

Reactions of InMe_3 with isocyanides in the presence of amines: chemical and mass spectrometric evidence of unprecedented insertion into In–N bonds

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Abstract

InMe_3 reacts with CNR ($\text{R}=\text{C}_6\text{H}_4\text{-}p\text{-OMe}$, $\text{C}_6\text{H}_4\text{-}p\text{-Me}$) affording the corresponding adducts Me_3InCNR , which are formed even in the presence of an excess of CNR. Me_3InCNR reacts with pyrrolidine to give the $[\text{Me}_2\text{InC(=NR)(Pyr)}]$ products [Pyr = conjugated base of pyrrolidine], which form through the insertion of CNR into the In–N_{Pyr} bond. These insertion products decompose easily to give the corresponding formamidines. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Isocyanides; Pyrrolidine; Formamidines

1. Introduction

The synthesis of indium complexes containing nitrogen ligands which, in principle, can behave as precursors to InN in various deposition processes [1–3], have been extensively studied. In particular, the preparation and thermal behavior of indium/alkyl/amino [4], indium/azide and nitride [5] have been described. The studies reported in the literature mostly concern the reactivity of InCl_3 [6], InMe_3 [7] or InMe_2Cl [8] with amines or Li-amides to form monomers or dimers depending on the reaction conditions [9].

While the chemistry of the transition elements with isocyanides has been extensively developed [10], few data have been collected on their complexes with Group 13 elements: aryl isocyanides are known to insert in Al–Al or Ga–Ga bonds of some organometallic Al or Ga compounds, to give $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{AlC}$

$(=\text{NPh})\text{C}(=\text{NPh})\text{Al}[\text{CH}(\text{SiMe}_3)_2]_2$ [11] and $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{GaC}(=\text{NR})\text{C}(=\text{NR})\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$ ($\text{R} = \text{aryl}$, $t\text{-Bu}$) [12], respectively, while *tert*-butyl isocyanide forms the adduct $\text{AlCp}_3(\text{CNCMe}_3)$, Cp = cyclopentadienyl [13] with Al.

As for indium, to the best of our knowledge, only one reaction has been described between an indium substrate, tetraalkyldiindane, $\text{R}_2\text{In–InR}_2$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$), with *tert*-butyl and phenyl-isocyanides to afford the corresponding addition products $(\text{ArN}\equiv\text{C})\text{R}_2\text{In–InR}_2(\text{C}\equiv\text{NAr})$ [14].

In this area we thought it would be of interest to investigate the reactivity of InMe_3 and InMe_2Pyr (Pyr = conjugated base of pyrrolidine) with aryl isocyanides.

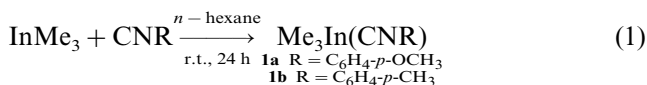
2. Results and discussion

InMe_3 reacted slowly with CNR ($\text{R}=\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3$, $\text{C}_6\text{H}_4\text{-}p\text{-CH}_3$) at room temperature in *n*-hexane to form the 1:1 adducts, according to Eq. (1). The products

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were brown solids, which must be handled under an inert atmosphere and decompose easily even in the solid state



The compounds **1a** and **1b** have been characterized via elemental analyses, IR and NMR spectroscopy.

The IR spectra clearly indicate the coordination of the CNR ligands, showing strong absorptions at 2174 and 2173 cm⁻¹ for **1a** and **1b**, respectively, ca. 50 cm⁻¹ at higher frequencies with respect to the corresponding free ligands (2126 and 2124 cm⁻¹, respectively), as reported for CNR coordination to metal centers in high oxidation state [10c]. These values are in agreement with those reported for the adduct (ArN≡C)R₂In–InR₂(C≡NAr) [14] where the C≡N stretchings of the coordinated Me₃N≡C and PhN≡C are observed at 2187 and 2168 cm⁻¹, respectively.

The ¹H-NMR spectra show singlets at 0.03 and 0.10 ppm for **1a** and **1b**, respectively, due to the methyl groups bonded to the In center. As expected, the signals are shifted downfield with respect to InMe₃ (–0.23 ppm), as a consequence of coordination of a donor ligand [4,15].

FAB mass spectrometric measurements confirmed the coordination of CNR and formation of **1a** and **1b**, showing the corresponding molecular ions at *m/z* 293 (18%) and *m/z* 277 (7%), respectively, together with fragmentation processes involving the subsequent methyl and isocyanide losses. In both spectra the ions at *m/z* 145 corresponding to [InMe₂]⁺, which represent the base peak in EI spectra previously reported for Me₃InL adducts [3c,6,16,17], are well evident (ca. 15%). Ions at *m/z* 381, corresponding to [In(CNC₆H₄-*p*-OMe)₂]⁺ are also evident in the FAB mass spectrum of **1a**. These ions presumably originate by a gas phase reaction occurring in the mass spectrometer due to the presence of free isocyanide. All of these results are consistent with the reported mass spectral data for other Me₃InL adducts [4,15,16]. This behavior indicates

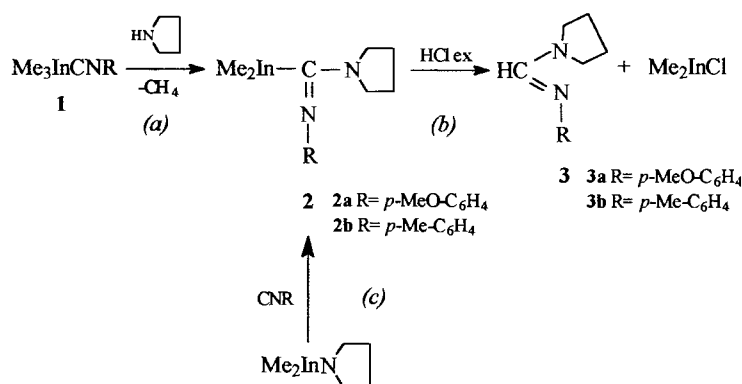
an easy dissociation of CNR ligands comparable to the dissociation that occurs in adducts containing amine ligands even if data for heats of formation of CNR adducts are not available. In the case of Me₃InNMe₃ gas phase studies give Δ*H*_f value of –83.3 kJ mol⁻¹ [4a].

The reactions of Eq. (1), which were followed by IR spectroscopy, are complete in 24 h. It is noteworthy that reactions performed in the presence of an excess (1:2) of CNR at room temperature do not provide evidence for the insertion process. This observation is in agreement with the behavior previously described for R₂In–InR₂, which did not give insertion into the In–C or In–In bonds, even when mixtures containing an excess of CNR were heated in *n*-hexane under reflux [14]. On the contrary, twofold insertion of isocyanide has been observed for [(Me₃SiCH)₂M]₂ (M = Ga, Al) with aryl and alkyl isocyanides to form the corresponding bridged 1,4-diazabutadiene derivatives (Me₃SiCH)₂-M[C(=NR)C(=NR)]M(CHSiMe₃)₂ [11,12].

However, the reactions of Eq. (1) performed in refluxing *n*-hexane or acetonitrile gave rise to a small quantity of the products **1a** and **1b**, with significant amounts of free isocyanides also being produced, indicating that the isocyanide dissociation is a favored process at higher temperatures.

Compounds **1a** and **1b** react slowly at room temperature with one equivalent of pyrrolidine according to Scheme 1 forming the imino derivatives **2a** and **2b** (route *a*).

The reactions have been followed by IR spectroscopy: a preliminary step involves the substitution of coordinated CNR with pyrrolidine, as indicated by the appearance of the ν_{C=N} of free CNR and by the shift of ν_{N–H} from 3284 cm⁻¹ in free pyrrolidine to 3261 cm⁻¹. Then, a slow increase of new C=N absorptions at 1634 and 1631 cm⁻¹ for **2a** and **2b**, respectively, is observed, suggesting the occurrence of insertion processes. The IR and ¹H-NMR spectra of **2a** and **2b** do not contain a signal attributable to N–H, indicating that the reactions proceed with elimination of CH₄, to yield the corre-



Scheme 1.

sponding dialkylamido derivatives, as previously reported for reactions of InMe_3 with secondary amines [4c,8,17].

It is noteworthy that reactions described by route *a* do not occur with formation of carbene species by nucleophilic attack of the amine on the carbon atom of the coordinated isocyanide, even if the increasing of the intensity of $\nu_{\text{C=N}}$ may indicate an activation of the isocyanide towards this process [18a]. This observation may be related to the fact that the only method reported in the literature for the preparation of indium carbene complexes involves the reaction of stable carbenes with suitable indium substrates [18b,c].

NMR data are in agreement with the proposed structures of **2a** and **2b** and a $^1\text{H}/^{13}\text{C}$ heteronuclear correlation 2D experiment allowed the peak assignments. The ^1H -NMR spectrum exhibits singlets at 0.072 and 0.019 ppm corresponding to the methyl groups bonded to indium for **2a** and **2b**, respectively. These signals are shifted downfield with respect to InMe_3 , complexes **1** and InMe_2Pyrr [19]. Methyl groups in complexes **2a** and **2b** give rise in ^{13}C -NMR spectra singlets at ca. -10 ppm. The signals corresponding to the CH_2 pyrrolidine ring appear as multiplets at ca. 1.4 ppm (CH_2) and 2.9 (NCH_2) in the ^1H -NMR spectra. The C=N carbon is evident only in the ^{13}C -NMR spectrum of **2a** at 163.8 ppm.

The FAB mass spectra of compounds **2a** and **2b** show the presence of the molecular ions at m/z 348 (15%) and 332 (15%), respectively. The base peak in both spectra is represented by In^+ at m/z 115 and ions at m/z 145 corresponding to Me_2In^+ . The ions corresponding to the losses of pyrrolidine are also present at m/z 278 (29%) for **2a** and 262 (25%) for **2b**.

Compounds **2a** and **2b** are brown powders, which decompose giving rise to the corresponding formamidines **3a** and **3b** (Scheme 1, route *b*).

Compounds **2a** and **2b** can also be prepared by reacting InMe_2Pyrr **4** [19] with the corresponding isocyanide (Scheme 1, route *c*). InMe_2Pyrr has been previously prepared by reacting InMe_3 and PyrrH (pyrrolidine) with CH_4 elimination [18] and has been completely characterized. The reactions (*c*) have been studied by IR spectroscopy by following the appearance of the $\nu_{\text{C=N}}$ stretching bands of compounds **2**.

Free formamidines **3a** and **3b** have been quantitatively obtained by reaction of compounds **2a** and **2b**, respectively, with HCl_{exc} (route *b*, Scheme 1). The formation of InMe_2Cl was checked by comparison with previously reported ^1H -NMR data (a singlet at 0.418 ppm for methyl groups in C_6D_6).

3a and **3b** have been also characterized by IR, ^1H - and ^{13}C -NMR. The $^1\text{H}/^{13}\text{C}$ heteronuclear correlation 2D spectra show the imine protons at 7.87 ppm with the corresponding carbon atom at 167.7 ppm for **3a** and at 7.90 ppm with the corresponding carbon atom at

166.8 ppm for **3b**. The mass spectra of **3a** and **3b** show the molecular ions at m/z 204 and 188 for **3a** and **3b**, respectively, together with the fragments originated by the loss of the pyrrolidine moiety.

Both reactions *a* and *c* of Scheme 1 affording the imino derivatives **2**, can be interpreted assuming that slow insertion processes of the isocyanides CNR occurs in the $\text{In-N}_{\text{Pyrr}}$ bond of Me_2InPyrr previously prepared according to route *c* or generated “in situ” according to route *a*.

Even if complexes **2a** and **2b** easily decompose, the process is confirmed by the isolation and characterization of the corresponding formamidine derivatives **3a** and **3b**, suitably formed by the unprecedented insertion of CNR into the In-N bond.

3. Experimental

Pyrrolidine (PyrrH) was purchased from Aldrich. The solvents and amine have been purified and dried according to the procedures reported in the literature [20].

InMe_3 , *p*-tolyl isocyanide and *p*-methoxyphenyl isocyanide were prepared according to procedures reported in the literature [21,22]. InMe_2Pyrr was prepared according to the method of Ref. [19]. The synthesis of InMe_2X was achieved by following a similar procedure to that reported in Ref. [23] which involves the reaction of InMe_2Cl with LiPyrr ($\text{Pyrr}=\text{NCH}_2-(\text{CH}_2)_2-\text{CH}_2$) [24]. LiPyrr was prepared by reacting *n*-BuLi (Fluka) and pyrrolidine.

Elemental analyses (C, H, N) were performed on a Fisons EA 1108 elemental analyzer. IR spectra were recorded on a Mattson 3030 Fourier-transform spectrometer ($4000-400\text{ cm}^{-1}$) using KBr disks. NMR spectra were collected on a Bruker AC-200 instrument. The mass spectrometric measurements were performed on a triple quadrupole (VG Quattro, VG Fisons, Altrincham, UK) instrument and on ZAB 2F (VG, Altrincham, UK) instrument equipped with a FAB source (8 keV Xe atoms), bombarding the sample deposited on the probe by evaporation of its Et_2O solution.

The FAB cesium gun in the VG Quattro Mass Spectrometer operated from 2 to 10 kV. Positive ion mass spectra were obtained with MS-1 scanning over m/z 50–1500 at 9.6 s decade^{-1} . GC/MS determinations were carried out on a QMD 1000 instrument (column PS 264, 30 m, 1 ml/min He flow, from 80 to 280°C , $10^\circ/\text{min}$).

3.1. $\text{InMe}_3\cdot\text{CNC}_6\text{H}_4\text{-}p\text{-OMe}$ (**1a**)

The isocyanide $\text{CNC}_6\text{H}_4\text{-}p\text{-OMe}$ (0.089 g, 0.68 mmol) was added to a solution of InMe_3 (0.109 g, 0.68 mmol) in freshly distilled *n*-hexane (15 ml). After stirring for a day at room temperature, the solution was evaporated

in vacuo yielding a brown powder. The product was recrystallized by dissolution in *n*-hexane and filtration from a cold (-10°C) suspension of ca. 2 ml of *n*-hexane. Yield 175 mg (87%).

IR (*n*-hexane): ν_{CN} 2174 cm^{-1} . $^1\text{H-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 3.21 (s, 3H, Ar-OCH₃), 0.03 (s, 9H, InCH₃). $^{13}\text{C-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): -7.66 (In(CH₃)₃), 55.03 (OCH₃), and 117.15 (InCN). FAB mass spectrum (ZAB 2F); m/z : 293 (18%) [M]⁺, 278 (2%) [M - CH₃]⁺, 263 (5%) [M - 2CH₃]⁺, 248 (2%) [M - 3CH₃]⁺, 133 (100%) [CNC₆H₄-*p*-OMe]⁺, 145 (15%) [Me₂In]⁺, 381 (5%) [In(CNC₆H₄-*p*-OMe)₂]⁺. Anal. Found: C, 45.56; H, 5.02; N, 4.75. Calc. for C₁₁H₁₆NOIn: C, 45.07; H, 5.55; N, 4.78%.

3.2. InMe₃·CNC₆H₄-*p*-Me (**1b**)

The isocyanide CNC₆H₄-*p*-Me (0.171 g, 1.46 mmol) was added to a solution of InMe₃ (0.233 g, 1.46 mmol) in *n*-hexane (30 ml). After stirring for a day at room temperature, the solution was evaporated in vacuo yielding a brown powder. The product was recrystallized by dissolution in *n*-hexane and filtration from a cold (-10°C) suspension of ca. 2 ml of *n*-hexane. Yield 339 mg (84%). IR (*n*-hexane): ν_{CN} 2173 cm^{-1} . $^1\text{H-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 1.82 (s, 3H, Ar-CH₃), 0.10 (In(CH₃)₃). $^{13}\text{C-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): -7.55 (InCH₃), 21.08 (Ar-CH₃), and 121.86 (InCN). FAB mass spectrum (ZAB 2F); m/z : 277 (7%) [M]⁺, 262 (2%) [M - CH₃]⁺, 247 (5%) [M - 2CH₃]⁺, 232 (2%) [M - 3CH₃]⁺, 117 (100%) [CNC₆H₄-*p*-Me]⁺, 145 (15%) [Me₂In]⁺, 349 (5%) [In(CNC₆H₄-*p*-Me)₂]⁺. Anal. Found: C, 47.38; H, 5.71; N, 4.90. Calc. for C₁₁H₁₆NIn: C, 47.68; H, 5.83; N, 5.06%.

3.3. InMe₂{C(=NC₆H₄-*p*-OCH₃)[N(CH₂)₃CH₂]} (**2a**)

Route (a): pyrrolidine (45 μl , $d = 0.83 \text{ g l}^{-1}$, 1 mmol) was added to a solution of **1a** (0.155 g, 0.53 mmol) in *n*-hexane (3 ml). After stirring for 33 days at room temperature, the solution was dried to yield a dark brown powder.

Route (b): the isocyanide CNC₆H₄-*p*-OCH₃ (0.124 g, 0.93 mmol) was added to a solution of InMe₂Pyrr (0.200 g, 0.93 mmol) in *n*-hexane (3 ml). After stirring for two months at room temperature, the solution was dried to yield a brown powder.

IR (*n*-hexane): ν_{CN} 1634 cm^{-1} . $^1\text{H-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 0.072 (s, 6H, InCH₃), 1.38 (m, 4H, CH₂), 2.97 (m, 4H, NCH₂), 3.26 (s, 3H, O-CH₃). $^{13}\text{C-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): -10.3 (InCH₃), 25.2 (CH₂), 53.0 (NCH₂), 55.0 (OCH₃), 163.8 (C=N). FAB mass spectrum (VG Quattro); m/z : 348 (22%) [M]⁺, 333 (10%) [M - CH₃]⁺, 317 (20%) [M - OCH₃]⁺, 278 (29%) [M - Pyrr]⁺, 145 (25%) [Me₂In]⁺, 115 (100%) [In]⁺.

3.4. InMe₂{C(=NC₆H₄-*p*-CH₃)[N(CH₂)₃CH₂]} (**2b**)

Route (a): pyrrolidine (45 μl , $d = 0.83 \text{ g l}^{-1}$, 1 mmol) was added to a solution of **1b** (0.147 g, 0.53 mmol) in *n*-hexane (3 ml). After stirring for three weeks at room temperature, the solution was dried to yield a dark brown powder.

Route (b): the isocyanide CNC₆H₄-*p*-CH₃ (0.124 g, 0.93 mmol) was added to a solution of InMe₂Pyrr (0.200 g, 0.93 mmol) in *n*-hexane (3 ml). After stirring for two months at room temperature, the solution was dried to yield a dark brown powder.

IR (*n*-hexane): ν_{CN} 1631 cm^{-1} . $^1\text{H-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 0.019 (s, 6H, InCH₃), 1.40 (m, 4H, CH₂), 2.07 (s, 3H, CH₃), 2.95 (m, 4H, NCH₂). $^{13}\text{C-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): -10.3 (InCH₃), 20.7 (ArCH₃), 25.3 (CH₂), 53.3 (NCH₂). FAB mass spectrum (VG Quattro); m/z : 332 (30%) [M]⁺, 318 (15%) [M - CH₃]⁺, 303 (45%) [M - 2CH₃]⁺, 262 (30%) [M - Pyrr]⁺, 247 (20%) [M - Pyrr - CH₃]⁺, 145 (25%) [Me₂In]⁺, 115 (100%) [In]⁺.

3.4.1. Reaction of **2a** with HCl

A C₆H₆-*d*₆ solution of **2a** (50 mg, 0.14 mmol) was reacted with HCl_{exc}. An immediate reaction was noted as the reaction mixture changed color from brown to yellow. $^1\text{H-NMR}$ spectra of the reaction mixture showed the quantitative formation of Me₂InCl (singlet at 0.418 ppm).

3a was identified on the basis of spectroscopic NMR and mass spectrometric data.

$^1\text{H-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 7.53 (s, 1H, HC=N), 1.40 (m, 4H, CH₂), 3.00 (m, 4H, NCH₂), 3.40 (s, 3H, OCH₃). $^{13}\text{C-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 149.6 (HCN), 20.7 (ArCH₃), 26.2 (CH₂), 53.3 (NCH₂), 55.0 (OCH₃). Mass spectrum; m/z : 204 (10%) [M]⁺, 188 (80%) [M - CH₃]⁺.

3.4.2. Reaction of **2b** with HCl

A C₆H₆-*d*₆ solution of **2b** (50 mg, 0.15 mmol) was reacted with HCl_{exc}. An immediate reaction was noted as the reaction mixture changed color from brown to yellow. $^1\text{H-NMR}$ spectrum of the reaction mixture shows the quantitative formation of Me₂InCl (singlet at 0.418 ppm).

3b was identified on the basis of spectroscopic NMR and mass spectrometric data.

$^1\text{H-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 7.50 (s, 1H, HC=N), 1.65 (m, 4H, CH₂), 2.85 (m, 4H, NCH₂), 2.12 (s, 3H, CH₃). $^{13}\text{C-NMR}$ (C_6H_6-d_6 , r.t., δ ppm): 149.8 (HCN), 20.8 (ArCH₃), 25.8 (CH₂), 51.5 (NCH₂). Mass spectrum; m/z : 188 (70%) [M]⁺, 159 (30%) [C₁₀H₁₁N₂]⁺, 118 (30%) [C₈H₈N₂]⁺.

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