Journal of Organometallic Chemistry, 265 (1984) 9–15
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ELECTROCHEMICAL STUDIES OF GROUP III ALKYL DERIVATIVES

II *. SYNTHESIS OF ADDUCTS OF TRIMETHYLINDIUM AND TRIMETHYLGALLIUM

ANTHONY C. JONES, NEIL D. GERRARD, DAVID J. COLE-HAMILTON
A. KENNETH HOLLIDAY*

Donnan Laboratories, University of Liverpool, P.O. Box 147, Liverpool, L69 3BX (Great Britain)

and J.B. MULLIN

Royal Signals Research Establishment, St. Andrews Road, Great Malvern, Worcs. W14 3PS (Great Britain)

(Received November 4th, 1983)

Summary

Electrolysis of methylmagnesium chloride or dimethylmagnesium in tetrahydrofuran (thf) with an indium anode yields the spectroscopically characterised adduct $Me_3In \cdot thf$ directly; the adducts $Me_3In \cdot L$ ($L = NEt_3$, PMe_3, PEt_3) are obtained by direct addition of excess L to $Me_3In \cdot thf$.

In the growth of gallium arsenide by metalorganic chemical vapour deposition (MOCVD), the technology of co-decomposing trimethylgallium, Me_3Ga, and arsine, AsH_3, is well-developed and layers with good morphology, low carrier concentration and high electron mobilities can be grown [1].

However, MOCVD growth of indium phosphide from Me_3In and PH_3 has not been so successful, since these compounds react together in the vapour phase at room temperature to give an involatile polymer $[MeInPH]_n$ [2]. This problem has been circumvented [3] by introducing the indium in the form of a preformed adduct $Me_3In \cdot L$ ($L = NR_3$ or PR_3, R = alkyl); this is then decomposed in the presence of PH_3 [3] or PCl_3 [4]. Accordingly, we have investigated methods for the production of these adducts, $Me_3In \cdot L$, for use in MOCVD.

Conventional methods for the preparation of Me_3In, or its adducts, involve synthesis either of air-sensitive $InCl_3$ prior to alkylation by MeLi [5] or MeMgX (X = halogen) [6], or of a homogeneous InMg alloy prior to reaction with methyl

---

* For part I see ref. 14.

iodide [7]. We have sought an electrochemical route by which Me_3In adducts may be synthesised directly, in one-step, from indium metal.

The electrolysis of organomagnesium compounds with sacrificial metal anodes has provided a facile route to a number of organometallic compounds [8]. More specifically, electrochemical methods of preparation have been used for the production of $RInX_2$ and R_2InX ($R =$ alkyl, $X =$ halogen) compounds using an indium anode [9] or cathode [10] and indium alkyls have been produced by electrolysis of $NaF \cdot AlR_3$ [11], or mixtures of zinc and aluminium alkyls containing alkali metal halides [12], using an indium anode.

The successful production of alkyl lead compounds by electrochemical means [13] encouraged us to study the application of similar methods to Group III alkyls and we have previously reported [14] the electrochemical synthesis of Me_3Ga adducts directly from gallium metal. Although $Me_3Ga \cdot$ thf can be prepared in reasonable yield by the electrolysis of thf solutions of Me_2Mg and Et_4NClO_4 using a gallium anode we have now found that this process suffers from a number of disadvantages.

(i) In the electrolysis of Me_2Mg current densities were very low, even at high applied voltages, so that very long reaction times were required for the production of usable quantities of the desired product.

(ii) the requirement for a carrying electrolyte, R_4MClO_4, not only meant the addition of an extra component to the system but also led to problems associated with product recovery, particularly on account of the dangers associated with heating organic perchlorates. Problems were also encountered with break-down of the carrying electrolyte [14] so that the major products from electrolyses employing $Bu^n_4NClO_4$ as carrying electrolyte were $Me_3Ga \cdot NBu^n_3$ [14] and $Me_3In \cdot NBu^n_3$ (this work) rather than the thf adducts.

When this method is used to prepare adducts of Me_3In, yields of $Me_3In \cdot$ thf are invariably low (25–30% based on indium consumption). We have now established the reason for this low yield. Initially, as in the reaction using a gallium anode [14], magnesium is deposited at the cathode. However, after a short time the appearance of the metal depositing at the cathode becomes fibrous and more silvery. We have identified this metal as indium. Apparently when the concentration of $Me_3In \cdot$ thf reaches a certain level it is electrolysed in preference to Me_2Mg; the net effect is that any more indium that dissolves at the anode is deposited at the cathode, steady state conditions are reached and only low yields of $Me_3In \cdot$ thf are achieved.

We have thus developed an alternative electrochemical synthesis which does not suffer from the disadvantages outlined above and which allows us to prepare $Me_3In \cdot$ thf or $Me_3Ga \cdot$ thf in high yield.

Results and discussion

Electrolysis of Grignard reagents

We find that the electrolysis of methylmagnesium chloride in thf solution using an indium or gallium anode produces $Me_3M \cdot$ thf in good yield (80% based on indium consumption). This route has a number of advantages over the route based on the electrolysis of Me_2Mg. These include:

(i) The reaction can be carried out in one pot and obviates the need to isolate and purify any magnesium containing compounds such as Me_2Mg.

(ii) Much higher current densities are obtained for the Grignard electrolysis, thus eliminating the need for supporting electrolyte. The higher current densities mean that reaction times are much shorter than in the corresponding reaction with Me_2Mg. These higher current densities presumably arise because of the more efficient self-ionisation of MeMgCl than of Me_2Mg.

(iii) Very high current efficiencies are obtained. Assuming that each indium atom dissolved loses three electrons, apparent current efficiences in the indium[*] electrolysis are 110–120%. These values are artificially high due to some mechanical loss of indium at the anode in addition to anodic dissolution.

(iv) High yields (60–80% based on metal consumed) are obtained for $Me_3In \cdot$ thf and $Me_3Ga \cdot$ thf.

(v) Addition of excess alkyl halide to the Grignard solution prevents build up of magnesium metal at the cathode and regenerates the Grignard reagent thus increasing the efficiency of the process with respect to magnesium.

Preparation and characterisation of adducts $Me_3In \cdot L$ ($L =$ thf, PMe_3, PEt_3 and NEt_3)

The final product of the electrolysis of Me_2Mg/Et_4NClO_4 mixtures or MeMgCl in thf using an indium anode and a platinum cathode is an air sensitive colourless liquid which is readily purified by vacuum distillation. ^1H NMR, mass spectral and infra-red studies show that this oil has the limiting composition $Me_3In \cdot$ thf, but problems associated with the isolation of volatile liquid metal alkyls [14] have precluded reproducible elemental microanalysis.

Addition of excess of a Lewis base (PMe_3, PEt_3 or NEt_3) to $Me_3In \cdot$ thf gives, on evaporation of excess base and liberated thf, volatile solids $Me_3In \cdot QR_3$ ($Q = P$ or N). Analytical as well as spectroscopic data (Tables 1 and 2) confirm the 1 : 1 stoichiometry. In addition these adducts show a characteristic strong absorption in their infrared spectra between 475–482 cm^{-1} attributable [15] to $\nu_{asym}(InC_3)$. The preparation of the analogous adducts for $GaMe_3$ has previously been described [14].

Use of adducts in MOCVD

A sample of $Me_3In \cdot PMe_3$, prepared by our new route, has been successfully [16] employed in the production of epitaxial InP by MOCVD. The layers so grown have

TABLE 1

^1H NMR SPECTRA OF $Me_3In \cdot L$ IN TOLUENE-d_8 AT 298 K

L	InMe δ(I)	L protons		
		QCH_2 [a]	CH_2 [b]	CH_3
thf [c]	0.0s(9)	4.2t(4)	2.3m(4)	
PMe_3	−0.1s(9)			0.8d(9)
PEt_3	0.0s(9)	1.2m(6)		0.85m(9)
NEt_3	−0.1s(9)	2.3q(6)		0.9t(9)
NBu^n_3	0.1s(9)	2.6t(6)	1.5m(12)	1.0t(9)

[a] Methylene protons adjacent to donor atom. [b] Methylene protons remote from donor atom. [c] Neat liquid.

---

[*] There is no evidence for indium deposition at the cathode, cf. electrolysis of Me_2Mg. This may be because of the different applied voltages or current densities but since viable routes to the metal alkyls were being sought, no attempt was made to compare the reactions under controlled conditions.

TABLE 2

MASS SPECTRAL DATA FOR $Me_3In \cdot L$ COMPOUNDS

L	*m/e* (Assignment)[a]
(a) thf	71$[C_4H_7O]^+$; 72$[C_4H_8O]^+$; 115$[In]^+$; 130$[MeIn]^+$; 145$[Me_2In]^+$; 160$[Me_3In]^+$ (*s* 70, *I* 15)
(b) PMe_3	61$[C_2H_6P]^+$; 76$[C_3H_9P]^+$; 115$[In]^+$; 130$[MeIn]^+$; 145$[Me_2In]^+$; 160$[Me_3In]^+$ (*s* 100, *I* 30)
(c) PEt_3	61$[C_2H_6P]^+$; 62$[C_2H_7P]^+$; 75$[C_3H_8P]^+$; 90$[C_4H_{11}P]^+$; 103$[C_5H_{12}P]^+$; 115$[In]^+$; 118$[C_6H_{15}P]^+$; 130$[MeIn]^+$; 145$[Me_2In]^+$; 160$[Me_3In]^+$; 233$[In \cdot PEt_3]^+$; 263$[Me_2In \cdot PEt_3]^+$ (*s* 50, *I* 25)
(d) NEt_3	86$[C_5H_{12}N]^+$; 101$[C_6H_{15}N]^+$; 115$[In]^+$; 130$[MeIn]^+$, 145$[Me_2In]^+$ (*s* 170, *I* 30)
(e) NBu^n_3	86$[C_5H_{12}N]^+$; 100$[C_6H_{14}N]^+$; 115$[In]^+$; 130$[MeIn]^+$; 142$[C_9H_{20}N]^+$; 145$[Me_2In]^+$, 185$[C_{12}H_{27}N]^+$ (*s* 200, *I* 70)

[a] *s* = source temperature (°C); *I* = ionisation energy (eV). All mass spectra were recorded using the solid probe of the mass spectrometer.

TABLE 3

EPITAXIAL InP FROM $Me_3In \cdot PMe_3$ [16]; THE ELECTRICAL PROPERTIES OF LAYERS FROM 3 GROWTHS

Run	Carrier concentration ($cm^{-3} \times 10^{15}$)		Electron mobility ($cm^2\ s^{-1}\ V^{-1}$)	
	298K	77 K	298 K	77 K
989	6.4	4.2	3296	5542
990	12.1	7.1	3581	9850
991 (A)	10.9	6.2	2206	7732
(B)	16.4	8.6	3374	11 725

shown good surface morphology and reasonable electrical properties in terms of carrier concentration and electron mobilities (Table 3), and compare favourably with InP grown by similar routes [3,4,17] using trimethylindium adducts.

Experimental

Microanalyses were by Elemental Microanalysis Limited.

Mass spectra were carried out on a VG Micromass 13 mass spectrometer using a solid probe. Proton NMR spectra were recorded on a PE R12B spectrometer at 60 MHz whilst infrared spectra were recorded on a PE 577 spectrometer using thin films or Nujol mulls between caesium iodide plates. Melting points were measured on an Electrothermal melting point apparatus in sealed capillaries under vacuum and are uncorrected.

All preparations and manipulations were carried out in an atmosphere of dry deoxygenated dinitrogen using Standard Schlenk-tube/catheter techniques.

All chemicals and solvents were dried, purified and deaerated by standard methods before use except for trimethylphosphine and triethylphosphine (Strem. Chem. Co. Ltd.) which were used without further purification.

The electrochemical cell was a three-neck flask fitted with a water condenser, platinum cathode (1 × 1 cm plate) and an indium wire anode. The D.C. power supply used in the electrolyses was a Solartron Vari-Pack Model SRS 153.

Methylmagnesium chloride was prepared by addition of gaseous methyl chloride to a stirred suspension of magnesium turnings (3.0 g, 0.12 mol) in tetrahydrofuran (250 cm^3). Dimethylmagnesium was prepared by the precipitation of the dioxane-magnesium iodide complex from an ether solution of methylmagnesium iodide [18].

Electrochemical preparations

Trimethylindium-tetrahydrofuran adduct

(a) From dimethylmagnesium. A mixture of dimethylmagnesium (0.8 g, 14.8 mmol) and tetraethylammonium perchlorate (1.0 g, 4 mmol) in thf (100 cm^3) was electrolysed at ambient temperature using a Pt cathode and indium wire anode. Initially, a current of 4 mA was obtained at an applied voltage of 50 V. The reaction was continued until 2.3 g of indium wire had been consumed. During the course of the reaction the current rose to 75 mA at 50 V and a mixed metal deposit formed at the cathode.

The mixture was filtered and the thf was removed in vacuo. The pure colourless liquid product was separated from residual dimethylmagnesium and Et_4NClO_4 by vacuum distillation (60°C) into a ca. -196°C cold trap. *Danger*: perchlorate.

Yield of $Me_3In \cdot$ thf 30% (based on indium consumption).

IR max (cm^{-1}): 2960vs, 2910vs, 2880vs, 2840vs(sh) 2270vw, 1460m, 1365w, 1340vw, 1290vw, 1245vw, 1180w(br), 1150m, 1070s(sh), 1050vs(sh), 1040vs, 915m, 880s, 840w(sh) 680vs(br), 515vw(sh), 485vs. (Thin film).

(b) From methylmagnesium chloride. A solution of methylmagnesium chloride (0.12 mol dm^{-3} in magnesium) in thf (250 cm^3) * was electrolysed at ambient temperature using a Pt cathode and an indium wire anode. Applied voltages of 50 V gave a current of 15 mA. The reaction was continued until 8.0 g of indium wire had been consumed when the current was 95 mA at 20 V. There was no metal deposit at the cathode.

The mixture was filtered and the thf was removed in vacuo. The pure product was separated from residual Grignard reagent and magnesium chloride by vacuum distillation (60–100°C) into a ca. -196°C cold trap. In a separate experiment, dissolution of 1.336 g of indium required the passage of 3,087 coulombs – current efficiency = 111% (some mechanical loss of indium was observed).

Trimethylgallium-tetrahydrofuran adduct was similarly prepared but using a gallium pool anode (40 g). Initially a current of 25 mA at 40 V was obtained but this rose to 140 mA at 20 V after 24 h. The colourless liquid product had spectroscopic properties identical to those previously described [14].

Trimethylindium-trimethylphosphine adduct

Trimethylphosphine (5 g, 66 mmol) was added to the liquid product, $Me_3In \cdot$ thf, obtained as described in (b). The mixture was stirred for 30 min at ambient temperature. Excess trimethylphosphine and liberated thf were then removed in

---

* Containing excess MeCl.

vacuo to leave a colourless crystalline solid. The final product (m.p. 43–45°C) was obtained by vacuum sublimation (80°C) of the crude product into a ca. −196°C cold trap. Yield 13.0 g (79%) based on indium consumed during electrolysis.

Found: C, 30.46; H, 7.89; In, 49.6. $C_6H_{18}InP$ calcd.: C, 30.50; H, 7.63; In, 48.9%.

IR max (cm^{-1}) 1300w, 1280m, 1160vw, 1140m, 950vs, 940vs, 850vw, 840vw, 735vs, 720s, 680vs, 630(br,sh), 520vw, 482vs, 470m(sh). (Nujol mull).

The adducts $Me_3In \cdot L$ ($L = PEt_3$ and NEt_3) were prepared as described above by the addition of excess phosphine or amine to $Me_3In \cdot$ thf. Both adducts were purified by vacuum sublimation (80–100°C) into a −196°C cold trap.

$L = PEt_3$. M.p. 33–36°C. Found: C, 39.2; H, 9.1; In, 41.1; P, 10.1. $C_9H_{24}InP$ calcd.: C, 38.8; H, 8.6; In, 41.5; P, 11.1%.

IR max (cm^{-1}) 1300vw, 1255w, 1240w(sh), 1145m, 1040s, 1010w, 950w, 770s, 750s, 730s(sh), 720s(sh), 685vs, 630w(sh), 475 vs, 460m(sh). (Nujol mull)

$L = NEt_3$. M.p. 94–96°C. Found: C, 41.1; H, 9.0; In, 44.6; N, 5.2; $C_9H_{24}InN$ calcd.: C, 41.4; H, 9.1; In, 44.1; N, 5.4%.

IR max (cm^{-1}) 1330vw, 1320vw, 1290w, 1190m, 1170s, 1150s, 1090m, 1055m, 1025w, 1005w, 900vw (br) 800vw, 790vw, 730m, 680vs, 620w (br, sh), 550w, 475vs, 455m(sh), 475vs, 455m(sh) 420vw (Nujol mull).

Trimethylindium-tri-n-butylamine adduct

A mixture of dimethylmagnesium (0.5 g, 9 mmol) and tetrabutylammonium perchlorate (2.0 g, 6 mmol) in thf (100 cm^3) was electrolysed as described in (a). A voltage of 120 V gave a current of 50 mA. After consumption of 1.6 g of indium the mixture was filtered and the thf was removed in vacuo. The pure product was obtained by vacuum sublimation (50–60°C) into a −196°C cold trap. Found: C, 49.1 *; H, 10.5; In, 32.8; N, 3.8. $C_{15}H_{35}InN$ calcd.: C, 52.2; H, 10.4; In, 33.3; N, 4.1%.

Acknowledgment

We are grateful to the Ministry of Defence for the support of this work, Mr. A. Mills for recording mass spectral data, and to Dr. S. Bass for communicating his epitaxial results.

References

1 T. Nakanisi, T. Udagawa, A. Tanaka and K. Kamei, J. Cryst. Growth, 55 (1981) 255.
2 R. Didchenko, J.E. Alix and R.H. Toeniskoettler, J. Inorg. Nucl. Chem., 14 (1960) 35.
3 R.H. Moss and J.S. Evans, J. Cryst. Growth, 55 (1981) 129.
4 K.W. Benz, H. Renz and J. Weidlein, J. Electronic Materials, 10 (1) (1981) 185.
5 H.C. Clark and A.L. Pickard, J. Organomet. Chem., 8 (1967) 427.
6 F. Runge, W. Zimmerman, H. Pfeiffer and I. Pfeiffer, Z. Anorg. Allgem. Chem., 267 (1951) 39.
7 E. Todt and R. Doetzer, Z. Anorg. Allgem. Chem., 321 (1963) 120.
8 For a review see Technique of Electroorganic Synthesis", N.L. Weinberg (Ed.), Wiley, 1975, Vol. II, p. 492 et seq.
9 D.G. Tuck, J.J. Habeeb and F.F. Said, J. Organomet. Chem., 190 (1980) 325.

---

* Some photochemical decomposition to a brown product was observed.

10 A.P. Tomilov and I.N. Chernikh, Elektrokhimiya, 10 (1974) 1971.

11 K. Zeigler, Brit. Pat., 814, 609 (1959).

12 B.E. Roetheli and I.B. Simpson, Brit. Pat., 797, 093 (1958).

13 A.J. Owen in A.T. Kuhn (Ed.), The Electrochemistry of Lead, Academic Press, 1979, Ch.7, pp. 163–193.

14 A.C. Jones, D.J. Cole-Hamilton, A.K. Holliday and M.M. Ahmad, J. Chem. Soc., Dalton Trans. (1983) 1047.

15 F. Schindler and H. Schmidbauer, Chem. Ber., 100 (1967) 3655.

16 S.J. Bass, (RSRE Malvern), Private communication.

17 A.K. Chatterjee, M.M. Faktor, R.H. Moss and E.A.D. White in International Meeting on the Relationship between Epitaxial Growth Conditions and the Properties of Semi-conductor Epitaxial Layers, Perpignan, France, 1982.

18 E. Weiss, J. Organomet. Chem., 2 (1964) 314 and references therein.