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The Electrochemical Synthesis of some Ph_3SnMCl Adducts (M = Zn, Cd, Hg)

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The electrochemical oxidation of Zn, Cd or Hg (= M) in a non-aqueous solution of Ph_3SnCl yields the metal–metal bonded insertion product Ph_3SnMCl, which can be easily isolated as an adduct present in the solvent phase. The mechanism of this direct electrochemical synthesis is discussed. The far infrared spectra (500–50 cm^{-1}) of these compounds are also reported.

Introduction

The chemistry of metal–metal bonded compounds of main group metals, and especially of Group IIB and IVA elements has been the subject of a number of studies in recent years (see [1], and refs. therein). The preparation of such compounds, and hence their adducts, typically involves the attack of a triorganotin hydride on dialkyl zinc or cadmium, or their adducts with some bidentate neutral donor ligand, whereupon the formation of $(R_3Sn)_2Cd\cdot L$ is accompanied by the release of alkane [1]. The mechanism of such reaction has been discussed, as has the importance of the corresponding halide complexes (*e.g.* $R_3SnZnX\cdot L$), which can be prepared by the reaction [2]

$$Ph_3SnH + EtZnCl\cdot L \longrightarrow Ph_3SnZnCl\cdot L + C_2H_6$$

The role of the donor L in preventing 1,2-shifts of phenyl groups has been emphasised [3].

We have now shown that the metal–metal bonded triphenyltin halide compounds of zinc, cadmium and mercury can be readily prepared by a direct electrochemical synthesis involving the oxidation of the Group IIB metal in a non-aqueous solution of triphenyltin chloride. The preparation of RCdX, $RCdX\cdot L$ and $RZnX\cdot L$ compounds by similar direct electrochemical methods has been successfully carried out in this laboratory [4–6], and the overall reaction

$$RX + M \longrightarrow RMX$$

which describes the stoichiometry of these reactions also applies to those described below, with $R = Ph_3Sn$. The preparations are simple, require no elaborate apparatus, and can be carried out at room temperature.

Experimental

Materials

Zinc (M5N) and cadmium (M4N) were used as plates, approx. 2 × 0.5 × 0.2 cm, made by mechanically flattening metal rods of the appropriate size. Mercury was triple-distilled. Triphenyltin chloride (Aldrich), 2,2′-bipyridine (bipy) and N,N,N′,N′-tetramethylethylenediamine (TMED) were used as supplied, except that TMED was dried. Acetonitrile and benzene were dried over phosphorus pentoxide and distilled before use. The exclusion of moisture from the reaction media is a most important experimental precaution.

Procedure

The experiments were all carried out in a two-arm (H-form) cell, each arm being approx. 10 cm long and 1.5 cm diameter. One arm served for the out-gassing of the solution *in vacuo* by a series of evacuation/freezing cycles to remove dissolved oxygen. The degassed solution was then decanted under vacuum into the second arm which served as the electrochemical cell. In the case of zinc and cadmium, the anode was suspended on a platinum wire entering through a Teflon plug, and was sited above a tungsten wire ring fused into the side of the vessel and acting as the cathode. For the mercury compound, a pool of mercury in the bottom of the cell was the anode. Other aspects of the electrochemical method were essentially as described in previous publications. Details of solution composition, electrical conditions, *etc.* are given in Table I.

In a typical experiment ($Cd/TMED/Ph_3SnCl$), a white material formed in the cell during electrolysis. This was collected and further quantities of product were obtained by adding petroleum ether dropwise to the filtrate. The material was washed several times

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TABLE I. Experimental Conditions for the Electrochemical Synthesis of $Ph_3SnMCl \cdot L$ Compounds.

Product	Vol (cm^3)[a]		Mass of Ph_3SnCl (g)	Mass of L (g)	Initial Voltage (V)	Initial Current (mA)	Time of Electrolysis (h)	Mass of Metal Dissolved (g)	Mass of Product (g)	% Yield[b]
	CH_3CN	C_6H_6								
$Ph_3SnZnCl \cdot TMED$	6	8	0.8	1.1	30	25	3.0	0.084	0.73	~100
$Ph_3SnCdCl \cdot TMED$	2.5	5	0.5	1.0	?	30	4.5	0.35	0.65	30
$Ph_3SnCdCl \cdot bipy$	2	2	0.27	0.3	8	18	1.5	0.080	0.2	43
$Ph_3SnHgCl \cdot bipy$	6	8	0.8	1.5	30	25	4.0	0.078	?	?

[a] All solutions contained *ca.* 15 mg Et_4NClO_4. [b] Based on mass of metal dissolved.

TABLE II. Analytical Results for $Ph_3SnMCl \cdot L$ Compounds.[a]

Compound	Sn (%)	M (Zn, Cd, Hg) (%)	Cl (%)
$Ph_3SnZnCl \cdot TMED$	21.1 (21.0)	11.5 (11.5)	6.3 (6.3)
$Ph_3SnCdCl \cdot TMED$	19.3 (19.3)	18.3 (18.3)	5.8 (5.8)
$Ph_3SnCdCl \cdot bipy$	18.4 (18.2)	17.2 (17.1)	5.6 (5.4)
$Ph_3SnHgCl \cdot TMED$	17.1 (16.9)	–	5.2 (5.0)

[a] Calculated values given in parentheses.

with petroleum ether, and dried *in vacuo*. All chemical procedures were carried out under dry nitrogen.

Analysis for metals was by atomic absorption spectrophotometry and for chlorine by Volhard titration (results in Table II). Proton n.m.r. spectra in $CDCl_3$ at 60 MHz and infrared spectroscopy confirmed the presence of phenyl groups and of the neutral ligand; integration of the n.m.r. spectra for each of the TMED adducts showed NCH_3 (singlet) CH_2 (singlet) and C_6H_5 (multiplet) in the calculated intensity ratios.

Far infrared spectra (500–50 cm^{-1}) were recorded on a Perkin-Elmer 180 Spectrometer, with the samples as Nujol mulls between polyethylene plates.

Results and Discussion

The experiments described show that the electrochemical oxidation of zinc, cadmium or mercury in the presence of Ph_3SnCl provides a simple preparative route to the Ph_3SnMCl compounds. The percentage yields are adequate, except that in the case of zinc the yield approaches theoretical, and in general are similar to, but lower than, those reported by des Tombe, van der Kerk and Noltes [2]. The scale of the electrochemical experiment can be easily increased if larger quantities of product are desired.

The chemistry of the Sn–Zn species has been discussed by the previous authors [2, 3], and some spectroscopic information is also available on these and the related cadmium compounds [7]. Our studies allow us to add briefly to these results. Firstly, we find that the bipy adduct of $Ph_3SnCdCl$ is much less stable at room temperature even under nitrogen than is the TMED analogue. The decomposition product has Cd 30.9%, Cl 20.1%, close to the values for $CdCl_2 \cdot bipy$ (Cd 32.9; Cl 20.9%). It seems likely that the difference in stability between the bipy and TMED adducts lies in the differing bite of these two ligands, reflecting the extra flexibility of the latter. Because of this finding, we reserved our preparative and other studies to the addition compounds with TMED.

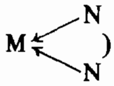
The far infrared spectra of the three TMED adducts have been recorded in the region 500–50 cm^{-1}. The results and our tentative assignments are given in Table III. The $\nu(SnPh_3)$ region is almost invariant in the three spectra, showing only some slight dependence on M. The ν(M–Cl) vibrations are assigned by comparison with other halides of the Group IIB elements, and there are two other metal-dependent bands which we assign to the complex stretching modes of the  moiety. The remaining low frequency band is then identified as the Sn–M stretching vibration; the frequencies assigned to ν(Sn–Zn) and ν(Sn–Cd) are close to those reported [1] for ν_{as} in Sn_2Zn and Sn_2Cd com-

TABLE III. Far Infrared Spectra of $Ph_3SnMCl \cdot TMED$ Compounds (in cm^{-1}).

M	$\nu(SnPh_3)$	$\nu(M–Cl)$	$\nu(M–N_2)$	$\nu(Sn–M)$
Zn	452 sh 446 s 435 sh	335	250, 310	200
Cd	460 sh 450 s	260	190, 205	150
Hg	453 ms 445 sh	272	190, 210	155

pounds. It is also worth noting that the ν(Sn–Cd) frequencies in both types of compounds are close to the value [8] for the stretching mode of the isoelectronic In–In bond in $In_2Cl_6^{2-}$.

We have also measured the ^1H n.m.r. spectra of the three $Ph_3SnMCl \cdot TMED$ compounds, and of TMED itself, in $CdCl_3$. The free ligand spectrum consists of two sharp singlets at $\delta = 1.08$ (NMe_2) and 1.15 (CH_2) ppm from TMS. The three adducts have multiplet resonance absorptions due to the Ph_3Sn group centred at approx. 7.35 (Zn), 7.2 (Cd) and 7.8 (Hg) ppm. The TMED resonances show substantial downfield shifts on complexation, with the CH_2 resonances at $\delta = 2.68$ (Zn), 2.53 (Cd) and 3.10 (Hg), and the NMe_2 resonances at 2.55 (Zn), 2.40 (Cd) and 2.80 (Hg). These absorptions are all sharp singlets, except that the CH_2 resonance of the mercury compound shows a reproducible absorption approx. 0.05 ppm downfield of the main resonance. There is no obvious relationship between the complexation shifts of TMED and the properties of the Group IIB metals involved, since for each resonance the order is Cd > Zn > Hg. It seems probable that in addition to factors such as charge density, the size of the metal may be involved, since this will affect the bond angles (and hence resonance frequencies) in the NC_2N chain of the ligand. Further work on this point would be of interest.

Reaction Mechanism

As in other electrochemical work, the efficiency of the reaction can be measured in electrical, as well as chemical, terms. Following normal practice, the loss of weight of both zinc and cadmium electrodes was therefore measured at constant current (20 mA) over a period of 2 h; the current efficiencies for each system was found to be 0.61 ± 0.02 mmol M per Faraday.

The electrochemical reduction of Ph_3SnCl at a dropping mercury electrode has been discussed by Dessy and co-workers [9–11], who suggest that the processes are either

$$Ph_3SnCl \xrightarrow{e^-} Ph_3Sn\cdot + Cl^- \qquad (1)$$

$$2Ph_3Sn\cdot \longrightarrow Ph_6Sn_2 \qquad (2)$$

or

$$Ph_3SnCl \xrightarrow{e^-} Ph_3Sn^- + Cl \qquad (3)$$

$$Ph_3Sn^- + Ph_3SnCl \longrightarrow Ph_6Sn_2 + Cl^- \qquad (4)$$

Reactions (1), or (3) + (4), both of which are possible under our experimental conditions, give rise to chloride ions whose migration to the anode would be followed, according to our previous postulates, by the reactions

$$Cl^- \longrightarrow Cl\cdot + e^- \qquad (5)$$

$$Cl\cdot + M \longrightarrow MCl \qquad (6)$$

and the reaction of M^ICl on the Ph_3SnCl substrate would give the primary product

$$Ph_3SnCl + M^ICl \longrightarrow Ph_3SnMCl + Cl\cdot \qquad (7)$$

with a chain reaction sequence of (6) + (7) then expected.

Such sequences have been identified by the resulting current efficiencies, which are greater than unity, and sometimes considerably so [12]. In the present case, the current efficiency obviously does not demonstrate such reactions, despite the earlier evidence [9–11] as to the cathode reactions. We suggest that chlorine atoms generated in (5) may react with Ph_3SnCl to give Ph_2SnCl_2, or $Ph_3Sn\cdot + Cl_2$, and so remove chlorine from the systems more efficiently than by attack on the anode. The fact that the current efficiencies are identical for two different metals points to some metal-independent process being responsible for the lowering of the current efficiency below that observed in otherwise formally similar systems. Work on the electrochemical behaviour of other R_3M^- anions is continuing.

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