*Journal of Organometallic Chemistry*, 185 (1980) 117–127
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# The Electrochemical Synthesis of Neutral and Anionic Organozinc Halides

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(Received July 9th, 1979)

## Summary

A series of 2,2´-bipyridine adducts of organozinc(II) halides RZnX has been prepared by the electrochemical oxidation of zinc in the presence of organic solutions of RX ($R = CH_3$, $C_2H_5$, $CF_3$, $C_3H_3$, $C_6H_5$, $C_6F_5$, $C_6H_5CH_2$; X = Cl, Br, I (not all combinations)). Similar methods have been used to prepare the anions $RZnX_2^-$ ($R = CH_3$, $C_2H_5$, $C_6H_5$, $CF_3$; X = Cl, Br, I (not all combinations)) as the tetra-n-propylammonium salts.

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## Introduction

The reaction of metallic zinc or zinc/copper couple with alkyl halides to yield organozinc(II) halides is one of the classical reactions of organometallic chemistry. This simple synthetic route is not however available for the preparation of the corresponding aryl halides, since zinc does not react with these compounds under normal conditions [1], and the usual method involves the reaction of anhydrous zinc chloride with the appropriate Grignard reagent. Following work on the direct synthesis of neutral and anionic organocadmium halides [2-4], we have now investigated the application of this technique to zinc and find that the metal can be oxidised electrochemically in the presence of either alkyl or aryl halides, and certain fluoro analogues, to give the corresponding RZnX compounds, which are conveniently prepared and stabilised as the addition compounds with 2,2′-bipyridine (bipy). Alternatively, oxidation in the presence of RX and $R'_4NX$ gives the salts $R'_4N[RZnX_2]$, which are the first examples of dihalogeno-organozincate(II) anions.

## Experimental

### General

Zinc metal (m4N5) was used in the form of discs, approx. 1x1 x 0.2 cm, obtained by hammering pieces of zinc rod. The purification of solvents, etc., and the spectroscopic investigation of product materials, followed techniques described previously [3-5]. All experiments were carried out in an atmosphere of dry nitrogen.

### Electrochemical Synthesis

A piece of zinc, *ca.* 1 x 1 x 0.1 $cm^2$ suspended on a platinum wire formed the anode for the cell. The experiments were carried out in a two-arm cell. The solution phase was first frozen, degassed, thawed, and flushed with nitrogen several times in one arm, and then decanted into the second arm which contained the anode; a ring of tungsten wire fused into the cell wall formed the cathode. Operations with this type of cell are conveniently carried out with *ca.* 15 $cm^3$ total solution phase, and approx. half a gram of product can be obtained in a few hours. The solution phase composition, electrochemical conditions, time of electrolysis, and yields are given in Table 1 for the neutral RZnX.bipy compounds, and in Table 2 for the tetrapropylammonium salts of $[RZnX_2]^-$ anions.

In the case of the 2,2´-bipyridine adducts, the solution resulting from the electrochemical oxidation was filtered, and petroleum ether added dropwise to the filtrate. The yellow precipitate which formed was washed several times with benzene to remove excess bipy and then dried in vacuo. With the anionic complexes, addition of diethyl ether to the filtrate precipitated both the product and excess tetrapropylammonium bromide or iodide, but the latter was removed by successive washing with dry chloroform. In the case of the chloride, only the product was precipitated by diethyl ether, and this solid was washed with petroleum ether and dried.

Analysis for zinc was by atomic absorption spectrophotometry, and for halogen by Volhard titration; the analytical results are given in Tables 3 and 4. In compounds where R = $CH_3$ or $C_2H_5$, decomposition by the addition of dilute acid released $CH_4$ or $C_2H_6$ which was collected and whose volume was measured. (See Table 5). The presence of bipy, or of the tetrapropylammonium cation was demonstrated in every case by established infrared spectroscopy.

## Results and Discussion

As with the previous studies on cadmium compounds [2-4], the direct electrochemical synthesis gives compounds in good purity and yield, using only simple apparatus and conventional procedures. In addition, arylzinc halides

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Table 1. Reaction conditions for the direct electrochemical synthesis of neutral organozinc halides.

| Compound (a) | Vol. of RX ($cm^3$) | Vol. of 2:1(v/v) $CH_3CN + C_6H_6$ ($cm^3$) (b) | Initial voltage (V) | Initial current (mA) | Time of electrolysis (h) | Zn dissolved (mg) | Wt. of product (g) | % yield (d) |
|---|---|---|---|---|---|---|---|---|
| $CH_3ZnI.L$ | 2.5 | 15 | 40 | 25 | 6 | 105 | 0.42 | 72 |
| $C_2H_5ZnBr.L$ | 2.5 | 15 | 50 | 25 | 8 | 78 | 0.25 | 63 |
| $C_2H_5ZnI.L$ | 2.5 | 15 | 40 | 25 | 6 | 125 | 0.60 | 86 |
| $CF_3ZnI.L$ | 2.5 | 15 | 10 | 10 | 1.5 | 152 | 0.75 | 77 |
| $C_3H_3ZnBr.L$ | 2.5 | 15 | 30 | 30 | 3 | 101 | 0.25 | 68 |
| $C_6H_5ZnCl.L$ | 3.0 | 15 | 40 | 25 | 6 | 65 | 0.20 | 61 |
| $C_6H_5ZnBr.L$ | 3.0 | 15 | 45 | 25 | 6 | 75 | 0.30 | 67 |
| $C_6H_5ZnI.L$ | 3.0 | 15 | 40 | 25 | 6 | 86 | 0.41 | 73 |
| $C_6F_5ZnBr.L$ | 3.0 | 16 (c) | 45 | 30 | 8 | 98 | 0.38 | 54 |
| $C_6H_5CH_2ZnCl.L$ | 2.5 | 16 (c) | 40 | 25 | 7 | 130 | 0.58 | 84 |
| $C_6H_5CH_2ZnBr.L$ | 2.5 | 16 (c) | 40 | 30 | 8 | 105 | 0.47 | 76 |
| $C_6H_5CH_2ZnI.L$ | 1.0(g) | 13 | 40 | 25 | 6 | 130 | 0.70 | 84 |

(a) L = 2,2′-bipyridine; (b) plus 0.8 g bipy in each case; (c) 1:1 (v/v) $CH_3CN + C_6H_6$ (d) based upon metal dissolved

Table 2. Reaction conditions for the direct electrochemical synthesis of organodihalogenozincate(II) anions

| Anion [(a)] | Vol$(cm^3)$ |  |  | $(C_3H_7)_4NX$ (g) | Initial voltage (v) | Initial current (mA) | Time of electrolysis (h) | Zn dissolved (mg) | % yield |
|---|---|---|---|---|---|---|---|---|---|
|  | RX | $CH_3CN$ | $C_6H_6$ |  |  |  |  |  |  |
| $CH_3ZnI_2^-$ | 1.5 | 10 | 3 | 1.5 | 20 | 25 | 3 | 101 | 91 |
| $C_2H_5ZnBr_2^-$ | 2.5 | 10 | 5 | 2.0 | 30 | 25 | 4 | ? | 67 |
| $C_2H_5ZnI_2^-$ | 1.5 | 10 | 3 | 1.5 | 20 | 25 | 4 | 125 | 79 |
| $C_6H_5ZnCl_2^-$ | 2.0 | 10 | 5 | 1.2 | 40 | 30 | 6 | 65 | 69 |
| $C_6H_5ZnBr_2^-$ | 2.0 | 10 | 5 | 1.3 | 40 | 30 | 5 | 77 | 67 |
| $C_6H_5ZnI_2^-$ | 2.0 | 10 | 5 | 1.5 | 30 | 30 | 6 | 115 | 73 |
| $CF_3ZnI_2^-$ | 2.0 | 10 | 5 | 1.5 | 20 | 15 | 2 | 86 | 60 |

[(a)] As the tetra-n-propylammonium salt

Table 3. Analytical results for 2,2′-bipyridine adducts of organozinc halides.

| Compound[a] | Colour | Analysis (Found (calcd)) (%) Zinc | Halogen |
|---|---|---|---|
| $CH_3ZnI.L$ | yellow | 18.1 (18.0) | 35.1 (35.0) |
| $C_2H_5ZnBr.L$ | pale yellow | 20.0 (19.8) | 24.6 (24.2) |
| $C_2H_5ZnI.L$ | pale yellow | 17.5 (17.3) | 33.8 (33.7) |
| $C_3H_3ZnBr.L$ | brown-yellow | 19.8 (19.9) | 24.4 (24.3) |
| $C_6H_5ZnCl.L$ | green-yellow | 19.7 (19.6) | 10.6 (10.6) |
| $C_6H_5ZnBr.L$ | yellow | 17.2 (17.3) | 21.3 (21.1) |
| $C_6H_5ZnI.L$ | yellow | 15.5 (15.4) | 29.9 (29.8) |
| $C_6F_5ZnBr.L$ | off-white | 14.2 (14.0) | 17.2 (17.1) |
| $C_6H_5CH_2ZnCl.L$ | yellow | 18.7 (18.8) | 23.2 (23.0) |
| $C_6H_5CH_2ZnBr.L$ | pale yellow | 16.6 (16.7) | 20.3 (20.4) |
| $C_6H_5CH_2ZnI.L$ | orange-yellow | 14.8 (14.9) | 29.0 (28.9) |
| $CF_3ZnI.L$ | brown | 15.7 (15.7) | 30.4 (30.4) |

(a) L = 2,2′-bipyridine.

Table 4. Analytical results for tetra-n-propylammonium salts of organodihalogenozincate(II) anions.

| Anion | Colour | Analysis (Found (Calcd)) (%) Zinc | Halogen |
|---|---|---|---|
| $CH_3ZnI_2^-$ | pale yellow | 12.6 (12.5) | 48.9 (48.8) |
| $C_2H_5ZnBr_2^-$ | pale orange | 14.7 (14.8) | 36.3 (36.3) |
| $C_2H_5ZnI_2^-$ | pale yellow | 12.3 (12.2) | 47.4 (47.5) |
| $C_6H_5ZnCl_2^-$ | off-white | 16.4 (16.3) | 17.7 (17.7) |
| $C_6H_5ZnBr_2^-$ | yellow-orange | 13.4 (13.4) | 32.7 (32.7) |
| $C_6H_5ZnI_2^-$ | pale yellow | 11.2 (11.2) | 43.7 (43.6) |
| $CF_3ZnI_2^-$ | yellow | 11.5 (11.4) | 44.4 (44.2) |

Table 5. Analysis of organozinc halides by acid decomposition

| Compound | Wt. cpd. (mg) | Vol. of gas ($cm^3$, STP) Found / Calcd. |
|---|---|---|
| $CH_3ZnI.bipy$ | 87.3 | 5.8 (5.9) |
| $C_2H_5ZnBr.bipy$ | 95.0 | 7.0 (6.8) |
| $C_2H_5ZnI.bipy$ | 91.2 | 5.9 (5.7) |
| $[CH_3ZnI_2]^-$ (a) | 80.0 | 3.5 (3.7) |
| $[C_2H_5ZnBr_2]^-$(a) | 75.3 | 4.0 (4.1) |
| $[C_2H_5ZnI_2]^-$(a) | 121.0 | 5.3 (5.5) |

(a) As the tetra-n-propylammonium salt.

are now available by this route as readily as are the alkyl analogues. The adducts all involved the bidentate donor 2,2´-bipyridine, but there is no doubt on the basis of our previous work [3], and that of others [1], that compounds with other neutral ligands could readily be prepared by this route. The addition compounds of 2,2´-bipyridine with organozinc halides are yellow-white solids, stable in dry nitrogen, insoluble in acetone, benzene, diethyl ether or petroleum ether, and slightly soluble in acetonitrile. All show some solubility in a mixture of acetonitrile and the parent organohalide.

The method also yields a series of new $RXnX_2^-$ anions, with R = alkyl or aryl, and here again there seems every reason to assume that experiments with organic halides other than those actually used would give rise to analogous complexes. The formulation of these compounds as salts was confirmed by measuring the molar conductivities for nM solutions in acetonitrile. For the salts of $CH_3ZnI_2^-$, $C_2H_5ZnBr_2^-$ and $C_2H_5ZnI_2^-$, the values were in the range 135 ± 5 ohm$^{-1}$ cm$^{2}$ mol$^{-1}$, which is within the limits of 120 - 160 ohm$^{-1}$ cm$^{2}$ mol$^{-1}$ regarded as being typical of 1:1 electrolytes in this solvent [6]. While questions still remain as to the molecularity of the complexes, the conductivity and analytical results establishes the ionic structures with certainty. The salts have similar stabilities, and solubilities, to the neutral adducts discussed above. In both cases, the low solubilities may reflect some degree of polymerisation in the solid state (cf. ref 1).

Spectroscopic Measurements

The information which can be obtained in the potassium bromide region of the infrared spectrum is limited, and can be quickly summarised. Firstly, the presence of 2,2´-bipyridine, or the tetra-n-proplyammonium cation as appropriate was clearly demonstrated by the standard tests [7,8], and the presence of $CF_3$ or $C_6F_5$ was equally shown by $\nu$(C-F). The $\nu(Zn-CH_3)$ band at 510 cm$^{-1}$ was readily identified in $CH_3ZnI$.bipy, as was $\nu(Zn-C_2H_5)$ at 515 ($C_2H_5ZnI$.L) or 545 ($C_2H_5ZnBr$.L) cm$^{-1}$. We made no attempt to identify $\nu$(Zn-X) or $\nu$(Zn-N) modes at this stage of the work.

The low solubility of the neutral adducts prevented studies of the n.m.r. spectra of these compounds, and only limited investigation of the $RZnX_2^-$ salts was possible. In $CD_3CN$, the compound $Pr_4N[C_6H_5ZnI_2]$ shows the expected resonances due to the cation plus a multiplet at $\delta = 7.2$ ppm relative to TMS (60 MHz); this is assigned to the phenyl group of the anion. The corresponding chloro- and bromo-compounds are insufficiently soluble for any comparative studies. For $Pr_4N[CH_3ZnI_2]$, the triplet at $\delta = 0.9$ of the $CH_3$ group of the cation shows some distortion and extra intensity compared to the spectrum of (say) $Pr_4NI$, and we therefore deduce that the $CH_3$ group attached to zinc has a $^1H$ resonance in this region.

These spectroscopic results confirm the nature of the reaction products, but it is clear that unambiguous structural identification will require more rigorous methods such as an X-ray determination.

## Electrochemical oxidation of zinc

Following previous practice, we have measured the current efficiency, $E_F$, expressed as mol metal dissolved per Faraday of electricity, for a number of $Zn_{(+)}/RX$ systems. The results of experiments lasting 2-3h at a constant current of 20-30 mA were

| | |
|---|---|
| $CH_3I$ | 0.99 |
| $C_2H_5I$ | 1.08 |
| $CH_3I$/bipy | 0.89 |
| $C_2H_5I$/bipy | 0.76 |
| $CH_3I/Pr_4NI$ | 0.83 |
| $C_2H_5I/Pr_4NI$ | 0.79 |

These values are remarkably constant, and significantly lower than those found for the corresponding cadmium systems [3]. In this latter case, as with tin [5], the high current efficiency was explained in terms of the following scheme

cathode $RX + e^- \rightarrow R^\cdot + X^-$ (1)

anode $X^- + M \rightarrow MX + e$ (2)

$MX + RX \rightarrow MRX + X$ (3)

$X + M \rightarrow MX$ (4)

with (3) and (4) constituting a chain process whose length is independent of the electrochemical anode reaction (2). In the simplest system studied for zinc, namely those involving $CH_3I$ or $C_2H_5I$ in the absence of ligand, the $E_F$ values are unity, within experimental error, which implies that reaction (4) is of little importance. Any halogen formed in a process such as in eq. (3) will then most likely go to $I_2$, and in keeping with this, a purple colour was observed near the anode in unstirred solutions. The other systems give $E_F$ values below unity, and these low values in the presence of bipy or $Pr_4NI$ may be due to the formation of insoluble reaction products on the metal surface. One possible rationalisation for the difference between zinc on the one hand and cadmium and tin on the other may lie in the energetics of reaction (4); further work on this topic is planned.

Acknowledgement. This work was supported in part by Operating Grants (to DGT) from the National Research Council of Canada.

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