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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 $RNXNR^-$ (X = 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 $[In(CyNC(H)NCy)_nR_{3-n}]_2$ ($n = 2, 1$; R = Cl, Me).

Reaction of an ethereal suspension of $InCl_3$ with 2 equiv of Li(CyNCHNCy)[18] (Cy = 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 $[In(CyNC(H)NCy)_2Cl]_n$. On the basis of the ready solubility of **1** in organic solvents, the comparable ionic radius of In(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 (In1−In1A = 3.142(5) Å) 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)°; Cl1−In1−N1, 102.0(4)°; N1−In1−N1b, 156.1(6)°; N1−In1−N1c, 87.5(6)°; In1−N1−C1, 124.1(13)°; In1−N1−C2, 116.8(11)°].[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 In1−N1−C1−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 V(III) dimer, $[V(CyNC(H)NCy)_2(\mu\text{-}Cl)]_2$.[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.

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(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 °C. Anal. Calcd for $C_{52}H_{92}Cl_2In_2N_8$: 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), $a = 22.678(7)$ Å, volume = 11663(4) Å^3, fw = 1129.90, $Z = 6$, $F(000) = 3552$, $D_{calc} = 0.979 Mg.m^{-3}$, 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.

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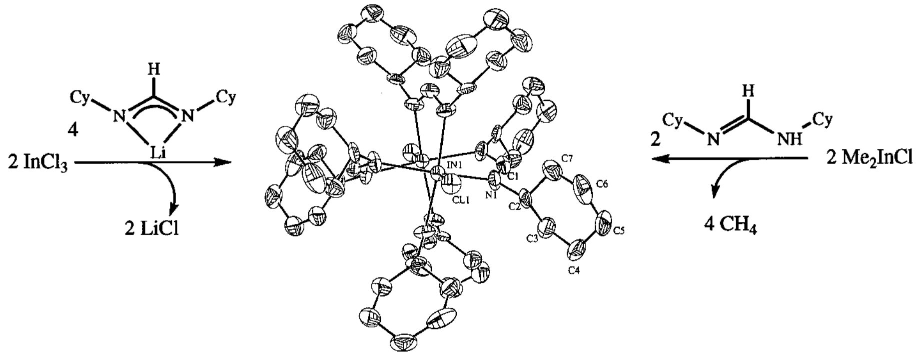
Scheme 1

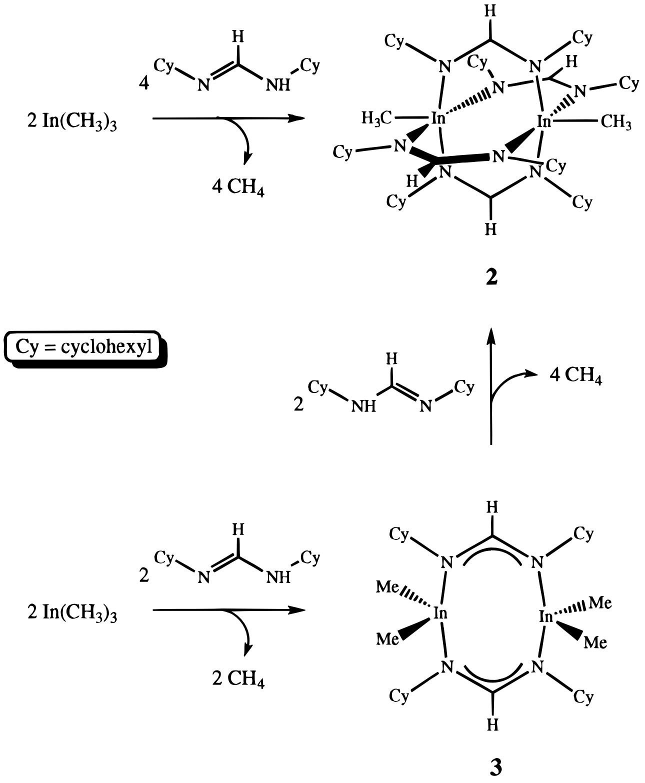


Due to the uniqueness of **4**, direct comparison of the In−N [2.226(14) Å] and In−Cl [2.383(9) Å] distances with other structurally characterized species is not straightforward. A majority of the reported five-coordinate In complexes have relatively long range intramolecularly coordinated nitrogen centers.[9a−c] 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 [$(C_6H_5N)_2N$] 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 $(CH_3)_2InCl$ with 2 equiv of free formamidine and elimination of two molecules of methane (Scheme 1). Interestingly, compound **1** does not react directly with Me_4Sn or MeLi, a feature likely due to the steric congestion caused by the four cyclohexyl substituents. However, the methyl analog $[In(CyNC(H)NCy)_2(CH_3)]_2$, **2**, can be prepared by the reaction of $In(CH_3)_3$ 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 $In(CH_3)_3$ with 1 equiv of CyN(H)C(H)NCy proceeds to yield an intermediate cyclic species $[Me_2In(CyNC(H)NCy)]_2$ (**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*′-dimethylacetamidinate complexes of aluminum and gallium, $[Me_2M(MeNC(Me)NMe)]_2$ (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 $In(CH_3)_3$ (−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.

Scheme 2



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

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(22) Spectroscopic data for **2**. IR (Nujol, cm^{-1}): 1571 (s). ^1H NMR (C_6D_6, 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). ^{13}C NMR (C_6D_6, 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 $C_{54}H_{98}In_2N_8$: 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 (C_6D_6, 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). ^{13}C NMR (C_6D_6, 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 $C_{30}H_{58}In_2N_4$: C, 51.15; H, 8.30; N, 7.95. Found: C, 51.33; H, 8.31; N, 7.94.

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