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THE DIRECT ELECTROCHEMICAL SYNTHESIS OF ORGANOMETALLIC HALIDES OF ZINC AND CADMIUM WITH SUBSTITUTED PHENYL HALIDES

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Summary

The electrochemical oxidation of zinc or cadmium into acetonitrile solutions of RC_6H_4X (R = CN, NO_2; X = Cl, Br, I; not all combinations) gives the corresponding RC_6H_4MX compounds, which form stable 1 : 1 adducts with 2,2′-bipyridine. The method provides a simple and direct synthesis of these and related compounds.

Introduction

In previous papers we have described the application of simple electrochemical methods for the direct synthesis of neutral and anionic organozinc [1] and organocadmium [2,3] halides. Both alkyl and aryl radicals were used sucessfully, and the aryl groups included pentafluorophenyl, demonstrating that the method is in no way restricted to unsubstituted aryl species. We have now shown that the synthesis of aryl organometallic halides derived from substituted phenyl halides is also readily achieved by the electrochemical route, even when the substituents are potentially reactive. To put the method to a searching test, we have concentrated upon nitro- and cyano-substituted compounds.

The recommended route to such compounds is via mercuration, involving the reaction of aromatic compounds with mercury(II) salts. Nitrobenzene reacts slowly under these circumstances [4]. One difficulty is that a mixture of *ortho*, *meta* and *para* derivatives is obtained by such reactions, but there is evidence that in the electrochemical reaction the product is formed with retention of the original substitution pattern.

Experimental

General

Metals, organic halides, solvents etc., were as in previous work, and the spectroscopic and analytical methods followed earlier descriptions [1,2,3].

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Electrochemical synthesis

Following our usual approach we have been concerned to establish the viability and simplicity of the method, and no attempt has been made to work on a large scale. The cells were of the general type

$$Pt_{(-)}/CH_3CN + RX + bipy/M_{(+)}$$

where RX = o-NCC_6H_4X (X = Cl, Br) or o-$O_2NC_6H_4X$ (X = Cl, Br, I) and M = Zn or Cd. The presence of 2,2′-bipyridine (bipy) served to stabilize the RMX product for easy handling in subsequent analysis, etc. In addition, approx. 25 mg of the appropriate tetraethylammonium halide was added to increase the conductivity; the actual cell compositions, and other experimental details, are given in Table 1. Benzene was necessary in two cases noted in Table 1 because of the poor solubility of the aryl halide in acetonitrile.

The experiment followed a similar course in each of the eight systems reported in Table 1. As the electrolysis proceeded, a small quantity of yellow or brown solid precipitated, and metal analysis and infrared spectra suggest that this is the appropriate $MX_2 \cdot 2$ bipy adduct, amounting in quantity to ~10% of the metal consumed. This material was separated by filtration, and the resultant brown solution treated with diethyl ether, or pumped in vacuo to reduce the volume, until a brown solid formed. This was washed with benzene and diethyl ether to remove starting materials, dried in vacuo, and analysed. The analytical results are shown in Table 2. The nitro compounds proved very difficult to dissolve for analysis, even in conc. aqueous acids. The product yields were typically 60—70%, based on metal dissolved.

Experiments were also run with pyridine or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine replacing 2,2′-bipyridine in the cell. In each case the product obtained by following the above procedure was a brown oil in which metal, halide, substituted phenyl group and neutral ligand were identified. None of these oils gave crystalline products at room temperature. The ^1H NMR spectrum of the product of the Zn/o-NCC_6H_4Cl/py reaction was identical to that of a

TABLE 1

EXPERIMENTAL CONDITIONS FOR THE ELECTROCHEMICAL PREPARATION OF SUBSTITUTED PHENYL-ZINC AND -CADMIUM HALIDES

Metal	RX	Solution composition [a]		Initial		Time of electrolysis (h)	Metal dissolved (g)
		CH_3CN (cm^3)	RX (g)	Voltage	Current (mA)		
Zn	o-NCC_6H_4Cl	50	0.5	25	20	14	0.13
	o-NCC_6H_4Br	50	0.5	25	30	14	0.13
	o-$O_2NC_6H_4Cl$	50	0.5	20	20	6	0.07
	o-$O_2NC_6H_4I$	25	0.5 [b]	25	10	9	0.09
Cd	o-NCC_6H_4Cl	50	0.5	25	20	7	0.12
	o-NCC_6H_4Br	50	0.5	20	30	13	0.22
	o-$O_2NC_6H_4Cl$	40	0.5	25	20	20	0.28
	o-$O_2NC_6H_4Br$	20	1.0 [b]	25	10	12	0.10

[a] Plus 25 mg $(C_2H_5)_4NX$ and 0.5 g 2,2′-bipyridine. [b] Plus 25 cm^3 benzene.

TABLE 2

ANALYTICAL RESULTS FOR 2,2'-BIPYRIDINE ADDUCTS OF SUBSTITUTED PHENYL-ZINC AND -CADMIUM

Compound	Analysis. Found (calculated) (%)	
	Metal	Halogen
o-$NCC_6H_4ZnCl \cdot$ bipy [a]	17.7 (18.2)	10.2 (9.8)
o-$NCC_6H_4ZnBr \cdot$ bipy	16.5 (16.2)	19.8 (19.8)
o-$NCC_6H_4CdCl \cdot$ bipy	26.8 (27.6)	8.9 (8.6)
o-$NCC_6H_4CdBr \cdot$ bipy	23.8 (24.9)	17.3 (17.7)
o-$O_2NC_6H_4ZnCl \cdot$ bipy	18.0 (17.2)	9.1 (9.3)
o-$O_2NC_6H_4ZnI$ bipy	14.1 (13.8)	26.1 (27.0)
o-$O_2NC_6H_4CdCl \cdot$ bipy	24.9 (26.4)	7.7 (8.2)
o-$O_2NC_6H_4CdBr \cdot$ bipy	21.9 (23.8)	16.7 (17.0)

[a] Microanalysis: C, 55.8 (56.9); H, 4.1 (3.4); N, 11.7 (11.7).

mixture of pyridine and o-NCC_6H_4Cl, demonstrating that the zinc is bonded to the ring at the site originally occupied by the chlorine atom.

Results and discussion

The syntheses described offer a straightforward route to substituted phenyl halides of zinc and cadmium. The reactions of other elements have also been examined briefly. Tin is oxidised under very similar conditions to give $(NCC_6H_4)_2SnCl_2 \cdot$ bipy, and work on this is proceeding, but with indium on the other hand, the reaction products were of variable composition, and could not be characterised, in contrast to the behaviour of this element with other aryl halides [5]. Nickel reacted smoothly to give $NCC_6H_4NiCl \cdot$ bipy, and work on this and other transition metal derivatives is proceeding.

The electrochemical reactions are assumed to be those discussed in earlier publications [1—3,6] namely the cathodic reduction of RX to yield $R^{\cdot}$ and X^-, followed by discharge of the halide ion at the anode and subsequent reaction of X and M. The current efficiencies, defined as moles of metal dissolved per Faraday of electricity for the cells

$$Pt_{(-)}/CH_3CN + \text{bipy} + o\text{-}O_2NC_6H_4Cl/M_{(+)}$$

(M = Zn or Cd) were 0.46 ± 0.05 mol F^{-1}, close to the values required for Faradaic behaviour, but lower than the results obtained for systems involving zinc or cadmium with simple organohalides [1—3]. This suggests that reactions between RMX and RX do not occur as easily with R = substituted phenyl as with R = alkyl or phenyl, which is in keeping with the stability of these substituted phenyl derivatives.

The products are brown solids, stable to air and moisture, and in the case of the nitro compounds resistant to acid hydrolysis. Characterisation involved analysis (See Table 2), and infrared spectroscopy. The IR spectra showed the typical weak $\nu(C{\equiv}N)$ band at 2230 ± 10 cm^{-1} for the derivatives of NCC_6H_4X (X = Cl or Br), shifted only slightly from the same mode in the parent halide. Similarly the ν_{as} and ν_s of the nitro group shows little change between product and starting material in the $O_2NC_6H_4X$ series. The ^1H NMR spectra also demonstrated the presence of the substituted phenyl group and of the ligand, and further confirmation of the bonded 2,2′-bipyridine was obtained from the infrared spectra.

In general then, this work shows that the direct electrochemical synthesis of substituted phenyl halides derivatives of zinc and cadmium is a simple and straightforward procedure, with certain advantages over established methods.

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References

1 J.J. Habeeb, A. Osman and D.G. Ruck, J. Organometal. Chem., 185 (1980) 117.
2 J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 146 (1978) 213.
3 A. Osman and D.G. Tuck, J. Organometal. Chem., 169 (1979) 255.
4 G.E. Coates and K. Wade, Organometallic Compounds, Vol. 1, The Main Group Elements, Methuen, London, 3rd ed., 1967, pp. 152—153.
5 J.J. Habeeb, F.F. Said and D.G. Tuck, J. Organometal. Chem., 190 (1980) 325.
6 D.G. Tuck, Pure Appl. Chem., 51 (1979) 2005.