Coordination Complexes

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Synthesis of Square-Planar Aluminum(III) Complexes**

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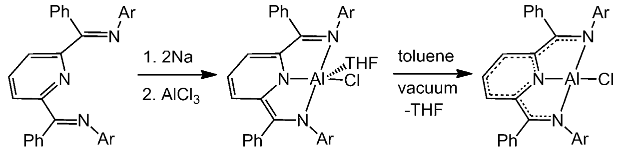
Abstract: *The synthesis of two four-coordinate and square planar (SP) complexes of aluminum(III) is presented. Reaction of a phenyl-substituted bis(imino)pyridine ligand that is reduced by two electrons, $Na_2(^{Ph}I_2P^{2-})$, with $AlCl_3$ afforded five-coordinate $[(^{Ph}I_2P^{2-})Al(THF)Cl]$ (**1**). Square-planar $[(^{Ph}I_2P^{2-})AlCl]$ (**2**) was obtained by performing the same reaction in diethyl ether followed by lyphilization of **2** from benzene. The four-coordinate geometry index for **2**, τ_4, is 0.22, where 0 would be a perfectly square-planar molecule. The analogous aluminum hydride complex, $[(^{Ph}I_2P^{2-})AlH]$ (**3**), is also square-planar, and was characterized crystallographically and has $\tau_4 = 0.13$. Both **2** and **3** are Lewis acidic and bind 2,6-lutidine.*

Widespread use of the aluminum(III) ion is driven primarily by its exceptionally potent Lewis acidic properties.[1] Al^{III} is probably best known to synthetic chemists as $AlCl_3$, a strongly Lewis acidic reagent that accepts a fourth ligand to form the preferred class of coordination compound for Al^{III}: the four-coordinate tetrahedral metal ion.[2] Recent work in frustrated Lewis pair (FLP) chemistry has extended the scope of Al^{III} chemistry by using steric effects to lengthen and weaken one of the aluminum–ligand interactions in tetrahedral Al^{III} complexes, thereby greatly increasing their reactivity.[3] Efforts to study unusual reactivity using Al ions have also focused on the low-coordinate complexes of both Al^{I} and Al^{III},[4] including several three-coordinate and planar Al complexes.[5] Four-coordinate Al complexes have also been used as Lewis acidic catalysts that associate a fifth ligand and display remarkable reactivity.[6] However, even these distorted and acidic four-coordinate complexes possess a pseudo tetrahedral geometry ($\tau_4 = 0.88$, where 0 would be perfectly square-planar (SP), and 1 is perfectly tetrahedral),[6b] and these results further highlight the uniqueness of targeting the SP geometry of Al^{III} in this work. Herein, we demonstrate that tridentate bis(imino)pyridine ligands (I_2P)[7] can be used to access SP complexes of Al^{III}, and that these complexes are Lewis acidic enough to bind 2,6-lutidine.

The Cambridge Crystallographic Data Centre (CCDC) reveals that out of 3582 four-coordinate Al^{III} complexes, none approach SP. The Al^{III} complex with the most distorted coordination geometry from tetrahedral is $[L^1L^2Al]$, where L_1 and L_2 are two bidentate N and C donor ligands.[8] The τ_4 for $[L^1L^2Al]$ is 0.59,[9] and this indicates that the observed distortion from tetrahedral is not large. According to the CCDC, all of Group 13 provides just one example of a SP M^{III} coordination complex, and that contains In^{III} in $[(bpy)InCl_2]^+$,[10] which has $\tau_4 = 0.25$.

The reaction of two-electron-reduced, phenyl-substituted bis(imino)pyridine $Na_2(^{Ph}I_2P)$ with $AlCl_3$ afforded, upon work-up, $[(^{Ph}I_2P^{2-})Al(THF)Cl]$ (**1**) in 62 % yield (Scheme 1).



$^{Ph}I_2P$ **1** **2**

Scheme 1. Synthesis of **1** and **2**.

The solid-state structure of **1** was obtained from crystals grown by diffusion of pentane into a concentrated THF solution of **1** (Supporting Information, Figure S1, Tables S1, S2).[11] The bond lengths and angles in **1** depict an electronic structure for $^{Ph}I_2P^{2-}$ that is asymmetric. Formally, the three *N*-donor atoms of $^{Ph}I_2P^{2-}$ could be described as amido, anionic pyridyl, and imino. Closed-shell electronic structures for the twice-reduced I_2P ligand have previously been observed in Al^{III} and Mn^{II} complexes.[12,13] The asymmetry of the $^{Ph}I_2P^{2-}$ ligand is not apparent in the ^1H NMR spectrum of **1** where one triplet (1 H) and one doublet (2 H) were assigned to the protons in the pyridyl ligand. This NMR response presumably stems from averaging on the timescale of the experiment, and is persistent down to −70 °C in low-temperature experiments.

The THF solvate molecule in **1** is tightly bound to Al^{III}, and addition of a variety of non-coordinating solvents, followed by their removal in vacuo was not sufficient to produce the base free, four-coordinate analogue of **1**. Multiple cycles of lyophilization of **1** from benzene likewise had no effect. Successful synthesis of four-coordinate $(^{Ph}I_2P^{2-})AlCl$ (**2**) was achieved in diethyl ether, followed by lyophilization of the complex from benzene. Recrystallization from toluene afforded **2**. The ^1H NMR spectrum of **2**, collected in C_6D_6, indicated that base-free SP **2** was obtained, and this is most apparent from the proton resonances of the pyridyl portion of $^{Ph}I_2P^{2-}$: these are shifted downfield by 0.46 ppm relative to those for **1**, consistent with a decrease in electron density at the Al^{III} center.

The solid-state structure of **2** revealed an Al^{III} ion with a SP coordination geometry (Figure 1; Supporting Informa-

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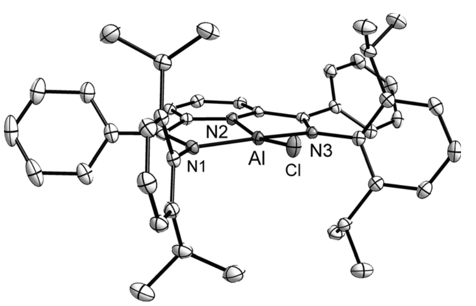


Figure 1. Solid-state structure of $[(^{\mathrm{Ph}}\mathrm{I_2P^{2-}})\mathrm{AlCl}]$ (**2**).[11] Unlabeled atoms are C atoms; ellipsoids are set at 50%, H atoms are omitted for clarity.

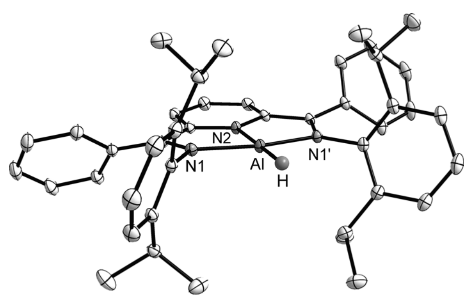
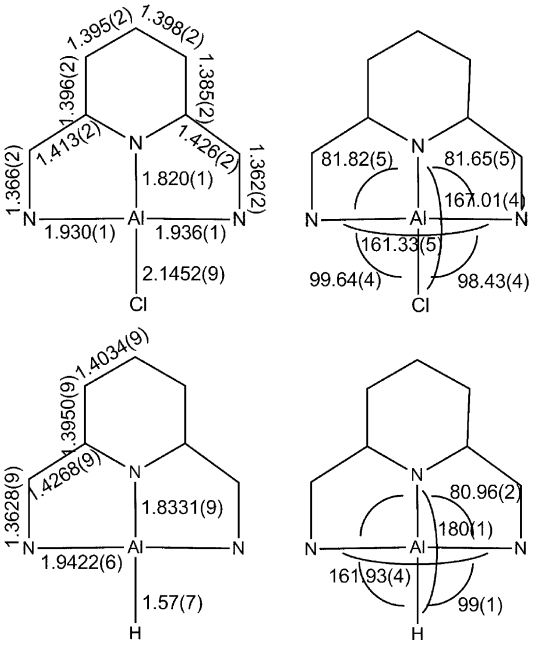


Figure 2. Solid-state structure of $[(^{\mathrm{Ph}}\mathrm{I_2P^{2-}})\mathrm{AlH}]$ (**3**).[11] Unlabeled atoms are C atoms; ellipsoids are set at 50%, H atoms except the hydride are omitted for clarity.

tion, Tables S1, S2). The structure contained no disorder, and was refined to $R_1 = 0.0354$ and $wR_2 = 0.0878$ in the space group $P2_1/n$. The ligand in **2** has approximate mirror symmetry across the Cl-Al-N_{py} plane. For example, the two C_{im}–N_{im} bond lengths in **2** are 1.3664(18) and 1.3622(17) Å, and the two C_{im}–$C_{py(o)}$ bond lengths are 1.4128(18) and 1.4261(18) Å. The crystallographic metrics for the $^{\mathrm{Ph}}\mathrm{I_2P^{2-}}$ ligand suggested an extensively delocalized electronic structure for **2**. The ligand backbone is planar, and characterized by very uniform C–C bond lengths in the pyridyl ring, which span just 1.385(2)–1.398(2) Å over all four C–C bonds (Scheme 2). The bond angles about the $\mathrm{Al^{III}}$ ion confirm the visual impression that **2** has an unusual geometry that is very close to SP. The N_{py}-Al-Cl angle is 167.01(4), and the N_{im}-Al-$N_{im'}$ angle is 161.33(5). The τ_4 value for **2** is 0.22.



Scheme 2. Bond lengths and angles in **2** (top) and **3** (bottom).

The foregoing results prompted us to reinvestigate the four-coordinate complex $[(^{\mathrm{Ph}}\mathrm{I_2P^{2-}})\mathrm{AlH}]$ (**3**), which we have previously characterized spectroscopically.[12] We were eventually able to crystallize **3** from a hexane/toluene mixture, which afforded brown block-shaped crystals suitable for a single-crystal X-ray diffraction experiment. The solid-state structure of **3** revealed another SP $\mathrm{Al^{III}}$ complex (Figure 2). In this example, the molecule lies on a crystallographically imposed C_2 axis in the $C2/c$ space group (Scheme 2). The crystallographically imposed value of τ_4 for **3** is 0.13. As in compound **2**, the bond lengths around the backbone of the $^{\mathrm{Ph}}\mathrm{I_2P^{2-}}$ ligand indicate extensive delocalization of the π system: in this case, all of the C–C bonds in the pyridyl ring have bond lengths that fall between 1.3950(9) and 1.4034(9) Å, and these are slightly longer than those for **2** (Scheme 2).

In general, these and other bond lengths for the ligands in **2** and **3** are consistent with an observation that the ligand in **3** is more reduced than that in **2**, because the localization of more electron density over the $^{\mathrm{Ph}}\mathrm{I_2P^{2-}}$ ligand causes lengthening and shortening of various internal ligand bond lengths. In particular, the C_{im}–N_{im} bond in **3** is 0.012 Å shorter, and the C_{im}–$C_{py(o)}$ bond is 0.0073 Å longer than the corresponding bond length averages in **2**. These observations are consistent with the less electron-withdrawing character of the hydrido ligand compared with the chloro ligand, and are consistent with observations that we have previously made in trigonal bipyramidal Al complexes containing two bidentate iminopyridine ligands (IP), and of the form $[(\mathrm{IP^-})_2\mathrm{AlX}]$.[14]

We are aware of two previously reported examples of diamagnetic twice-reduced bis(imino)pyridine ligands coordinated to diamagnetic metal ions, namely $\mathrm{Ni^{II}}$ and $\mathrm{Al^{III}}$.[12,15] In both of those instances, the coordination environment about the metal center approximated tetrahedral, and the $\mathrm{I_2P^{2-}}$ ligand deviated significantly from planarity (N_{im}-C_{im}-$C_{py(o)}$-N_{py} torsion angles were 11.87° and 11.45° for the $\mathrm{Ni^{II}}$, and 5.2° and 8.1° for the $\mathrm{Al^{III}}$ complex). Characterization of **2** and **3** has demonstrated that when the $^{\mathrm{Ph}}\mathrm{I_2P^{2-}}$ ligand possesses a planar geometry, the $S = 0$ ground state spin persists.[16]

To assess the Lewis acidity of each of the SP Al complexes, we probed the interactions of **2** and **3** with base. Proton NMR spectroscopy measurements indicated that there is an interaction between the Al center and 2,6-lutidine (lut). The proton NMR resonance that arises from the para pyridyl proton on the backbone of the $^{\mathrm{Ph}}\mathrm{I_2P^{2-}}$ ligand is very sensitive to the coordination environment at the Al center: it is shifted upfield by 0.61 ppm in **2**-lut, and by just 0.13 ppm upfield in **3**-

lut, as compared with **2** and **3**, respectively (Supporting Information, Figure S2 and S3). Consistent with our earlier comment that the Al center in **3** is more electron-rich than in **2**, the interaction with lut by **2** is stronger, as indicated by the relative chemical shifts. Furthermore, the resonance on the py ring observed for **2**-lut is a well-defined triplet, and the resonance for the *para* pyridyl proton in **3**-lut is a broad singlet and this suggests that the interaction between the Al center in **3** and lut is fluxional at the temperature of the experiment. Fluxional behavior is often associated with the Lewis acid–Lewis base adducts sometimes denoted as FLPs.[3]

In summary, the isolation of **2** and **3**, which are SP Al^{III} complexes, reveals that an unusual coordination geometry arises using the chelating phenyl-substituted bis(imino)pyridine ligand. The origin of the energetic driving force for this square planarity is currently unknown and will be interrogated by using theoretical methods in the future. These four-coordinate Al centers are Lewis acidic and form adducts with the base 2,6-lutidine. Future work will probe the potential for these complexes to display the reactivity often associated with FLP chemistry.

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