$$(CF_3)_3COOC(O)F + ClF \xrightarrow{CsF, -78\ ^\circ C} (CF_3)_3COOCF_2OCl$$

$$(CF_3)_3COOCF_2OCl \xrightarrow{-65\ ^\circ C} (CF_3)_3COOCl + COF_2$$

$$(CF_3)_3COOCl \xrightarrow{22\ ^\circ C} CF_3Cl + (CF_3)_2CO + {}^1/_2O_2$$

$$(CF_3)_3COOCF_2OCl \xrightarrow{22\ ^\circ C} CF_3Cl + COF_2 + (CF_3)_2O + {}^1/_2O_2$$

This supports our earlier contention that the reactions of $R_fOOC(O)F$ with $F_2$ and ClF in the presence of CsF are identical, but the OF derivatives are stable. However, it was most disappointing to find the thermal stability of $(CF_3)_3COOCl$ so low. Both $CF_3OOCl$ and $SF_5OOCl$ are unstable at 22 °C, but they can be prepared and isolated pure in reasonable quantities. Both are very useful reagents for the direct synthesis of fluorinated peroxides.[17]

**General Properties.** All the new compounds except $(CF_3)_3COOCl$ and $(CF_3)_3COOCF_2OCl$ have been characterized by IR and NMR and physical properties. Each exhibits IR and NMR spectra consistent with the presence of a $(CF_3)_3CO-$ group[7,9] and different from those of the related nonperoxides, where known [$(CF_3)_3COH$,[22] $(CF_3)_3COC(O)F$,[7] and $(CF_3)_3COCl$[5]]. The peroxide link in $(CF_3)_3COOH$ is supported by its Raman band at 885 $cm^{-1}$,[23] which is absent in the corresponding alcohol run under identical conditions. The molecular weights of all compounds were close to the expected values.

Except for $(CF_3)_3COOCl$ and $(CF_3)_3COOCF_3OCl$ as discussed above, all the compounds are stable colorless liquids at 22 °C. However, the presence of the peroxide linkage provides a relatively low energy path for decomposition. As has been observed previously for $(CF_3)_3CO$ derivatives containing a weak bond, a major decomposition product is hexafluoroacetone. Considering the clean thermal decomposition of $(CF_3)_3COX$ (X = Cl, F) to $CF_3X$ and $(CF_3)_2CO$, the peroxides decompose in a predictable way.

$$(CF_3)_3COOC(O)F \xrightarrow{80\ ^\circ C} (CF_3)_2CO + CF_3OC(O)F$$

$$(CF_3)_3COOC(O)OCF_3 \xrightarrow{80\ ^\circ C} (CF_3)_2CO + CO_2 + CF_3OCF_3$$

$$(CF_3)_3COOH \xrightarrow{120\ ^\circ C} COF_2 + HF + (CF_3)_2CO$$

$$(CF_3)_3COOCl \xrightarrow{22\ ^\circ C} CF_3Cl + (CF_3)_2CO + {}^1/_2O_2$$

The effect of a peroxide or OX bond on thermal stability is illustrated by the fact that $(CF_3)_3COC(O)CF_3$ does not decompose readily even at 500 °C. While the latter is expected to be more stable, it is formally the dimer of hexafluoroacetone.

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**Registry No.** $(CF_3)_3COOC(O)F$, 64957-47-7; $(CF_3)_3COOC(O)OCF_3$, 64957-48-8; $(CF_3)_3COOH$, 64957-49-9; $(CF_3)_3COOCF_2OF$, 64957-50-2; $(CF_3)_3COOCl$, 64957-51-3; $(CF_3)_3COOSO_2F$, 55064-77-2; $COF_2$, 353-50-4; $F_2$, 7782-41-4; ClF, 7790-89-8.

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# Electrochemical Preparation of Anhydrous Halides of Transition Metals (Mn–Zn)

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Elemental manganese, iron, cobalt, nickel, copper, and zinc can be oxidized electrochemically at room temperature with halogen ($Cl_2$, $Br_2$, $I_2$) dissolved in an organic solvent mixture. The final products are the anhydrous metal halides, which are important starting materials for synthetic work. In most cases the halides are recovered as solvates of $CH_3OH$ or $CH_3CN$, which can be removed by heating in vacuo. Adducts of the halides can be prepared in situ in the electrochemical cell or preferably by subsequent reaction. The mechanism of the electrochemical oxidation processes is discussed.

## Introduction

Anhydrous halides of metals are important starting materials in many synthetic routes to inorganic and organometallic compounds, but the preparation of the halides themselves is not always a simple problem. Many hydrated halides decompose rather than dehydrate on heating, and the removal of water from such salts requires treatment with thionyl chloride or a similar reagent, although the product may even then be unsatisfactory for some purposes.[1] The alternative routes involve high-temperature reactions between metal and halogen, metal oxide and hydrogen halide, etc. We return to this point later but note here that such procedures have obvious disadvantages.

The present paper is one of a series reporting the preparation of metal halides, anionic halide complexes, and organometallic compounds by electrochemical oxidation of a metal in the

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**Table I.** Experimental Conditions for Electrochemical Preparation of Transition-Metal Halides

| Elements | Soln-phase compn (volumes in cm$^3$) | Amt of $Et_4NClO_4$, mg | Initial Voltage, V | Initial Current, mA | Time of electrolysis, h | Wt of metal dissolved, g | Yield of final product, % |
|---|---|---|---|---|---|---|---|
| Mn/Br | $C_6H_6$, 56; $CH_3OH$, 14; $Br_2$, 2 | 15 | 50 | 20 | 18 | 2.73 | |
| | $CH_3CN$, 50; $Br_2$, 3 | 10 | 5 | 40 | 19.5 | 1.21 | 75 |
| Fe/Cl | $CH_3CN$, 50; $Cl_2$(g) | 0 | 1 | 50 | 1 | 1.39 | |
| Fe/Br | $C_6H_6$, 56; $CH_3OH$, 14; $Br_2$, 2 | 15 | 50 | 40 | 1.25 | 0.99 | 55 |
| | $C_6H_6$, 10; $CH_3CN$, 40; $Br_2$, 2 | 10 | 3 | 2.5 | 19 | 0.97 | 90 |
| Fe/I | $CH_3CN$, 50; $I_2$, 1.5 g | 0 | 12 | 100 | 24.5 | 1.28 | |
| Co/Br | $C_6H_6$, 56; $CH_3OH$, 14; $Br_2$, 3.5 | 15 | 42 | 60 | 6 | 0.46 | 95 |
| Ni/Cl | $CH_3CN$, 60; $Cl_2$(g) | 12 | 30 | 80 | 1 | 0.21 | 97 |
| Ni/Br | $C_6H_6$, 48; $CH_3OH$, 12; $Br_2$, 2 | 15 | 50 | 15 | 13.4 | 1.09 | |
| Ni/I | $CH_3CN$, 60; $I_2$, 1 g | 0 | 50 | 125 | 25 | 0.71 | 22 |
| Cu/Br | $C_6H_6$, 56; $CH_3OH$, 14; $Br_2$, 2 | 15 | 50 | 50 | 27.6 | 1.81 | 95[a] |
| Zn/Br | $C_6H_6$, 56; $CH_3OH$, 14; $Br_2$, 2 | 15 | 50 | 15 | 19 | 0.86 | 77 |

[a] CuBr + $CuBr_2$.

**Table II.** Analytical Results for Anhydrous Metal Halides and Adducts

| Compd | % calcd Metal | % calcd Halogen | % found Metal | % found Halogen |
|---|---|---|---|---|
| $MnBr_2 \cdot 2CH_3OH$ | | 57.4 | | 55.1 |
| $MnBr_2 \cdot CH_3CN$ | 21.5 | 62.5 | 21.5 | 61.8 |
| $MnBr_2$ | 25.6 | 74.4 | 25.2 | 74.8 |
| $FeCl_2 \cdot CH_3CN$ | | 42.3 | | 42.3 |
| $FeCl_2$ | 44.1 | 55.9 | 44.1 | 56.6 |
| $FeBr_2 \cdot 2CH_3CN$ | 18.8 | 53.7 | 19.0 | 53.4 |
| $FeBr_2 \cdot 2$phen[a] | | 27.8 | | 27.2 |
| $FeBr_2$ | 25.9 | 74.1 | 26.0 | 74.0 |
| $FeI_2 \cdot 2CH_3CN$ | | 64.8 | | 64.6 |
| $FeI_2$ | 18.0 | 82.0 | 17.9 | 82.0 |
| $CoBr_2$ | 26.9 | 73.1 | 27.2 | 73.5 |
| $CoBr_2 \cdot 2CH_3CN$ | 19.6 | 53.1 | 19.7 | 52.1 |
| $CoBr_2 \cdot$diphos[a] | | 25.9 | | 25.9 |
| $NiCl_2 \cdot CH_3CN$ | 34.4 | 41.5 | 34.4 | 40.8 |
| $NiCl_2$ | 45.3 | 54.7 | 45.3 | 54.3 |
| $NiBr_2 \cdot 2CH_3OH$ | | 57.0 | | 57.8 |
| $NiBr_2$ | 26.9 | 73.1 | 26.0 | 73.1 |
| $NiBr_2 \cdot$bpy[a] | 15.6 | 42.7 | 15.6 | 42.6 |
| $NiI_2 \cdot 4CH_3CN$ | | 53.2 | | 53.9 |
| $NiI_2 \cdot 2CH_3CN$ | | 64.4 | | 66.0 |
| $NiI_2 \cdot CH_3CN$ | | 71.8 | | 74.6 |
| $NiI_2$ | 18.8 | 81.2 | 18.2 | 82.0 |
| CuBr | 44.3 | 55.7 | 44.2 | 56.1 |
| $CuBr_2$ | 28.4 | 71.6 | 28.4 | 71.4 |
| $ZnBr_2$ | 29.0 | 71.0 | 29.0 | 70.4 |

[a] bpy = 2,2′-bipyridine; diphos = 1,2-bis(diphenylphosphino)ethane; phen = 1,10-phenanthroline

presence of a solution of appropriate ligands in an organic solvent mixture. Complexes of indium,[2,3] organocadmium compounds,[4] and anionic bromometalate complexes of transition- and main-group metals[5] have been prepared for this method, as have vanadium(II) halides[6] and titanium(IV) halides and their adducts.[7] Of direct relevance to the present work is the room-temperature preparation of chromium(III) bromide; the material obtained is highly reactive, and cationic and anionic chromium(III) complexes are readily obtained by direct reaction in solution with the appropriate ligand.[8] We now report the electrochemical oxidation of the metals manganese, iron, cobalt, nickel, copper, and zinc to give the anhydrous halides or their simple adducts. Anhydrous bromides of all elements in question and sufficient chlorides and iodides have been prepared to establish the generality of the method.

## Experimental Section

The experimental methods were essentially those described earlier.[5] In the preparation of the metal chlorides, chlorine gas was bubbled through the solution with a nitrogen carrier at a rate of approximately 25 cm$^3$/min.

Halogen analysis was done by Volhard titration or the Oakdale–Thompson[9] method. Metal analysis was done by atomic absorption; we are grateful to Dr. C. Riddle (Department of Geology, University of Windsor) for help in this aspect of the work. The presence of acetonitrile and other neutral ligands in certain compounds (see below) was confirmed by infrared spectroscopy.

Typical experimental conditions are detailed in Table I, and the analytical results for the reported compounds are given in Table II.

## Results and Discussion

**Manganese ($MnBr_2$).** The electrolytic oxidation of manganese in $CH_3OH/C_6H_6/Br_2$ yielded a precipitate of beige crystals whose bromine content corresponded to $MnBr_2 \cdot 2MeOH$. This compound does not appear to have been reported previously, although the corresponding $C_2H_5OH$ and *i*-$C_3H_7OH$ bis adducts are known.[10] The thermal desolvation of this preparation was not investigated. Oxidation using unstirred acetonitrile as the solvent led to the formation of yellow crystals which redissolved in the reaction mixture as the reaction proceeded; stirred solutions gave no such precipitate. Complete removal of solvent and bromine from the reaction mixture yielded a pale pink solid which was dried in vacuo at 40–60 °C. This compound had a bromine content close to that calculated for $MnBr_2 \cdot CH_3CN$, and further heating (240 °C, 10 min) yielded pink hygroscopic $MnBr_2$. The monoacetonitrile adduct of $MnBr_2$ has not been reported previously, but the bis adduct is known, having been obtained by Hathaway and Holah[11] either by the direct action of $CH_3CN$ on the halide or by refluxing manganese powder with bromine in acetonitrile. Further experiments (not reported in Table II) using a benzene/acetonitrile solution phase yielded a solid containing 56.9% bromine, suggesting a mixture of $MnBr_2 \cdot CH_3CN$ (62.5%) and $MnBr_2 \cdot 2CH_3CN$ (53.9% Br). The composition of these and other acetonitrile adducts is discussed below.

In the benzene/methanol experiments, a total current of 13.5 × $10^{-3}$ faraday caused 2.73 g, or 49.7 mmol, of manganese to dissolve, a current efficiency of 3.68 mol/faraday. In acetonitrile, the calculated efficiency is 0.78 mol/faraday over the 19.5-h experiment, but more detailed studies with other metals suggest that this value should not be taken as a true indication of the reaction mechanism.

**Iron ($FeCl_2$, $FeBr_2$, $FeI_2$).** Freshly cleaned (hot KOH) iron wire dissolves readily in $CH_3CN/Cl_2$ at voltages much lower than those found necessary in other work, to give a yellow solution. The current efficiency (9.5 mol/faraday) and the visible continuance of the reaction after switching off the voltage suggest that some chemical attack of chlorine on iron is also occurring. When cooled overnight (0 °C), the solution deposited yellow crystals which were collected and dried at 100 °C (45 min); this material, $FeCl_2 \cdot CH_3CN$, decomposed on further heating (220 °C, 20 min) to give light brown anhydrous $FeCl_2$. As with $MnBr_2$, the monoacetonitrile adduct of $FeCl_2$ has not been reported previously, but the existence of series of adducts $FeCl_2 \cdot L_n$ ($n$ = 4–0.67) of differing thermal stabilities with other ligands is well established.[12]

The product of electrochemical oxidation in cells containing benzene/methanol/bromine was a dark brown crystalline material, with bromine content varying between 68 and 73%. This system was not pursued further, except to show that addition of 1,10-phenanthroline (phen) to the solution (after removal of excess bromine by a stream of nitrogen) yielded $FeBr_2 \cdot 2phen$. No doubt other adducts could be obtained by similar procedures, following the preparation of chromium(III) compounds previously noted. Electrochemical oxidation of iron in acetonitrile proceeds smoothly, with air-sensitive brown-yellow crystals forming in the cell; the analytical results (after magnetic removal of particles of iron metal) showed this substance to be $FeBr_2 \cdot 2CH_3CN$ (cf. ref 11) which on heating (300 °C, 5 min) decomposed to anhydrous dark brown $FeBr_2$. The average current efficiency in this system corresponded to the dissolution of 0.96 mol of Fe/faraday.

Iron can be oxidized electrochemically in the presence of iodine. Removal of the solvent precipitated fine, almost black, crystals of $FeI_2 \cdot CH_3CN$ which on heating (300 °C, 2 min) yielded unsolvated $FeI_2$. Excessive heating causes thermal decomposition, with evidence of iodine vapor appearing above the solid.[13] The current efficiency in a separate experiment (1.7 h, 40 mA) was 2.3 mol of Fe dissolved/faraday.

**Cobalt ($CoBr_2$).** Cobalt metal reacts with bromine in the cell used (Table I). Removal of the solvent in vacuo resulted in the deposition of green crystals; further heating of this solid (200 °C, 10 min) produced anhydrous $CoBr_2$. The current efficiency in a second experiment (2.16 h, 40 mA) was 2.54 mol/faraday.

Anhydrous $CoBr_2$ dissolves in acetonitrile; removal of excess solvent yields blue crystals of $CoBr_2 \cdot 2CH_3CN$ (mp 243 °C). The reaction of $CoBr_2$ in benzene/methanol (1/1) with 1,2-bis(diphenylphosphino)ethane in the same solvent produced an immediate precipitate of $CoBr_2 \cdot diphos$. The ready formation of these adducts emphasizes the synthetic usefulness of anhydrous transition-metal halides.

**Nickel ($NiCl_2$, $NiBr_2$, $NiI_2$).** Nickel dissolves easily with acetonitrile/$Cl_2$(g) at an applied voltage of 30 V; the air-sensitive yellow crystals deposited in the cell were found to be $NiCl_2 \cdot CH_3CN$, which turns green (presumably forming $NiCl_2 \cdot 6H_2O$) on exposure to air. Prolonged heating (2 h) at 100 °C, followed by 10 min at 200 °C, gave yellow-gold crystalline $NiCl_2$. The current efficiency for the dissolution of nickel was 0.83 mol/faraday. Hathaway and Holah[11] have reported the chemical attack of chlorine on nickel in acetonitrile, but the low current efficiency implies that the electrochemical process is the dominant one under our conditions.

Nickel dissolved electrochemically in a cell containing methanol, benzene, and bromine; addition of ether precipitated a gold-yellow solid whose bromine content (55.9%) is close to that calculated for $NiBr_2 \cdot 2CH_3OH$. Analyses in better agreement with the calculated value were obtained by removing the solvents in vacuo. Addition of 2,2′-bipyridine to the reaction mixture after removal of excess bromine gave orange crystals of $NiBr_2 \cdot bpy$. The presumed $NiBr_2 \cdot 2CH_3OH$ decomposed on heating (3 min, 200 °C) to give yellow anhydrous $NiBr_2$. The dimethanol adduct of $NiBr_2$ does not seem to have been reported previously; Osthoff and West[14] showed that nickel powder is oxidized by chlorine gas in ether and obtained inter alia the compound $NiCl_2 \cdot 2EtOH$ which is stoichiometrically analogous to the $NiBr_2 \cdot 2MeOH$ obtained above. The current efficiency for the dissolution of nickel in a short experiment (22 V, 40 mA, 1.67 h) was 8.6 mol/faraday.

With a cell containing iodine in acetonitrile, the product obtained on removing the solvent in vacuo corresponded to $NiI_2 \cdot 4CH_3CN$ which decomposed on heating (1 h at 100 °C, followed by 1 min at 200 °C) to $NiI_2 \cdot 2CH_3CN$; further heating (10 min at 200 °C) yielded $NiI_2$, apparently via $NiI_2 \cdot CH_3CN$. The analytical results for the two intermediate (mono and bis) acetonitrile adducts do not exactly agree with the calculated values, but this no doubt reflects the relatively crude temperature control. No attempt was made to prepare these adducts by precise control of the conditions, given that the prime aim was to obtain $NiI_2$. The current efficiency for dissolving nickel under the conditions described was 1.3 mol/faraday.

**Copper ($CuBr$, $CuBr_2$).** Electrochemical oxidation of copper in a cell containing bromine led to the isolation of two products. At the end of the reaction period, the gray crystals which had collected in the flask were separated from the black solution, washed with methanol, and dried in vacuo; this material was shown to be CuBr. Addition of diethyl ether to the filtrate resulted in the precipitation of almost black, unsolvated $CuBr_2$, which was dried in vacuo. In later experiments, the current efficiency for dissolution of copper was determined as 7.03 mol/faraday. The distribution of copper between CuBr and $CuBr_2$ was found to be $Cu^I/Cu^{II}$ = 0.28/0.72.

**Zinc ($ZnBr_2$).** Zinc metal dissolved easily in the cell used, and the solution deposited a white–gray solid which was collected by filtration and heated in vacuo (5 min, 200 °C). The resultant product was unsolvated $ZnBr_2$.

**General Comments.** As emphasized in the Introduction, the electrochemical technique provides a simple room-temperature route to a variety of anhydrous metal halides, which can then be used as the starting point for other synthetic work. The present and earlier work demonstrates that adducts with neutral ligands can be easily prepared, either in situ or preferably by subsequent reactions with the pure halide.

It is appropriate to comment here on the identity of the solvates obtained, especially in the acetonitrile systems. In only a few cases do the solids identified correspond to the adducts previously reported in the literature. The stabilizing factors to be considered are the solution conditions, which are known to affect the composition of solid phases in many such systems, and, more importantly, the temperature at which the product was desolvated in vacuo following removal from the reaction mixture. A number of studies[15] have shown that neutral adducts of transition-metal halides decompose in stepwise manner on heating

$$MX_2L_n \rightarrow MX_2L_{n-1} \rightarrow \cdots \rightarrow MX_2$$

and it should therefore come as no surprise that different preparative routes yield different solvates for a given halide. The case of $NiI_2$ is especially instructive, in that 4,2,1, or 0 molecules of $CH_3CN$ may be bound at different stages of thermal decomposition. In terms of the production of anhydrous metal halides, however, the most important point is that the last acetonitrile molecule can be removed under relatively mild conditions. In any case, it is possible that the acetonitrile adducts would be as useful in synthetic work as the parent anhydrous halides.

**Current Efficiency and Reaction Mechanism.** In each series of experiments, we have determined the current efficiency of the process, expressed in terms of the quantity of metal dissolved per faraday. The first point that should be made about such experiments is that our experience shows that the numerical values are somewhat dependent upon the detailed experimental arrangement (electrode area, separation between electrodes) and, more importantly, upon the length of electrolysis. This latter effect is presumably due inter alia to changes in solution composition and in the surface characteristics of the electrode (e.g., precipitation of product). We therefore restrict the present discussion to results obtained in short experiments of the order of 1–2 h, although even here one cannot rule out the possible influence of the factors just noted. In general, the current efficiencies in such experiments are in the order 2–10 mol/faraday.

The discussion must address two problems—the high current efficiency, which suggests a free-radical mechanism, and the striking preparative result that low oxidation states ($Fe^{II}$, $Co^{II}$, $Cu^{I}$) are produced instead of, or as well as, the higher states which one might have predicted, given the oxidizing nature of the solution phase. In this latter context we should note that previous work on vanadium[6] showed that vanadium(II) halides are formed in the electrochemical oxidation, whereas chemical attack of halogens on vanadium gives rise to vanadium(III) species.[11] We should also note in this context that both InI and $InI_3$ are produced in the electrochemical oxidation of indium in the presence of iodine.[2] Finally, it is relevant that work on the electrochemical oxidation of tin to yield $R_2SnX_2$ species (R = alkyl, aryl; X = Cl, Br, I) points to a free-radical mechanism being involved in the formation of RSnX in the first stage of the reaction.[16]

We suggest that the reactive species formed in our experiments is the dihalide anion $X_2^-$. There have been a number of investigations (spectral,[17] kinetic,[18] electron spin resonance[19]) of such radical anions in aqueous systems, and the main properties are well established. We frame the discussion in terms of $Br_2^-$ for convenience and propose that the primary formation at the cathode is

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

An alternative would be to postulate the formation of $S^-$ anions from acetonitrile or methanol, followed by electron transfer to $Br_2$, but this does not alter the overall argument. A lack of appropriate solution-phase electron-capture data hinders any discussion of this point for the present. The main reaction by which $Br_2^-$ would decompose in solution, by analogy with the aqueous solution chemistry,[18] is

$$Br_2^- + Br_2^- \rightarrow Br_3^- + Br^- \qquad (2)$$

but this can be neglected, as a consideration of the current density shows. A typical current of 20 mA generates approximately $2 \times 10^{-5}$ mol of $Br_2^-$/s into a total volume of ~50 $cm^3$; given that $Br_2^-$ is consumed at the anode (see below), the steady-state concentration of $Br_2^-$ should be sufficiently small for reaction 2 to be negligible.

The cathode process is believed to be

$$M + Br_2^- \rightarrow MBr + Br + e^- \qquad (3a)$$

followed by

$$M + Br \rightarrow MBr \qquad (3b)$$

so that if MBr were the only product, the current efficiency should be 2 mol of M dissolved/faraday. Further oxidation of MBr may occur by the sequence

$$MBr + Br_2 \rightarrow MBr_2 + Br \qquad (4a)$$

$$M + Br \rightarrow MBr \qquad (4b)$$

which gives rise by a chain of $n$ events to $n$ mol of $MBr_2$; this molecule can also be formed by

$$MBr + Br \rightarrow MBr_2 \qquad (5)$$

The chain in (4a) and (4b) can be terminated by

$$Br + Br \rightarrow Br_2 \qquad (6)$$

$$Br + Br_2^- \rightarrow Br_3^- \qquad (7)$$

or by reaction 5.

Thus in addition to the 2 mol of M which dissolves per faraday by (3a) + (3b) to give MBr, $n$ mol dissolves by the chain (4a) + (4b), giving $n$ mol of $MBr_2$. A further quantity of $MBr_2$ is formed by eq (5); this process removes a fraction $m$ of MBr ($\rightarrow m$ mol of $MBr_2$). In addition, a quantity of MBr is formed by chain termination, a process identical to (3b). This quantity ($p$), which will probably be small, will in turn generate $pn$ mol of $MBr_2$. The ratio $MBr{:}MBr_2$ ($R$) should therefore be given by

$$R = \frac{2 - m + p}{n + m + pn} \qquad (8)$$

The only system for which the experimental results allow any evaluation of $R$ is for copper for which $CuBr{:}CuBr_2 = 0.39$. If we assume that $p$ and $m$, being fractional, are small relative to $n$, we then obtain a value of $n = 5.1$ for the copper system. The total quantity of metal dissolved is $2 + n = 7.1$ mol/faraday. The agreement with the measured value (7.03) is beyond all expectation, given the nature of the experiment, but does establish that the overall mechanism is a reasonable one.

For the other metals studied, the MBr species was not isolated, implying that oxidation by (4a) and (5) is more important than in the case of copper. Under such circumstances the assumptions $n \gg m$ and $n \gg p$ are clearly invalid. The case for which $m = p \rightarrow 1$ gives $MBr{:}MBr_2 \rightarrow 0$, so that the apparently total conversion to $MBr_2$ for metals other than copper is ascribed to the ready oxidation of MBr by $Br_2$, in keeping with the chemistry of the 1+ states of these elements. The current efficiency remains at $2 + n$; the range of values reported above (2–10) presumably reflects both differing values of the chain length and the other factors noted at the beginning of this section.

The lack of oxidation beyond the M(II) state in the present experiments has been noted. It is interesting to note that studies[20] of aqueous solutions showed that under such conditions $Br_2^-$ oxidizes Co(I) to Co(II) but not Co(II) to Co(III). Iron(II) is oxidized to Fe(III) via inner-sphere association to $FeBr_2^+$, and a similar mechanism presumably applies for Mn(II) → Mn(III). On balance, these conclusions neither prove nor disprove the mechanism postulated above for nonaqueous conditions but are important in the main because they establish that oxidation of transition-metal species by $Br_2^-$ does not necessarily generate high oxidation states. In general, we believe that the mechanism proposed offers a satisfactory rationale for the present results and provides a basis for further experimentation.

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**Registry No.** $MnBr_2{\cdot}2CH_3OH$, 64715-16-8; $MnBr_2{\cdot}CH_3CN$, 64715-17-9; $MnBr_2$, 13446-03-2; $FeCl_2{\cdot}CH_3CN$, 64715-18-0; $FeCl_2$, 7758-94-3; $FeBr_2{\cdot}2CH_3CN$, 64715-19-1; $FeBr_2{\cdot}2phen$, 14322-36-2; $FeBr_2$, 7789-46-0; $FeI_2{\cdot}2CH_3CN$, 64715-20-4; $FeI_2$, 7783-86-0; $CoBr_2$, 7789-43-7; $CoBr_2{\cdot}2CH_3CN$, 17992-27-7; $CoBr_2{\cdot}diphos$, 34775-49-0; $NiCl_2{\cdot}CH_3CN$, 18897-44-4; $NiCl_2$, 7718-54-9; $NiBr_2{\cdot}2CH_3OH$, 64715-21-5; $NiBr_2$, 13462-88-9; $NiBr_2{\cdot}bpy$, 46389-47-3; $NiI_2{\cdot}4CH_3CN$, 15628-83-8; $NiI_2{\cdot}2CH_3CN$, 15305-84-7; $NiI_2{\cdot}CH_3CN$, 64715-22-6; $NiI_2$, 13462-90-3; CuBr, 7787-70-4; $CuBr_2$, 7789-45-9; $ZnBr_2$, 7699-45-8.

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# Complexes of the Platinum Metals. 13.[1] β-Diketonato Derivatives of Ruthenium, Osmium, and Iridium

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β-Diketones react with platinum metal hydrides and with $[Ru(CO)_3(PPh_3)_2]$ in boiling 2-methoxyethanol or toluene to give β-diketonato derivatives of ruthenium, osmium, and iridium. Products obtained in this manner include the O,O′-coordinated acetylacetonato complexes $[M(acac)H(CO)(PPh_3)_2]$ and $[M(acac)_2(PPh_3)_2]$ (M = Ru or Os), $[Ru(acac)Cl(CO)(PPh_3)_2]$, $[Ir(acac)H_2(PPh_3)_2]$, and $[Ir(acac)ClH(PPh_3)_2]$, together with the corresponding trifluoroacetylacetonato (facac) and hexafluoroacetylacetonato (facfac) derivatives. Stereochemical assignments have been made on the basis of $^1H$ and $^{31}P$ NMR data.

The acidolysis of platinum metal hydrides (eq 1) has re-

$$L_nM\text{-}H + HR \rightarrow L_nM\text{-}R + H_2 \qquad (1)$$

cently gained favor as an alternative to the classic halide metathesis reactions (eq 2) for the introduction of anionic

$$L_nM\text{-}X + M'R \rightarrow L_nM\text{-}R + M'X \qquad (2)$$
$$M' = Na, Ag, Tl^I, \text{etc.}$$

ligands, R, into platinum metal phosphine complexes. The method can also be applied to selected zero oxidation state complexes (eq 3 and 4). Reactions of this type are now being

$$L_{n+1}M + HR \rightarrow L_nMHR + L \qquad (3)$$

$$L_nMHR + HR \rightarrow L_nMR_2 + H_2 \qquad (4)$$

commonly used to introduce a variety of anionic ligands into platinum metal complexes. Examples from our own laboratory involve the formation of carboxylato,[2,3] perfluorocarboxylato,[2,4] 1,3-diaryltriazenido,[5] and, as described in the present paper, β-diketonato derivatives. A similar reaction involving oxidative addition of acetylacetone to the molybdenum complex $[Mo(Ph_2PCH_2CH_2PPh_2)_2(C_2H_4)]$ has previously been reported.[6]

Our interest in β-diketonato complexes derives in part from the variety of bonding modes displayed by β-diketonate anions when coordinated to transition metals in general and platinum metals in particular.[7] In the present work, introduction of β-diketonate ligands into crowded coordination environments containing three or four bulky triphenylphosphine ligands was intended to encourage monodentate O or C coordination to the metal. However, the conditions required to induce reaction proved sufficiently vigorous to cause phosphine displacement, and all metal complexes synthesized contain β-diketonate anions bound in conventional fashion as O,O′ donor chelates. Moreover, attempts to convert β-diketonate ligands from O,O′-bidentate coordination to γ-C-monodentate coordination by addition of triphenylphosphine or pyridine were unsuccessful.

## Experimental Section

The complex $[IrCl_2H(PPh_3)_3]$ was prepared as described by Vaska,[8] and all other platinum metal complexes employed in this work were synthetized using the single-stage techniques developed in our laboratory.[9] The β-diketones were obtained from BDH and Fluorochem and were used without further purification. Reagent grade organic solvents were dried over molecular sieves and degassed before use. The light petroleum used had a boiling range of 60–80 °C. Reactions were performed under a nitrogen atmosphere, but products were worked up in air. Analyses, by the microanalytical laboratory, University College, London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. Infrared spectra were run as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Proton and phosphorus NMR spectra were obtained at 90 and 36.43 MHz, respectively, using a Bruker HFX90 NMR spectrometer. Spectroscopic data are recorded in Table II or are given in the text ($^{31}P$ NMR). $^{31}P$ NMR data are referenced to external $H_3PO_4$ and are reported in ppm with a positive value indicating a resonance at low field relative to the $H_3PO_4$.

**(Acetylacetonato)carbonylhydridobis(triphenylphosphine)ruthenium(II), $[Ru(acac)H(CO)(PPh_3)_2]$. Method I.** A mixture of carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.2 g), acetylacetone (0.05 g), and triethylamine (1 mL) in 2-methoxyethanol (15 mL) was heated under reflux for 15 min. After the resultant yellow solution was cooled overnight, the required product separated and was washed with methanol and light petroleum to yield yellow crystals (0.134 g, 85%).

**Method II.** Acetylacetone (0.05 g) was added to a suspension of carbonyldihydridotris(triphenylphosphine)ruthenium (0.2 g) in 2-methoxyethanol (15 mL), and the mixture was heated under reflux for 30 min. The required product separated from the yellow solution on cooling and was purified as described above to yield yellow crystals (0.131 g, 80%).

**Method III.** A mixture of acetylacetone (0.05 g) and tricarbonylbis(triphenylphosphine)ruthenium (0.2 g) in 2-methoxyethanol (15 mL) was heated under reflux for 6 h. The resultant yellow solution was evaporated to dryness and the residue washed with methanol and then recrystallized from dichloromethane/methanol to yield the required product as yellow crystals (0.169 g, 80%).

Similarly prepared using any of the above methods were: **carbonylhydrido(trifluoroacetylacetonato)bis(triphenylphosphine)ruthenium(II)** as lime yellow crystals (ca. 85%) and **carbonyl(hexafluoroacetylacetonato)hydridobis(triphenylphosphine)ruthenium(II)** as yellow crystals (ca. 80%).

**(Acetylacetonato)carbonylchlorobis(triphenylphosphine)ruthenium(II), $[Ru(acac)Cl(CO)(PPh_3)_2]$.** A mixture of acetylacetone (0.05 mL) and carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.2 g) in 2-methoxyethanol (15 mL) was heated under reflux for 30 min and then cooled overnight. The resultant precipitate was

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