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ELECTROCHEMICAL PREPARATION OF NEUTRAL ORGANOCADMIUM HALIDES

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Summary

The electrochemical oxidation of cadmium metal in the presence of methyl or ethyl iodide leads to the formation of unstable RCdI. These, and related species, can be stabilised with neutral ligands, and a series of adducts of alkyl-, aryl- and perfluoroaryl-cadmium halides have been prepared. The oxidation apparently involves a free radical mechanism. The results support previous studies of solution equilibria involving R_2Cd and CdX_2 species.

Cadmium differs from zinc and mercury in a number of respects, one of which is in the ability of the latter two elements to undergo direct catalytic or photochemical reactions with organic halides to give the organometallic halide compounds. The preparation of zinc and mercury compounds by this route is thus well established, but attempts to prepare cadmium complexes in this way have not been successful. Chenault and Tatibouet [1] showed that cadmium will react with alkyl iodides (= RI) (but not chlorides or bromides) in hexamethylphosphoramide (= HMPA), and isolated both $CdI_2 \cdot 2$ HMPA and $CdR_2 \cdot 2$ HMPA from the reaction mixture. Evans and Phillips [2] later established that solutions prepared by treating cadmium (and zinc) with C_6F_5I in donor solvents contain $(C_6F_5)_2Cd$ and C_6F_5CdI, whose exchange reactions were studied by ^{19}F NMR. No solids were isolated in this work.

The preparation of RCdX species has generally involved exchange between the appropriate diorganocadmium compound and a cadmium halide, a method which is satisfactory but has the obvious problem that the organocadmium halide must be separated from an equilibrium mixture with the starting materials [2,3]. Studies of Schlenk-type equilibria involving dialkylcadmium and cadmium dihalides have been carried out by both ^1H NMR [4] and vibrational spectroscopy [5], and by molecular weight determinations [6]; all these investigations established that RCdX species are readily formed in donor solvents.

We now report details of the electrochemical oxidation of cadmium metal in the presence of alkyl and aryl halides, a technique which yields the corresponding organocadmium halides in high yield. The compounds are highly reactive, but fortunately can be stabilized with bidentate neutral ligands, giving rise to thermally stable addition compounds. The preparative technique is similar to one which has been used successfully in this laboratory for the preparation of organotin compounds [7], in which case the products were diorganotin dihalides and their adducts, and more recently in the preparation of organo-transition metal halides [8]. We note below the advantages of this method. The mechanism appears to be very similar to that identified in the preparation of organotin compounds, in that measurements of current efficiency suggest a free radical mechanism. A preliminary report of this work has appeared elsewhere [9].

Experimental

General

Cadmium metal (Alfa Inorganics, m4N) was used in the form of a rod (8 cm long, 0.25 cm diameter), or beaten into a sheet (2 X 2 cm). Solvents and neutral ligands were as described in previous work [7].

Infrared spectra were recorded on a Beckman IR-12 instrument, using Nujol mulls between caesium iodide plates. We found that the spectra of compounds pressed into a disc after grinding with caesium iodide powder showed no ν(Cd—C) vibration, and believe that this is due to replacement of the organic group to give CdX_2 compounds; certainly such behaviour is known to occur in solution [5]. Attempts to record the Raman spectra of solid compounds were frustrated by extensive charring of samples in the laser beam.

Metal analysis was by atomic absorption spectrophotometry, and halide analysis by the Volhard method. In a number of cases, the methyl and ethyl groups were determined by decomposing the compound with acetic acid and measuring volumetrically the quantity of methane or ethane produced.

Electrochemical preparations

The method was essentially that described previously in terms of the preparation of diorganotin dihalides; details of the experimental conditions are listed in Table 1. The colourless or off-white products precipitated in the cell, which was operated under nitrogen, and were washed with dry benzene (for bipyridine and phenanthroline compounds only) and dry ether and dried in vacuo.

All the compounds prepared are extremely air sensitive, and were handled in a nitrogen atmosphere. We also noted that methyl- and ethyl-cadmium halides in particular decompose on contact with a nickel spatula, producing a black deposit (cadmium metal?) on the surface of the spatula; the use of glass or plastic spatulas is therefore recommended.

We observed that the surface of the cadmium metal electrodes tended to disintegrate physically during long electrolyses, and especially at high (>20 V) voltages. Perceptible particles of cadmium metal contaminate the product in these circumstances, and are difficult to remove, since the adducts of RCdX species are insoluble in most common organic solvents. The situation can be avoided by restricting the operation to low voltage and short (i.e. <3 h) periods of electrolysis. When more extreme conditions were necessary, it was found possible to

TABLE 1

ANALYTICAL RESULTS FOR ORGANOCADMIUM HALIDES, AND THEIR ADDUCTS

Compound [a]	Analysis (Found (calcd.)(%))	
	Cd	Halogen
CH_3CdI [b]	44.4 (44.1)	49.7 (49.9)
C_2H_5CdI	41.8 (41.9)	47.1 (47.3)
$CH_3CdI \cdot$ bipy [c]	27.3 (27.3)	30.9 (30.9)
$CH_3CdI \cdot 2$ dmso [d]	27.1 (27.3)	31.1 (30.9)
$C_2H_5CdBr \cdot$ bipy [e]	29.4 (29.8)	21.2 (21.3)
$C_2H_5CdBr \cdot$ phen	28.2 (28.0)	20.3 (19.9)
$C_2H_5CdBr \cdot$ diox	36.6 (36.4)	25.8 (25.9)
$C_2H_5CdI \cdot$ diox	32.0 (31.5)	35.6 (35.7)
n-$C_4H_9CdCl \cdot$ bipy	31.4 (31.0)	9.7 (9.8
$C_6H_5CdBr \cdot$ diox	32.2 (31.5)	22.1 (22.4)
$C_6F_5CdBr \cdot$ bipy	21.6 (21.8)	15.4 (15.5)

[a] bipy = 2,2'-bipyridine; dmso = dimethyl sulphoxide; phen = 1,10-phenanthroline; diox = 1,4-dioxane. [b] Acid decomposition of 0.428 g gave 37.5 cm^3 of gas (NTP); calcd. 37.7 cm^3. [c] Acid decomposition of 0.217 g gave 11.4 cm^3 of gas (NTP); calcd. 11.8 cm^3. [d] Values are for freshly prepared material (see text). [e] Acid decomposition of 0.173 g gave 10.2 cm^3 of gas (NTP); calcd. 10.2 cm^3.

effect a separation of cadmium particles from the product by collecting the former in a small vial placed immediately below the cadmium rod; the cadmium particles fall into this vial, whilst most of the lighter insertion product falls outside it.

Results and discussion

Methyl-, and ethyl-cadmium iodide

Cadmium metal dissolves readily in methyl iodide/methanol mixtures, and a white, highly air-sensitive product deposits in the reaction vessel. Elemental and gas analysis established that this material is CH_3CdI; C_2H_5CdI was similarly prepared. In view of their sensitivity, and the ease with which the much more stable addition compounds can be prepared (see below), we did not attempt to investigate these compounds further. We should note here that RCdX compounds are formal analogues of Grignard reagents; the electrochemical preparation of RCOR' compounds from RCOX and R'X represents one application of this analogy [10]. The preparation of C_6F_5CdX adducts (and the $CF_3CdI_2^-$ anion [11]) suggests that the parent R_fCdX compounds could be used in circum-

TABLE 2

REACTION CONDITIONS FOR DIRECT ELECTROCHEMICAL SYNTHESIS OF ORGANOCADMIUM HALIDES

Compound [a]	Vol. of organic halide (cm^3)	Vol. of acetone (cm^3) [b]	Wt., or volume, of ligand	Voltage (V)	Initial current (mA)	Time (h)	Cd dissolved (g)	Wt. of product recovered (g)	Yield (%)
CH_3CdI	70	30 [d]	0	50	60	2	0.42	0.71	74
C_2H_5CdI	60	20 [d]	0	45	50	2	0.37	0.72	81
$CH_3CdI \cdot$ bipy	5	40	0.7 g	35	100	2.5	0.26	0.9	95
$CH_3CdI \cdot$ 2 dmso	25	0	25 cm^3	25	100	12	[e]	[e]	—
$C_2H_5CdBr \cdot$ bipy	15	30	0.7 g	40	80	2	0.26	0.84	96
$C_2H_5CdBr \cdot$ phen	15	30	0.75 g	40	90	2	0.27	0.93	97
$C_2H_5CdBr \cdot$ diox	15	10 [c]	15 cm^3	14	40	10	0.46	1.21	96
$C_2H_5CdI \cdot$ diox	15	10	15 cm^3	15	40	8	0.35	0.87	78
n-$C_4H_9CdCl \cdot$ bipy	30	15 [d]	0.5 g	10	20	5	[e]	[e]	—
$C_6H_5CdBr \cdot$ diox	30	10	30 cm^3	18	40	6	[e]	1.19	—
$C_6F_5CdBr \cdot$ bipy [f]	2	0.5 [d]	0.35 g	17	8	2	0.13	0.38	64

[a] Abbreviations as in Table 1. [b] 15 mg of $(C_2H_5)_4NClO_4$ added in each experiment. [c] Plus 5 cm^3 CH_3OH to reduce voltage. [d] Methanol used instead of acetone. [e] Not recorded. [f] Experiment performed in small cell.

stances in which the preparation of the perfluoroalkyl-Grignard reagent is troublesome.

Addition compounds

Electrochemical oxidation of cadmium under the various conditions described in Table 2 gave rise to the series of adducts noted. We first note that the infrared spectra of the 2,2′-bipyridine and 1,10-phenanthroline adducts confirm the bidentate coordination of these ligands, and we therefore formulate these compounds as the four-coordinate RCdX · bipy etc. species. In view of the instability of the dmso adduct (see below), we believe that 1,4-dioxane is also acting as a bidentate ligand in these complexes. Thus we have obtained these thermally stable compounds in high yield by the simple syntheses described. The compound CH_3CdI · 2 dmso was prepared by a similar method, but proved to be unstable; two days after the original preparation, the iodine content of the solid was 62.0%, approaching the value for unsolvated CdI_2 (calcd. 69.4%). We suggest that loss of dmso from the compound is followed (or accompanied) by rearrangement to $(CH_3)_2Cd$ (volatile) and CdI_2. A similar loss of dmso from adducts of Main Group organometallic compounds has been observed previously [7].

The C_6F_5Br system is especially interesting because of its relevance to the postulated Schlenk equilibria in solution. Under the conditions outlined in Table 2, colourless crystals of $C_6F_5CdBr \cdot$ bipy formed in the reaction vessel and were collected. When the electrolysis was carried out with a solution phase of C_6F_5Br and CH_3CN, cadmium dissolved but the material which precipitated contained acetonitrile (identified by infrared absorption at 2284 cm^{-1}). No vibrations of the C_6F_5 group were detected in the ether-washed solid, and the analytical results (Found: Cd, 25.3; Br, 36.1%) are in good agreement with those for $CdBr_2 \cdot 2\,CH_3CN$ (Calcd.: Cd, 25.5; Br, 36.3%). We therefore propose that in the presence of CH_3CN, the initial product is $C_6F_5CdBr \cdot 2\,CH_3CN$, which is soluble in excess acetonitrile, and dissociates via equilibrium 1, which is followed by precipitation of the cadmium dibromide adduct. This mechanism is similar to that proposed by Chenault and Tatibouet [1] for the reaction of cadmium with alkyl iodides in HMPA, and also with the NMR studies of Evans and Phillips [2] on C_6F_5I/Cd systems.

$$2\,C_6F_5CdBr \cdot L_2 \rightleftharpoons (C_6F_5)_2Cd \cdot L_2 + CdBr_2 \cdot L_2 \qquad (1)$$

Vibrational spectroscopy

The infrared spectra of the addition compounds in the ν(Cd—C) region are shown in Table 3. The results show some dependence on the mass of the alkyl group, and equally show that $\nu(Cd{-}C_2H_5)$ is unaffected by change in bidentate ligand or halogen. Because of the decomposition of these compounds in the laser beam, we were unable to record the Raman spectra.

Cavanagh and Evans [5] have studied the infrared and Raman spectra of solutions prepared by mixing $(CH_3)_2Cd$ and CdX_2 (X = Cl, Br, I) in tetrahydrofuran or dimethylformamide (X = I only). They identified vibrations between 475 and 482 cm^{-1} as $\nu(Cd{-}CH_3)$ in these systems. These values are slightly higher than the 445 cm^{-1} found for $CH_3CdI \cdot$ bipy, but this may be accounted for by the difference between the crystalline and solution phases in question.

TABLE 3

ν(Cd—C) MODES IN THE INFRARED SPECTRA OF RCdX ADDITION COMPOUNDS

Compound	ν(Cd—C) (cm^{-1})
$CH_3CdI \cdot$ bipy	445
$C_2H_5CdBr \cdot$ bipy	478
$C_2H_5CdBr \cdot$ phen	479
$C_2H_5CdBr \cdot$ diox	474
$C_2H_5CdI \cdot$ diox	471
n-$C_4H_9CdCl \cdot$ bipy	472

Reaction mechanism

It has been pointed out in previous papers that measurements of the current efficiency, expressed as mol metal dissolved per Faraday of electricity, can lead to an understanding of the reaction mechanism. To be meaningful, such measurements must be carried out at constant current, and under conditions which prevent both build up of product on the anode surface and disintegration of the cadmium electrode. Experiments of this nature were performed on a number of systems, with the following results: C_2H_5Br/bipy; current efficiency = 1.1 mol Cd F^{-1}; CH_3I/bipy; current efficiency = 2.4 mol Cd F^{-1}; and C_6F_5Br/bipy; current efficiency = 2.0 mol Cd F^{-1}.

These values are similar to, although slightly lower than, those reported for tin dissolving in CH_3I or C_2H_5I, and lead to a similar mechanism, the gist of which is that radicals are generated at the cathode (eq. 2), followed by the anodic processes (eq. 3a, 3b, 3c).

$$RX + e^- \rightarrow R^\cdot + X^- \qquad (2)$$

$$X^- \rightarrow X^\cdot + e^- \qquad (3a)$$

$$X^\cdot + Cd \rightarrow CdX \qquad (3b)$$

$$CdX + RX \rightarrow RCdX + X^\cdot \qquad (3c)$$

The relatively high current efficiencies observed are in keeping with short chains in which $X^\cdot$ is the chain carrier. Unlike the tin system, the product RCdX does not react to give higher oxidation states. The details of the chain termination and other reactions have been discussed elsewhere [7].

General

It is clear that RCdX species, which can be stabilised in the solid state, will indeed exist in solution, especially of donor solvents, and the present work therefore serves as confirmation of earlier spectroscopic studies [2,5]. Equally, the work demonstrates that the synthesis of these compounds in good yield is easily achieved. The compounds may serve as convenient substitutes for Grignard reagents in certain situations.

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