Electronic Supplementary Information

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

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I. General Considerations

Unless otherwise specified, all reactions and manipulations were carried out inside an argon-filled glove box or using Schlenk line techniques. Toluene and pentane were dried and deoxygenated via the solvent purification system and stored over molecular sieves in the glove box filled with argon. C_6D_6 were dried over NaK /Ph_2CO/18-crown-6, distilled and stored over molecular sieves in an Ar-filled glove box. Fluorobenzene and C_6D_5Br were dried over CaH_2, distilled and stored over molecular sieves in an Ar-filled glove box. NMR spectra were recorded on a Varian Inova 500 spectrometer (^1H NMR, 499.703 MHz, ^{13}C NMR 125.580 MHz, ^{19}F NMR, 469.854 MHz), Varian Inova 400 (^{11}B NMR, 128.191 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^1H spectra, the residual solvent peak was used as an internal reference (δ 7.16 for C_6D_6, 7.30 for C_6D_5Br).1H-pyrrole was purchased from Oakwood chemicals, then was dried with CaH_2 and distilled before use. Other chemicals were purchased from commercial vendors and used without further purification. $AgCHB_{11}Cl_{11}$[1] and N-tris(2-diisopropylphophinopyrrolyl)alane[2] (**1** AlP_3) ligand was synthesized according to the literature.

II. Synthesis of Silver Complexes

Synthesis of Ag(AlP$_3$OTf) (2). To a toluene solution containing 540 mg (0.94 mmol) Al$_3$P, 240 mg AgOTf (0.94 mmol, 1.0 equiv) was added. The resulting mixture was stirred at r.t. for 2 h. The light orange solution was then filtered through a short pad of Celite. The filtrate was concentrated under vacuum, and then layered with pentane to allow slow diffusion in the freezer. 600 mg of **2** (77%) was obtained as colorless crystal. ^{1}H NMR (500 MHz, C$_6$D$_6$, Figure S1): δ 8.10 (brs, 3H, pyrrole-C*H*), 6.52 (t, *J* = 3.0 Hz, 3H, pyrrole-C*H*), 6.39 (d, *J* = 3.2 Hz, 3H, pyrrole-C*H*), 2.20 - 2.12 (m, 3H, (CH$_3$)$_2$C*H*), 1.61 – 1.52 (m, 3H, (CH$_3$)$_2$C*H*), 1.07 – 1.02 (m, 9H, (C*H*$_3$)$_2$CH), 0.85 – 0.81 (m, 9H, (C*H*$_3$)$_2$CH), 0.78 – 0.75 (m, 9H, (C*H*$_3$)$_2$CH), 0.04 – 0.01 (m, 9H, (C*H*$_3$)$_2$CH). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$, Figure S2): δ 7.43 (d, $J_{107\text{Ag-P}}$ = 287 Hz, $J_{109\text{Ag-P}}$ = 331 Hz). ^{19}F (470 MHz, C$_6$D$_6$, Figure S3): δ -75.7. calcd for C$_{35}$H$_{59}$AgAlN$_3$P$_3$O$_4$SF$_3$: C 46.57; H 6.59, N 4.65; found: C 46.16; H 6.54; N 4.53.

Synthesis of Ag(AlP$_3$)CHB$_{11}$Cl$_{11}$ (3). 287 mg (0.50 mmol) of Al$_3$P was loaded in a culture tube with 10 mL fluorobenzene. 315 mg (0.50 mmol, 1 equiv) AgCHB$_{11}$Cl$_{11}$ was added to the above toluene solution. The mixture was stirred at r.t. for 2 h. The light orange solution was then filtered through a short pad of Celite. The filtrate was concentrated under vacuum, and slow diffusion of pentane would result in 420 mg (70%) colorless crystal of **3**. ^{1}H NMR (500 MHz, C$_6$D$_5$Br, Figure S4): δ 7.61 (brs, 1H, pyrrole-C*H*), 7.21 (brs, 2H, pyrrole-C*H*), 6.67 (t, J = 2.4 Hz, 1H, pyrrole-C*H*), 6.56 (t, J = 2.5 Hz, 2H, pyrrole-C*H*), 6.52 (d, J = 3.2 Hz, 1H, pyrrole-C*H*), 6.45 (d, J = 3.2 Hz, 2H, pyrrole-C*H*), 2.92 (m, 1H, (CH$_3$)$_2$C*H*), 2.25 - 2.16 (m, 1H, (CH$_3$)$_2$C*H*), 2.11 – 2.04 (m, 2H, (CH$_3$)$_2$C*H*), 1.81 – 1.73 (m, 2H, (CH$_3$)$_2$C*H*), 1.08 (dd, *J* = 18.9, 7.0 Hz, 6H, (C*H*$_3$)$_2$CH), 0.81 – 0.60 (m, 30H, (C*H*$_3$)$_2$CH). ^{31}P{^{1}H}

NMR (202 MHz, C_6D_5Br, Figure S5): δ 19.5 (d, $J_{107Ag\text{-}P}$ = 424 Hz, $J_{109Ag\text{-}P}$ = 489 Hz, 2P), -1.8 (brs, 1P).

III. NMR Spectra

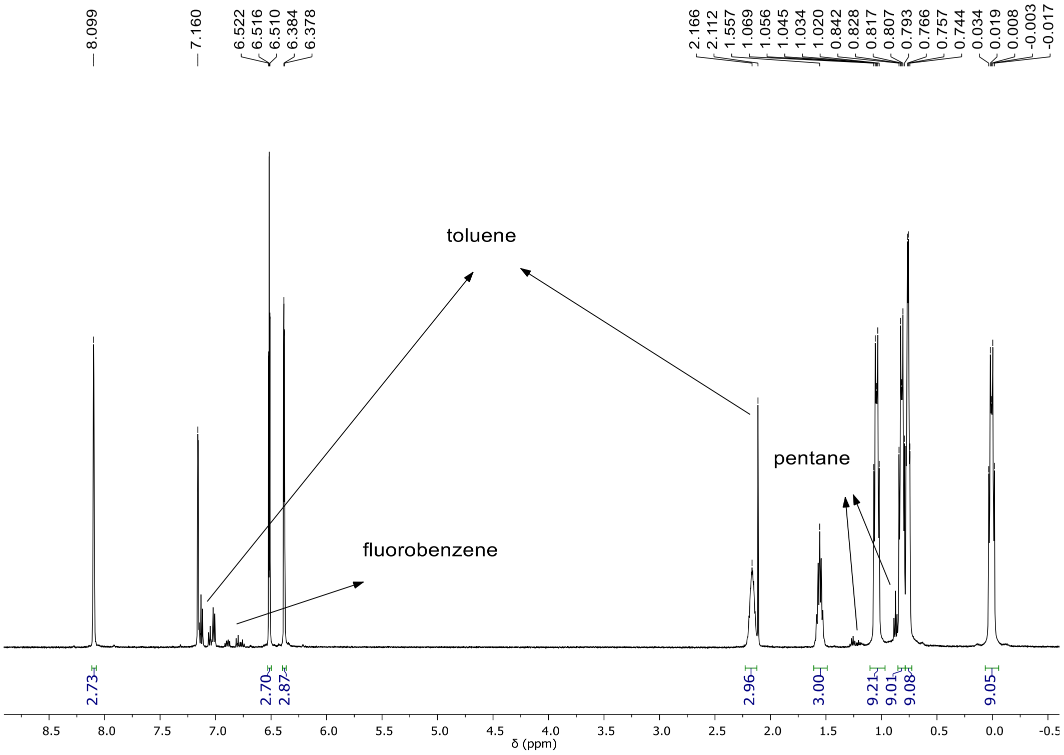

Figure S1. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **2**

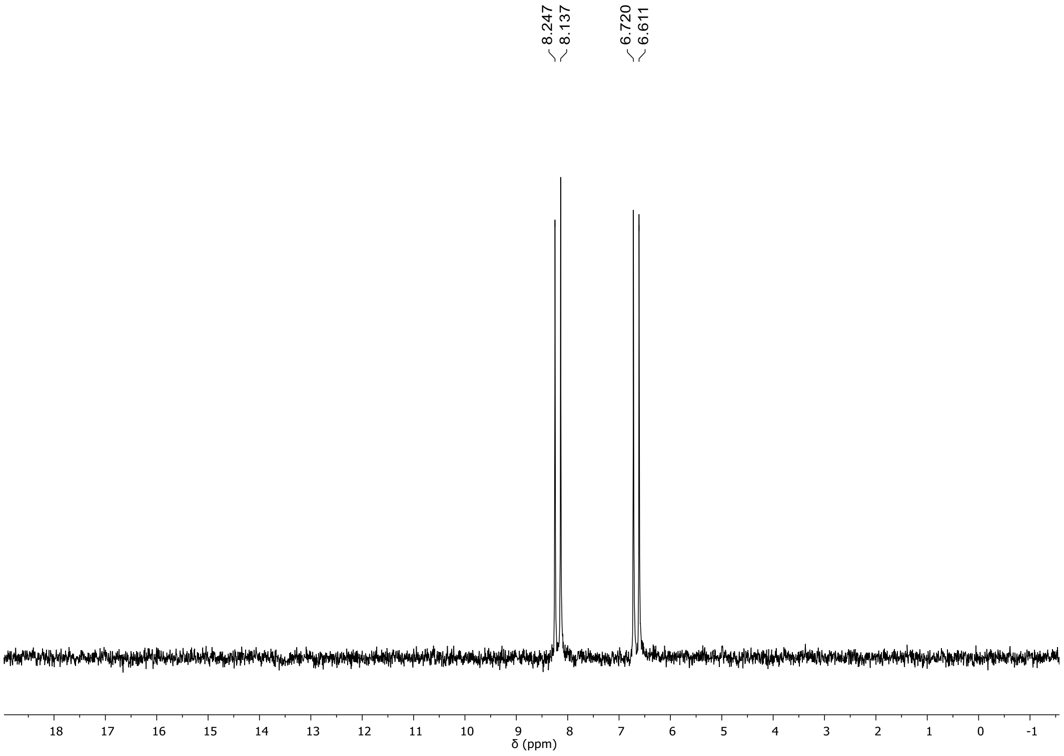

Figure S2. $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6) spectrum of **2**

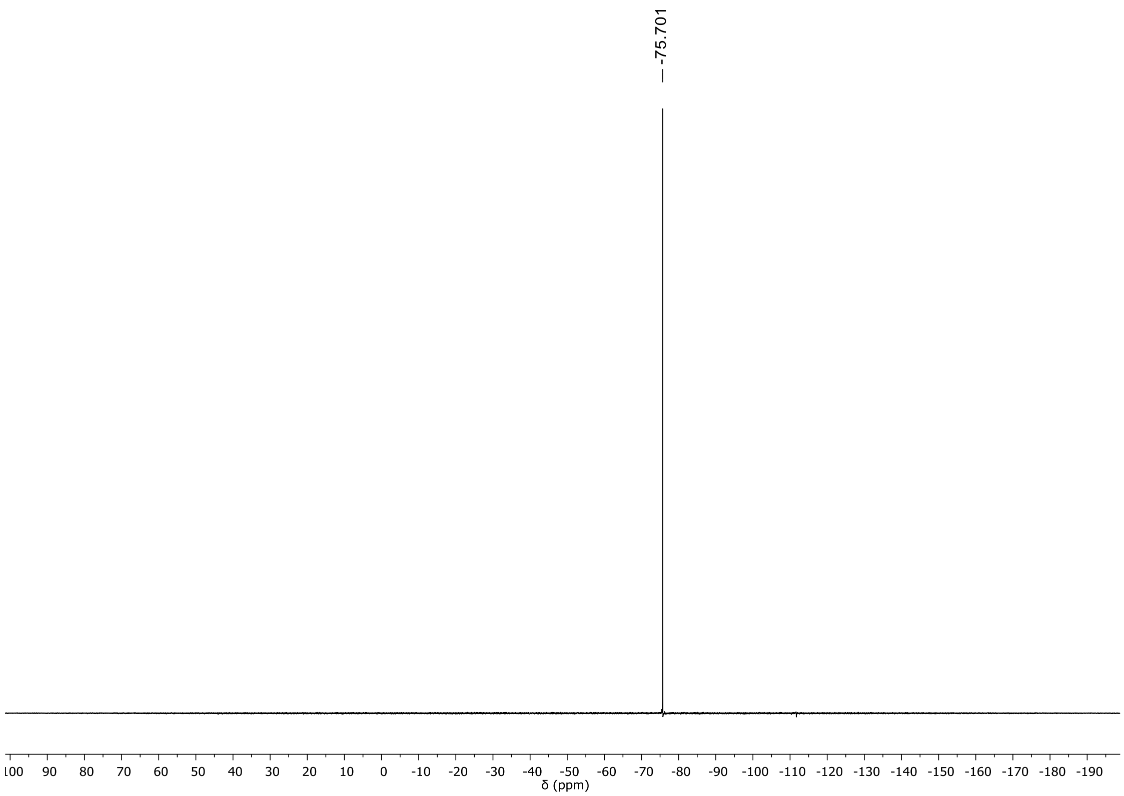

Figure S3. ^{19}F NMR (470 MHz, C_6D_5Br) spectrum of **2**

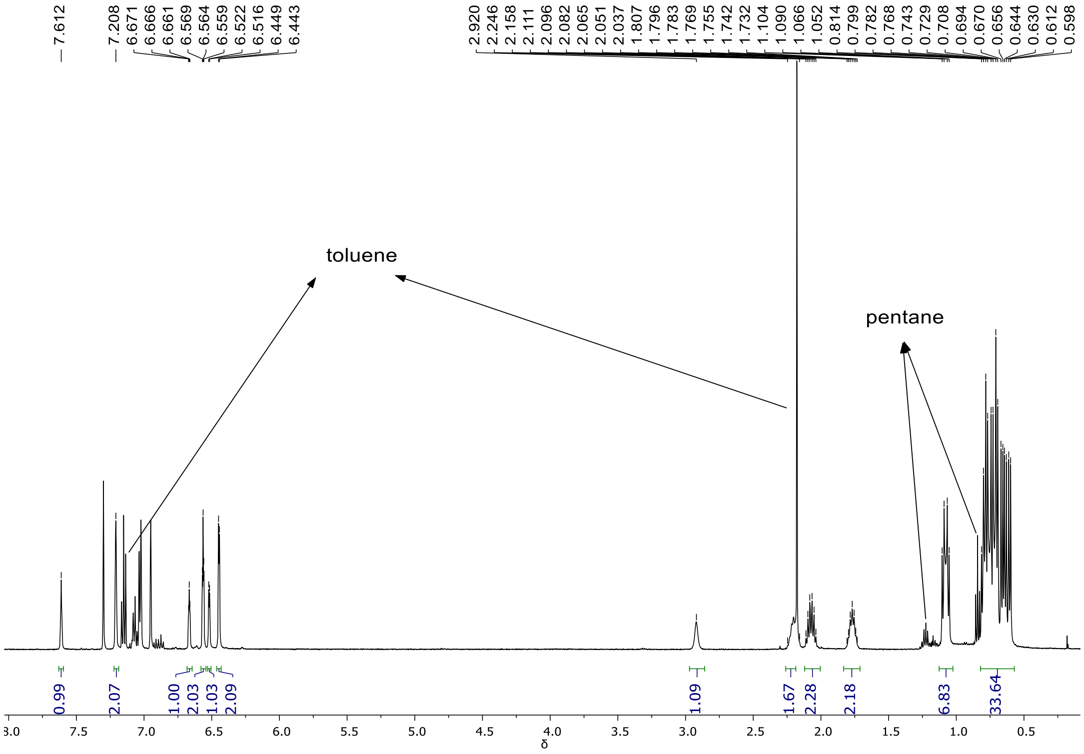

Figure S4. ^{1}H NMR (500 MHz, C_6D_5Br) spectrum of **3**

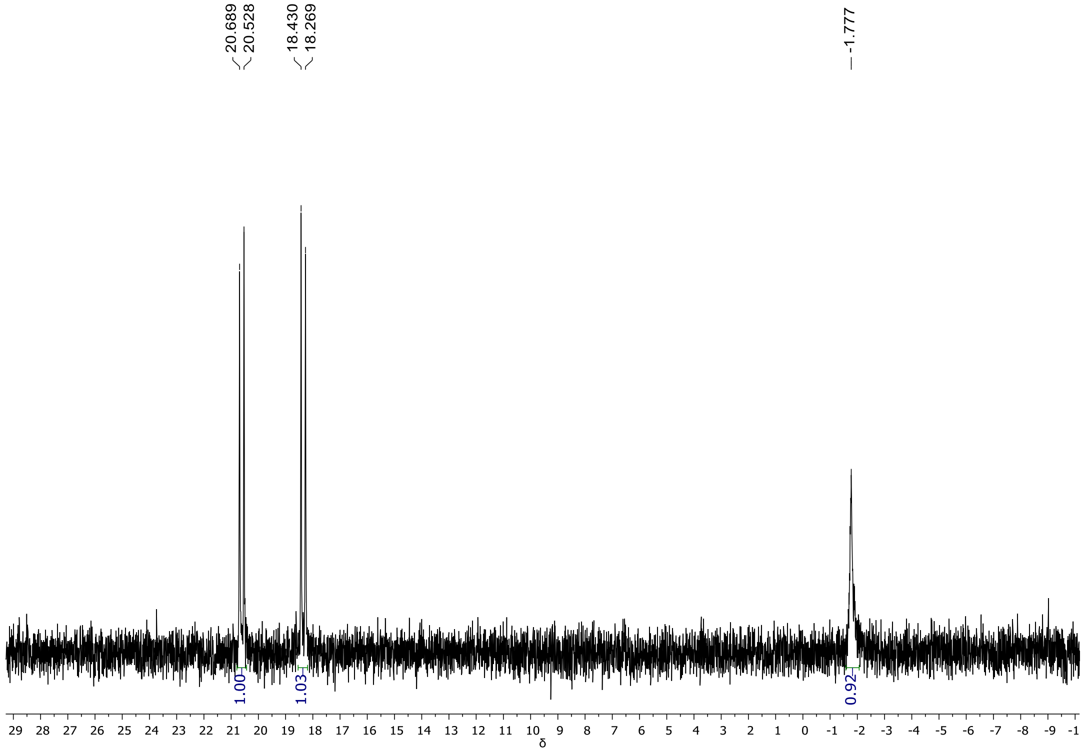

Figure S5. ^{31}P{^{1}H} NMR (202 MHz, C_6D_5Br) spectrum of **3**

IV. X-Ray Structural Determination Details

Colorless block crystals of **2 (CCDC 1915843)** was mounted onto a nylon loop and placed in a cold stream of nitrogen respectively. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, Kα = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[3] An absorption correction was applied using SADABS.[4] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic P21/n space group using XS/XT[5] (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model with the exception of the hydrogen bridged to iron and carbon which was located from the difference map. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.[6]

Colorless block crystals of **3 (CCDC 1915844)** were mounted onto a nylon loop and placed in a cold stream of nitrogen respectively. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, Kα = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[3] An absorption correction was applied using SADABS.[4] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[1] The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[2] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group *P*-1. A solution was obtained readily using XT/XS in APEX2.[3,5] Two molecules of toluene were found solvated. One of them located on a symmetry element and hence disordered, which was modeled successfully. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Also, residual electron density (Q) peaks suggested the isopropyl group (C26, C27, C28) was disordered and was modeled between two positions with an occupancy ratio of 0.88 : 0.12. Appropriate restraints and/or constraints were added to keep the bond distances, angles, and thermal ellipsoids meaningful. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).[6] The structure was refined (weighted least squares refinement on F^2) to convergence.[3, 7] Olex2 was employed for the final data presentation and structure plots.[7]

V. DFT Calculations

The Gaussian suite of programs[8] was used for the ab initio electronic structure calculations. The structures were fully optimized by the B97-D3,[9] B3LYP-D3,[10,11] M06,[12] and wB97XD[13] functional in the gas phase, and harmonic vibrational frequency calculations were performed to ensure that a minimum was obtained. The Los Alamos basis set and the associated effective core potential (ECP) was used for Ag atom, and an all-electron 6-31G(d) basis set was used for all the other atoms. Unless otherwise stated, the Gibbs free energy and enthalpy reported in this paper are under 298.15 K and 1 atm.

Atom-in-molecules (AIM)[14] analyses were carried out to study the interaction between Ag atom and Al atom. According to the topological analysis in AIM theory, the position where the electron density gradient disappears to zero is called the critical points (CPs). Bond CPs (BCPs) is a key CP which is usually found among the pairs of atoms that are attracted to each other. The bond path between a BCP and the pairs of atoms shows various bonding pathways of the atoms. AIM analyses were performed by Multiwfn code.[15] The figures are presented by VMD software.[16]

Table S1. DFT Calculated energies and Ag-Al interatomic distances.

Compound #	DFT Functional	Calculated free energy (G), in a.u.	Calculated enthalpy (H), in a.u.	Ag-Al distance, Å	ΔG_{298} of isomerization from **3** to **4**, kcal/mol	ΔH of isomerization from **3** to **4**, kcal/mol
2	B3LYP-D3	-3711.628272	-3711.48465	3.263		
3	B3LYP-D3	-8125.122937	-8124.940271	3.200		
4	B3LYP-D3	-8125.11042	-8124.929758	2.605	7.9	6.6
2	B97-D3	-3710.499213	-3710.353316	3.279		
3	B97-D3	-8124.144435	-8123.959237	3.154		
4	B97-D3	-8124.133921	-8123.949751	2.600	6.6	6.0
2	M06	-3710.030253	-3709.887303	3.281		
3	M06	-8123.164281	-8122.981603	3.065		
4	M06	-8123.153556	-8122.975304	2.662	6.7	4.0
2	wB97XD	-3710.767233	-3710.626907	3.318		
3	wB97XD	-8124.105328	-8123.923747	3.321		
4	wB97XD	-8124.089442	-8123.910819	2.656	10.0	8.1

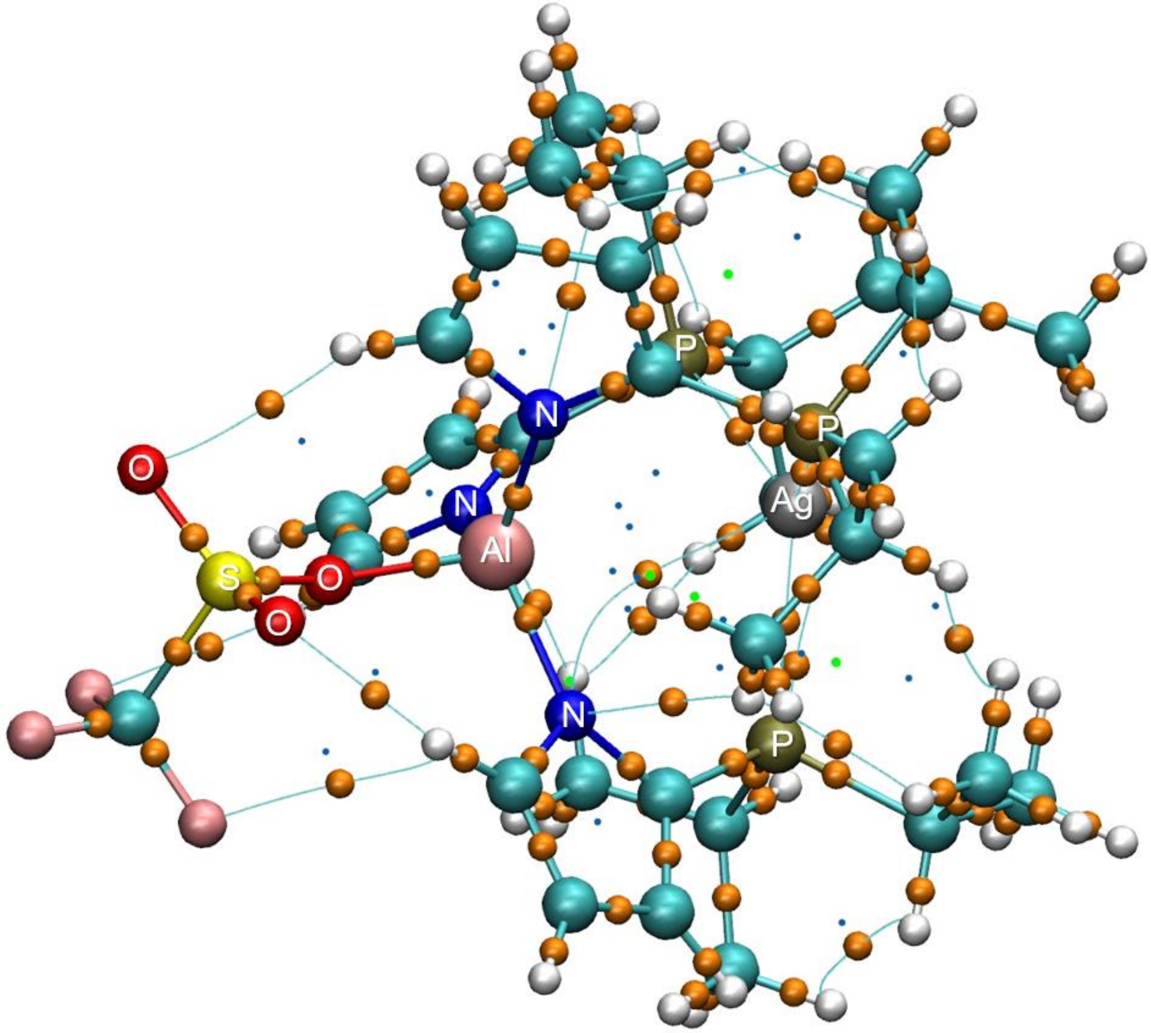

Figure S6. AIM topological analysis of compound **2**. Bond critical points (orange dots) and bond paths (cyan lines) are shown. Selected atoms are labeled.

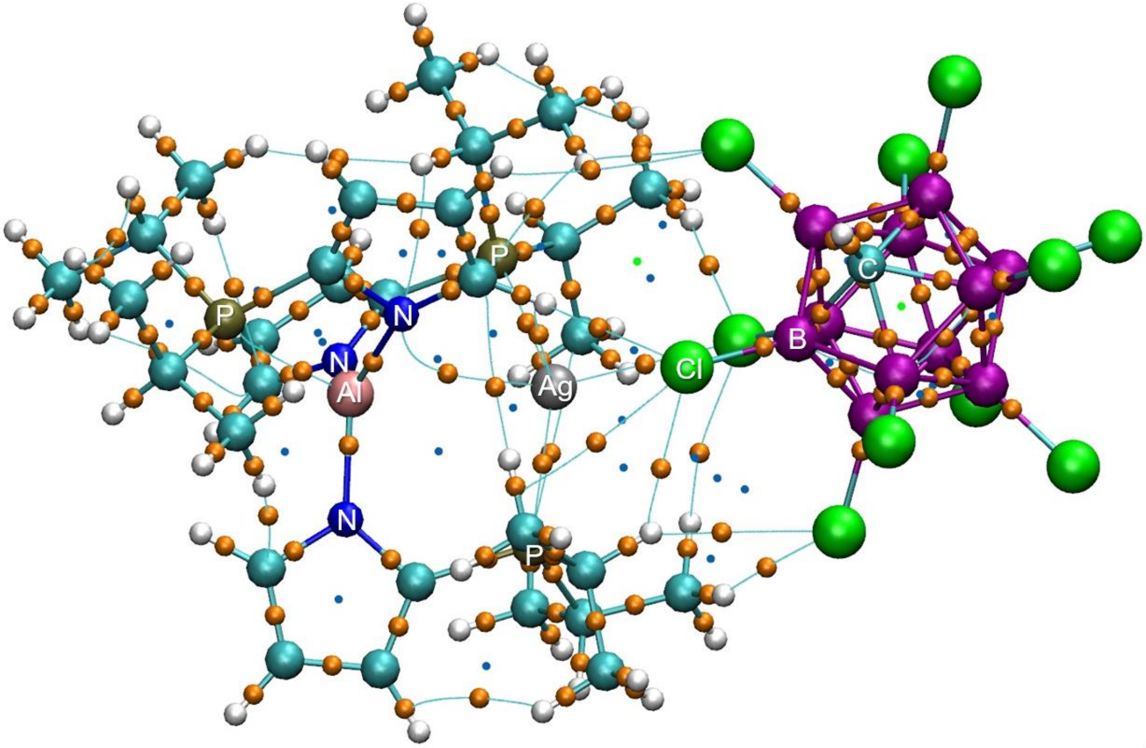

Figure S7. AIM topological analysis of compound **3**. Bond critical points (orange dots) and bond paths (cyan lines) are shown. Selected atoms are labeled.

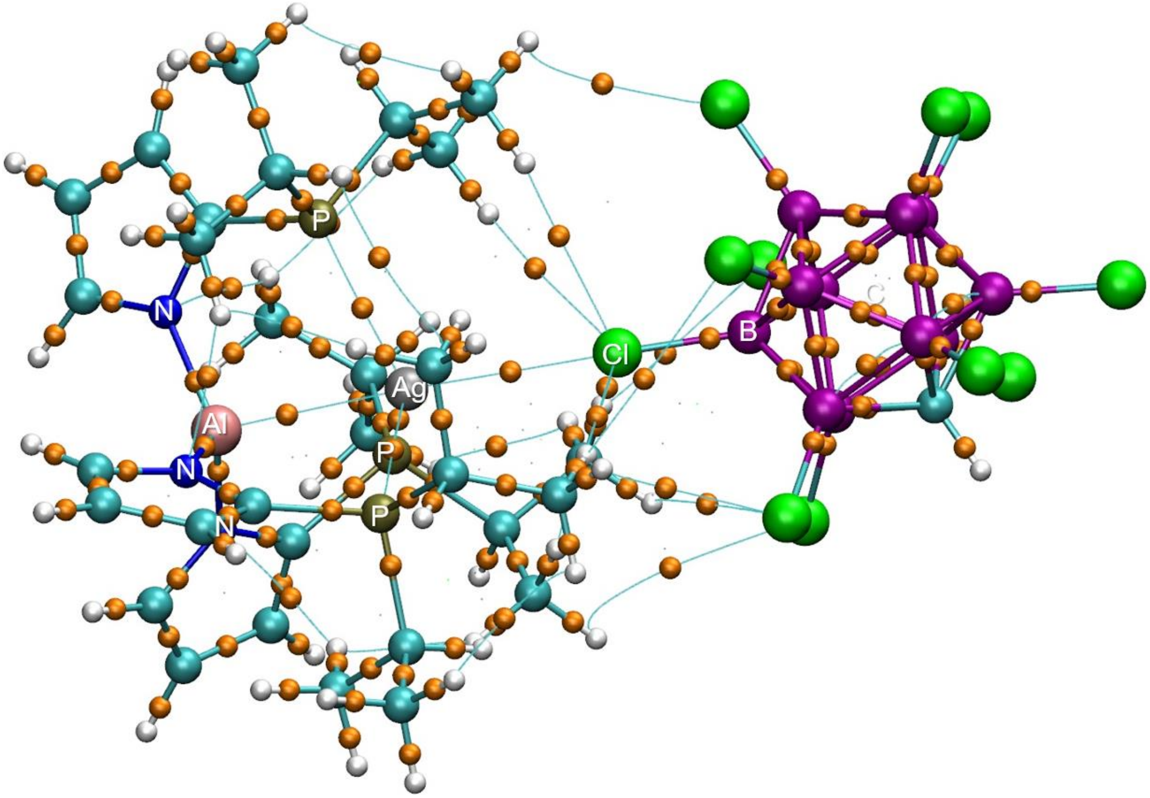

Figure S8. AIM topological analysis of compound **4**. Bond critical points (orange dots) and bond paths (cyan lines) are shown. Selected atoms are labeled. The electron density value for the Ag…Al BCP is 0.0264 a.u. and the Laplacian value is 0.0311 a.u.

VI. ESI References.

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