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2018 (vw), 1990 (w, sh), 1964 (s), 1948 (vs), 1920 (s), 1896 (m, sh), 1653 (m); for $Ru_6(CO)_{18}^{2-}$, $\tilde{\nu}$ (cm^{-1}) = 2003 (vs), 1986 (vs), 1963 (m, sh), 1937 (m, sh), plus weak bands attributable to about 15% unreacted $Ru_3CO)_{12}$ (2060 and 2030 cm^{-1}). $Ru(CO)_5$ was prepared from $Ru_3(CO)_{12}$ by the photochemical method of Lewis et al.,[28] purified by vacuum line distillation, and stored under CO in a freezer until use. Infrared bands were observed at $\tilde{\nu}$ (cm^{-1}) = 2036 (s), 2004 (vs).

Solutions for electrochemical studies were freshly prepared from the reagents purified as described above. Unless otherwise specified, such solutions were 1.0 mM in the electroactive compound and 0.15 M in supporting electrolyte and were deoxygenated with and kept under argon during the experiments.

Electrochemical Measurements. dc polarograms were recorded with a PAR 174 polarographic analyzer in the three-electrode configuration with *iR*-drop compensation. Cyclic voltammograms, recorded on a Bascom-Turner 2120 digital recorder (for $\upsilon \geq 200$ mV s^{-1}) or on a Hewlett-Packard x-y recorder (for slower scan rates), employed a Pt-wire counter electrode, a Ag/AgCl reference electrode making contact with the solution through a Luggin probe, and a Pt-button (ca. 2 mm diameter) working electrode. The Pt working electrode was surface polished and anodized in a solution of the supporting electrolyte for 45 s at +2.0 V before use. The reference electrode contained a Ag/AgCl reference element with 0.1 M TBAP in acetone, saturated in LiCl ($E_{1/2}$ = 0.66 V for ferrocene in acetone solution with 0.1 M TBAP). Low-temperature work in CH_2Cl_2 used a Ag/AgCl electrode with 0.1 M TBAFB in CH_2Cl_2, saturated in LiCl ($E_{1/2}$ = 0.60 V for ferrocene in CH_2Cl_2 solution with 0.1 M TBAFB). Unless otherwise noted, potentials reported here are relative to the acetone Ag/AgCl electrode.

Room-temperature cyclic voltammograms were obtained by using a standard BAS cell. Cyclic voltammograms at −56 °C employed a jacketted cell and acetone coolant circulated through a dry ice/acetone bath. Cyclic voltammograms at −90 °C were recorded with a Metrohm cell immersed in a liquid nitrogen/CH_2Cl_2 slush bath.

In a series of experiments in which the potential of the $Ru_3(CO)_{12}$ reduction peak was measured as a function of scan rate, the solutions contained an equimolar concentration of ferrocene; the separation of the ferrocene oxidation and reduction peaks were used to estimate the solution resistance, which was used to correct the $Ru_3(CO)_{12}$ reduction peak potentials for ohmic potential drop in the solution.

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Direct Electrochemical Synthesis of X_2InCH_2X Compounds (X = Br, I) and a Study of Their Coordination Chemistry

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The electrochemical oxidation of indium in CH_2X_2/CH_3CN media (X = Cl, Br, I) gives InX. Indium(I) chloride disproportionates, but InBr or InI react with CH_2X_2 to give X_2InCH_2X (X = Br, I) derivatives. Treatment of the latter with Et_4NX gives the 1:1 electrolytes $Et_4N[X_3InCH_2X]$. With triphenylphosphine, Br_2InCH_2Br forms the phosphonium ylid derivative $Br_3InCH_2P(C_6H_5)_3$, whose structure has been established by X-ray crystallography: cell constants a = 14.076 (4) Å, b = 7.610 (2) Å, c = 12.931 (2) Å; space group $Pna2_1$; R = 0.034, R_w = 0.034. Reaction between *N*,*N*,*N′*,*N′*-tetramethylethanediamine (tmen) and Br_2InCH_2Br also gives a cyclized nitrogen ylid $Br_3\overline{InCH_2NMe_2CH_2N}Me_2$: cell constants a = 12.814 (3) Å, b = 15.721 (4) Å, c = 21.343 (5) Å; space group $Pbca$; R = 0.045, R_w = 0.047. The iodo species I_2InCH_2I undergoes redistribution in solution, and two tmen derivatives were isolated, $I_3\overline{InCH_2NMe_2CH_2N}Me_2$ and $[I\overline{In(CH_2NMe_2CH_2N}Me_2)_2](I)_2$. The latter has two identical cyclized ylid ligands: a = 11.414 (4) Å, b = 14.592 (6) Å, c = 16.144 (7) Å, β = 110.1 (4)°; space group $P2_1/c$; R = 0.051, R_w = 0.051. The ^1H and ^{13}C NMR spectra show that the CH_2 group in X_2InCH_2X is electron-poor, in keeping with the tendency for nucleophilic ligands to react at this site as well as at the metal.

Introduction

The method of direct electrochemical synthesis consists of oxidizing a metal anode in a nonaqueous solution containing a ligand or ligand precursor to produce the appropriate metal–ligand complex. One of the many advantages of the technique is that the compound is often a derivative of a low oxidation state of the metal in question, and examples of this include chromium(III) bromide.[1] tin(II) and lead(II) thiolates,[2] hexahalogenodigallate(II) anions,[3] thorium diiodide,[4] copper(I) thiolates,[5] and indium(I) derivatives of thiols,[6] dithiols,[7] and diols.[8]

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Table I. Electrochemical Oxidation of Indium Metal in CH_2X_2/CH_3CN Solutions

CH_2X_2	vol, mL	Et_4NPF_6 mass, mg	time of electrolysis, min	current, mA	mass of metal dissolved, mg	E_f, mol F^{-1} [b]
CH_2Cl_2	neat	100	33	60	143	1.01
CH_2Br_2	5[c]	57	280	30	614	1.02
CH_2I_2	2[c]	39	280	30	622	1.03

[a] Voltage adjusted in the 20–30-V range to maintain constant current. [b] Defined as moles of metal lost from anode per faraday of charge. [c] Dissolved in 30 mL of CH_3CN.

In many cases, the metal–ligand product precipitates directly in the cell, making for easy isolation, so that the technique is both direct and simple, and, in addition, the product yields are very high. In some systems, the low oxidation state compound that is formed undergoes subsequent reaction, as was observed in the synthesis of alkylindium dihalides, when the reaction sequence involved the oxidation of an indium metal anode to give InX, which subsequently reacted with RX to give $RInX_2$.[9]

We now report that the electrochemical oxidation of indium in solutions containing a dihalogenomethane also yields InX (X = Cl, Br, I) and that in the case of X = Br or I further reaction leads to X_2InCH_2X compounds. Some interesting adducts of these species have been prepared and structurally characterized. These derivatives are related to the $X_2InCH_2InX_2$ compounds previously studied in this laboratory.[10]

Experimental Section

Indium metal (in the form of a rod, ca. 0.6-cm diameter), CH_2I_2, tetraethylammonium halides, *N,N,N′,N′*-tetramethylethanediamine (tmen), and triphenylphosphine were used as supplied (Aldrich). All other liquid compounds, including CH_2X_2 (X = Cl, Br), were dried, distilled, and stored over appropriate drying agents.

Indium analysis was by atomic absorption spectrophotometry using an IL-251 instrument, and halide analysis was by the Volhard method, involving silver halide precipitation and back-titration with potassium thiocyanate solution. Microanalysis was by Guelph Chemical Laboratories Ltd. Proton and ^{13}C NMR spectra were recorded on a Bruker AC300L spectrometer. Conductivities were measured in a standard platinum electrode cell, standardized with 1 mol dm^{-3} aqueous KNO_3.

Electrochemical Synthesis. The electrochemical techniques were essentially those used in previous work. The solution phase was contained in a 100-mL round-bottomed Schlenk flask; an indium rod suspended through a rubber septum formed the anode of the cell, and a platinum wire was the cathode. Details of solution composition and electrochemical conditions are given in Table I. We have found that Et_4NPF_6 is the preferred supporting electrolyte in these experiments, since the use of Et_4NClO_4 with indium anodes in the media used may give rise to explosive oxidative reactions at the metal surface. As soon as current flowed in the cell, the formation of the appropriate indium monohalide at the surface of the anode was apparent. Indium(I) chloride undergoes disproportionation, forming elemental indium as the electrolysis proceeds, but InBr and InI slowly dissolve in the electrolyte solution at rates that depend generally on the initial concentration of CH_2X_2; typical times for dissolution of InX after the completion of electrolysis were 1 h (InBr) and 6 h (InI) under the conditions described in Table I. We found that it was possible to minimize the disproportionation of InCl by carrying out the electrolysis at low temperatures (ice–salt bath, −8 °C) and for short period of time (approximately 30 min), but it was not possible to suppress this reaction completely by such procedures. Other approaches such as changing the solution composition to CH_2Cl_2/CH_2CN (1:1 or 1:6) or CH_2Cl_2/toluene (1:1), or working in a cell with two compartments in which the two electrodes were separated, were equally unsuccessful, and Cl_2InCH_2Cl could not be prepared in this way.

Table II. Analytical Results

compd	In, % found	In, % calcd	halogen, % found	halogen, % calcd
InCl	76.0	76.4	22.7	23.6
$Br_2InCH_2Br\cdot{}^1/_2(C_2H_5)_2O$	28.6	28.3	58.8	59.1
$I_2InCH_2I\cdot CH_3CN$	21.1	20.9	68.6	69.1
$(C_2H_5)_4N[Br_3InCH_2Br]$	19.9	19.9	55.0	55.3
$(C_2H_5)_4N[I_3InCH_2I]$[a]	15.0	15.0	*b*	
$Br_2InCH_2Br\cdot P(C_6H_5)_3$[c]	18.5	18.2	37.0	38.0
Br_2InCH_2Br·tmen[d]	23.8	19.9	49.6	49.5
I_2InCH_2I·tmen[e]	18.7	18.3	*b*	
$IIn(CH_2I)_2$·2tmen[f]	15.5	15.2	50.8	50.4

[a] Found: C, 13.8; H, 2.71; N, 2.10. Calcd: C, 14.1; H, 2.89; N, 1.83. [b] Visible loss of iodine during dissolution of sample. [c] Found: C, 35.9; H, 2.51. Calcd: C, 36.2; H, 2.72. [d] tmen = *N,N,N′,N′*-tetramethylethanediamine. [e] Found: C, 14.1; H, 2.50; N, 4.72. Calcd: C, 13.4; H, 2.90; N, 4.48. [f] Found: C, 22.6; H, 5.01; N, 7.92. Calcd: C, 22.2; H, 4.80; N, 7.41.

The final products of the reactions involving methylene bromide and iodide were X_2InCH_2X derivatives, isolated by the following techniques.

(i) The solution obtained from the electrolysis with CH_2Br_2 was filtered to remove a small quantity of white cloudiness, and the filtrate was pumped under vacuum to achieve complete removal of all volatile substances. The resultant colorless oil was redissolved in diethyl ether, and the supporting electrolyte, which is insoluble in this ethereal solution, was removed by filtration. Diethyl ether was pumped off in vacuo to leave a colorless oil, identified as $Br_2InCH_2Br\cdot{}^1/_2Et_2O$. (See Table II for analytical results.)

(ii) The mixture resulting from the electrochemical reaction involving CH_2I_2 was worked up in a similar way, except that the elimination of the volatiles required much stronger conditions, namely 24 h of pumping under vacuum at 50 °C. The isolation of the final product was also complicated by the fact that it is not soluble in Et_2O and therefore could not be separated from the supporting electrolyte. Solutions in acetonitrile obtained by this direct electrochemical synthesis were suscessfully used as the starting point for the preparation of I_2InCH_2I derivatives (see below).

(iii) The formation of $I_2InCH_2I\cdot CH_3CN$ via InI was demonstrated by treating InI (2.02 g, 8.26 mmol) with excess CH_2I_2 (2 mL, 6.65 g) in CH_3CN (15 mL). After InI had completely dissolved (2 h, room temperature), volatile compounds were removed by pumping in vacuo at 50 °C for 24 h to give 3.65 g (6.6 mmol; 80% yield) of $I_2InCH_2I\cdot CH_3CN$. The ^1H NMR spectrum of this material in $CDCl_3$ showed two singlet resonances at 1.67 and 1.77 ppm from Me_4Si. (See below.)

Preparation of Derivatives of X_2InCH_2X. (i) $Et_4N[Br_3InCH_2Br]$. Electrochemical oxidation of indium in CH_2Br_2/CH_3CN was carried out under the conditions given in Table I until 0.28 g (2.43 mmol) of indium had dissolved. After the InBr had completely dissolved, solid Et_4NBr (0.51 g, 2.43 mmol) was added to the mixture, the resultant solution filtered to remove any solid impurities, and the filtrate concentrated to approximately 10 mL. Upon addition of Et_2O to turbidity, and subsequent cooling, colorless crystals of $Et_4N[Br_3InCH_2Br]$ were obtained; these were filtered out, washed with Et_2O, and dried in vacuo. Yield: 1.17 g, 84%.

(ii) $Et_4N[I_3InCH_2I]$. A similar procedure, following an electrolysis in which 0.32 g (2.78 mmol) of indium dissolved, involved the addition of 0.71 g (2.78 mmol) of Et_4NI to give $Et_4N[I_3InCH_2I]$ as colorless crystals (yield 1.63 g, 79%).

(iii) $Br_2InCH_2Br\cdot PPh_3$. Electrolysis was carried on until 0.33 g (2.87 mmol) of indium dissolved, and the electrolyte phase was then pumped to dryness to remove all the volatiles completely. The oil so obtained was redissolved in CH_3CN (10 mL), and a

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solution of Ph_3P (0.74 g, 2.82 mmol) in CH_3CN (10 mL) was added dropwise over 30 min. The resultant yellow solution was concentrated to 5 mL; addition of Et_2O (50 mL) caused the precipitation of a small quantity of solid, which was removed by filtration and discarded. The filtrate was pumped to dryness to give an oil, which was triturated with Et_2O (10 mL) and pentane (10 mL) and again pumped to dryness to give $Br_2InCH_2Br{\cdot}PPh_3$ (1.20 g, 67%) as a white fluffy solid, conveniently recrystallized from CH_3CN.

(iv) $I_2InCH_2I{\cdot}PPh_3$. The solution from an electrolysis with CH_2I_2 in which 0.47 g of indium dissolved was pumped under vacuum for 24 h at 50 °C. The pasty solid that was obtained was redissolved in acetonitrile (10 mL), and Ph_3P in the same solvent (1.08 g in 10 mL) was added dropwise over 30 min. Traces of solid formed up to this point were removed and discarded, and the filtrate was pumped to dryness; the residue was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O to yield 2.09 g of a white solid. The ^1H and ^{13}C NMR spectra demonstrated the presence of $I_2InCH_2I{\cdot}PPh_3$ in this material, but the analytical results were consistently low (Calcd for $C_{19}H_{17}PInI_3$: C, 29.56; H, 2.22. Found: C, 26.26–26.77; H, 1.62–1.87), suggesting the presence of InI_3 in the product, which would be in keeping with the redistribution reaction discussed below. This aspect of the work was not pursued further.

(v) $Br_2InCH_2Br{\cdot}tmen$. The solution from an electrolysis in CH_2Br_2 in which 0.44 g (3.8 mmol) of indium dissolved was pumped under vacuum to ensure complete removal of the volatiles. The oily residue was dissolved in CH_3CN (10 mL), and tmen (2 mL, 1.54 g, 13.3 mmol) in the same solvent (10 mL) was added dropwise over a period of 30 min. The solution was concentrated to 50% of its initial volume, small quantities of solid were removed and discarded, and Et_2O was added to the point of turbidity. On standing, the solution deposited $Br_2InCH_2Br{\cdot}tmen$ as colorless crystals (yield 1.28 g, 70%).

(vi) $I_2InCH_2I{\cdot}tmen$ and $IIn(CH_2I)_2{\cdot}2tmen$. This preparation can be carried out by following the procedure just described but is equally conveniently done with use of InI as the starting material. Indium(I) iodide (2.0 g, 8.27 mmol), CH_2I_2 (4 mL, 13.3 g, 50 mmol), and CH_3CN (15 mL) were stirred together to give a clear solution, after which the volatile components were removed by pumping in vacuo for 24 h at 50 °C. The resultant pale green oil was redissolved in CH_3CN (20 mL), neat tmen (5 mL, 3.85 g, 33.3 mmol) syringed into this solution, and the mixture stirred for 6 h at room temperature. At the end of this period, the colorless solid (A) that had formed was collected by filtration and dried in vacuo (1.20 g); we were not able to characterize this material. A sample was dissolved in boiling water; when this solution cooled to room temperature, colorless crystals of $IIn(CH_2I)_2{\cdot}2tmen$ (0.31 g) precipitated and were collected and dried in vacuo. A crystal from this batch was the subject of X-ray crystallographic analysis.

The mother liquor remaining after removal of the solid A was taken to dryness in vacuo. The sticky solid residue was dissolved in CH_2Cl_2 (20 mL), and Et_2O was added to precipitate a yellow solid (2.12 g), which was recrystallized from boiling acetone/ethanol (3:2 v/v); the colorless crystals that formed at 0 °C were collected, dried in vacuo, and identified as $I_2InCH_2I{\cdot}tmen$ (0.66 g).

Crystallographic Measurements. The diffraction data for $Br_2InCH_2Br{\cdot}PPh_3$, or $Br_3InCH_2PPh_3$ (1), and $Br_2InCH_2Br{\cdot}tmen$, or $Br_3InCH_2N(CH_3)_2C_2H_4N(CH_3)_2$ (2), were collected at the University of Oklahoma on an Enraf-Nonius CAD 4 diffractometer at 22 °C, using monochromated Mo Kα radiation (λ = 0.71069 Å), by the standard methods of that laboratory.[11] The data were corrected for Lorentz and polarization effects, and absorption corrections were applied in the case of 1. The atomic scattering factors were taken from ref 12. Both structures were solved by heavy-atom methods and refined anisotropically by the full-matrix least-squares method (SHELX-76),[13] minimizing the function $\sum w(|F_o| - |F_c|)^2$. Hydrogen atoms could not be located in the difference Fourier maps and were not included in the refinement of 1 and 2. The crystal and other experimental data are summarized in Table III. The atomic coordinates are given in Tables IV and VI, and the interatomic distances and angles in Tables V and VII. Figures 1 and 2 show the molecular structures.

Table III. Summary of Crystal Data, Intensity Collection, and Structural Refinement

	1	2	3
formula	$C_{19}H_{17}PBr_3In$	$C_7H_{18}N_2Br_3In$	$C_{14}H_{36}N_4I_3In$
fw, M_r	630.9	434.8	756.0
cryst system	orthorhombic	orthorhombic	monoclinic
space group	*Pbca*	*Pna*2	$P2_1/c$
a, Å	12.814 (3)	14.076 (4)	11.414 (4)
b, Å	15.721 (4)	7.610 (2)	14.592 (6)
c, Å	21.343 (5)	12.931 (2)	16.144 (7)
β, deg			110.1 (4)
V, Å^3	4299.5	1438.9	2525.1
d_c, g cm^{-3} (calcd/found)	1.95/1.90	2.24/2.30	1.99/2.05
Z	8	4	4
cryst dimens, mm	0.3 × 0.2 × 0.2	0.25 × 0.15 × 0.13	0.4 × 0.3 × 0.2
abs coeff, cm^{-1}	65.5	96.7	43.0
temp, °C	22	22	21
data collcn range (2θ), deg	3–50	3–50	4–45
total no. of rflcns measd	3762 (h,k,l)	3164 (h,k,l)	3625 ($h,k,\pm l$)
no. of unique data	1654 ($I > 2\sigma(I)$)	1228 ($I > 2\sigma(I)$)	2891 ($I > 3\sigma(I)$)
$R = (\sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert)$	0.045	0.031	0.051
$R_w = [\sum_w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum_w \lvert F_o\rvert^2]^{1/2}$	0.047	0.034	0.051
max Δ/δ in final cycle	0.1	0.1	0.01
ρ_{max} in final diff map, e/Å^3	0.58	0.63	1.71

Table IV. Final Atomic Coordinates for Non-Hydrogen Atoms of $Br_3InCH_2P(C_6H_5)_3$ (1)

atom	x	y	z
In	0.12873 (7)	0.06620 (6)	0.17525 (4)
Br(1)	−0.0374 (1)	−0.0163 (1)	0.1906 (1)
Br(2)	0.0932 (1)	0.1585 (1)	0.0817 (1)
Br(3)	0.1576 (1)	0.1673 (1)	0.2646 (1)
P(1)	0.3533 (2)	−0.0148 (2)	0.1125 (1)
C(1)	0.2570 (8)	−0.0244 (7)	0.1726 (5)
C(11)	0.3054 (8)	−0.0637 (9)	0.0416 (5)
C(12)	0.3612 (10)	−0.1308 (9)	0.0137 (6)
C(13)	0.3213 (11)	−0.1686 (9)	−0.0414 (7)
C(14)	0.2308 (11)	−0.1356 (11)	−0.0700 (7)
C(15)	0.1761 (10)	−0.0690 (12)	−0.0412 (7)
C(16)	0.2142 (9)	−0.0315 (8)	0.0149 (5)
C(21)	0.3805 (8)	0.0962 (7)	0.0982 (6)
C(22)	0.3809 (9)	0.1284 (9)	0.0373 (6)
C(23)	0.3984 (9)	0.2154 (10)	0.0280 (7)
C(24)	0.4151 (10)	0.2667 (9)	0.0805 (9)
C(25)	0.4152 (11)	0.2366 (10)	0.1400 (9)
C(26)	0.3986 (10)	0.1487 (9)	0.1504 (7)
C(31)	0.4727 (8)	−0.0648 (8)	0.1347 (5)
C(32)	0.5681 (8)	−0.0223 (9)	0.1287 (6)
C(33)	0.6606 (9)	−0.0611 (11)	0.1471 (7)
C(34)	0.6568 (10)	−0.1453 (11)	0.1725 (7)
C(35)	0.5618 (10)	−0.1887 (9)	0.1811 (7)
C(36)	0.4686 (10)	−0.1444 (9)	0.1627 (6)

The corresponding determination of the structure of $IIn(CH_2I)_2{\cdot}2tmen$, or $\{IIn[CH_2N(CH_3)_2C_2H_4N(CH_3)_2]_2\}(I)_2$ (3), was carried out at the University of Windsor on a four-circle Syntex $P2_1$ diffractometer with monochromatized Mo Kα radiation. Machine parameters, crystal data, and data collection parameters are summarized in Table III. The initial orientation was obtained from 15 machine-centered reflections selected from rotation photographs, and subsequently 30 strong reflections in the range 15° < 2θ < 30° were used to obtain the final lattice parameters and the orientation matrices. The observed extinctions were consistent with the space group $P2_1/c$. Three standard reflections

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Table V. Interatomic Distances (Å) and Angles (deg) for $Br_3InCH_2P(C_6H_5)_3$ (1)

In–Br(1)	2.514 (2)	C(15)–C(16)	1.42 (2)
In–Br(2)	2.510 (2)	C(21)–C(22)	1.39 (2)
In–Br(3)	2.511 (2)	C(21)–C(26)	1.41 (2)
In–C(1)	2.18 (1)	C(22)–C(23)	1.40 (2)
P(1)–C(1)	1.79 (1)	C(23)–C(24)	1.40 (2)
P(1)–C(11)	1.80 (1)	C(24)–C(25)	1.36 (3)
P(1)–C(21)	1.81 (1)	C(25)–C(26)	1.41 (2)
P(1)–C(31)	1.78 (1)	C(31)–C(32)	1.40 (2)
C(11)–C(12)	1.41 (2)	C(31)–C(36)	1.39 (2)
C(11)–C(16)	1.40 (2)	C(32)–C(33)	1.39 (2)
C(12)–C(13)	1.41 (2)	C(33)–C(34)	1.43 (2)
C(13)–C(14)	1.41 (2)	C(34)–C(35)	1.41 (2)
C(14)–C(15)	1.40 (2)	C(35)–C(36)	1.44 (2)
Br(1)–In–Br(2)	104.36 (6)	C(14)–C(15)–C(16)	120 (1)
Br(1)–In–Br(3)	110.63 (6)	C(11)–C(16)–C(15)	119 (1)
Br(1)–In–C(1)	107.8 (3)	P(1)–C(21)–C(22)	121 (1)
Br(2)–In–Br(3)	105.40 (6)	P(1)–C(21)–C(26)	118 (1)
Br(2)–In–C(1)	119.7 (3)	C(22)–C(21)–C(26)	122 (1)
Br(3)–In–C(1)	108.8 (3)	C(21)–C(22)–C(23)	119 (1)
C(1)–P(1)–C(11)	109.4 (5)	C(22)–C(23)–C(24)	118 (1)
C(1)–P(1)–C(21)	109.6 (5)	C(23)–C(24)–C(25)	123 (1)
C(1)–P(1)–C(31)	111.3 (5)	C(24)–C(25)–C(26)	119 (1)
C(11)–P(1)–C(21)	109.7 (6)	C(21)–C(26)–C(25)	118 (1)
C(11)–P(1)–C(31)	109.1 (6)	P(1)–C(31)–C(32)	121 (1)
C(21)–P(1)–C(31)	107.7 (6)	P(1)–C(31)–C(36)	118 (1)
In–C(1)–P(1)	118.9 (6)	C(32)–C(31)–C(36)	120 (1)
P(1)–C(11)–C(12)	120.1 (9)	C(31)–C(32)–C(33)	121 (1)
P(1)–C(11)–C(16)	118.2 (9)	C(32)–C(33)–C(34)	119 (1)
C(12)–C(11)–C(16)	122 (1)	C(33)–C(34)–C(35)	122 (1)
C(11)–C(12)–C(13)	119 (1)	C(34)–C(35)–C(36)	117 (1)
C(12)–C(13)–C(14)	120 (1)	C(31)–C(36)–C(35)	121 (1)
C(13)–C(14)–C(15)	120 (1)		

Table VI. Final Atomic Coordinates for Non-Hydrogen Atoms of $Br_3\overline{InCH_2N(CH_3)_2C_2H_4N}(CH_3)_2$ (2)

atom	x	y	z
In	−0.12173 (4)	−0.07757 (8)	0.50000
Br(1)	0.0030 (1)	0.1832 (1)	0.5187 (1)
Br(2)	−0.1081 (1)	−0.0691 (2)	0.3022 (1)
Br(3)	−0.2647 (1)	0.0874 (2)	0.5701 (1)
N(1)	−0.2278 (6)	−0.3373 (11)	0.4762 (5)
N(2)	−0.0928 (6)	−0.3524 (10)	0.6868 (6)
C(1)	−0.2500 (7)	−0.4036 (13)	0.5847 (8)
C(2)	−0.1658 (8)	−0.4813 (14)	0.6439 (8)
C(3)	−0.0403 (7)	−0.2528 (15)	0.6033 (7)
C(11)	−0.1793 (8)	−0.4733 (14)	0.4122 (9)
C(12)	−0.3188 (7)	−0.2911 (15)	0.4243 (8)
C(21)	−0.0204 (9)	−0.4611 (17)	0.7470 (9)
C(22)	−0.1384 (10)	−0.2255 (17)	0.7614 (8)

Table VII. Interatomic Distances (Å) and Angles (deg) for $Br_3\overline{InCH_2N(CH_3)_2C_2H_4N}(CH_3)_2$ (2)

In–Br(1)	2.661 (1)	N(1)–C(12)	1.49 (1)
In–Br(2)	2.566 (1)	N(2)–C(2)	1.53 (1)
In–Br(3)	2.539 (1)	N(2)–C(3)	1.51 (1)
In–N(1)	2.450 (8)	N(2)–C(21)	1.53 (1)
In–C(3)	2.21 (1)	N(2)–C(22)	1.51 (1)
N(1)–C(1)	1.52 (1)	C(1)–C(2)	1.53 (1)
N(1)–C(11)	1.49 (1)		
Br(1)–In–Br(2)	91.28 (4)	N(1)–In–C(3)	84.7 (3)
Br(1)–In–Br(3)	97.00 (4)	In–N(1)–C(1)	105.7 (5)
Br(1)–In–N(1)	175.2 (2)	In–N(1)–C(11)	110.1 (6)
Br(1)–In–C(3)	93.0 (3)	In–N(1)–C(12)	112.5 (6)
Br(2)–In–Br(3)	113.7 (1)	C(1)–N(1)–C(11)	112.1 (8)
Br(2)–In–N(1)	86.7 (2)	C(1)–N(1)–C(12)	108.5 (7)
Br(2)–In–C(3)	125.4 (3)	C(11)–N(1)–C(12)	108.0 (8)
Br(3)–In–N(1)	87.8 (2)	C(2)–N(2)–C(3)	113.0 (7)
Br(3)–In–C(3)	119.7 (3)	C(2)–N(2)–C(21)	106.6 (8)
N(1)–C(1)–C(2)	115.5 (8)	C(2)–N(2)–C(22)	111.0 (8)
N(2)–C(2)–C(1)	117.1 (8)	C(3)–N(2)–C(21)	108.0 (8)
In–C(3)–N(2)	118.8 (6)	C(3)–N(2)–C(22)	110.1 (8)
		C(21)–N(2)–C(22)	107.8 (8)

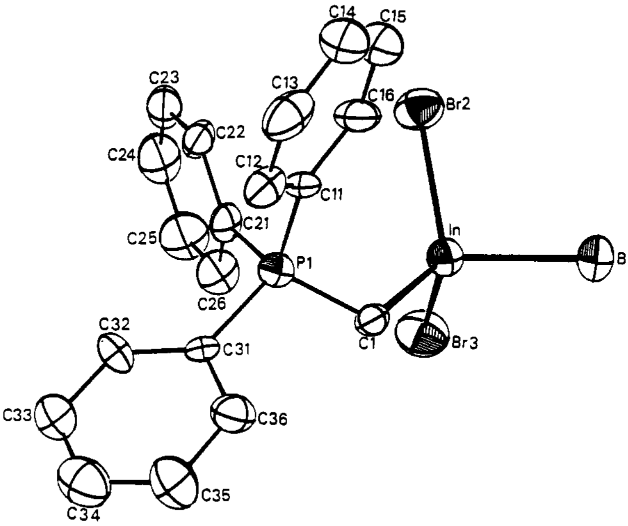

Figure 1. Molecular structure of 1 (ORTEP diagram) with atoms shown as 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

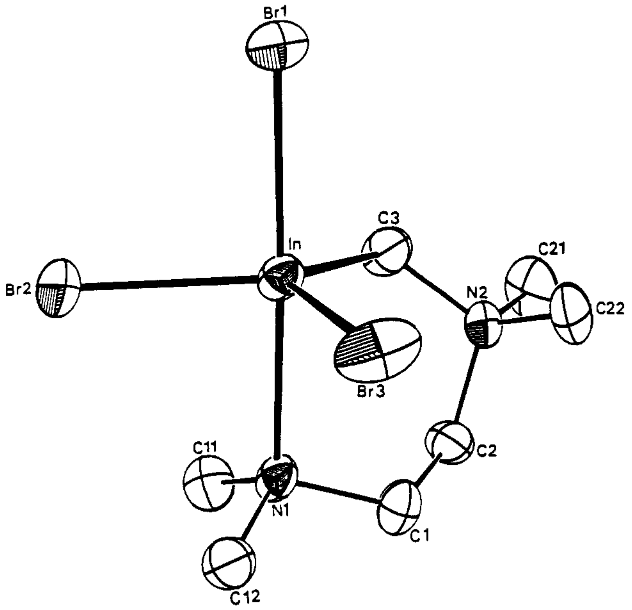

Figure 2. Molecular structure of 2. Conditions are as in Figure 1.

for each reflection were recorded regularly throughout data collection. No significant decay was observed. The data were processed (SHELX-76)[13] on the computing facilities at the University of Windsor. Non-hydrogen atomic scattering factors were taken from the literature.[12] Initial positions for In and I atoms were obtained by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinements were carried out by using full-matrix least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$. In the final cycles of refinement, all non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were allowed to ride on the appropriate bonded carbon, assuming r(C–H) = 0.95 Å, and temperature factors were fixed at 1.10 times the thermal parameter of the carbon atom. Table VIII gives the atomic coordinates for 3, interatomic distances and angles are in Table IX, and Figure 3 shows the molecular structure.

For 1–3, tables of anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates and isotropic thermal parameters, and observed and calculated structure factors are available as supplementary material.

Results

Electrochemical Synthesis. The oxidation of an indium anode in the presence of CH_2X_2 (X = Cl, Br, I)

Table VIII. Final Atomic Coordinates for Non-Hydrogen Atoms of $\{IIn[CH_2N(CH_3)_2C_2H_4N(CH_3)_2]_2\}(I)_2$ (3)

atom	x	y	z
I(1)	0.1747 (1)	0.8166 (1)	0.0321 (1)
I(2)	0.2292 (1)	−0.3699 (1)	0.9040 (1)
I(3)	0.4305 (1)	−0.1143 (1)	0.8476 (1)
In	0.2522 (1)	0.0019 (1)	0.7445 (1)
N(1)	0.4015 (7)	0.0731 (5)	0.6206 (5)
N(2)	0.3871 (8)	0.1387 (5)	0.8127 (5)
N(3)	0.1120 (7)	−0.1221 (5)	0.6692 (5)
N(4)	0.0343 (7)	−0.0242 (5)	0.8271 (5)
C(1)	0.1057 (9)	0.0458 (6)	0.7945 (6)
C(2)	0.2755 (9)	0.0492 (7)	0.6216 (6)
C(11)	0.4835 (10)	−0.0109 (7)	0.6400 (8)
C(12)	0.3888 (11)	0.1035 (7)	0.5278 (8)
C(13)	0.4594 (11)	0.1511 (7)	0.6810 (7)
C(14)	0.4935 (10)	0.1396 (8)	0.7787 (8)
C(15)	0.4409 (12)	0.1329 (8)	0.9089 (7)
C(16)	0.3116 (11)	0.2231 (7)	0.7908 (8)
C(21)	0.1195 (10)	−0.0674 (7)	0.9095 (6)
C(22)	−0.0650 (10)	0.0243 (8)	0.8513 (8)
C(23)	−0.0300 (10)	−0.0920 (7)	0.7597 (7)
C(24)	0.0502 (10)	−0.1588 (7)	0.7287 (7)
C(25)	0.1776 (10)	−0.2008 (7)	0.6436 (7)
C(26)	0.0208 (9)	−0.0833 (7)	0.5880 (6)

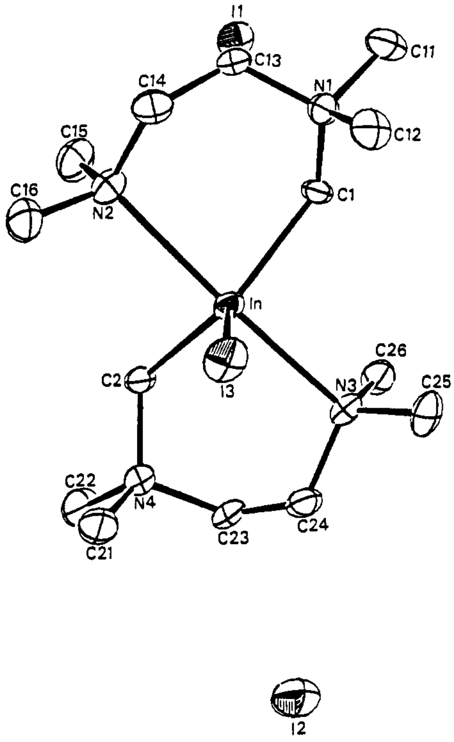

Figure 3. Molecular structure of 3. Conditions are as in Figure 1.

clearly produces InX, and the simplest stoichiometry is then

cathode:

$$CH_2X_2 + 2e \rightarrow CH_2 + 2X^- \tag{1}$$

anode:

$$2X^- + 2In \rightarrow 2InX + 2e \tag{2}$$

An analogous pathway in which eq 1 is replaced by

$$CH_2X_2 + e \rightarrow CH_2X + X^- \tag{3}$$

is also possible, but we have not investigated the nature of the cathode processes. The anodic oxidation has an electrochemical efficiency (defined as moles of indium dissolved/faraday of charge) of 1.02 ± 0.01 mol F^{-1}, which is obviously compatible with eq 2.

Table IX. Interatomic Distances (Å) and Angles (deg) for $\{IIn[CH_2N(CH_3)_2C_2H_4N(CH_3)_2]_2\}(I)_2$ (3)

In–I(3)	2.730 (1)	In–C(2)	2.193 (9)
In–C(1)	2.187 (9)	In–N(3)	2.445 (9)
In–N(2)	2.533 (8)	N(4)–C(2)	1.50 (1)
N(1)–C(1)	1.48 (1)	N(4)–C(21)	1.50 (1)
N(1)–C(11)	1.48 (1)	N(4)–C(22)	1.53 (1)
N(1)–C(12)	1.54 (1)	N(4)–C(23)	1.47 (1)
N(1)–C(13)	1.52 (1)	C(23)–C(24)	1.51 (2)
C(13)–C(14)	1.49 (2)	N(3)–C(24)	1.48 (1)
N(2)–C(14)	1.51 (1)	N(3)–C(25)	1.51 (1)
N(2)–C(15)	1.46 (1)	N(3)–C(26)	1.45 (1)
N(2)–C(16)	1.46 (1)		
I(3)–In–C(1)	116.4 (3)	I(3)–In–C(2)	117.1 (3)
I(3)–In–N(2)	90.4 (2)	I(3)–In–N(3)	93.8 (2)
C(1)–In–N(2)	84.5 (3)	C(2)–In–N(3)	87.2 (3)
C(1)–In–N(3)	92.4 (3)	C(2)–In–N(2)	92.2 (3)
N(2)–In–C(2)	92.2 (3)	N(3)–In–C(1)	92.4 (3)
In–C(1)–N(1)	120.2 (7)	In–C(2)–N(4)	120.7 (6)
N(2)–In–N(3)	175.4 (4)	C(2)–In–C(1)	125.8 (6)
C(1)–N(1)–C(11)	110.1 (8)	C(2)–N(4)–C(21)	109.9 (8)
C(1)–N(1)–C(12)	108.5 (8)	C(2)–N(4)–C(22)	107.8 (8)
C(1)–N(1)–C(13)	112.8 (8)	C(2)–N(4)–C(23)	113.5 (7)
C(11)–N(1)–C(12)	106.2 (8)	C(21)–N(4)–C(22)	108.2 (8)
C(11)–N(1)–C(13)	111.9 (8)	C(21)–N(4)–C(23)	113.5 (7)
C(12)–N(1)–C(13)	107.0 (8)	C(22)–N(4)–C(23)	106.9 (8)
N(1)–C(13)–C(14)	119.4 (9)	N(4)–C(23)–C(24)	118.3 (9)
C(13)–C(14)–N(2)	116.0 (9)	C(23)–C(24)–N(3)	117.7 (9)
C(14)–N(2)–C(15)	105.7 (9)	C(24)–N(3)–C(25)	107.5 (8)
C(14)–N(2)–C(16)	113.1 (9)	C(24)–N(3)–C(26)	112.2 (8)
C(14)–N(2)–In	107.3 (6)	C(24)–N(3)–In	108.0 (6)
C(15)–N(2)–C(16)	108.8 (9)	C(25)–N(3)–C(26)	108.4 (8)
C(15)–N(2)–In	112.7 (7)	C(25)–N(3)–In	113.2 (6)
C(16)–N(2)–In	109.3 (7)	C(26)–N(3)–In	107.6 (6)

Indium(I) chloride prepared in this way disproportionates rapidly, even at low temperatures, giving In^0 and $InCl_3$, in keeping with earlier studies of this compound.[14] The monobromide slowly dissolves in the cell solution to give a clear solution from which the compound $Br_2InCH_2Br\cdot 0.5Et_2O$ was subsequently recovered, and this dissolution process therefore represents the oxidative insertion of InBr into the C–Br bond of CH_2Br_2. A similar reaction has been reported briefly in a previous paper,[10] and such oxidative reactions have now been identified for a number of M–X and M–M systems.[14-17]

The reaction between freshly prepared InI and CH_2I_2 is more complicated. The solution that is formed as InI dissolves in the CH_2I_2/CH_3CN mixture yields the solid insertion product $I_2InCH_2I\cdot CH_3CN$ on removal of the volatile components, and this oxidative insertion into the C–I bond is in keeping with a number of earlier studies of similar reactions.[18-22] The ^1H NMR spectrum of $I_2InCH_2I\cdot CH_3CN$ in $(CD_3)_2SO$ shows two resonances in the $InCH_2$ region (see Table X), and this is attributed to the establishment in solution of the equilibrium

$$2I_2InCH_2I \rightleftarrows InI_3 + IIn(CH_2I)_2 \tag{4}$$

The isolation of tmen adducts of each of these iodo-

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Table X. ^1H and ^{13}C NMR Spectra of X_2InCH_2X Compounds and Their Derivatives in CD_2Cl_2

compd	$^1H^a$	$^{13}C^a$	assgnt
CH_2Br_2	5.0, s	20.3	
CH_2I_2	3.84, s^b	−62.5	
$Br_2InCH_2Br{\cdot}{}^1/_2Et_2O$	4.06, q (2)	68.7	OCH_2CH_3
	3.07, s (2)	17.6, br	$InCH_2Br$
	1.39, t (3)	14.9	OCH_2CH_3
$I_2InCH_2I{\cdot}CH_3CN^c$	2.05, s (3)	1.7	CH_3CN
	1.67, s 1.77, s } (2)	−8.3, br	$InCH_2I$
		118.1	CH_3CN
$(C_2H_5)_4N[Br_3InCH_2Br]$	3.25, q (4)	53.3	NCH_2CH_3
	2.75, s (1)	18.3, br	$InCH_2Br$
	1.35, t (6)	8.2	NCH_2CH_3
$Br_2InCH_2Br{\cdot}P(C_6H_5)_3$	7.7, m (15)	134.5	C(para)
		133.0, 132.9	C(meta)
		130.2, 130.0	C(ortho)
		122.8, 121.6	C–P
	2.3, s (2)	10.2	$InCH_2$
$I_2InCH_2I{\cdot}P(C_6H_5)_3{}^d$	7.7, m (15)	136.0	C(para)
		133.4	C(meta)
		131.1	C(ortho)
		119.2, 118.0	C–P
	2.3, s (2)	11.4, 10.6	$In{-}CH_2$
$Br_2InCH_2Br{\cdot}tmen^e$	3.90, br (1)	66.5	$^+NCH_2CH_2N$
	3.71, br (1)	62.6	$^+NCH_2CH_2N$
	3.31, s (3)	56.9	$^+N(CH_3)_2$
	3.07, s (1)	52.1	$^+NCH_2In$
	2.98, s (3)	45.1	$N(CH_3)_2$
$IIn(CH_2I)_2{\cdot}2tmen^e$	3.66, br (1)	62.5	$^+NCH_2CH_2N$
	3.40, s (3)	58.6, br	$^+N(CH_3)_2$
	3.31, s (1)	54.8	$^+NCH_2In$
	3.14, br (1)	59.8, br	$^+NCH_2CH_2N$
	2.58, s (3)	45.9	$N(CH_3)_2$

[a] In ppm from $\delta(Me_4Si) = 0$; s = singlet, t = triplet, q = quartet, m = multiplet, br = broad. Numbers in parentheses show relative integrated intensities. [b] In CD_3CN. [c] In $(CD_3)_2SO$. [d] See text (Experimental Section). [e] In D_2O.

methylene derivatives (see below) is in keeping with these results, and the problems reported in the Experimental Section in isolating an analytically pure product from the reaction of "I_2InCH_2I" with triphenylphosphine presumably arise from this redistribution reaction. Such reactions are a common feature of the solution chemistry of indium(III) compounds.

Adduct Formation. The addition of halide anion X^- (as the tetraethylammonium salt) to a freshly prepared solution of X_2InCH_2X (obtained by the electrolysis of indium in CH_2X_2) yielded the corresponding salts of $[X_3InCH_2X]^-$ in yields of ca. 80%. The molar conductivities of these compounds (Table XI) show them to be 1:1 electrolytes in acetonitrile, and their ^1H and ^{13}C NMR spectra (Table X) are in good agreement with the postulated structure. In addition, a single-crystal X-ray diffraction study of the iodide derivative unquestionably identified the $[I_3InCH_2I]^-$ anion, although we were not able to refine the structure completely due to severe problems of disorder in the tetraethylammonium cation.

With the neutral ligands triphenylphosphine and tmen, the addition reaction leads to products that are formally 1:1 or 1:2 adducts. These products have been shown in three cases discussed below to the ylid derivatives, rather than the conventional adducts formed by indium(III) halides or organometallic halides, and it seems reasonable to conclude that this is a general reaction of X_2InCH_2X compounds with such ligands. The spectroscopic properties of these derivatives are discussed below.

Crystallographic Results. The structure of $Br_3InCH_2P(C_6H_5)_3$ (Figure 1) shows clearly that this molecule involves four-coordinate indium(III) and a phosphonium ylid ligand. The stereochemistry at both indium and phosphorus is slightly distorted tetrahedral in each case (sum of all angles at In is 656.7° and at P is 656.8°). The angle P–C(1)–In (118.9 (6)°) is obviously greater than the ideal value for an sp^3 carbon atom, but this is presumably due to the steric interaction between Br(2) and the phenyl groups of $P(C_6H_5)_3$. The In–Br bond distances are slightly greater than those in $InBr_4^-$,[23] for which In–Br = 2.479 (2) Å, and the In–C distance (2.18 (1) Å) is close to those in other tetrahedral species such as $CH_3InCl_3^-$ (2.19 (2) Å)[24] and $C_2H_5InI_3^-$ (2.213 (9) Å).[25]

Table XI. Molar Conductivities of X_2InCH_2X Derivatives^a

compd	molar conductivity, Ω^{-1} cm^2 mol^{-1}	compd	molar conductivity, Ω^{-1} cm^2 mol^{-1}
$Et_4N[Br_3InCH_2Br]$	152	$Br_2InCH_2Br{\cdot}tmen$	20.6
$Et_4N[I_3InCH_2I]$	157	$I_2InCH_2I{\cdot}tmen$	20.0
$Br_2InCH_2Br{\cdot}PPh_3$	15.6	$IIn(CH_2I)_2{\cdot}2tmen$	230
$I_2InCH_2I{\cdot}PPh_3$	88.9		

[a] All the measurements were done in CH_3CN solutions with concentrations ca. 1 mmol dm^{-3}. Standard value for 1:1 electrolytes in CH_3CN 120–160 Ω^{-1} cm^2 mol^{-1} and for 2:1 electrolytes 220–300 Ω^{-1} cm^2 mol^{-1} (Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81).

The compound formed in the reaction of tmen with Br_2InCH_2Br has been shown to be a five-coordinate species in which the bidentate donor is coordinated to the metal through only one nitrogen atom, the other having quarternized to give an $In{-}CH_2{-}NMe_2$ linkage (Figure 2). The bond lengths in the $InCNBr_3$ kernel, which has essentially pentagonal-bipyramidal stereochemistry, are again compatible with earlier results. The values for $C_2H_5InBr_2{\cdot}tmen$[25] are In–C = 2.17 (1) Å, In–Br = 2.531 (2) Å (eq) and 2.688 (2) Å (apic), and In–N = 2.30 (1) Å (eq) and 2.49 (1) Å (apic), and here, as in **2**, there is a marked difference between equatorial and apical In–Br distances.

Finally, the reaction between I_2InCH_2I and tmen yields a species in which two quaternized tmen molecules are coordinated to the indium(III) center of a five-coordinate cation (Figure 3). The InC_2N_2I kernel is again a distorted trigonal bipyramid with an equatorial InC_2I plane. The bond lengths for In–C and In–N are similar to those in **2**, and *r*(In–I) (2.730 (1) Å) to close to that for the equatorial In–I bond of $C_2H_5InI_2{\cdot}tmen$ (2.750 (1) Å).[25] The appropriate C–C and C–N bond distances and angles in both **2** and **3** are all similar to each other, and to those in $C_2H_5InX_2{\cdot}tmen$ (X = Br, I),[25] and in particular, N–C(In) is not significantly different in length from other N–C bonds.

Spectroscopic Results. Table X shows the ^1H and ^{13}C NMR spectra of the compounds prepared in this work. We first note significant changes between CH_2X_2 and both the solvated neutral X_2InCH_2X compounds and the anionic $X_3InCH_2X^-$ derivatives, corresponding in each case to increased shielding of the protons relative to CH_2X_2. In the case of I_2InCH_2I, the presence of two ^1H resonances in this region is probably due to the establishment of equilibrium 4 in dimethyl sulfoxide solution. The ^{13}C spectra of these compounds were difficult to detect, due to the breadth of the resonance signal, and it was necessary to use an unusually large line-sharpening parameter in recording the spectra. This is no double due to the presence of neigh-

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boring atoms with high nuclear spin (^{115}In, $I = {}^{9}/_{2}$; $^{79,81}Br$, $I = {}^{3}/_{2}$; ^{127}I, $I = {}^{5}/_{2}$).

The NMR spectra of the two triphenylphosphine derivatives confirm the structural identity of these two compounds as $InCH_2PPh_3$ species, although it should again be noted that this only applies to the solution phase, since the iodo compound was not isolated as a pure solid. With the tmen derivatives 2 and 3, there are substantial downfield shifts in the In–CH_2 resonance frequency, relative to X_2InCH_2X, and some interesting changes in the tmen region of the spectrum. Previous work on the tmen adducts of $C_2H_5InX_2$[25] or $X_2InCH_2InX_2$[10] showed that in such compounds the methylene groups are equivalent, as are the N–CH_3 sites, with ^1H resonances at ca. 2.8 and 2.6 ppm, respectively; the corresponding ^{13}C values are ca. 57 and 48 ppm. In the present cases, both methylene and methyl regions of tmen each show two sets of resonances in both ^1H and ^{13}H spectra, corresponding to N and N^+ sites. The signals are appreciably shifted downfield and correspond to those of α- and β-methylene groups and methyl groups of a quaternary nitrogen atom.[26] These results are in keeping with the crystal structure results, which show that this quaternization has indeed occurred at one nitrogen of tmen in each case.

Discussion

Synthetic Aspects. The electrochemical oxidation of indium metal in CH_2X_2/CH_3CN mixtures provides a simple route to X_2InCH_2X compounds in the cases of X = Br or I. The inherent instability of InCl under the experimental conditions clearly bars any study of the corresponding behavior of Cl_2InCH_2Cl by similar techniques. The reaction of InX with CH_2X_2 (X = Cl, Br) was briefly studied in earlier work,[10] and for X = Cl disproportionation to In and $InCl_3$ was again significant at temperatures above -80 °C. In that work, a 1:3 adduct of Br_2InCH_2Br and Me_2SO was isolated, presumably analogous to the etherate found in the present investigations.

The initial reaction corresponds to the oxidative addition of InX to one C–X bond of CH_2X_2, and the subsequent formation of anionic $X_3InCH_2X^-$ derivatives and the redistribution reaction (eq 4) are typical features of indium(III) chemistry in nonaqueous media. On the other hand, the derivatives formed by reaction with either triphenylphosphine or tmen are clearly ylidic rather than the coordinated adducts identified for such donors and indium(III) halides[27] or organometallic[28] compounds. These unusual compounds are interesting both in their own right and in terms of the reactions by which they are produced. Phosphonium ylid derivatives of transition metals are well-known,[29] but the small number of main group analogues that have been structurally characterized include $[Li(CH_2)PPh_3(CH_2)]_2$,[30] $Me_3PCH_2BH_3$,[31] $[Me_2AlCH_2PMe_2]_2$ and related compounds,[32,33] the metallocycle $Me_2Ga(CH_2PMe_2)_2CH$,[34] and two tin(IV) compounds.[35,36] The present results therefore add a mononuclear indium(III) species to this list of complexes in which a phosphonium ylid functions as a ligand. Earlier studies of the synthesis of phosphonium ylid derivatives of gallium, indium, and thallium were reported by Schmidbaur et al.[37,38] In a related investigation, Yamamoto[39] studied the reaction of $(C_6H_5)_3PCH_2$ with a number of main group halides, including $InCl_3$, and reported the formation of $Cl_3In[CH_2P(C_6H_5)_3]_2$, which was formulated as a dimer with a 4+ cation $\{[(C_6H_5)_3PCH_2]_2InCl_2In[CH_2P(C_6H_5)_3]_2\}^{4+}$. This unusual formulation is based on the ^1H NMR spectrum, which identifies the presence of the ylid ligand, and on the conductivity in nonaqueous solution. The details of these latter measurements are unfortunately not given, but in any case Table XI demonstrates that the molar conductivity is sometimes a poor guide to solid-state structure, since compounds that are unambiguously nonionic in the solid state may give measurable conductivities. Similar behavior has been demonstrated for neutral adducts of indium trihalides[40] and can be explained by rearrangement reactions that give rise, inter alia, to ionic species such as

$$X_3InCH_2PPh_3 \rightleftarrows X^- + X_2InCH_2PPh_3^+ \qquad (5)$$

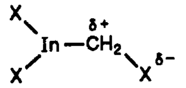
or

$$X_3In(CH_2PPh_3)_2 \rightleftarrows X^- + [X_2In(CH_2PPh_3)_2]^+ \qquad (6)$$

Table XI shows that for $I_3InCH_2P(C_6H_5)_3$, the molar conductivity is approximately 50% of that found for 1:1 electrolytes. In the light of these results, it seems reasonable to conclude that the crystalline compound prepared by Yamamoto is probably a five-coordinate mononuclear neutral species rather than the dimer originally proposed.

The ylid derivatives 2 and 3 appear to have no previous analogue in the chemistry of group III but provide examples of five-coordinate indium(III) complexes, an increasing number of which are now known.

Spectroscopy and Reaction Pathway. The results of the structural analyses imply that the reaction of X_2InCH_2X with the neutral donor Ph_3P involves nucleophilic attack at the CH_2 site rather than at the metal atom. Similarly with tmen, the basic nitrogen atoms bond both to CH_2 and the metal, even to the extent of replacing halide ligand at the metal. The simplest structure of X_2InCH_2X could be written as



in which the CH_2 group is electron-poor, in contrast to the electron-rich character found in methylene derivatives of transition metals.[35] This difference is nicely illustrated by the NMR results. The ^1H resonances of X_2InCH_2X and $X_3InCH_2X^-$ are in the 1.35–1.77 ppm region, and the ^{13}C spectra show corresponding absorptions at ca. 18 ppm (X = Br) or −(8–17) ppm (X = I), values that are in marked contrast to those reported for $M{=}CR_2$ or $M{-}CH_2{-}M$ derivatives of transition metals.[41] The spectra of the

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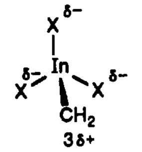
triphenylphosphonium or tmen derivatives show that ylid formation results in only a slight deshielding of the CH_2 protons relative to those in X_2InCH_2X, so that there is clearly little change in the electron density at the CH_2 site on ylid formation.

The structural results show that ylid formation is accompanied (or followed) by halide transfer, so that, whatever the ground state, the products are in fact derivatives of the formal structure



The synthetic consequences of the electronic structures and reactivities of these X_2InCH_2X species will be discussed elsewhere.

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Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic temperature factors (5 pages); tables of calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

Synthesis and Fluxional Behavior of Protonated 1,3-Diene Complexes of Ruthenium(0), Osmium(0), Rhodium(I), and Iridium(I) Containing 2,3-Dimethylene-5,6,7,8-dibenzobicyclo[2.2.2]octane (ddbo, $C_{18}H_{14}$). Single-Crystal X-ray Study of the Agostic Complex $[Ru(C_{18}H_{15})(\eta\text{-}C_6H_3Me_3)]PF_6$

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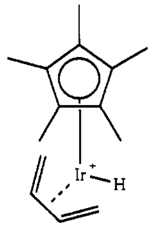
The 1,3-diene 2,3-dimethylene-5,6,7,8-dibenzobicyclo[2.2.2] octane (ddbo, $C_{18}H_{14}$, **6**) forms complexes $Ir(\eta\text{-}C_5H_5)(C_{18}H_{14})$ (**7**), $M(\eta\text{-}C_5Me_5)(C_{18}H_{14})$ [M = Rh (**8**), Ir (**9**)], and $M(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(C_{18}H_{14})$ [M = Ru (**10**), Os (**11**)], which react with aqueous HPF_6 or triflic acid to give fluxional monoprotonated cations $[Ir(\eta\text{-}C_5H_5)(C_{18}H_{15})]^+$ (**14**), $[Rh(\eta\text{-}C_5Me_5)(C_{18}H_{15})]^+$ (**12**), $[Ru(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]^+$ (**13**), and $[Os(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})]^+$ (**15**). Crystals of **13·PF$_6$** are orthorhombic, space group $P2_12_12_1$, with a = 14.243 (2) Å, b = 13.554 (2) Å, c = 12.894 (2) Å, and Z = 4. The structure was solved by heavy-atom methods and refined by least-squares analysis to R = 0.034 and R_w = 0.043 for 2020 unique observed reflections. The $C_{18}H_{15}$ moiety is bound to a (η^6-mesitylene)ruthenium unit through a η^3-enyl linkage [Ru–C(1) = 2.180 (8) Å, Ru–C(2) = 2.196 (7) Å, Ru–C(17) = 2.148 (7) Å] and a two-electron, three-center interaction Ru–H(18C)–C(18) to the terminal methyl group of the butenyl moiety [Ru–C(18) = 2.357 (9) Å, C(18)–H(18C) = 0.98 (8) Å, Ru–H(18C) = 1.81 (8) Å, ∠C(17)–C(18)–H(18C) = 108 (5)°, ∠C(18)–H(18C)–Ru = 112 (6)°]. The NMR (^1H, ^{13}C) spectra of the rhodium complex **12** at −60 °C are consistent with a similar ground-state agostic η^3-methallyl structure, but unexpectedly, the ^1H NMR spectrum of **13** at −100 °C resembles that expected for a hydrido (1,3-diene) structure. It is suggested that in **13** reversible C–H bond cleavage occurs more easily than M–H bond cleavage, whereas **12** shows the more usual reverse behavior. The NMR and IR spectra of **14** show this complex to have a hydrido 1,3-diene structure; the same is probably true for **15**, although a η^3-methallyl structure with a strong agostic interaction cannot be excluded. Treatment of **13** and **15** with *tert*-butyl isocyanide causes irreversible hydride transfer to ddbo, giving $[M(\eta\text{-}C_6H_3Me_3)(C_{18}H_{15})(CN\text{-}t\text{-}Bu)]PF_6$ [M = Ru (**17**), Os (**16**)].

It has been shown[1] that protonation of 1,3-diene complexes of the type $Ir(\eta\text{-}C_5Me_5)$(diene) and $Os(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)$(diene) (diene = 1,3-cyclohexadiene or 2,3-dimethylbutadiene) with strong acids containing poorly coordinating anions gives cationic hydrido diene complexes **1** and **2**. These are fluxional only above room temperature owing to reversible migration of the hydride ligand between the metal atom and the diene. Similar protonation of the rhodium(I) complexes $Rh(\eta\text{-}C_5Me_5)$(1,3-diene) gives highly fluxional species whose ^1H and ^{13}C NMR spectra at low temperature are consistent with an agostic structure **3** similar to those established by single-crystal X-ray and



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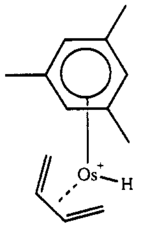

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