Direct Electrochemical Synthesis of Neutral and Anionic Organocadmium Halides

By JACOB J. HABEEB, AHKTAR OSMAN, and DENNIS G. TUCK*
(*Department of Chemistry, University of Windsor, Windsor, Ontario* N9B 3P4, *Canada*)

Summary Adducts of organocadmium halides with neutral bidentate ligands, *e.g.* EtCdBr.dioxan, are readily synthesised by the electrochemical oxidation of the metal; salts of anions such as $[MeCdI_2]^-$ have also been prepared by this method.

ALTHOUGH zinc and mercury undergo direct catalytic or photochemical reaction with alkyl halides to give compounds of the type RMX, the analogous alkylcadmium halides cannot be prepared in this way, and the preferred route involves an exchange reaction between cadmium dihalide and the appropriate dialkylcadmium.[1] Relatively little work has been done on these interesting substances. We now report that these compounds can be synthesised, and stabilised as their adducts with various bidentate ligands, through a direct electrochemical method. The same procedure also gives rise, under the appropriate conditions, to a series of tetra-alkylammonium salts of anionic cadmium complexes of the type $RCdX_2^-$, which appear to be the first organocadmium complexes of this type to be prepared. The experimental techniques are similar to those reported for the direct synthesis of a wide range of anionic and neutral complexes and organometallic compounds of the main group and transition elements;[2,3] the method has been successfully applied to the preparation of compounds of Ti, Zr, Hf, V, Cr, Mn, Fe, Co, Ni, Cu, Au, Cd, Ga, In, Tl, and Sn.

The electrochemical cell is essentially a simple one, in which metallic cadmium (1—2 g) forms the anode and a stout platinum wire forms the cathode, with a solution phase which, in the case of the neutral complexes, was normally pure dry acetone (20—40 cm^3). To this solution was added the alkyl halide (10—20 cm^3), together with Et_4NClO_4 (15 mg) in order to ensure sufficient flow of current. Applied voltages in the range 10—40 V gave a current between 20 and 100 mA. Solutions were degassed before electrolysis, and a stream of N_2 ensured the absence of O_2 and moisture throughout the experiment; all products were handled under dry N_2.

In our first experiments, we attempted the preparation of the simple compound methylcadmium iodide and found that electrolysis of cadmium in the presence of methyl iodide in acetone resulted in oxidation of the metal to yield a very unstable white material, whose halide content corresponded to that of methylcadmium iodide. We were unable to characterize this highly reactive material further. Analogous experiments differing only in that bidentate ligands were added to the electrolytic cell yielded the following compounds: MeCdBr.bipy, EtCdBr.bipy, EtCdBr.phen, EtCdBr.diox, EtCdI.diox, PhCdBr.diox and Bu^n-CdCl.bipy (bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, and diox = 1,4-dioxan). These adducts are obtained as white crystalline materials, which in the cases of the 2,2′-bipyridyl and 1,10-phenanthroline adducts are stable at room temperature under N_2. The dioxan adducts appear to decompose slowly on standing, probably due to the loss of ligand.† The presence of the bidentate ligand was demonstrated in each case by i.r. spectroscopy. Although the exact structures of these adducts have not yet been established, the analogy with the adducts of dimethylcadmium with dioxan and other chelating ligands[1] suggests that we are dealing with a series of four-co-ordinate species.

The amount of cadmium reacting is readily determined by the change in weight of the anode; in a typical experiment 0·3—0·5 g of cadmium dissolved, and the yield of the adduct (*ca.* 1 g), based on the loss of cadmium, was *ca.* 90%. The products were obtained in sufficiently good crystalline form and no further purification was necessary.

In an analogous series of experiments, we have obtained the salts $Pr^n_4N\cdot EtCdBr_2$ and $Pr^n_4N\cdot MeCdI_2$, which appear to be the first examples of organocadmium anions. In these experiments, the solution phase was benzene–methanol (2:1) (50 cm^3) containing the alkyl halide and the appropriate tetrapropylammonium halide (in gram quantities). Electrolysis for 6—7 h at 15—20 V yielded the salt in gram quantities, which was recrystallized from acetonitrile–acetone or acetronitrile–methanol (1:1) to give a white ($MeCdI_2^-$) or pale yellow ($EtCdBr_2^-$) solid, which decomposed slowly (2—3 days) at room temperature under N_2.† I.r. spectroscopy confirmed the presence of the tetra-n-propylammonium cation in these salts. Reaction of $Pr^n_4N\cdot MeCdI_2$ with dil. acetic acid released an equimolar volume of methane.

In view of this evidence, we believe that these anions are analogous of CdX_3^- (X = Cl, Br, or I) and CdX_2Y^- ($X \neq Y$ = Cl, Br, or I), recently prepared as the tetra-n-propylammonium salts, and shown to exist as discrete cadmium(II) species of C_{2v} symmetry.[4]

(*Received*, 16*th February* 1976; *Com.* 157.)

---

† Satisfactory microanalytical data were obtained for these compounds.

[1] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' 3rd edn., Methuen, London, 1967, Vol. 1, Ch. 2.

[2] J. J. Habeeb and D. G. Tuck, *J.C.S. Chem. Comm.*, 1975, 808.

[3] J. J. Habeeb, L. Neilson, and D. G. Tuck, *Synth. Inorg. Metal-Org. Chem.*, in the press; J. J. Habeeb, D. G. Tuck, and F. H. Walters, unpublished results.

[4] J. G. Contreras and D. G. Tuck, *Canad. J. Chem.*, 1975, **53**, 3487, and unpublished results.