COORDINATION COMPOUNDS OF INDIUM

XXXVI *. THE DIRECT ELECTROCHEMICAL SYNTHESIS OF NEUTRAL AND ANIONIC ORGANOINDIUM HALIDES

JACOB J. HABEEB, FAROUQ F. SAID and DENNIS G. TUCK

Department of Chemistry, University of Windsor, Windsor, Ontario, N9B 3P4 (Canada)

(Received October 19th, 1979)

Summary

The electrochemical oxidation of indium metal in cells of the type $Pt_-|RX + CH_3CN|In_+$ leads to the formation of $RInX_2$ compounds; if 2,2'-bipyridine is also present, the products are the adducts $RInX_2 \cdot bipy$ ($R = CH_3$, C_2H_5, C_6H_5, $C_6H_5CH_2$, C_6F_5; $X = Cl$, Br, I (not all combinations)). When R'_4NX is present instead of bipy, the products are the salts $R'_4N[RInX_3]$. The electrochemical oxidation apparently proceeds via the general mechanism discussed previously. Anomalous results with CH_3I or C_2H_5I are discussed in the light of the known solution chemistry of organoindium(III) compounds.

Introduction

Organometallic compounds of indium have been less widely studied than have the analogous derivatives of the other Group III elements, but alkyl- and aryl-indiums are known [1], and the neutral organohalides derivatives $RInX_2$ and R_2InX have also been prepared. The published synthetic routes to these compounds include the reaction of Grignard reagents [2] or organolithium compounds [3,4] with indium(III) halides, the titration of triphenylindium with stoichiometric quantities of either Br_2 or I_2 in benzene [5], and the oxidative insertion of InI into a C—I bond [6—8]. Diaryl indium iodides have also been prepared by the reaction of aryl iodides with activated indium powder, prepared by reducing $InCl_3$ with fresh potassium metal in dry xylene [9].

The Lewis acidity of the R_2InX and $RInX_2$ species allow complexation with Lewis bases, so that dimethylindium halides react with neutral donors such as pyridine, triphenylphosphine, 2,2'-bipyridine, 1,10-phenanthroline and ethyl-

enediamine to yield a series of four- and five-coordinate complexes [4,6]. Similarly, the adducts $C_6H_5InCl_2 \cdot L$ (L = 2,2'-bipy, 1,10-phen, terpy, diphos) have been prepared by reaction of $C_6F_5InCl_2 \cdot$ diox with the appropriate ligands [10]. A small number of anionic organoindium halides have also been reported, following the early work of Clark and Pickard [3,4]. The salts $(C_2H_5)_4N$-$[(CH_3)_2InCl_2]$ and $(C_6H_5)_4As[(CH_3)_2InCl_2]$ were prepared from the reaction of $(CH_3)_2InCl$ and the appropriate tetraalkylammonium halide, while $[(CH_3)_4Sb]$-$[CH_3InCl_3]$ and $[(CH_3)_4As][CH_3InCl_3]$ were obtained by treating $(CH_3)_3SbCl_2$ and $(CH_3)_3AsCl_2$, respectively, with $(CH_3)_2InCl$ [11].

We have now shown that both neutral and anionic organoindium halides can be prepared by the electrochemical oxidation of the metal in a cell containing the appropriate organic halide, organic solvent(s) and a neutral ligand or tetra-alkylammonium halide. In general, the neutral compounds were most conveniently prepared and handled as their adducts with 2,2'-bipyridine (bipy). The method is similar to that used successfully to synthesise organohalides of tin [12], cadmium [13,14] and zinc [15], but there are some interesting ramifications which arise from the +III oxidation state of the metal in the products. Many of the compounds prepared are reported here for the first time.

Experimental

General

Indium (Alfa Inorganics, m4N) was hammered into thin sheets, ca. 0.5 mm thick; pieces ca. 1 X 1 cm^2 were supported on a platinum wire to form the anode of the cell. A stout platinum wire formed the cathode.

Acetonitrile was dried over Linde molecular sieves and then redistilled under nitrogen before use. Other compounds were used as supplied, or after drying at 110°C.

Indium analysis was by atomic absorption spectrophotometry, and halide analysis by Volhard titration. Carbon, hydrogen and nitrogen analyses were performed by Gygli Microanalytical Laboratories. Toronto. The analytical results are given in Table 1 for the neutral species, and in Table 2 for the salts of the anionic complexes.

Infrared spectra were recorded over the range 4000—250 cm^{-1} on a Beckman IR-12 instrument, using Nujol mulls between potassium bromide or polyethylene plates. NMR spectra were recorded with a Varian EM-360 spectrometer operating at 60 MHz.

Preparative

The details of solution composition, electrochemical conditions, etc. are given in Table 3, and it should be noted immediately that in the single case of ethyl bromide, experiments were run with indium as either anode or as cathode, with platinum as the counter-electrode in each case. In general, the electrochemical methods were essentially identical to those used in our earlier work [12—15]. Most of the experiments involved solution phases in the 50 cm^3 order, but small scale preparations were also carried out, using a cell of the type described previously [16].

We give details below for typical isolation procedures for neutral and anionic

TABLE 1

ANALYTICAL RESULTS FOR NEUTRAL ORGANOINDIUM HALIDE COMPOUNDS

Compound [a]	Colour	Found (calcd.)(%)				
		C	H	N	Halogen	In
$(CH_3)_2InI \cdot bipy$	orange	—	—	—	29.2 (29.7)	27.1 (26.9)
$CH_3InI_2 \cdot bipy$	yellow	—	—	—	46.9 (47.0)	21.8 (21.3)
$(C_2H_5)_2InI \cdot bipy$	yellow	36.9 (36.9)	3.9 (3.9)	5.9 (6.1)	27.7 (27.9)	25.4 (25.2)
$C_2H_5InBr_2 \cdot bipy$ [b]	light yellow	30.8 (31.3)	2.4 (2.8)	5.7 (6.0)	34.7 (34.8)	—
$C_2H_5InBr_2 \cdot bipy$ [c]	light yellow	—	—	—	35.0 (34.8)	24.8 (25.0)
$C_6H_5CH_2InCl_2 \cdot bipy$	yellow	46.8 (47.1)	3.7 (3.5)	5.5 (6.5)	16.0 (16.2)	26.2 (26.6)
$C_6H_5CH_2InBr_2 \cdot bipy$	yellow	—	—	—	30.5 (30.6)	22.1 (22.0)
$C_6H_5CH_2InI_2 \cdot bipy$	yellow	—	—	—	40.9 (41.2)	18.2 (18.6)
$C_6H_5InCl_2 \cdot bipy$	off white	—	—	—	16.5 (16.7)	27.9 (27.5)
$C_6H_5InBr_2 \cdot bipy$	off white	—	—	—	31.7 (31.5)	23.0 (22.6)
$C_6H_5InI_2 \cdot bipy$	brown	31.3 (31.9)	2.9 (2.2)	4.0 (4.7)	42.0 (42.2)	20.0 (19.1)
$C_6F_5InBr \cdot bipy$	off white	—	—	—	26.4 (26.7)	19.3 (19.4)

[a] bipy = 2,2'-bipyridine. [b] Indium cathode, platinum anode. [c] Platinum cathode, indium anode.

TABLE 2

ANALYTICAL RESULTS FOR SALTS OF ANIONIC ORGANOINDIUM HALIDE COMPLEXES

Compound	Colour	Found (calcd.)(%)	
		Halogen	In
$(C_2H_5)_4N[CH_3InI_3]$ [a]	faint yellow	59.6 (59.5)	17.4 (17.9)
$(C_4H_9)_4N[(CH_3)_2InI_2]$	colourless	39.5 (39.6)	18.5 (18.0)
$(C_2H_5)_4N[C_2H_5InBr_3]$	colourless	46.3 (46.7)	23.0 (22.4)
$(C_2H_5)_4N[C_2H_5InI_3]$	colourless	58.4 (58.2)	17.5 (17.6)
$[C_2H_5)_4N[C_6H_5InCl_3]$	colourless	25.1 (24.6)	27.7 (26.9)
$(C_2H_5)_4N[C_6H_5InBr_3]$	yellow	42.7 (42.7)	21.1 (20.5)
$(C_2H_5)_4N[C_6H_5InI_3]$	brown	54.7 (54.2)	15.9 (16.4)
$(C_4H_9)_4N[C_6H_5InI_3]$	yellow	46.3 (46.7)	14.3 (14.1)
$(C_2H_5)_4N[C_6H_5CH_2InCl_3]$	colourless	23.2 (23.8)	27.0 (26.1)

[a] Found: C, 17.6; H, 3.8; N, 2.3; calcd.: C, 16.9; H, 3.6; N, 2.2%.

TABLE 3

EXPERIMENTAL CONDITIONS FOR ELECTROCHEMICAL PREPARATION OF NEUTRAL ORGANOINDIUM HALIDE COMPLEXES

RX	Solution composition (cm³)		2,2'-bipyridine (g)	R'_4NX added (mg)	Initial		Time of electrolysis (h)	In dissolved (g)
	CH_3CN	RX			Voltage (V)	Current (mA)		
CH_3I	See text	See text	See text	See text	30	10	See text	See text
C_2H_5Br [a]	20	20	0.5	30	25	25	3.5	0.2
C_2H_5Br [b]	20	15	1.0	30	30	30	14	0.15
C_2H_5I [c]	2	1	0.3	10 [e]	4	10	4	0.06
$C_6H_5CH_2Cl$	10	15 [d]	0.5	30	30	10	9	0.19
$C_6H_5CH_2Br$	40	5	1.0	30	25	30	5	0.72
$C_6H_5CH_2I$	40	0.7 [g]	1.0	30	25	35	4	0.29
C_6H_5Cl	40	10	1.0	30	25	20	12	0.35
C_6H_5Br	40	10	1.0	30	25	20	8.5	0.37
C_6H_5Br [c]	1.8 [f]	2	0.3	10 [e]	5	10	1	0.09
C_6H_5I	15	15 [d]	0.5	40	30	7	9	0.10
C_6F_5Br [c]	0.4	0.5	0.35	15 [c]	23	10	14	0.05

[a] Indium cathode, platinum anode. [b] Platinum cathode, indium anode. [c] Small cell: see text. [d] Plus 15 cm³ benzene. [e] Tetraethylammonium perchlorate. [f] Methanol used in place of acetonitrile.

indium derivatives of ethyl bromide, as being typical of the method. In addition, those systems involving methyl and ethyl iodides are singled out for detailed description since the products are stoichiometrically different from those with other organic halides.

$C_2H_5InBr_2 \cdot bipy$

The solution resulting from the anodic electrolysis of indium was treated with diethyl ether to precipitate a light yellow solid which was filtered off under nitrogen and dried in vacuo.

$(CH_3)_2InI \cdot bipy$ and $CH_3InI_2 \cdot bipy$

The solution phase (10 cm^3 CH$_3$CN, 15 cm^3 CH$_3$I, 0.5 g bipy, 30 mg tetraethylammonium perchlorate) gradually developed a dark brown colour as the electrolysis proceeded, and a small quantity of yellow-red solid deposited on both electrodes. This material was detached from the surface of the cathode by reversing the polarity of the electrodes for a short time. After an electrolysis lasting 3.5 h, when 0.06 g In had dissolved, the solution was filtered, but the amount of yellow solid recovered was too small to permit characterization. The filtrate was therefore then evaporated in vacuo, to yield a fluffy orange solid which was thoroughly washed with benzene in order to remove excess 2,2'-bipyridine. The orange powder which was collected and dried in vacuo analysed as $(CH_3)_2InI \cdot bipy$.

In another experiment indium was electrolysed in a mixture of 40 cm^3 CH$_3$-CN, 5 cm^3 CH$_3$I, 0.7 g bipy, and 30 mg $(C_2H_5)_4$NBr for 20 h; 0.57 g indium dissolved. In this experiment the large quantity of a yellow solid which deposited in the cell was collected and dried in vacuo, and identified as $CH_3InI_2 \cdot bipy$. When the filtrate was treated with petroleum ether, then concentrated and triturated, a yellow-orange solid precipitated. This solid was recrystallized from acetonitrile, dried in vacuo, and identified as $(CH_3)_2InI \cdot bipy$.

$(C_2H_5)_2InI \cdot bipy$

During the early stages of the electrolysis, a yellow/gray precipitate formed in the cell and was later removed by filtration. Later experiments suggested that the gray material is a decomposition product, whose formation can be avoided by keeping the temperature of the cell below 10°C. Dry ether was added dropwise to the filtered electrolyte, producing a yellow precipitate, which on further addition of ether changed to an oil. Addition of benzene caused crystallisation to take place; the resultant solid was collected and dried in vacuo.

$(C_2H_5)_4N[C_2H_5InBr_3]$

When the colorless solution resulting from electrolysis was treated with diethyl ether, a colorless solid precipitated and was washed thoroughly with chloroform to remove excess tetraethylammonium bromide. The product is insoluble in chloroform, acetone or benzene, slightly soluble in acetonitrile, and soluble in methanol.

$(C_2H_5)_4N[CH_3InI_3]$

Within a few minutes of beginning the electrochemical oxidation, the anode

became covered with a red-violet solid, which we believe to be indium(I) iodide. At the end of the electrolysis (20 h), the colorless solution was filtered and the solvent was then removed in vacuo. When the resulting colorless solid was thoroughly washed with chloroform, some of the material dissolved leaving a residue which was characterized as tetraethylammonium iodide. The chloroform solution was evaporated to dryness to yield the compound $(C_2H_5)_4N$-$[CH_3InI_3]$.

$(C_4H_9)_4N[(CH_3)_2InI_2]$

As in the above experiment, the colorless solid which precipitated when the solution resulting from electrolysis was treated with diethyl ether was characterized as tetrabutylammonium iodide. This was filtered off and the filtrate evaporated to dryness to yield a salt containing the $[(CH_3)_2InI_2]^-$ anion.

$(C_2H_5)_4N[C_2H_5InI_3]$

The solution became yellow during the first hour of electrolysis, and the anode was gradually covered with a purple deposit. At the end of the electrolysis, the cell contained a colorless solution, and a deposit of colorless crystals mixed with the indium metal and indium(I) iodide. This solid was treated with hot ethanol, the crystals subsequently obtained from this extract by evaporation proved to be $(C_2H_5)_4N[C_2H_5InI_3]$.

The electrolyte solution phase was evaporated to dryness, and the resultant crystals washed with ethanol to remove $(C_2H_5)_4NI$. The final product was shown to be $(C_2H_5)_4N[InI_4]$. (Found: In, 15.4; I, 67.3; calcd.: In, 15.3; I, 67.5%).

Results and discussion

Preparative

The advantages of the direct electrochemical syntheses of organoindium halides are those advanced in previous cases, namely that the method is convenient and efficient, involves simple apparatus and readily available chemicals, and is a significant improvement over previously described routes. The chemical yields are generally in the order of 80—90%, based on the mass of indium dissolved, except of course in those systems where two products are obtained (e.g. For $C_6H_5CH_2Cl/CH_3CN$, 0.186 g of In dissolved, giving 0.65 g of C_6H_5-$CH_2InCl_2 \cdot$ bipy, a yield of 92%). There is no reason to suppose that the method is confined to those alkyl and aryl halides studied, or to 2,2'-bipyridine (as neutral ligand) and tetraethyl- and tetrabutyl-ammonium salts for the anionic complexes. Variation of these conponents may lead to changes in product stoichiometry because of solution chemistry effects (see below), and the use of the same neutral ligand throughout minimizes any such problems.

Reaction pathway

(a) Anodic oxidation. The mechanism involved in the direct electrochemical synthesis of RMX compounds has been discussed in previous publications from this laboratory [12—14]. The first step is the cathodic reduction of RX (eq. 1) and while there is some dispute [17] as to the details of this process, the overall

reaction is well established. The anodic oxidation is assumed to involve the halide ion generated in eq. 1 and we note that in the case of $In_{(+)}/RI$ systems,

$$RX + e \rightarrow R^{\bullet} + X^- \tag{1}$$

the formation of a purple-red deposit, believed to be InI, is in keeping with eq. 2. Further reaction of InX with RX should then yield $RInX_2$ by an oxida-

$$M_+ + X^- \rightarrow MX + e \tag{2}$$

$$InX + RX \rightarrow RInX_2 \tag{3}$$

tive insertion reaction (eq. 3). This product then undergoes complexing with 2,2'-bipyridine or halide anion to give the observed products.

The current efficiency E_F (defined as moles of metal dissolved per Faraday of electricity) resulting from the sum of eqs. 1 + 2 + 3 should be unity. Unfortunately, it was not possible to measure current efficiencies accurately in these systems, since a visible deposit of product adhered strongly to the anode in all the relevant experiments. In a measurement involving the cell $Pt_-|CH_3CN + C_2H_5I|In_+$, the loss of indium (2 h, 20 mA) corresponded to $E_F = 0.45$, but this value is low, since visible amounts of purple material were present on the surface of the electrode. The metal was then treated with methyl iodide under reflux in an attempt to remove any InI (cf. ref. 6); but this was only partially successful, for although some further weight loss did occur, leading to a revised value of $E_F = 0.55$, subsequent examination of the metal revealed substantial amounts of occluded purple solid. A careful mechanical cleaning of the metal surface with mild abrasives caused further weight loss, with E_F raised to ~1.5, but some indium metal was certainly removed in this abrasion. In the light of these difficulties, an accurate value of E_F was clearly not obtained, but the limits of $0.55 < E_F < 1.5$ are in keeping with the predicted value of 1.0 insofar as the experimental difficulties permit. In the system $Pt_-|CH_3CN + CH_3I + Bu_4NI|In_+$, E_F after mechanical cleaning of the electrode was 1.3.

Finally, in further support of this reaction scheme, we note that eq. 3 represents an established thermal reaction [6—8] for InI/RI (R = CH_3, C_2H_5, n-C_3H_9) and InBr/RBr (R = CH_3, $C_6H_5CH_2$). The fact that the indium(I) halide is freshly formed on the anode surface may well facilitate the reaction, since it is known that monohalide prepared by room temperature methods is more reactive than the material obtained in high temperature processes [18].

(b) Cathodic reaction. The production of alkylmetals and other compounds at sacrificial cathodes is well-known [19], and in one experiment indium served as the cathode in the cell $In_-|CH_3CN + C_2H_5Br + bipy|Pt_+$. The product, C_2H_5-$InBr_2 \cdot bipy$, is the same as that from cells in which the metals had the opposite polarity. The mechanism suggested here is:

$$In_- + RX + e \rightarrow InR + X^- \tag{4}$$

followed by:

$$InR + RX \rightarrow R_2InX \tag{5}$$

We return below to the conversion of R_2InX to the $RInX_2$ species actually isolated, but point out here that the current efficiency for this process is again

1.0. The observed value was 0.8, in reasonable agreement with the proposed mechanism, given that the process $2 R^{\cdot} \to R_2$ must be in competition with eq. 4. The detailed mechanism of eq. 4, and in particular the number of intermediate steps, are not at issue at this point.

(c) Rearrangement reactions in solution. While the schemes outlined above explain the main features of the electrochemical reactions, they do not explain why in some cases, and in particular for experiments involving CH_3I and C_2H_5I, the stoichiometry of the products is not that required by eqs. 3 and 5 (i.e. $RInX_2$, $RInX_3^-$). We believe that these problems find an explanation in the ease with which indium compounds undergo rearrangement reactions in solution. In particular, it has previously been suggested [6] that the equilibrium 6 explains the products obtained in the thermal reaction between InI and CH_3I. In fact, adducts of both CH_3InI_2 and $(CH_3)_2InI$ were obtained from the electrolytic oxidation of indium in the presence of CH_3I, implying that the redistribution (eq. 6) follows eq. 3. The equilibrium position of eq. 6, or of the analogous

$$2 CH_3InI_2 \rightleftharpoons (CH_3)_2InI + InI_3 \qquad (6)$$

equations for other organoindium dihalides, may depend both on the organic group and the halide involved, and must also be affected by the formation of, and solubility of, the 2,2'bipyridine adducts. In the case of ethyl iodide, the product is again the diorganoindium halide and we note that the preparative method includes precipitation of this material from the reaction solution, a process well known to disturb solution equilibria involving indium compounds.

This is not an appropriate place at which to discuss the factors which govern the equilibrium constants for reactions such as eq. 6, but it is worth pointing out that with one exception the systems studied here yield R_2InX compounds only when $X = I$. The exception is that involving the cathode reactions 4 and 5, where the product is not the predicted $(C_2H_5)_2InBr$, but rather $C_2H_5InBr_2$, and again an equilibrium similar to eq. 6 provides a reasonable explanation.

(d) Anionic complexes. The dependence of the nature of the anionic com-

TABLE 4

EXPERIMENTAL CONDITIONS FOR ELECTROCHEMICAL PREPARATION OF ANIONIC ORGANOINDIUM HALIDE COMPLEXES

System RX/R₄NX	Solution composition (vol. cm³)		R₄NX (g)	Initial		Time of electrolysis (h)	Metal dissolved (g)
	CH₃CN	RX		Voltage (V)	Current (mA)		
$CH_3I/C_2H_5)_4NI$	50	5	1.0	15	70	20	0.36
$CH_3I/(C_4H_9)_4NI$	30	5 ^{a}	3.0	10	60	21.5	0.69
$C_2H_5Br/(C_2H_5)_4NBr$	50	10	2.0	5	80	20	1.62
$C_2H_5I/(C_2H_5)_4NI$ ^{b}	1.5	2 ^{c}	0.5	4	15	20	0.10
$C_6H_5I/(C_2H_5)_4NI$	50	5	1.0	5	20	20	0.26
$C_6H_5I/(C_4H_9)_4NI$	40	10 a	2.0	5	40	18	0.19
$C_6H_5Br/(C_2H_5)_4NBr$	40	10	2.0	5	80	6	0.50
$C_6H_5Cl/(C_2H_5)_4NCl$	40	10	2.0	5	90	10	0.70
$C_6H_5CH_2Cl/(C_2H_5)_4NBr$	40	5	2.0	20	60	16	0.50

^{a} Plus 10 cm³ benzene. ^{b} Small cell: see text. ^{c} Plus 1 cm³ ethanol.

plexes in the $CH_3I/In/I^-$ systems is also explicable in terms of eq. 6. Both CH_3-InI_2 and $(CH_3)_2InI$ can react with excess iodide to give $CH_3InI_3^-$ and $[(CH_3)_2$-$InI_2]^-$, respectively, and these must be in equilibrium with each other. The product which precipitates on evaporation of the solvent, or addition of petroleum ether, will depend in part on the properties of the resultant solid phase, and hence on the cation employed as counterion. Thus $(C_2H_5)_4N^+$ apparently favours $CH_3InI_3^-$, whereas $(C_4H_9)_4N^+$ favours $[(CH_3)_2InI_2]^-$. This effect of cation upon the stoichiometry of anionic complexes of indium is well-established in systems [20] involving InX_4^-, InX_5^{2-}, etc.

Further confirmation of the existence of redistribution reactions in solution comes from experiments involving C_2H_5I and $(C_2H_5)_4NI$. Here in addition to the product $[C_2H_5InI_3]^-$, evidence was obtained for the presence of InI_4^- in the electrolyte phase; this species is clearly the result of the interaction of excess iodide ion with InI_3 produced in the analogue of eq. 6.

Finally, in the case of $[C_6H_5InI_3]^-$, a variation of cation from tetraethyl- to tetrabutyl-ammonium has no effect on the stoichiometry of the product. Again there are analogues in the coordination chemistry of indium for systems [20] where such a situation holds.

In general then the nature of the products isolated in this work is in keeping both with the known solution chemistry of indium, and with our previous experience of the direct electrochemical synthesis of organometallic halides.

Structural investigations

As part of the characterisation of the products obtained, we have carried out various spectroscopic examinations. We should first note, however, that the formulation of the anionic complexes, or more properly of their salts, was confirmed by measuring the molar conductivity of 10^{-3} M solutions in acetonitrile. The results of three compounds ($(C_2H_5)_4N[C_2H_5InBr_3]$ 138 ohm^{-1} cm^2 mol^{-1}, $(C_2H_5)_4N[C_6H_5InCl_3]$ 117 ohm^{-1} cm^2 mol^{-1}, and $(C_4H_9)_4N[(CH_3)_2InI_2]$ 148 ohm^{-1} cm^2 mol^{-1}) are in good agreement with the range of values for 1/1 electrolytes in this solvent. The compound $C_6H_5CH_2InCl_2 \cdot$ bipy had a molar conductivity of 17 ohm^{-1} cm^2 mol^{-1} in nitromethane, confirming the non-ionic nature of this substance.

TABLE 5

^{1}H NMR SPECTRA ^{a} OF SALTS OF ANIONIC ORGANOINDIUM HALIDE COMPLEXES

Compound	Solvent	Cation ^{b} resonances	Other ^{b}	Assignment
$(C_2H_5)_4N[CH_3InI_3]$	$CDCl_3$	1.45, 3.35	0.72s	In—CH_3
$(C_4H_9)_4N[(CH_3)_2InI_2]$	CD_3CN	0.75, 1.25, 1.75, 2.85	0.43s	In—CH_3
$(C_2H_5)_4N[C_2H_5InBr_3]$	CD_3OD	1.35, 3.35	0.8(br), 2.2s	In—C_2H_5
$(C_2H_5)_4N[C_6H_5InBr_3]$	CD_3OD	1.0, 3.0	7.3(br)	In—C_6H_5
$(C_2H_5)_4N[C_6H_5InI_3]$	$CDCl_3$	1.35, 3.20	6.75m, 7.1(br), 7.2(br)	In—C_6H_5
$(C_4H_9)_4N[C_6H_5InI_3]$	$CDCl_3$	0.9, 1.1, 1.7, 3.1	7.1(br), 7.3(br), 7.6(br)	In—C_6H_5

^{a} Chemical shifts (δ) in ppm, relative to external TMS, at 60 MHz. ^{b} s, singlet; (br), broad. Other results refer to mid-point of doublet, triplet, etc., as appropriate.

The infrared spectra of the compounds confirmed the presence of 2,2'-bipyridine, or of the tetraalkylammonium cation. In some compounds, and especially in those containing In—CH_3, it was also possible to identify ν(In—C) in the 500 cm^{-1} region. We hope to present a more detailed analysis of the vibrational spectra of these compounds elsewhere.

The ^1H NMR spectra of certain of the anionic complexes are listed in Table 5, the neutral complexes not being amenable to such investigation because of their poor solubility in suitable solvents. The results show that the In—CH_3 and In—C_2H_5 protons have resonance absorptions close to TMS, as previously noted for other organoindium compounds [21—23]. The resonance of In—C_6H_5 groups show a complex pattern, which we have not attempted to analyse but which is clearly in keeping with the structure proposed.

Acknowledgement

References

1 G.E. Coates and K. Wade, Organometallic Compounds, Vol. I, Methuen, London, 1967, p. 357 et seq.
2 A. Victorova, Dokl. Akad. Nauk SSSR, 177 (1967) 103.
3 H.C. Clark and A.L. Pickard, J. Organometal. Chem., 8 (1967) 427.
4 H.C. Clark and A.L. Pickard, J. Organometal. Chem., 13 (1968) 61.
5 W. Schumb and H. Crane, J. Amer. Chem. Soc., 60 (1938) 306.
6 J.S. Poland and D.G. Tuck, J. Organometal. Chem., 42 (1972) 315.
7 L. Waterworth and I.J. Worrall, Chem. Commun., (1971) 569.
8 M.J.S. Gynane, L.J. Waterworth and I.J. Worrall, J. Organometal. Chem., 40 (1972) C9.
9 L. Chao and R.D. Rieke, Synth. React. Inorg. Met.-Org. Chem., 5 (1975) 165.
10 G.B. Deacon and J.C. Parrott, Austr. J. Chem., 27 (1974) 2547.
11 H.J. Wilder, H.D. Hausen and J. Weidlein, Z. Naturforsch. B, 30 (1975) 645.
12 J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 134 (1977) 363.
13 J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 146 (1978) 213.
14 A. Osman and D.G. Tuck, J. Organometal. Chem., 169 (1979) 255.
15 J.J. Habeeb, A. Osman and D.G. Tuck, J. Organometal. Chem., 185 (1980) 117.
16 J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 139 (1977) C17.
17 M.R. Rifi, in M.M. Baizer (Ed.), Organic Electrochemistry, Marcel Dekker, New York, 1973, p. 279 et seq.
18 B.H. Freeland and D.G. Tuck, Inorg. Chem., 15 (1976) 476.
19 H. Lehmkuhl, in M.M. Baizer (Ed.), Organic Electrochemistry, Marcel Dekker, New York, 1973, p. 621 et seq.
20 D.J. Gislason, M.H. Lloyd and D.G. Tuck, Inorg. Chem., 10 (1971) 1907.
21 J.J. Habeeb and D.G. Tuck, Can. J. Chem., 52 (1974) 3950.
22 J.J. Habeeb and D.G. Tuck, J. Organometal. Chem., 101 (1975) 1.
23 A.F. Berniaz and D.G. Tuck, J. Organometal. Chem., 46 (1972) 243.