

Synthesis and Structure of Novel Bridged Dinuclear Indium Complexes

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Due to the Lewis acidity of three-coordinate complexes of aluminum, gallium, and indium, the organometallic chemistry of these metals is dominated by the appearance of four-coordinate monomeric species and four-membered-ring dimers.¹ Recently, several alkyl complexes with unusual coordination geometries have been reported. For example, there are now several structurally characterized polynuclear and monomeric five- and six-coordinate complexes.^{2–16} The dominant profile of aluminum among these examples is illustrated by the fact that the first structurally characterized five- and six-coordinate organometallic complexes of indium have been only very recently reported.^{7,8}

While the steric and electronic effects that dictate the formation of transition metal dinuclear species have been heavily investigated, similar investigations of the post-transition metals are lacking.¹⁶ Bidentate, three atom bridging ligands such as RNXR^- ($\text{X} = \text{CR}'$, CH , or N) are among the species that have been commonly employed in these investigations and have been important in preparing a wide variety of dinuclear transition metal complexes.¹⁷ Modification of the organic substituents on these ligands should allow tuning of their electronic properties and steric bulk.

With these facts in mind, we have initiated a systematic study of the complexes of formamidinate and related ligand systems with post transition metals. Herein we report, as part of our ongoing investigation, the synthesis and characterization of a novel family of dimeric In^{III} compounds of the general formula $[\text{In}(\text{CyNC}(\text{H})\text{NCy})_n\text{R}_{3-n}]_2$ ($n = 2, 1$; $\text{R} = \text{Cl}$, Me).

Reaction of an ethereal suspension of InCl_3 with 2 equiv of $\text{Li}(\text{CyNCHNCy})^{18}$ ($\text{Cy} = \text{cyclohexyl}$) afforded a new species (**1**) in 74% yield after crystallization from diethyl ether. Both ^1H and ^{13}C NMR are consistent with the presence of one environment for the formamidinate ligands as clearly indicated by the single resonances for the methyne proton (7.45 ppm) and carbon (162.1 ppm).¹⁹ Elemental analysis confirmed the formula of this species as $[\text{In}(\text{CyNC}(\text{H})\text{NCy})_2\text{Cl}]_n$. On the basis of the ready solubility of **1** in organic solvents, the comparable ionic radius of $\text{In}(\text{III})$ to the transition metals, and the ability of indium to accommodate 5- or 6-fold coordination, we anticipated that this complex was a dinuclear species. In order to confirm the level of aggregation for this species, the structure of **1** was determined by single-crystal X-ray diffraction analysis, and the result is shown in Scheme 1.²⁰

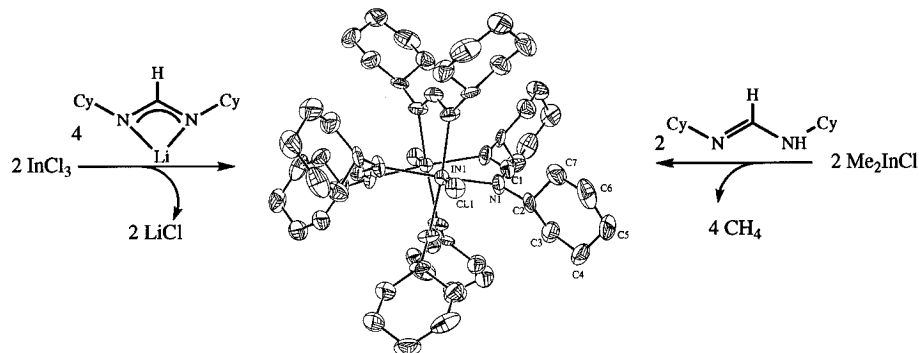
Complex **1** crystallizes in the cubic space group $Pn\bar{3}n$ with six molecules in the unit cell. The molecular geometry and atom-numbering scheme are shown in Scheme 1. The molecule exhibits a nonbonded binuclear In-In unit ($\text{In1-In1A} = 3.142(5) \text{ \AA}$) which is bridged by four formamidinate ligands. The In centers are in an unusual square-based pyramidal, five-coordinate environment consisting of the four formamidinate N atoms with a terminal chloride occupying the apical position and completing the coordination sphere [In1a-In1-Cl1 , 180.0° ; In1a-In1-N1 , $78.0(4)^\circ$; Cl1-In1-N1 , $102.0(4)^\circ$; N1-In1-N1b , $156.1(6)^\circ$; N1-In1-N1c , $87.5(6)^\circ$; In1-N1-Cl1 , $124.1(13)^\circ$; In1-N1-C2 , $116.8(11)^\circ$].²¹ The molecule possesses a rigorous C_4 axis coincident with the In-In vector as well as 2-fold axes perpendicular to the higher order rotation axis. The obvious twist in the five-membered $\text{In1-N1-Cl1-N1A-In1A}$ rings is likely an effort to reduce the steric interactions between the bulky cyclohexyl substituents.

The lantern-type structure of **1** is, to our knowledge, unique among the group 13 elements. In addition, the solid state structure of **1** contrasts with that reported for the analogous $\text{V}(\text{III})$ dimer, $[\text{V}(\text{CyNC}(\text{H})\text{NCy})_2(\mu\text{-Cl})_2]_2$.¹⁷ This species exhibits one formamidinate ligand spanning the dinuclear core, bridging Cl atoms, and one terminal formamidinate ligands occupying a nonbridging chelating position with an overall octahedral coordination of the V atoms.

- (1) For a summary of Ga and In organometallic chemistry see: Tuck, D. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 1, Chapter 7.
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- (16) For a review, see: Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; J. Wiley & Sons: New York, 1982.
- (17) Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417 and references therein.

- (18) The lithium salt, LiCyNCHNCy (Cy : cyclohexyl), was prepared by the stoichiometric reaction of CyNHCHNCy with MeLi in Et_2O . CyNHCHNCy was prepared according to the published procedure: Saeed, A. H.; Selman, A. S. *J. Spectrosc.* **1982**, *27*, 123.
- (19) In a typical experiment, a Schlenk flask was charged with InCl_3 (0.40 g, 1.81 mmol), LiCyNCHNCy (0.77 g, 3.62 mmol), and diethyl ether (25 mL). Removal of solvent and crystallization in ether yielded 0.76 g (74%, 0.67 mmol) of **1**. Spectroscopic data for **1**. IR (Nujol, cm^{-1}): 1622 (s), 1581 (s). ^1H NMR (C_6D_6 , ppm): 7.45 (s, NCHN , 4H); 3.25–3.10 (m, Cy , 8H); 2.1–1.2 (m, Cy , 80H). ^{13}C NMR (C_6D_6 , ppm): 162.1 (s, NCHN); 57.4, 36.6, 26.0, 25.8 (4s, Cy). MP (sealed): 157–159 $^\circ\text{C}$. Anal. Calcd for $\text{C}_{52}\text{H}_{92}\text{Cl}_2\text{In}_2\text{N}_8$: C, 55.28; H, 8.21; N, 9.92. Found: C, 54.87; H, 8.37; N, 9.86.
- (20) Crystal data: $Pn\bar{3}n$ (cubic), $a = 22.678(7) \text{ \AA}$, volume = 11663(4) $\text{\AA}^3$, fw = 1129.90, $Z = 6$, $F(000) = 3552$, $D_{\text{calc}} = 0.979 \text{ Mg}\cdot\text{m}^{-3}$, no. of unique reflections = 1729, $R_F = 0.067$, and $R_w = 0.086$.
- (21) References 6, 8, 9, 14, and 15 present crystal structures of five-coordinate gallium and indium complexes in distorted trigonal bipyramidal coordination environments. The values for the angle along the pseudoaxial vectors in these reports fall in the range of 144.9 – 169.7° . In all cases the methyl group is in the equatorial plane.

Scheme 1



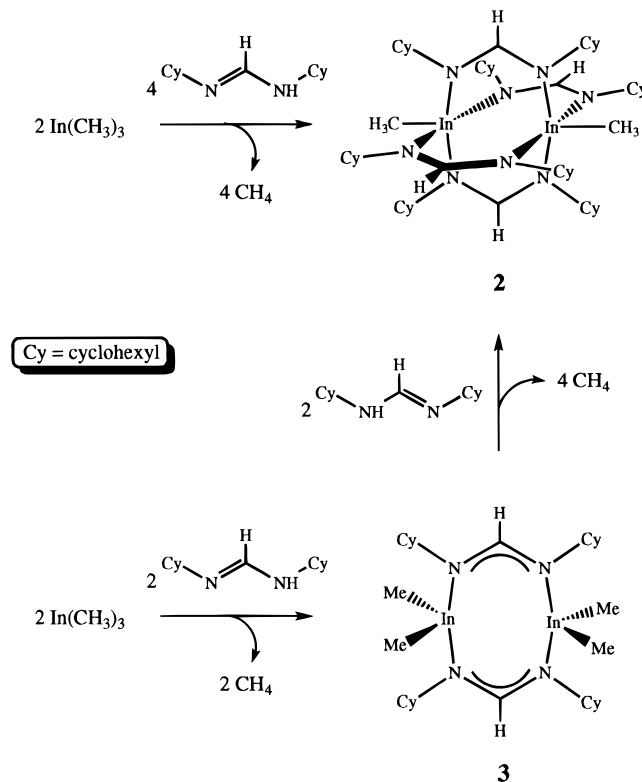
Due to the uniqueness of **4**, direct comparison of the In–N [2.226(14) Å] and In–Cl [2.383(9) Å] distances with other structurally characterized species is not straightforward. A majority of the reported five-coordinate In complexes have relatively long range intramolecularly coordinated nitrogen centers.^{9a–c} In these examples the average In–N distance of 2.55 Å is considerably longer than the sum of the covalent radii (2.19 Å) and than the In–N distance observed for **1**. The reported diphenyltriazenido [(C₆H₅N)₂N] complexes, while possessing only nonbridging, chelating ligands, have In–N bond lengths that span the value found for **1**.⁸ The In–Cl distance of **1** is, as expected, slightly shorter than for some recently reported six-coordinate complexes.^{11,12,13}

Complex **1** can be synthesized independently by the interaction of (CH₃)₂InCl with 2 equiv of free formamidine and elimination of two molecules of methane (Scheme 1). Interestingly, compound **1** does not react directly with Me₄Sn or MeLi, a feature likely due to the steric congestion caused by the four cyclohexyl substituents. However, the methyl analog [In(CyNC(H)NCy)₂(CH₃)₂], **2**, can be prepared by the reaction of In(CH₃)₃ with 2 equiv of CyN(H)C(H)NCy and elimination of methane.²²

The stepwise formation of **2** was confirmed by the series of reactions shown in Scheme 2. The reaction of In(CH₃)₃ with 1 equiv of CyN(H)C(H)NCy proceeds to yield an intermediate cyclic species [Me₂In(CyNC(H)NCy)]₂ (**3**).²³ We propose the connectivity shown in Scheme 1 based upon the spectroscopic data and by analogy with the reported tetrahedrally coordinated *N,N'*-dimethylacetamidate complexes of aluminum and gallium, [Me₂M(MeNC(Me)NMe)]₂ (M = Al, Ga).^{24,25} These species exhibited centrosymmetric puckered eight-membered ring structures. The downfield shift of the methyl protons (0.17 ppm) relative to In(CH₃)₃ (−0.18 ppm) is consistent with a four-coordinate structure of **3** but does not rule out another highly symmetrical structure.²⁶ Support for our formulation of complex **3** is provided by its facile conversion to **2**, in excellent yield (85%), by reaction with a second molecule of formamidine and elimination of methane.

We feel confident in assigning an analogous dimeric structure to **2** based upon comparison with **1** and **3** and its spectral

Scheme 2



features. In addition, the presence of a single methyl carbon signal at −6.1 ppm is consistent with the reported five-coordinate diphenyltriazenido–In species.⁸ The chemical shifts for the methyne proton (7.67 ppm) and carbon (161.2 ppm) are also in accord with a structure similar to that of **1**.

The use of the dicyclohexylformamidinate ligand leads to a family of unusual dinuclear indium complexes that are unique among the elements of group 13. Without the possibility of In–In interactions, it would appear that steric features are the primary cause for the formation of these compounds. We are currently expanding our work to investigate the replacement of both the N–R and C–H groups in the formamidinate ligand system with the goal of dissecting the features that influence the formation of dinuclear main group organometallic complexes.

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Supporting Information Available: Text providing experimental details and a description of the structural solution, tables of atomic positions, thermal parameters, crystallographic data, and bond distances and angles, and an ORTEP drawing for compound **1** (10 pages). Ordering information is given on any current masthead page.

- (22) Spectroscopic data for **2**. IR (Nujol, cm^{−1}): 1571 (s). ¹H NMR (C₆D₆, ppm): 7.67 (s, NCHN, 4H); 3.15–2.96 (m, Cy, 8H); 1.95–1.15 (m, Cy, 80H), 0.31 (s, Me, 6H). ¹³C NMR (C₆D₆, ppm): 161.2 (NCHN); 58.0, 37.1, 26.7, 26.0, (8s, Cy); −6.1 (s, Me). MP (sealed): 93–95 °C. Anal. Calcd for C₅₄H₉₈In₂N₈: C, 59.56; N, 9.07; N, 10.29. Found: C, 59.26; H, 9.24; N, 10.33.
- (23) Spectroscopic data for **3**. IR (Nujol, cm^{−1}): 1562. ¹H NMR (C₆D₆, ppm): 7.68 (s, NCHN, 2H); 2.97–2.83 (m, Cy, 4H); 1.75–1.00 (m, Cy, 40H); 0.17 (s, Me, 12H). ¹³C NMR (C₆D₆, ppm): 162.4 (s, NCHN); 57.4, 37.0, 26.0, 25.3 (4s, Cy); −5.3 (Me). MP (sealed): 97–98 °C. Anal. Calcd for C₃₀H₅₈In₂N₄: C, 51.15; H, 8.30; N, 7.95. Found: C, 51.33; H, 8.31; N, 7.94.
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