

Coordination Compounds of Indium. Part XXX. Pyrrole Complexes of Indium(III) and Dimethylindium(III)

HENRY L. CHUNG AND DENNIS G. TUCK

Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4

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Preparative and spectroscopic studies show that the interaction of 2-formylpyrrole, $C_4H_4N\cdot CHO$, and 2-acetylpyrrole, $C_4H_4N\cdot COCH_3$ ($=HL$), with $In(III)$ may involve the organic base as either a bidentate organic anion ligand to give InL_3 complexes, ($L = 2$ -acetylpyrrolate only) or as a neutral monodentate species to form $InCl_3\cdot 3HL$. The spectroscopic and kinetic properties of the organometallic derivatives Me_2InL are also discussed. The polarographic reduction of InL_3 ($L = 2$ -acetylpyrrole anion) involves three one-electron reduction steps.

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Des études de préparation et de spectroscopie permettent de montrer que l'interaction du formyl-2 pyrrole, C_4H_4NCHO , et de l'acétyl-2 pyrrole, $C_4H_4N\cdot COCH_3$ ($=HL$), avec $In(III)$ peut impliquer la base organique soit sous forme de ligand organique anionique bidentate conduisant à des complexes InL_3 , ($L =$ seulement l'acétyl-2 pyrrolate) ou sous forme d'espèces monodentates neutres amenant la formation de $InCl_3\cdot 3HL$. On discute aussi des propriétés spectroscopiques et cinétiques des dérivés organométalliques Me_2InL . La réduction polarographique de InL_3 ($L =$ anion acétyl-2 pyrrole) implique trois transferts d'un électron.

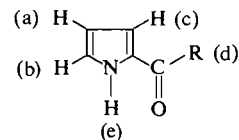
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Introduction

One of the interesting features of complexes of indium(III) with bidentate ligands is that polarographic reduction in nonaqueous solvents may take place via three one-electron steps, in contrast to the single three-electron reduction observed for simple $In(III)$ species in aqueous solution. The details of such reduction processes for $In(III)$ -dithiolate and $In(III)$ -diketonate species have been discussed elsewhere (1-3). The original aim of the present work was to prepare complexes of indium(III) with 2-formylpyrrole (**1**; $R = H$) and related compounds in order to investigate the effect of the group R on the reduction to the formally $In(II)$ and $In(I)$ states, but this was not in fact achieved because the synthesis of the InL_3 complexes proved much more difficult than expected. The preparative and spectroscopic work did, however, reveal that pyrrole derivatives may coordinate as either neutral or anionic ligands. We have also prepared the corresponding Me_2InL complexes, examples of an increasing number of dimethylindium(III) derivatives of bidentate organic bases.

Previous work with pyrrole compounds as ligands has been entirely concerned with transition metals. Emmert *et al.* (4) reported the prep-

aration of the copper(II) complex of 2-formylpyrrole; this compound, the cobalt(III) analog, and related compounds with $R = CH_3$, were studied spectroscopically by Perry and Weber (5). Davies and Gogan (6) obtained CrL_3 compounds of various pyrrole ligands, starting with $Cr(CO)_6$, and showed that in these compounds the ligand is bidentate and formally anionic, chelating through basic oxygen and nitrogen atoms. Later work by these authors (7), and others (8), established that pyrroles can also function as π -donors, in which the ligand donates electrons from the C_4H_4N ring. To these two modes of ligation can now be added a third, in which the basic oxygen bonds to the metal ion, with retention of the nitrogen acidic proton, which is involved in intramolecular hydrogen-bonding to a halide ligand also coordinated to the metal ion.



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$R = H$; Hpyr.CHO

$R = CH_3$; Hpyr.COCH₃

TABLE 1. Analytical results for pyrrole derivatives of indium(III)

Compound	Found (%)			Calculated (%)		
	C	H	In	C	H	In
Me ₂ In(pyr·CHO)*	35.1	4.1	48.1	35.2	4.2	48.2
Me ₂ In(pyr·COCH ₃)†	37.2	4.8	45.1	37.9	4.7	45.5
In(pyr·COCH ₃) ₃ ‡	48.0	4.6	26.9	49.2	4.1	26.2
InCl ₃ (Hpyr·CHO) ₃ §	36.0	3.0	22.3	35.5	3.0	22.7
InCl ₃ (Hpyr·COCH ₃) ₃	—	—	21.5	—	—	21.0

*pyr·CHO = 2-formylpyrrole anion.

†pyr·COCH₃ = 2-acetylpyrrole anion.

‡N; found 9.0%, calculated 9.6%.

§Cl; found 21.1%, calculated 21.1%.

||Cl; found 19.1%, calculated 19.5%.

Experimental

General, Materials

Spectroscopic and analytical methods were as described in previous work (1-3). Operations involving organoindium compounds were carried out in a dry oxygen-free glove box.

2-Formylpyrrole was prepared according to the method described by Silverstein *et al.* (9). 2-Acetylpyrrole was obtained by a modification of this method; *N,N*-dimethylacetamide (48 g) was treated with phosphorus oxychloride (85 g); after about 15 min, ethylene dichloride (125 ml) was added to the reaction mixture, followed by 34 g of freshly distilled pyrrole in ethylene dichloride (125 ml). This mixture was refluxed for 20 min, cooled to 25 °C, and aqueous sodium acetate (375 g in 500 ml) added. After refluxing for a further 20 min the organic phase was worked up to give a white crystalline material (m.p. 90 °C) which was sublimed *in vacuo*.

Trimethylindium was prepared by the reaction of indium(III) chloride and methyl lithium.

Preparation of Dimethylindium(III) Derivatives

When equimolar quantities of trimethylindium and 2-formylpyrrole were stirred together in dry ether at room temperature, a white precipitate formed after about 5 min. After 30 min, during which time the solution changed from colorless to yellow, the final precipitate was collected and dried *in vacuo*. The compound (dimethylindium(III)-2-formylpyrrolate) is soluble in acetone, methanol, ethanol, dimethylsulfoxide, chloroform, and hot benzene, but insoluble in ether, petroleum ether, carbon tetrachloride, carbon disulfide, and cyclohexane. The solid material darkened on standing over some weeks in a sealed tube. Analytical results for this and other compounds are given in Table 1. The preparation and properties of dimethylindium(III)-2-acetylpyrrolate were similar to those of the formyl compound.

An adduct of dimethylindium(III)-2-formylpyrrolate was prepared by mixing solutions of this compound and 2,2'-bipyridyl in acetone; addition of cyclohexane produced a yellow solid. We were unable to obtain this material in a form suitable for elemental analysis since attempted crystallization gave only gummy solids, but integration of the n.m.r. spectrum of the dissolved material showed that the bipy:pyrrole:CH₃ proton ratio was 8:4:6, as required for a Me₂In(pyr·CHO)(bipy) compound.

Attempted Preparations of In(pyr·CHO)₃

Via Indium(III) Carbonate

Following the work of Emmert *et al.* (4), a suspension of indium(III) carbonate (prepared from the reaction of indium(III) chloride and sodium carbonate) was refluxed with 2-formylpyrrole in xylene. After about 15 min orange crystals were visible, but these proved to be merely contaminated indium carbonate. After longer refluxing (~10 h), the solution phase was evaporated to yield a purple solid which appeared to be polymer contaminated with pyrrole.

Via Solvent Extraction

Indium(III) chloride was dissolved in water and the pH adjusted to 6; this solution was then refluxed with a chloroform solution of 2-formylpyrrole. Although this method works successfully for In(acac)₃ (10), refluxing over periods from 2 h to 3 days yielded only unchanged pyrrole in the organic phase of the present experiments.

Via Lithium 2-Formylpyrrolate

The lithium derivative of 2-formylpyrrole, prepared by the reaction of the parent compound and methyl lithium suspended in chloroform, was treated with indium chloride in the same solvent. The color of the suspension changed from white through orange to red, but the solution phase did not yield the desired InL₃ compound.

Via InCl₃(Hpyr·CHO)₃

This complex (see below) was treated with triethylamine in the hope of forming Et₃NH·Cl and In(pyr·CHO)₃. Reaction of these materials in acetone produced an immediate white precipitate, insoluble in water, and containing 18.1% Cl (calculated for Et₃NHCl, 25.8% Cl); the n.m.r. spectrum showed the presence of ethyl groups in the solid. The filtrate from this reaction yielded 2-formylpyrrole as the only significant solid.

Via Me₂In(pyr·CHO)

Dimethylindium(III)-2-formylpyrrolate and excess of 2-formylpyrrole in toluene were heated in a sealed tube at 110 °C for 10 min, after which the tube was opened and gaseous products removed by pumping. This cycle was repeated six times. The final solution produced brownish crystals on cooling, or on reduction in volume, but this material again proved to be 2-formylpyrrole, and contained no indium.

Preparation of In(pyr·COCH₃)₃

Dimethylindium(III)-2-acetylpyrrolate and 2-acetylpyrrole (1:3 mole ratio) were heated in benzene in a

sealed tube for 10 min, after which the mixture was degassed *in vacuo*. After repeating this cycle six times, the solution was held at 110 °C for 3 days. The solvent was then pumped off, leaving a yellow residue of $\text{In}(\text{pyr}\cdot\text{COCH}_3)_3$. The mass spectrum of this solid had strong peaks at m/e 115 (In^+), 223 (InL^+), 331 (InL_2^+), and 439 (InL_3^+).

Preparation of $\text{InCl}_3(\text{Hpyr}\cdot\text{CHO})_3$ and $\text{InCl}_3(\text{Hpyr}\cdot\text{COCH}_3)_3$

When ether solutions of $\text{InCl}_3\cdot 3\text{H}_2\text{O}$ and 2-formylpyrrole (1:3 mole ratio) were mixed and stirred at room temperature, a white precipitate began to form after 5 min. After 30 min the solid material was collected, washed, and dried *in vacuo*. This material, $\text{InCl}_3(\text{Hpyr}\cdot\text{CHO})_3$, m.p. 143 °C, is soluble in acetone, ethanol, and dimethylsulfoxide, but insoluble in carbon tetrachloride, benzene, ethylenedichloride, petroleum ether, and carbon disulfide.

The corresponding derivative of 2-acetylpyrrole was prepared by a similar reaction, but the resultant white crystalline solid decomposed very readily on removal of solvent at or below room temperature, so that only indium and chloride analyses were possible, and no spectroscopic results were obtained for this compound. This decomposition, which is not photodependent, involves the loss of a gas identified as hydrogen chloride. In a subsequent experiment, we collected the materials evaporating from the reaction mixture during the final removal of the solvent. No significant material was detected in the first (70 ml) or second (8 ml) fractions, but the final 2 ml contained both H^+ and Cl^- . We return to this point below.

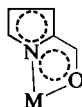
Results and Discussion

Preparative Studies

The present work apparently represents the first attempt to prepare derivatives of pyrrole compounds with main group elements. It is clear that the indium(III) tris(2-formylpyrrolate) complex was not obtained by any of the five methods investigated, despite the fact that the corresponding 2-acetylpyrrole compound is reasonably stable. The reason for the differing behavior of the two compounds is not immediately obvious.

The difficulty in stabilizing indium(III), relative to transition metal species, may reflect extra stabilization in the latter due to delocalization in the metal-ligand ring system. The ready formation of dimethylindium(III) derivatives of both pyrrole anions shows that there can be no steric barrier to the chelation of these ligands to indium(III).

The delocalization has been discussed by



Gogan and Davies (6, 7) in terms of the structure and to the extent that this structure depends upon the metal d_r -orbitals, the low stability of the indium(III) compounds may be due to charge being confined to the pyrrole ring.

In addition to the difficulties experienced in the preparation of neutral InL_3 species with these pyrroles, we have the formation of unusual adducts in which the pyrrole is a protonated monodentate ligand. The spectroscopic evidence on the structure of these compounds is reviewed below.

Nuclear Magnetic Resonance Spectroscopy

The n.m.r. (^1H) spectra of 2-formyl- and 2-acetylpyrrole are given in Table 2; that for the 2-formylpyrrole is in good agreement with published material (11).

The spectrum of 2-formylpyrrole shows little dependence on solvent apart from a slight shift in the broad and readily identifiable N—H proton signal (ϵ). Similarly, substitution of $-\text{CHO}$ by $-\text{COCH}_3$ at the 2-position causes a small downfield shift of ~ 0.40 p.p.m. in the ring proton resonances. The formation of the dimethylindium complexes $\text{Me}_2\text{In}(\text{pyr}\cdot\text{CHO})$ and $\text{Me}_2\text{In}(\text{pyr}\cdot\text{COCH}_3)$ produces a shift of ~ 0.1 p.p.m. in protons a, b, and c, corresponding to a deshielding associated with electron donation from the chelating oxygen atoms to the Me_2In group. Changes of similar magnitude were observed in the formation of γ -pyrone complexes of indium(III) (2).

It was necessary to obtain the spectrum of $\text{In}(\text{pyr}\cdot\text{COCH}_3)_3$ in benzene- d_6 and in consequence a direct comparison with that of $\text{Me}_2\text{In}(\text{pyr}\cdot\text{COCH}_3)$ in acetone- d_6 is not possible. The ring protons appear to be significantly more deshielded in the former (shifts ~ 0.3 p.p.m.), relative to the parent ligand. The compound formed by the direct addition of 2-formylpyrrole to indium(III) chloride shows virtually no shift in the resonance of any of the protons.

As part of the n.m.r. studies, we find that a solution of a mixture of $\text{Me}_2\text{In}(\text{pyr}\cdot\text{CHO})$ and 2-formylpyrrole in acetone- d_6 at 0 °C shows two resonances in the 9.3 p.p.m. region ($-\text{CHO}$). These resonances coalesce at 35 °C, and from this, and the measured frequency difference of 22.2 Hz between ligand and complex at 0 °C, we calculate that the free energy of ligand exchange in this system is $14.8 \text{ kcal mol}^{-1}$. This value is in the same order as that reported previously for

TABLE 2. Nuclear magnetic resonance spectra of pyrrole derivatives of indium(III), (values in p.p.m. from TMS)

Compounds	Solvent	Assignment*					Others
		a	b	c	d	e (all br)	
Hpyr·CHO	CDCl ₃	6.37	7.00	7.16	9.53	10.6	
Hpyr·CHO	DMSO- <i>d</i> ₆	6.09	6.78	7.02	9.31	11.5	
Hpyr·CHO	Acetone- <i>d</i> ₆	6.15	6.83	7.09	9.33	11.2	
Hpyr·COCH ₃	Benzene- <i>d</i> ₆	5.99	6.55	6.78	—	10.99	keto CH ₃ 1.99
Hpyr·COCH ₃	Acetone- <i>d</i> ₆	5.78	6.48	6.67	—	9.63	keto CH ₃ 1.92
Me ₂ In(pyr·CHO)	Acetone- <i>d</i> ₆	6.20	6.93	7.18	9.10	abs	CH ₃ (In) -0.35
Me ₂ In(pyr·COCH ₃)	Acetone- <i>d</i> ₆	5.67	6.40	6.54	—	abs	CH ₃ (In) 2.36 keto CH ₃ 1.78
InCl ₃ (Hpyr·CHO) ₃	Acetone- <i>d</i> ₆	6.15	6.88	7.10	9.29	11.2	
In(pyr·COCH ₃) ₃	Benzene- <i>d</i> ₆	6.29	6.81	7.08	—	abs	keto CH ₃ 1.83

*For key to assignments, see 1; abs = sought, but not detected; br = broad; sh = sharp.

ligand exchange involving dimethylindium complexes of β -diketonates (12).

We note finally that solutions of dimethylindium pyrrole species are rather unstable, depositing white solids after some hours at room temperature. The spectra reported are for freshly prepared solutions.

Vibrational Spectra

The vibrational spectrum of 2-formylpyrrole has been analyzed and assigned by Lord and Miller (13). The most important features relevant to the present work are $\nu(\text{N—H})$ at 3400 cm^{-1} (br) and $\nu(\text{C=O})$ at 1650 cm^{-1} . From our work, the corresponding values in 2-acetylpyrrole are $\nu(\text{N—H})$ 3275 and $\nu(\text{C=O})$ 1649 cm^{-1} .

The infrared spectra of the two dimethylindium(III) derivatives show an absence of $\nu(\text{N—H})$, and a lowering of approximately 50 cm^{-1} in $\nu(\text{C=O})$. A band at 725 cm^{-1} in $\text{Me}_2\text{In}(\text{pyr}\cdot\text{COCH}_3)$, and a shoulder at 720 cm^{-1} in $\text{Me}_2\text{In}(\text{pyr}\cdot\text{CHO})$, are assigned to $\delta(\text{In—CH}_3)$ by analogy with a number of other dimethylindium(III) derivatives. Both compounds have vibrations which can be assigned to $\nu(\text{In—CH}_3)$: $\text{Me}_2\text{In}(\text{pyr}\cdot\text{CHO})$, 545s + 480m (i.r.); 546m + 482m (R); $\text{Me}_2\text{In}(\text{pyr}\cdot\text{COCH}_3)$, 541m + 489mw (i.r.); 544m + 490s (R). Again, these values are in keeping with previous work.

The only interesting features of the infrared spectrum of the complex $\text{In}(\text{pyr}\cdot\text{COCH}_3)_3$ are the absence of $\nu(\text{N—H})$ and the shift in $\nu(\text{C=O})$ to 1640vs cm^{-1} . The latter is, on the face of it, surprisingly small, but mixing of vibrations is believed to hinder the analysis of vibrations in other bis- and tris-chelate systems (e.g. β -diketonates

(14)) and the same phenomenon may well be important in the present case. Finally, in $\text{InCl}_3(\text{Hpyr}\cdot\text{CHO})_3$, $\nu(\text{C=O})$ is at 1645vs cm^{-1} ; $\nu(\text{N—H})$ of the free ligand is absent, and a very broad absorption centered at about 2800 cm^{-1} may be the stretching mode of the N—H---Cl system (see below).

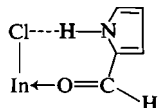
Structural Discussion

The spectroscopic and kinetic properties of $\text{Me}_2\text{In}(\text{pyr}\cdot\text{CHO})$ and $\text{Me}_2\text{In}(\text{pyr}\cdot\text{COCH}_3)$ are in keeping with those of other dimethylindium(III) complexes with bidentate chelate ligands, and require no special comment. It is probable that the solid phase involves polymerization via intermolecular bonding as in $\text{Me}_2\text{In}(\text{OAc})$ (15). By analogy with the behavior of the latter, the adduct $\text{Me}_2\text{In}(\text{pyr}\cdot\text{CHO})$ (bipy) should be one member of a series of adducts with neutral donors. The failure of the attempts to prepare $\text{In}(\text{pyr}\cdot\text{CHO})_3$ is puzzling and no specific reason is obvious. The compound $\text{In}(\text{pyr}\cdot\text{COCH}_3)_3$ has the properties to be expected of a six-coordinate InO_3N_3 chelate complex.

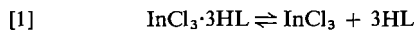
Finally, we turn to the unusual compounds $\text{InCl}_3(\text{HL})_3$ (HL = 2-formyl or 2-acetylpyrrole). The n.m.r. spectroscopic evidence (Table 2) shows unambiguously that there are five proton resonances per pyrrole in $\text{InCl}_3(\text{Hpyr}\cdot\text{CHO})_3$, in keeping with the presence of three chloride ligands in the molecule. The simplest assumption then is that intramolecular hydrogen bonding stabilizes the N—H proton. Hydrogen-bonding by pyrrole itself has been the subject of a number of studies. Infrared spectroscopy (16, 17) has been used to show that pyrrole interacts in

solution with various organic bases, and similar conclusions have been reached from dielectric polarization studies (18–20). Proton n.m.r. results in such systems have been discussed by Reeves (21), Freymann and Freymann (22), and Happe (23). None of these studies, unfortunately, refers to interactions in the solid state, or to pyrroles with substituted basic groups.

The structure

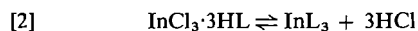


is proposed to explain the bonding in the solid state. Molecular models, based on reasonable interatomic distances, show that the overall molecular structure easily accommodates three such interactions, with three *cis* chlorides. The model appears free of significant strain. The intramolecular stabilization of acidic hydrogen atoms is not unusual; a relevant example is the molecule $[(\text{Meen})_2\text{Cu}(\text{CF}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{CF}_3)_2]$ (Meen = $(\text{CH}_3)_2\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2$) in which there are two monodentate β -diketonate ligands whose noncoordinated oxygens are each hydrogen-bonded to an NH_2 group of the diamine (24). The n.m.r. results (Table 2) are incompatible with the existence of the above structure in acetone solution, since the spectrum of a freshly prepared solution is almost identical with that of free $\text{Hpyr}\cdot\text{CHO}$. This could imply that the solution decomposition process is



The broad resonance at +11.2 is clearly that of a hydrogen-bonded system, but unfortunately the resonance frequency is an unreliable structural guide in such cases.

An alternative decomposition could be



and the reality of this process for the 2-acetylpyrrole adduct of InCl_3 is illustrated by the loss of HCl in the final stages of the preparative procedure (see Experimental). In this latter system, the existence of a stable InL_3 compound serves to move the equilibrium completely to the right. A solution of $\text{InCl}_3(\text{Hpyr}\cdot\text{CHO})_3$ in acetone turns red-brown on standing at room temperature, again suggesting decomposition by reaction 2. Thus we conclude that the failure to obtain a pure crystalline sample of $\text{InCl}_3(\text{Hpyr}\cdot\text{COCH}_3)_3$

is a consequence of the stability of $\text{In}(\text{pyr}\cdot\text{COCH}_3)_3$; equally the isolation of $\text{InCl}_3(\text{Hpyr}\cdot\text{CHO})_3$ may in part reflect the instability of $\text{In}(\text{pyr}\cdot\text{CHO})_3$.

The question of why substitution of H by CH_3 in the sidechain at the 2-position of pyrrole has such a pronounced effect on the ligating properties of these compounds must remain unanswered at the present time.

Polarographic Reduction

An initial aim of this work was to investigate polarographic reduction of $\text{In}(\text{III})$ pyrrole complexes; in the event we were only able to study $\text{In}(\text{pyr}\cdot\text{COCH}_3)_3$. In acetone solution containing the complex and 0.1 *M* $\text{Et}_4\text{N}\cdot\text{ClO}_4$, with Ag/AgCl and dropping mercury electrodes, we observed three one-electron reduction steps, with $E_{1/2}^{\text{I}}$ 0.37 V, $E_{1/2}^{\text{II}}$ -1.30 V, and $E_{1/2}^{\text{III}}$ -1.98 V. All three steps are polarographically irreversible (α^{I} 0.14, α^{II} 0.24, α^{III} 0.48). The reduction of 2-acetylpyrrole under the same conditions showed only one polarographic wave, $E_{1/2} = -1.60$ V ($\alpha = 0.31$), so that at least the first two reduction steps in InL_3 must be associated with reduction of the complex. In this respect then, $\text{In}(\text{pyr}\cdot\text{COCH}_3)_3$ behaves similarly to other neutral indium(III) complexes with bidentate chelating ligands.

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