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## Formation of an Ag→Al Dative Bond Is Avoided in Reactions of an Alane/tris(phosphine) Ligand with Monovalent Silver

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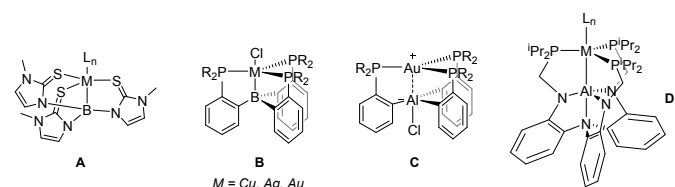
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**Abstract.** An alane/tris(phosphine) ligand reacts with AgOTf by coordination of three phosphines to the Ag center and transfer of triflate to the tris(pyrrrolyl) Al site. Reaction with Ag[HCB<sub>11</sub>Cl<sub>11</sub>] results in the coordination of two phosphines to Ag and one to Al, with no significant Ag–Al bonding in either structure.

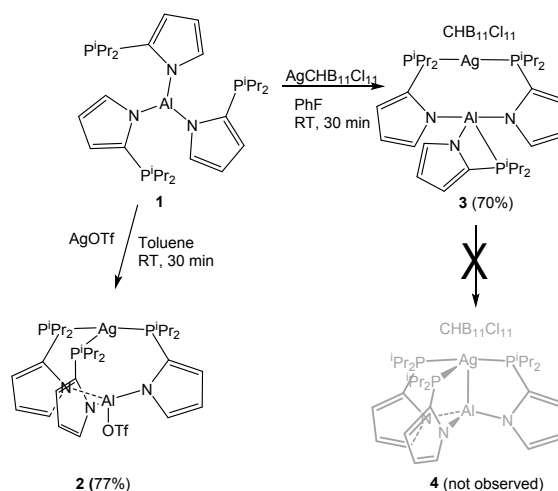
Tripodal ligands combining a central main group Lewis acid with three neutral outer donors (ZL<sub>3</sub>) have played a pivotal role in the development of the understanding of the nature of the interaction of Z-type ligands with transition metals,<sup>1</sup> and in the development of catalytic applications.<sup>2–7</sup> The ligands comprised of a central group 13 element and three phosphine donors (such as **A**, **B**, **C**, and **D** in Figure 1) have been particularly prominent.<sup>8–15</sup>



**Figure 1.** Selected literature examples of complexes of boron- and aluminum-centered ZL<sub>3</sub> ligands.

We have recently reported<sup>16</sup> a new AlP<sub>3</sub> ligand of this class which features one of the arguably strongest group 13 Lewis acids in the ZL<sub>3</sub> designs, courtesy of a tris(N-pyrrolyl) substitution about the Al center. Interactions of ZL<sub>3</sub> ligands with coinage metal-based MX or M<sup>+</sup> fragments with the system **B** (Figure 1) have been studied and generally showed that the ability to donate to the Lewis acid decreases in the order Au > Cu > Ag.<sup>12</sup> We became interested in whether the AlP<sub>3</sub> ligand and its higher central Lewis acidity can enforce a stronger

interaction with an Ag center. However, we discovered that the combination of AlP<sub>3</sub> with the AgOTf or Ag<sup>+</sup> fragments did not result in the expected tripodal complexes with a simple Ag→Al interaction. In this report, we present the structural changes that were observed instead.



**Scheme 1.** Synthesis of compounds **2** and **3**.

The reaction of AlP<sub>3</sub> with AgOTf proceeded smoothly to result in a single product **2** (Scheme 1), which was isolated in 77% yield. The <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were consistent with C<sub>3</sub> symmetry. In particular, we noted a single set of <sup>31</sup>P NMR resonances displaying characteristic coupling to the two S = ½ isotopes of Ag. However, the XRD study on a suitable single crystal (Figure 2) revealed that while the three phosphines are indeed bound to the Ag center, the triflate has migrated to Al. This has the apparent effect of quenching the Lewis acidity of Al towards the Ag center. The Al–Ag distance is quite long at 3.1834(7) Å vs 2.56 Å as the sum of covalent radii per Alvarez et al.<sup>17</sup> The Al center is displaced from the N<sub>3</sub> plane towards the oxygen of the triflate, but the geometry falls short of taking on a strictly tetrahedral (Σ<sub>N–Al–N</sub> = ca. 352.5°). The incomplete pyramidalization of Al may be related to the chelate constraint.

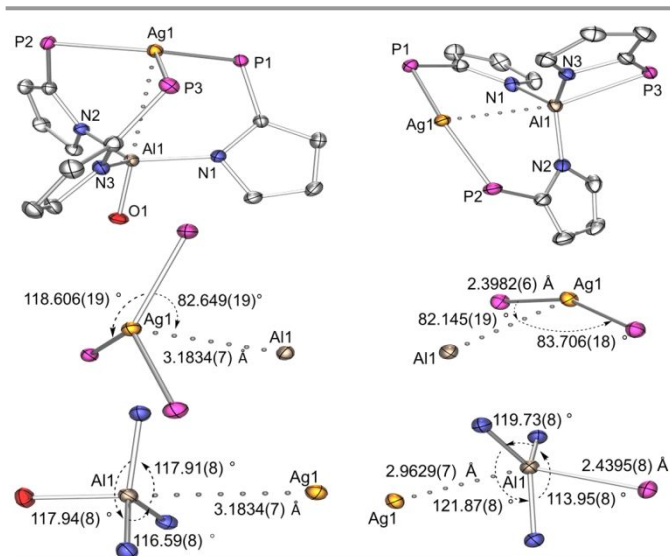
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The Ag center is slightly displaced from the P<sub>3</sub> plane, away from Al ( $\Sigma_{P-Ag-P} = \text{ca. } 354.9^\circ$ ). Based on these metrics, although some Al...Ag interaction cannot be excluded, it would clearly be quite weak at best.

The transfer of triflate to Al is reminiscent of the observation of Bourissou et al. who recorded the transfer of chloride from Au to Al resulting in structure **C** (Figure 1).<sup>18</sup> It is also related to the abstraction of the halide from group 11 metal halides by certain ZL<sub>2</sub> ligands.<sup>18,19</sup> We surmised that removing the triflate from the equation and instead utilizing a more weakly coordinating anion might result in the retainment of Lewis acidity at Al in the adduct with Ag<sup>+</sup>. To this end, AlP<sub>3</sub> was subjected to a reaction with Ag[HCB<sub>11</sub>Cl<sub>11</sub>].<sup>20</sup> It resulted in the clean formation of a single product, but it was apparent from the NMR spectra that it did not possess the expected tripodal symmetry of the targeted compound **4**. Two resonances in a 2:1 ratio were observed in the <sup>31</sup>P NMR spectrum, with only the larger resonance displaying the telltale coupling to <sup>107/109</sup>Ag. A single-crystal XRD study (Figure 2) revealed that in the product **3**, one of the phosphine arms has rotated away from Ag and brought the phosphine donor around to make a bond to Al (Figure 2). The 1,2-disposition of the Lewis acid (Al) and Lewis base (P) mimics some of the common designs for intramolecular frustrated Lewis pairs.<sup>21,22</sup>



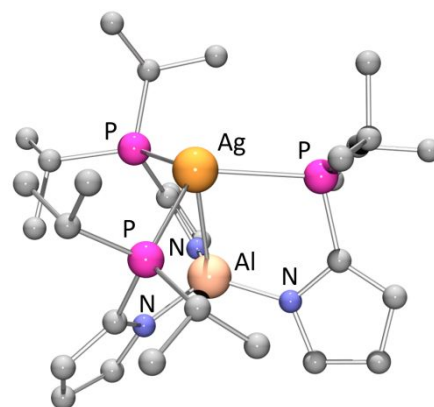
**Figure 2.** POV-Ray<sup>23</sup> rendition of the ORTEP drawing<sup>24</sup> (50% thermal ellipsoids) of **2** (left) and **3** (right). Top: A view showing selected atom labelling. Hydrogen atoms, solvent molecules, and isopropyl groups are omitted for clarity. Middle: Truncated molecules showing the Ag center and the atoms around Ag. Bottom: Truncated molecules showing the Al center and the atoms around Al.

Although the P-Al interaction should be challenged by the strain of the four-membered ring it creates, the P-Al distance in **3** (2.4395(8) Å) is not especially long. Barron et al. analysed Al-P distances in alane-phosphine adducts as a function of the number of carbon (R) vs heteroatom (X) substituents on Al and noted that X<sub>3</sub>Al-PR<sub>3</sub> adducts possess the shortest Al-P distance on the order of 2.40 Å, and the corresponding RX<sub>2</sub>Al-PR<sub>3</sub> giving rise to distances (2.44 Å) similar to that in **3**.<sup>25</sup> An adduct of an alkyl-diisopropylphosphine with AlCl<sub>3</sub> has been structurally

characterized by the Fryzuk group, revealing a ca. 2.41 Å Al-P distance.<sup>26</sup>

The value of  $\Sigma_{N-Al-N} = \text{ca. } 355.6^\circ$  in **3** is similar to that in **2**, indicating that Al largely remains in the N<sub>3</sub> plane. Thus it is also possible to contemplate that the structure can be viewed as trigonal bipyramidal about Al, with bonding interactions with both P and Ag. The Ag-Al distance in **3** (2.9629(7) Å) is shorter than in **2** but is still about 0.4 Å longer than the sum of the covalent radii.<sup>17</sup> Furthermore, the P-Ag-P angle is ca. 159°, but the deviation from linearity positions Ag away from Al.

To gain further insight into the possible Ag-Al interactions, we engaged DFT calculations. The structures of compounds **2-4** were optimized using Gaussian 09 (LANL2DZ/6-31G(d) basis set and the M06 functional in the gas phase). Satisfactory agreement between the geometries of the DFT-optimized **2** and **3** and the experimental XRD structures was found. Compound **4** (Figure 3) was calculated to possess a 2.662 Å Ag-Al distance and to lie higher than **3** in both enthalpy (by 4.0 kcal/mol) and in free energy (by 6.7 kcal/mol at 298 K). Utilization of other functionals similarly favoured **3** over **4** thermodynamically (see ESI). The AIM topological analysis of the computed structures revealed the presence of a bond critical point (BCP) in **4** but not in **2** or **3**. On the whole, the insight from DFT calculations is consistent with the experimental findings: there is essentially no bonding between Ag and Al in **2** or **3** and the structure in which Ag-Al bonding is present (**4**) is not the most stable isomer.



**Figure 3.** DFT-optimized geometry of the cation of compound **4** (The HCB<sub>11</sub>Cl<sub>11</sub> anion and the hydrogen atoms are not shown for clarity).

In summary, reactions of the AlP<sub>3</sub> ligand with AgOTf and Ag<sup>+</sup> do not lead to a well-defined Ag→Al bond. Instead, Al manages to abstract either the triflate anion or one of the phosphine donors away from silver. This reinforces the notion that monovalent silver is not a good partner for Z-type ligands. Employing a stronger Lewis acid such as in AlP<sub>3</sub> causes the Al center to seek alternatives to Ag as a Lewis basic partner, even in spite of the significant structural preorganization favouring a direct silver-aluminum contact.

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### Conflicts of interest

There are no conflicts to declare.

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