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Capturing In$^+$ Monomers in a Neutral Weakly Coordinating Environment

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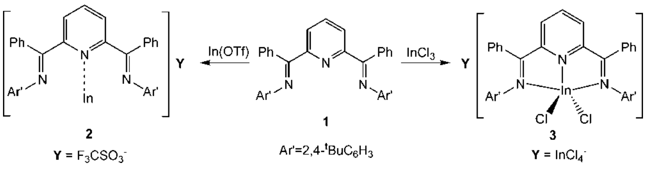
Fundamental bonding questions inspire the synthesis of increasingly challenging target molecules. The recent report of a cryptand-encapsulated Ge(II) cation demonstrated that with judicious choice of ligands, such reactive species can be isolated and crystallographically characterized while displaying nominal coordination.[1] In the case of indium(I), the exceptionally sterically encumbering *o*-terphenyl ligand 2,6-(Tripp)$_2$C$_6$H$_3$ (Tripp = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) allowed the isolation of the unique example of single coordination of this metal cation as 2,6-(Tripp)$_2$C$_6$H$_3$In(I).[2] Slightly reducing the bulk of the ligand to 2,6-(Dipp)$_2$C$_6$H$_3$ (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) yielded a "dimetallene" dimer, [2,6-(Dipp)$_2$C$_6$H$_3$In]$_2$, with an In−In bond.[3] The concept that sterically encumbered ligands can provide kinetic stabilization of highly reactive species with only weak coordination confronts the foundation of the current understanding of stability and bonding. Synergistic insight is provided through modern theoretical methods carried out in parallel with the synthesis.

With the goal of uncovering unprecedented structure and bonding arrangements and concomitant novel reactivity, we were attracted to the bis(imino)pyridine scaffold **1** and its potential for the isolation of reactive main-group metal centers. Our efforts were inspired by the modular steric and electronic features and the relative ease of synthesis of these species along with the fact that the application of this ligand in main-group chemistry is unrevealed.[4] We chose to avoid the established deprotonation reactivity of the imino methyl groups by employing phenyl substituents on this moiety.[5] Application of 2,4-^{t}Bu$_2$C$_6$H$_3$NH$_2$ in the synthesis of **1** was expected to maintain and perhaps enhance the steric demands of the *N*-aryl substituents. We demonstrate the isolation of the first low-valent main-group metal complex of this ligand scaffold, and a combined structural and density functional theory (DFT) analysis reveals an In(I) complex with minimal coordination.

The new bis(imino)pyridine **1** was prepared using a modified literature synthesis.[5] The steric demands of this architecture were demonstrated by the appearance of a complex set of singlets in the ^{1}H NMR spectrum of **1** (δ 1.55−0.92 ppm) whose integration intensities allowed their assignment as the ^{t}Bu groups. These observations were attributed to hindered dynamic solution conformers of **1**.[6]

Our targeted low-valent group 13 complex of **1** was achieved by allowing the soluble and readily accessible In(I) synthon In(OSO$_2$CF$_3$)[7] to react with **1** (Scheme 1) to provide an excellent isolated yield (76%) of bright-orange compound **2**. The relatively simple ^{1}H NMR spectrum of **2**, with only two ^{t}Bu singlets, suggested the formation of a symmetrical complex. The identity of **2** as the bis(imino)pyridine complex [{2,4-^{t}Bu$_2$C$_6$H$_3$N=CPh}$_2$(NC$_5$H$_3$)]In$^+$(OTf)$^-$ was established by single-crystal X-ray analysis, and the results for the cationic component are summarized in Figure 1.

Scheme 1



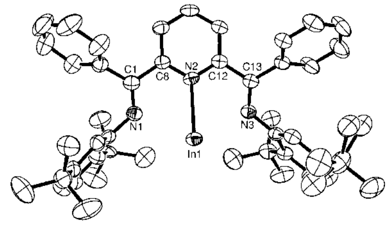


Figure 1. Structure of the [{2,4-^{t}Bu$_2$C$_6$H$_3$N=CPh}$_2$(NC$_5$H$_3$)]In$^+$ cation of compound **2**, with hydrogen atoms and the triflate counterion omitted for clarity. Selected bond distances (Å): In−N2, 2.495(5); N1−C1, 1.281(9); N3−C13, 1.283(9). Selected bond angles (deg): C8−N2−C12, 119.2(6); C8−N2−In1, 121.0(4); C12−N2−In1, 118.8(4).

Notably, this structure is monomeric, with a long In−N2 bond distance of 2.495(5) Å.[8,9] The most direct comparisons to **2** can be made with In(I) complexes of anionic ligands. For example, the In−N bond distance in the two-coordinate β-diketiminate complex [In{(NDippCMe)$_2$CH}] is 2.27Å.[10] Furthermore, for the three-coordinate complex tris(3,5-di-*tert*-butylpyrazolyl)hydroborato In(I), these distances averaged ~2.47 Å,[11] and for the four-coordinate amidinato species [DippNC(^{t}Bu)NDipp]In(I), an In−N distance of 2.329(5) Å was obtained.[12]

The In center in **2** lies slightly out of the pyridine plane (11.5°). The In−N$_{\text{imine}}$ distances are weakly coordinating, with In−N1 at 2.748(6) Å and In−N3 at 2.689(6) Å. Long In−O(triflate) distances [2.761(7) and 3.045(9) Å] are consistent with a well-separated triflate anion.[13] The observed structure of the cation of **2** is reminiscent of that of the In(terphenyl) monomer.[2] The imine C=N distances in **2** [N1−C1, 1.281(9) Å; N3−C13, 1.283(9) Å] are comparable to those for the free ligand, and the C1 and C13 centers of the imine moieties are planar.[6]

A DFT computational study was undertaken to obtain a thorough understanding of the electronic nature of the cation in **2**. Calculations were carried out with the B3LYP functional and the mixed DZVP/TZVP basis set. Only with the complete ligand array was the experimentally determined structure accurately modeled, thus supporting a significant steric origin for the observed structural features. The analysis of the electronic structure of the cation indicated that the In$^+$ ion accepts little covalent donor−acceptor interaction from the ligand. For example, the natural population analysis (NPA)-derived valence configuration for the In atom is 5s$^{1.93}$5p$^{0.20}$, and the Mayer bond orders for the In−N1/In−N3 and In−N2 interactions are only 0.23 and 0.28 respectively. These values are much lower than the indices of 1 expected for single bonds. The Wiberg bond indices calculated in the natural atomic

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orbital (NAO) basis are only 0.07−0.10, also consistent with very weak In−ligand interactions. These observations are in harmony with the extremely long In−N distances in **2**. The NPA-derived charge of the In atom is +0.86 au, which suggests that much of the cationic charge remains on the In ion, with only 0.14e transferred from the ligand to In^+ in the complex. In comparison, the NPA-derived charge of the Ge atom in the Ge(II)−cryptand complex, which displayed minimal coordination between the cryptand ligand and Ge(II), was +1.38 au.[1] This implies that 0.62e was donated to the Ge ion, a significantly stronger charge donation than obtained for **2**. The lone electron pair on In^+ is localized in the 5s orbital and has a clear destabilizing effect on the metal−ligand bonding (Figure 2). Because of mixing of the occupied π orbitals of the 2,4-$^tBu_2C_6H_3$ groups with In 5s orbital, the HOMO of the cation has a contribution of only 19% from In-localized orbitals. This effect may play an important role in stabilizing the structure of **2**. There is no back-donation from the metal into the extended π system, since the In 5s → L π^* transition is symmetry-forbidden (the overlap is zero; see Figure S1 in the Supporting Information). Finally, the In p_y orbital is empty and nonbonding with the ligand π framework.

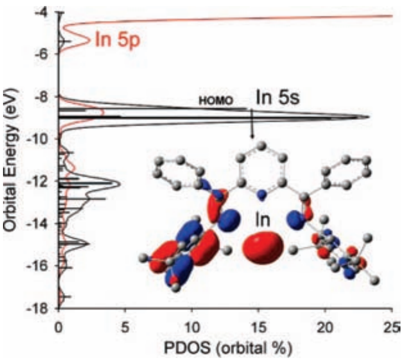

Figure 2. Partial density of states (PDOS) plot for the In s and p orbitals in the cation of **2** and (inset) the HOMO (with an isosurface contour value of 0.04).

Ligand **1** combines readily with $InCl_3$. A 1:2 stoichiometric ratio resulted in a red-orange solution that yielded a bright-yellow powder **3** in 73% yield (Scheme 1). Again, coordination of the ligand in a symmetrical fashion was clearly indicated by the appearance of a simplified ^1H NMR spectrum of the ^tBu subtituents as two singlets of appropriate integration.

Application of the related ligand 2,6-{DippN=C(Me)}$_2$(NC_5H_3) in the isolation of cationic Al(III) and Ga(III) halide complexes ($[LMX_2]^+MX_4^-$, M = Al, X = Cl; M = Ga, X = I) has been reported.[4c,g] The Al complex was formed from the direct reaction of the ligand with $AlCl_3$. Interestingly, the Ga species was derived from the reaction of a Ga(I) synthon, GaI,[14] through an apparent disproportionation to M(III).

Single-crystal X-ray analysis for this unique In complex revealed **3** to be $[\{2,4\text{-}^tBu_2C_6H_3N{=}CPh\}_2(NC_5H_3)]InCl_2^+InCl_4^-$ as a well-separated cation/anion pair; the cationic portion of compound **3** is shown in Figure 3. The geometry of the indium center within this constituent is distorted trigonal bipyramidal, with the threefold plane (∑angles = 359.9°) defined by the N2, Cl1, and Cl2 centers. The limitations of the ligand geometry lead to a pseudoaxial N1−In−N3 angle of only 142.6(6)°. The two five-membered rings resulting from the coordination of the pyridyl and imine moieties display values for the sum of internal angles that are ideal for planarity. As anticipated, the In−N_{py} distance of 2.23(2) Å is almost 0.27 Å shorter than the corresponding bond distance for **2**.

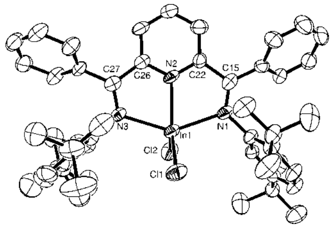

Figure 3. Structure of the $[\{2,4\text{-}^tBuC_6H_3N{=}CPh\}_2(NC_5H_3)]InCl_2^+$ cation of compound **3**, with hydrogen atoms and the $InCl_4^-$ counterion omitted for clarity.

Complex **2** is the first low-valent main-group metal complex of the bis(imino)pyridine scaffold. Moreover, a thorough analysis reveals this In(I) complex has minimal classical donor−acceptor coordination. We propose that mixing of the occupied 5s metal orbital with the occupied ligand orbitals reduces the reactivity of the central atom and thus stabilizes this species. Using this strategy, we are in the process of targeting low-valent species of other group 13 elements.

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Supporting Information Available: Crystallographic data for **1**, **2**, and **3** (CIF), experimental procedures, and additional computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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