that for ligands such as 2,4-pentanedionate, etc., this reaction goes directly when the metal is the anode of a non-aqueous solution cell (54). The results of these experiments are shown in Table 14. Similar preparations have also been carried out for Fe, Co and Ni/acac by Lehmkuhl and Eisenbach who have described very useful cells which allow continuous, high rate, complex production (55).

TABLE 14. Electrochemical synthesis of metal-chelate complexes

HL, CH ₃ OH or acetone	
$M_{(+)}$	$\xrightarrow[N_2]{} ML_n$
$CH_3COCH_2COCH_3$	$\longrightarrow TiL_3, ZrL_4, HfL_4, VL_3, CrL_3, MnL_2, FeL_3, CoL_2, NiL_2, CuL_2, ZnL_2, InL_3$
	$\longrightarrow FeL_3, CoL_2, NiL_2, CuL_2, InL_3$
	$\longrightarrow CrL_3, CoL_2, NiL_2, CuL_2, InL_3$

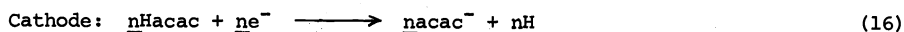
A number of points should be noted. With titanium, one can prepare $\text{Ti}(\text{acac})_3$ or $\text{TiO}(\text{acac})_2$, depending on the absence or otherwise of O_2 , and similar findings applied with vanadium. With zirconium and hafnium, on the other hand, one obtains $\text{M}(\text{acac})_4$, irrespective of the conditions, a finding which parallels much else of the inorganic chemistry in this group (Table 15).

TABLE 15. Titanium and vanadium acetylacetonate complexes



The preparation of the acetylpyrrole complexes is a useful alternative to many of the methods in the literature, although here, as elsewhere, decomposition of the parent pyrrole is a constant problem.

As with other electrochemical methods, the preparation is simple and usually rapid, and affords the products in gram quantities from the metal; here again the pyrrole complexes are the least satisfactory. The current efficiency is always low, and equal to $1/\underline{n}$ mol Faraday⁻¹, where \underline{n} is the oxidation number of the metal in the product. This leads to the overall stoichiometric equations

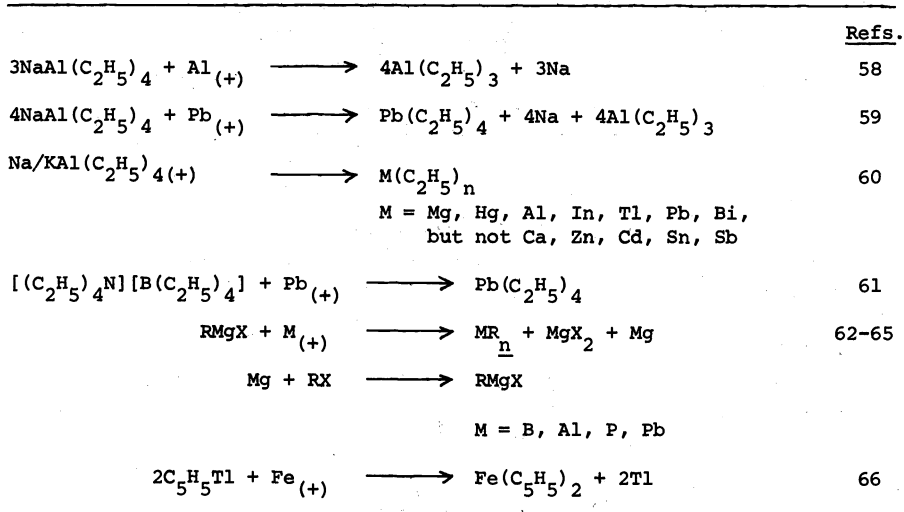


although these equations obviously beg the question as to the actual electrode reactions.

It will be useful to investigate the generality of these preparations for other ligands which are the conjugate bases of weak acids. For example, a number of acetates have been obtained in this way, and further experiments are planned.

(b) Reactions involving carbanions. The original experiments of Hein showed that alkali metal alkyls in solution with ZnR_2 or AlR_3 give conducting solutions which yield alkyl radicals on anodic oxidation (56,57). These radicals may attack the anode to yield compounds which may be stable metal alkyls, or which may disproportionate. Some examples of such methods are listed in Table 16. Organoboron and organomagnesium compounds have been used in similar processes, some of which are of commercial interest.

TABLE 16. Metal alkyl formation at sacrificial anodes

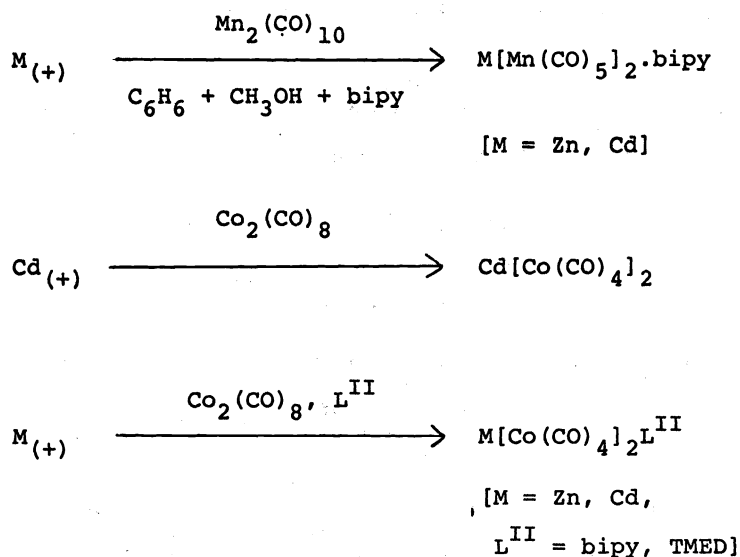


Although the main emphasis has very much been on lead, other elements (Mg, Hg, Al, In, Tl and Bi) have been successfully alkylated in this way. The preparation of ferrocene is formally similar to the cathodic reaction noted earlier (See Table 2), and again this process constitutes an electrochemical transmetallation reaction.

Where current efficiencies have been measured, it has been shown that the dissolution of anodic metal goes by Faraday's law, and the overall reactions are therefore formally similar to those set out above for chelating ligands. To the extent that an alkyl carbanion is the conjugate base of an extremely weak acid, this formalism is readily understood.

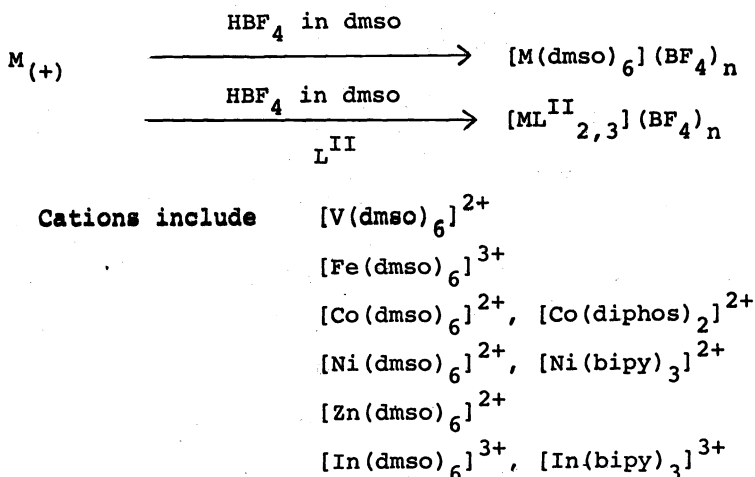
(c) Metal-metal bonded compounds. The reaction of cathodic mercury with M-M bonded dinuclear carbonyls giving rise to M-Hg-M systems was noted earlier (Table 2). The electrochemical behaviour of dinuclear carbonyls and similar compounds has been extensively investigated in polarographic and related experiments, from which it is known that reduction may yield $M(CO)_n^-$ anions (26). Migration to and reaction at a sacrificial anode can then give $M'[M(CO)_n]_2$ compounds. Table 17 lists the species which we have recently been able to prepare in this way, again using stabilisation by bidentate neutral ligands for ease of identification (67). The method should be of general application, and other systems are being investigated. The current efficiencies so far obtained again confirm the anionic mechanism proposed ($E_F = 0.5$ for $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ electrolysis).

TABLE 17. Electrochemical synthesis of $M-M^-$ at sacrificial anodes



(d) Cationic complexes.

TABLE 18. Electrochemical synthesis of cationic complexes



Even in systems with thermodynamically stable anions such as ClO_4^- or BF_4^- , discharge may result in dissolution of the anode by subsequent reaction. We have found that this provided a direct route to $[\text{In}(\text{dmsO})_6](\text{ClO}_4)_3$, but more recent (and safer) experiments with a non-aqueous solution of HBF_4 in the presence of neutral ligands yielded a series of BF_4^- salts of ML_6^{n+} complexes, which are readily obtained in crystalline form (46,20). Table 18 shows the promising results which have been obtained by this technique thus far.

One advantage of this direct synthesis of cationic complexes is that low oxidation states are again produced, as in the halide preparations. So far, we can sense no restriction other than solubility on the ligands which can be used, so that a large number of complexes should be available by this route. No current efficiency measurement has yet been made, and it is therefore idle to speculate upon the reactions involved.

V CONCLUDING REMARKS

The variety of experimental systems successfully investigated and the range of products obtained in the direct electrochemical syntheses described suggests that such methods have many advantages for the preparative chemist. Amongst these are that metals as starting materials are generally stable, easily stored and available in high purity, and whilst the other materials (solvent, organic halide, etc.) are generally used in excess, these remain available for further preparations if needed. The chemical yields are high in terms of metal consumption, and the amounts used are convenient for normal laboratory working; no doubt the scale of production could be readily increased if necessary to the 10-100 g scale for routine preparation.

Equally, the electrochemical cells are most conveniently run at or near room temperature, thereby offering considerable convenience over high temperature thermolytic preparations. The cells in general are electrochemically efficient, especially in those cases where radical reactions intervene (see Sections above).

Finally, we note that the direct electrochemical synthesis method has provided routes to some compounds not readily accessible, whilst in other cases the methods are simpler than the recommended literature syntheses, or give products which are more reactive than those obtained by conventional methods. This is not to claim that direct electrochemical synthesis is the answer to every preparative chemist's prayer, but there is certainly sufficient evidence to suggest that it is worth much more serious consideration than it has been given in the past. It is to be hoped that future results will justify this optimistic attitude.

Acknowledgement - It is a pleasure to acknowledge, with thanks, the support and co-operation of my co-workers (A. Osman, Lynn Neilson, F. F. Said, F. H. Walters, S. Zhandire, and especially J. J. Habeeb), and to thank the National Research Council of Canada for their financial support of our work.

REFERENCES

1. B. L. Laure and C. D. Schmulbach, *Prog. Inorg. Chem.*, **14**, 65 (1971).
2. H. Lehmkuhl, *Organic Electrochemistry*, M.M. Baizer (Ed), Marcel Dekker, N.Y. 621-678 (1973).
3. W. J. Settinieri and L. D. McKeever, *Technique of Electroorganic Synthesis*, N. L. Weinberg editor, Wiley-Interscience, New York, Part II, 397, 558 (1975).
4. P. L. Timms, *Adv. Inorg. Radiochem.*, **14**, 121 (1972).
5. G. A. Ozin and A. Van der Voet, *Prog. Inorg. Chem.*, **19**, 105 (1975).
6. K. J. Klabunde, *Accts. Chem. Res.*, **8**, 393 (1975).
7. T. Sekine, A. Yamura and K. Sugino, *J. Electrochem. Soc.*, **112**, 439 (1965).
8. J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. (B)*, 60 (1968).
9. C. K. Mann, J. L. Webb and H. M. Walborsky, *Tetrahedron Lett.*, **20**, 2249 (1966).
10. J. L. Webb, C. K. Mann and H. M. Walborsky, *J. Am. Chem. Soc.*, **92**, 2042 (1970).
11. E. F. Silversmith and W. J. Sloan, U.S. Patent 3 197 392 (1965).
12. H. J. Ulery, *J. Electrochem. Soc.*, **119**, 1474 (1972).
13. H. J. Ulery, *J. Electrochem. Soc.*, **120**, 1493 (1973).
14. O. R. Brown, E. R. Gonzalez and A. R. Wright, *Electrochim. Acta*, **18**, 369 (1973).
15. R. Galli, *Chem. Ind. (Milan)*, **50**, 977 (1968).
16. R. Galli, *J. Electroanal. Chem. Interfacial Electrochem.*, **22**, 75 (1969).
17. R. Galli and F. Olivani, *J. Electroanal. Chem. Interfacial Electrochem.*, **25**, 331 (1970).
18. A. P. Tomilov, Y. D. Smirnov and S. L. Varshavskii, *J. Gen. Chem. USSR*, **35**, 390 (1965).
19. A. P. Tomilov and Y. D. Smirnov, *Zh. Vses. Khim. Obshch. D. I. Mendeleeva*, **10**, 101 (1965).
20. J. J. Habeeb, F. Said and D. G. Tuck, unpublished results.
21. J. Tafel and K. Schmitz, *Z. Electrochem.*, **8**, 281 (1902).
22. T. Psarras and R. E. Dessy, *J. Am. Chem. Soc.*, **88**, 5132 (1966).
23. R. E. Dessy, R. King and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 5112 (1966).
24. R. E. Dessy, W. Kitching and T. Chivers, *J. Am. Chem. Soc.*, **88**, 453 (1966).
25. L. D. Gavrilova and S. I. Zhdanov, *Coll. Czech. Chem. Commun.*, **32**, 2215 (1967).
26. R. E. Dessy, F. E. Stary, R. B. King and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 471 (1966).
27. See, for example, G. Coates and K. Wade, *Organometallic Compounds. The Main Group*

- Elements, Methuen, London, Vol. I, p 144 (1967).
28. D. F. Evans and R. F. Phillips, J. Chem. Soc., Dalton Trans., 978 (1973).
 29. J. J. Habeeb, A. Osman and D. G. Tuck, Chem. Commun., 696 (1976).
 30. J. J. Habeeb and D. G. Tuck, J. Organometallic Chem., 146, 213 (1978).
 31. J. J. Habeeb, A. Osman and D. G. Tuck, J. Organometallic Chem., Inorg. Chim. Acta, in press.
 32. G. Coates and K. Wade, loc. cit., (ref. 27) p. 122.
 33. R. C. Poller, The Chemistry of Organotin Compounds, Logos Press, London, page 53 ff. (1970).
 34. K. N. Korotaevskii, E. N. Lysenko, Z. S. Smolyan, L. M. Monastyrskii and L. V. Armenskaya, Zh. Obshch. Khim., 13, 167 (1966).
 35. J. J. Habeeb and D. G. Tuck, J. Organometallic Chem., 134, 363 (1977).
 36. M. L. H. Green, Organometallic Compounds. The Transition Elements, Methuen, London, Vol. II 244 et seq., (1968).
 37. M. J. Piper and P. L. Timms, Chem. Comm., 50 (1972).
 38. J. J. Habeeb and D. G. Tuck, J. Organometallic Chem., 139, C17 (1977).
 39. J. R. Chadwick and E. Kinsella, J. Organometallic Chem., 4, 334 (1965).
 40. H. Lehmkuhl, Justus Liebig Ann. Chem., 40, 705 (1967).
 41. E. H. Mottus and M. R. Ort, J. Electrochem. Soc., 117, 885 (1970).
 42. F. J. A. Tombes, G. J. M. van der Kirk and J. G. Noltes, J. Organometallic Chem., 43, 323 (1972).
 43. R. Barbier, L. Pellerito, N. Bertazzi, G. Alonzo and J. G. Noltes, Inorg. Chim. Acta, 15, 201 (1975).
 44. R. B. King, Organometallic Syntheses, Academic Press, New York, Vol. I, p. 72 (1965).
 45. J. J. Habeeb, L. Neilson and D. G. Tuck, Inorg. Chem., 17, 306 (1978).
 46. J. J. Habeeb and D. G. Tuck, Chem. Commun., 808 (1975).
 47. J. J. Habeeb and D. G. Tuck, Inorg. Syntheses, 19, 257, (1979).
 48. J. J. Habeeb, F. F. Said and D. G. Tuck, Can. J. Chem., 55, 3882 (1977).
 49. J. J. Habeeb and D. G. Tuck, Inorg. Syntheses, 19, 123 (1979).
 50. J. J. Habeeb, L. Neilson and D. G. Tuck, Can. J. Chem., 55, 2631 (1977) and unpublished results.
 51. J. J. Habeeb, L. Neilson and D. G. Tuck, Synth. React. Inorg. Metl-org. Chem., 6, 105 (1976).
 52. J. J. Habeeb and D. G. Tuck, J. Chem. Soc., Dalton Trans., 866 (1976).
 53. B. J. Hathaway and D. G. Holah, J. Chem. Soc., 2400 (1964).
 54. J. J. Habeeb, D. G. Tuck and F. H. Walters, J. Coord. Chem., 8, 27 (1978).
 55. H. Lehmkuhl and W. Eisenbach, Justus Liebig Ann. Chem., 672 (1975).
 56. F. Hein, E. Petzschner, K. Wagler and F. A. Segitz, Z. Anorg. Allg. Chem., 141, 161, 224 (1924).
 57. F. Hein and F. A. Segitz, Z. Anorg. Allg. Chem., 158, 153, 159 (1926).
 58. K. Ziegler and H. Lehmkuhl, German Patent 1 150 078 (1963); C.A. 59, 4801a.
 59. K. Ziegler and H. Lehmkuhl, German Patent 1 181 220 (1964); C.A. 62, 6156c.
 60. W. Grimma, Dissertation, Technische Hochschule Aachen, (1960) (quoted in ref. 2).
 61. R. C. Pinkerton, U.S. Patent 3 028 325 (1962); C.A. 57, 4471b.
 62. J. W. Ryznar and J. C. Premo, U.S. Patent 3 100 181 (1963); C.A. 57, 11234d.
 63. W. V. Evans and R. Pearson, J. Am. Chem. Soc., 64, 2865 (1942).
 64. W. P. Hettinger, U.S. Patent 3 079 311 (1963); C.A. 57, 2859f.
 65. D. G. Braithwaite, U.S. Patent 3 007 957 (1961); C.A. 56, 3280f.
 66. S. Valcher and E. Alunni, Ric. Sci., 38, 527 (1968).
 67. J. J. Habeeb, D. G. Tuck and S. Zhandire, unpublished results.