Supporting Information

Cyclo-Dipnictadialanes

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1 Experimental

**General Information.** If not stated otherwise, all manipulations were performed under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk techniques or an inert atmosphere glovebox (MBraun LABstar ECO). All glassware was heated three times in vacuo using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, steel- or PE-canulas, which were purged with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in Table S1.

**Table S1:** Origin and purification of solvents and reactants.

| Substance       | Origin                  | Purification                                                                 |
|-----------------|-------------------------|------------------------------------------------------------------------------|
| Benzene         | local trade             | dried over Na/benzophenone freshly distilled prior to use, stored over molecular sieves. |
| n-hexane        | Geyer, CHROMASOLV®, for HPLC, ≥97.0% (GC) | purified with the Grubbs-type column system "Pure Solv MD-5" dried over Na/benzophenone/tetraglyme freshly distilled prior to use |
| n-pentane       | local trade             | dried over Na/benzophenone/tetraglyme freshly distilled prior to use           |
| Toluene         | Fisher Chemical, for HPLC | purified with the Grubbs-type column system "Pure Solv MD-5"                  |
| THF             | Sigma Aldrich, inhibitor-free, for HPLC, ≥99.9% | purified with the Grubbs-type column system "Pure Solv MD-5" dried over Na/benzophenone freshly distilled prior to use |
| C₆D₆            | euriso-top              | dried over Na/benzophenone freshly distilled prior to use                       |
| C₇D₈ (toluene-d₈) | euriso-top              | dried over Na/benzophenone freshly distilled prior to use                       |
| AlCp₃[1]        | synthesized             |                                                                              |
| (AlCp*)₄[2]     | synthesized             |                                                                              |
| (PMes)₃[3]      | synthesized             |                                                                              |
| (PDip)₃[4]      | synthesized             |                                                                              |
Table S1 continued.

| Substance     | Origin     | Purification |
|---------------|------------|--------------|
| (PTip)$_3$     | synthesized|              |
| (PtBu)$_3$     | synthesized|              |
| (PPh)$_3$      | synthesized|              |
| (AsDip)$_3$    | synthesized|              |
| (AsTip)$_3$    | synthesized|              |
| iPr$_2$        | synthesized|              |

NMR spectra were recorded on Bruker spectrometers (AVANCE 300, AVANCE 400 or Fourier 300) and were referenced internally to the deuterated solvent ($^{13}$C: C$_6$D$_6$ $\delta_{\text{ref}} = 128.06$ ppm; C$_7$D$_8$ $\delta_{\text{ref}} = 20.43$ ppm) or to protic impurities in the deuterated solvent ($^1$H: C$_6$HD$_5$ $\delta_{\text{ref}} = 7.16$ ppm; C$_7$D$_8$ $\delta_{\text{ref}} = 2.08$ ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable).

Elemental analyses were obtained using a Leco Tru Spec elemental analyser.

Mass spectra were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer and a Thermo Scientific Exactive Plus spectrometer in LIFDI mode using crystalline samples.

UV-Vis spectra were acquired on a METTLER TOLEDO UV-Vis-Excellence UV5 spectrometer using 6Q-quartz glass cuvettes.
2 Structure elucidation

**X-ray Structure Determination:** X-Ray quality crystals were immersed in a film of perfluoropolyether oil and selected at room temperature. The crystal data of 1a, 1c, 1d, 2, and 3a were collected on a **BRUKER D8 QUEST** diffractometer with a CMOS area detector and multi-layer mirror monochromated MoKα radiation. 1b were collected on a **BRUKER SMART-APEX** diffractometer with a CCD area detector and graphite monochromated MoKα radiation. X-ray quality crystals of 3c, 4a and 4b were selected in Fomblin® Y-1800 perfluoroether (Alfa Aesar) at room temperature. The samples were cooled to 150(2) K during measurement. The data were collected on a Bruker Kappa Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54178 Å) or on a STOE-IPDS II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. The crystal data of 5 were collected on a **RIGAKU OD XTALAB SYNERGY-S** diffractometer with a HPAD area detector and multi-layer mirror monochromated CuKα radiation. The structures were solved using intrinsic phasing method in **SHELXT**, refined with the **SHELXL** program, and expanded using Fourier techniques. Semi-empirical absorption corrections were applied (SADABS) or (LANA). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions.

The Mesityl-group of 1a is disordered, that's why the atomic displacement parameters of atoms C1 > C9 of the residues 4 and 14 were restraint with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used). The displacement parameters of atoms C1 > C9 of the residues 4 and 14 were restrained to the same value with similarity restraint SIMU. The 1-2 and 1-3 distances in Residue 4 and 14 were restrained to the same values with SAME.
One of the Cp* groups in 3a was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely and the geometry of the minor orientation was restrained to be equal with the major orientation. The atomic displacement parameters of atoms C1 > C10 of the residues 2 and 12 were restrained with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Values of 0.05 for both parameters were used). The displacement parameters of atoms C1 > C10 of the residues 2 and 12 were restrained to the same value with similarity restraint SIMU.

The solvent in 5 was found to be disordered. The atomic displacement parameters of atoms C1 to C6 of residues 8 and 18 (BENZ) were restrained with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used). The displacement parameters of atoms C1 to C6 of residues 8 and 18 (BENZ) were restrained to the same value with similarity restraint SIMU.
Table S2: Crystallographic details of 1a, 1b, 1c and 1d.

| Compound | 1a          | 1b          | 1c          | 1d          |
|----------|-------------|-------------|-------------|-------------|
| Empirical formula | C_{52}H_{80}Al_{2}P_{2} | C_{63}H_{102}Al_{2}P_{2} | C_{64}H_{102}Al_{2}P_{2} | C_{57}H_{74}Al_{2}P_{2} |
| Formula weight (g·mol⁻¹) | 821.06 | 975.34 | 989.37 | 815.01 |
| Temperature (K) | 133(2) | 100(2) | 145(2) | 100(2) |
| Radiation, λ (Å) | MoKα 0.71073 | MoKα 0.71073 | MoKα 0.71073 | MoKα 0.71073 |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic |
| Space group | P 1 | P 1 | P 1 | P2₁/c |
| a (Å) | 12.7191(7) | 11.877(2) | 12.2990(14) | 12.5124(4) |
| b (Å) | 13.7498(8) | 12.793(3) | 14.5074(19) | 15.2016(6) |
| c (Å) | 14.9235(7) | 21.259(5) | 19.780(2) | 12.6358(5) |
| α [°] | 95.548(2) | 100.954(13) | 83.201(7) | 90 |
| β [°] | 105.477(2) | 99.365(19) | 74.638(9) | 103.7210(10) |
| γ [°] | 99.048(2) | 104.194(16) | 67.989(8) | 90 |
| Volume (Å³) | 2457.5(2) | 2999.2(11) | 3154.4(7) | 2334.85(15) |
| Z | 2 | 2 | 2 | 2 |
| Calculated density (Mg·m⁻³) | 1.110 | 1.080 | 1.042 | 1.159 |
| Absorption coefficient (mm⁻¹) | 0.157 | 0.138 | 0.132 | 0.165 |
| F(000) | 896 | 1072 | 1088 | 884 |
| Theta range for collection | 2.340 to 26.372° | 1.691 to 26.499° | 2.338 to 31.569° | 2.145 to 26.022° |
| Reflections collected | 106714 | 54390 | 210511 | 21006 |
| Independent reflections | 10041 | 12313 | 21040 | 4603 |
| Minimum/maximum transmission | 0.7060/0.7454 | 0.6282/0.7454 | 0.7098/0.7462 | 0.6874/0.7456 |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data/parameters/restraints | 10041 / 614 / 420 | 12313 / 632 / 0 | 21040 / 643 / 0 | 4603 / 262 / 0 |
| Goodness-of-fit on F² | 1.032 | 1.018 | 1.079 | 1.034 |
| Final R indices [I>2 σ(I)] | R₁ = 0.0411, wR² = 0.0971 | R₁ = 0.0539, wR² = 0.1422 | R₁ = 0.0386, wR² = 0.0985 | R₁ = 0.0312, wR² = 0.0743 |
| R indices (all data) | R₁ = 0.0581, wR² = 0.1074 | R₁ = 0.0650, wR² = 0.1514 | R₁ = 0.0448, wR² = 0.1024 | R₁ = 0.0371, wR² = 0.0790 |
| Maximum/minimum residual electron density (e·Å⁻³) | 0.565 / −0.322 | 1.291 / −0.695 | 0.429 / −0.349 | 0.315 / −0.203 |
| CCDC # | 2102648 | 2102649 | 2102650 | 2102651 |
Table S3: Crystallographic details of 2, 3a, 3b and 3c.

| Compound | 2   | 3a  | 3b   | 3c   |
|----------|-----|-----|------|------|
| Empirical formula | C_{29}H_{56}AlP_{3} | C_{38}H_{52}Al_{2}P_{2} | C_{44}H_{64}Al_{2}P_{2} | C_{50}H_{76}P_{2}Al_{2} |
| Formula weight (g·mol\(^{-1}\)) | 524.62 | 624.69 | 708.85 | 793.00 |
| Temperature (K) | 101(2) | 100(2) | 100(2) | 150(2) |
| Radiation, \(\lambda\) (Å) | MoK\(\alpha\) 0.71073 | MoK\(\alpha\) 0.71073 | MoK\(\alpha\) 0.71073 | MoK\(\alpha\) 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Triclinic |
| Space group | \(P2_1/n\) | \(P\ \overline{1}\) | \(P\ \overline{1}\) | \(P\ \overline{1}\) |
| \(a\) (Å) | 9.555(6) | 8.347(4) | 10.558(4) | 9.3798(7) |
| \(b\) (Å) | 17.115(9) | 10.907(6) | 10.650(4) | 10.7625(8) |
| \(c\) (Å) | 20.101(12) | 11.736(5) | 11.317(4) | 12.4334(10) |
| \(\alpha\) [°] | 90 | 104.616(16) | 105.620(13) | 97.2100(10) |
| \(\beta\) [°] | 100.762(17) | 107.265(12) | 108.859(18) | 96.993(2) |
| \(\gamma\) [°] | 90 | 111.205(15) | 111.217(8) | 106.7070(10) |
| Volume (Å\(^3\)) | 3229(3) | 870.2(8) | 1009.2(7) | 1176.10(16) |
| \(Z\) | 4 | 1 | 1 | 1 |
| Calculated density (Mg·m\(^{-3}\)) | 1.079 | 1.192 | 1.166 | 1.120 |
| Absorbtion coefficient (mm\(^{-1}\)) | 0.226 | 0.198 | 0.181 | 0.162 |
| \(F(000)\) | 1152 | 336 | 384 | 432 |
| Theta range for collection | 2.380 to 30.942° | 2.286 to 26.367° | 2.282 to 26.022° | 1.674 to 30.000° |
| Reflections collected | 44496 | 32916 | 25448 | 34307 |
| Independent reflections | 10165 | 3551 | 3960 | 6865 |
| Minimum/maximum transmission | 0.5824/0.7462 | 0.6338/0.7454 | 0.6969/0.7454 | 0.967/0.994 |
| Refinement method | Full-matrix least-squares on \(F^2\) | Full-matrix least-squares on \(F^2\) | Full-matrix least-squares on \(F^2\) | Full-matrix least-squares on \(F^2\) |
| Data/parameters/restraints | 10165 / 316 / 0 | 3551 / 294 / 270 | 3960 / 226 / 0 | 6865 / 255 / 0 |
| Goodness-of-fit on \(F^2\) | 1.054 | 1.127 | 1.064 | 1.019 |
| Final R indices [I>2 \(\sigma(I)\)] | \(R_1 = 0.0477, \ wR^2 = 0.0983\) | \(R_1 = 0.0590, \ wR^2 = 0.1414\) | \(R_1 = 0.0347, \ wR^2 = 0.0853\) | \(R_1 = 0.0424, \ wR^2 = 0.1015\) |
| R indices (all data) | \(R_1 = 0.0910, \ wR^2 = 0.1214\) | \(R_1 = 0.0821, \ wR^2 = 0.1524\) | \(R_1 = 0.0423, \ wR^2 = 0.0912\) | \(R_1 = 0.0633, \ wR^2 = 0.1133\) |
| Maximum/minimum residual electron density (e·Å\(^{-3}\)) | 0.510 / −0.569 | 0.545 / −0.430 | 0.377 / −0.288 | 0.420 / −0.261 |
| CCDC # | 2102652 | 2102653 | 2102654 | 2102655 |
Table S4: Crystallographic details of 4a, 4b and 5.

| Compound | 4a | 4b | 5 |
|----------|----|----|---|
| Empirical formula | C₄₄H₆₄Al₂As₂ | C₅₀H₆₄As₂Al₂ | C₇₀H₁₀₆Al₂N₄P₂ |
| Formula weight (g·mol⁻¹) | 796.75 | 880.90 | 1119.48 |
| Temperature (K) | 150(2) | 100(2) | 100.01(10) |
| Radiation, λ (Å) | MoKα 0.71073 | CuKα 1.54178 | CuKα 1.54184 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | P 1 | P 1 | P 1 |
| a (Å) | 10.5930(7) | 9.2818(7) | 12.8734(2) |
| b (Å) | 10.8021(6) | 10.9613(8) | 13.83680(10) |
| c (Å) | 11.2879(8) | 12.4814(9) | 20.2087(2) |
| α [°] | 103.554(5) | 97.8090(22) | 72.3070(10) |
| β [°] | 108.100(5) | 96.8904(22) | 83.6160(10) |
| γ [°] | 113.866(5) | 106.8249(22) | 76.2490(10) |
| Volume (Å³) | 1021.88(11) | 1187.127(141) | 3328.19(7) |
| Z | 1 | 1 | 2 |
| Calculated density (Mg·m⁻³) | 1.295 | 1.232 | 1.117 |
| Absorbtion coefficient (mm⁻¹) | 1.707 | 2.322 | 1.157 |
| F(000) | 420 | 468 | 1220 |
| Theta range for collection | 2.085 to 29.282° | 2.282 to 26.022° | 3.433 to 77.475° |
| Reflections collected | 18893 | 35266 | 46738 |
| Independent reflections | 5501 | 4188 | 13732 |
| Minimum/maximum transmission | 0.675/0.848 | 0.737/0.955 | 0.71288/1.00000 |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data/parameters/restraints | 5501 / 226 / 0 | 4188 / 255 / 0 | 13732 / 712 / 24 |
| Goodness-of-fit on F² | 0.942 | 1.061 | 1.031 |
| Final R indices [I>2σ (I)] | R₁ = 0.0268, wR² = 0.0655 | R₁ = 0.0224, wR² = 0.0612 | R₁ = 0.0458, wR² = 0.1293 |
| R indices (all data) | R₁ = 0.0338, wR² = 0.0673 | R₁ = 0.0232, wR² = 0.0620 | R₁ = 0.0500, wR² = 0.1335 |
| Maximum/minimum residual electron density (e·Å⁻³) | 0.531 / -0.407 | 0.3336 / -0.247 | 0.411 / -0.811 |
| CCDC # | 2102656 | 2102657 | 2102658 |
Figure S1: Molecular structure of 1a. ORTEPs drawn at 50% probability, all H-atoms omitted for clarity.
Selected bond lengths (Å) and angles (°) of 1a: P2−Al2 2.3176(7), P2−Al2' 2.3317(7); Al2−P2−Al2' 90.11(2), P2−Al2−P2' 89.89(2).
Figure S2: Molecular structure of 1b. ORTEPs drawn at 50% probability, all H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°) of 1b: P1−P1 2.1677(9), Al1−P1 2.4057(9), Al2−P2 2.4090(9), Al1−Al2 2.6947(11); P2−P1−Al1 94.66(3), P1−P2−Al2 94.96(3), P1−Al1−Al2 82.58(3), P2−Al2−Al1 82.47(3).
**Figure S3**: Molecular structure of 1c. ORTEPs drawn at 50% probability, all H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°) of 1c: P1–P1 2.1676(4), Al1–P1 2.4090(5), Al2–P2 2.3977(5), Al1–Al2 2.6933(5); P2–P1–Al1 93.617(13), P1–P2–Al2 96.732(13), P1–Al1–Al2 83.846(13), P2–Al2–Al1 81.798(13).
**Figure S4:** Molecular structure of 1d. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (°) of 1d: C1–P1 1.8318(13), P1–Al1 2.3200(5), P1–Al1' 2.3389(5), Al1–Ct1 1.905; Al1–P1–Al1' 88.97(2), P1–Al1–P1' 91.03(2).
Figure S5: Molecular structure of 2. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (°) of 2: P1–Al1 2.376(1), P1–P2 2.217(1), P2–P3 2.208(1), P3–Al1 2.383(1), Al1–Ct1 1.935; P1–Al1–P3 89.66(2), Al1–P3–P2 84.96(2), P1–P2–P3 98.60(2), P2–P1–Al1 84.92(2).
**Figure S6**: Molecular structure of 3a. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (°) of 3a: C1–P1 1.839(4), P1–Al1 2.323(2), P1–Al1’ 2.322(2), Al1–Ct1 1.847; Al1–P1–Al1’ 86.06(4), P1–Al1–P1’ 93.94(4),
Figure S7: Molecular structure of 3b. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (°) of 3b: C1−P1 1.857(2), P1−Al1 2.307(1), P1−Al1’ 2.345(1), Al1−Ct1 1.910; C1−P1−Al1’ 127.11(6), C1−P1−Al1 118.49(6), Al1−P1−Al1’ 88.99(2), P1−Al1−P1’ 91.01(2).
Figure S8: Molecular structure of 3c. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (*) of 3c: C1–P1 1.8530(14), P1–Al1 2.3395(6), P1–Al1’ 2.3099(6), Al1–Ct1 1.9070(4); C1–P1–Al1’ 115.15(5), C1–P1–Al1 128.87(5), Al1–P1–Al1’ 88.796(19), P1–Al1–P1’ 91.205(18), P1–Al1–Ct1 133.893(21), P1’–Al1–Ct1 134.543(22); C2–C1–P1–Al1 -40.60(14).
Figure S9: Molecular structure of 4a. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (°) of 4a: C1−As1 1.9842(14), As1−Al1 2.4160(5), As1−Al1’ 2.4445(5), Al1−Ct1 1.9044(4); C1−As1−Al1’ 125.99(4), C1−As1−Al1 111.51(4), Al1−As1−Al1’ 86.990(15), As1−Al1−As1’ 93.009(15), As1−Al1−Ct1 134.539(21), As1’−Al1−Ct1 132.144(19); C2−C1−As1−Al1 104.89(108).
Figure S10: Molecular structure of 4b. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (°) of 4b: C1–As1 1.9863(15), As1–Al1 2.4106(8), As1–Al1’ 2.4462(16), Al1–Ct1 1.9012(4); C1–As1–Al1’ 124.93(5), C1–As1–Al1 116.31(5), Al1–As1–Al1’ 87.27(5), As1–Al1–As1’ 92.73(5), As1–Al1–Ct1 134.041(24), As1’–Al1–Ct1 133.227(22); C2–C1–As1–Al1 112.273(127).


**Figure S11**: Molecular structure of 5. ORTEPs drawn at 50% probability, all H-atoms omitted and for clarity. Selected bond lengths (Å) and angles (°) of 5: P2–Al1 2.3371(7), P2–Al3 2.3335(5), Al3–P4 2.4206(6), Al1–P4 2.4009(5), P2–C1 1.825(2), P4–C1 1.846(2), Al1–C1_4 2.084(1), Al3–C1_5 2.092(1), Al1–C1_6 2.100(2), Al3–C1_7 2.083(2); Al1–P2–Al3 91.49(2), P2–Al3–P4 87.98(2), Al3–P4–Al1 87.87(2), P4–Al1–P2 88.37(2), Al1–P2–C1 128.61(6), Al1–P4–C1 104.08(5).
3 Syntheses of compounds

3.1 [Cp³Al(μ-PMes)]₂ (1a)

A solution of Cp³Al (34.7 mg, 133 µmol) in C₆D₆ (0.6 mL) was added to P₃Mes₃ (20.0 mg, 44.4 µmol) in a J-Young-NMR tube resulting in an orange solution. After a few minutes the colour chanced to yellow. Afterwards the reaction mixture was transferred into a vial inside a glove box and was filtered. The solvent was evaporated and the residue was washed with n-pentane to give [Cp³Al(μ-PMes)]₂ (1a) (34.2 mg, 42.4 µmol, 64 %). Single crystals for X-ray diffraction were obtained by slow evaporation of a saturated C₇H₈ solution at −30°C.

^1H NMR (401 MHz, C₆D₆) δ [ppm] = 6.95 (s, 4H, aryl-CH), 6.29 (s, 4H, Cp-CH), 2.99 (s, 12H, CH₃), 2.17 (s, 6H, CH₃), 1.42 (s, 18H, Cp-C(CH₃)₃), 1.35 (s, 36H, Cp-C(CH₃)₃).

^27Al NMR (104 MHz, C₆D₆): No signal could be observed, probably due to its broadness.

^31P NMR (162 MHz, C₆D₆): δ [ppm] = −174.3 (s). HRMS (LIFDI): (m/z) Calculated for [C₅₂H₈₀Al₂P₂]⁺ 820.5361; Found 820.5344 [M]⁺
Figure S12: $^1$H NMR spectrum of [Cp$^{31}$Al($\mu$-PMes)]$_2$ (1a) in C$_6$D$_6$ at room temperature.

Figure S13: $^{31}$P($^1$H) NMR spectrum of [Cp$^{31}$Al($\mu$-PMes)]$_2$ (1a) in C$_6$D$_6$ at room temperature.
3.2 [Cp³Al−PDip]₂ (1b)

A solution of Cp³Al (27.1 mg, 104 µmol) in C₆D₆ (0.6 mL) was added to P₃Dip₃ (20.0 mg, 34.7 µmol) in a J-Young-NMR tube resulting in a yellow solution. The reaction shows a very slow conversion and colour change to intense red. At a certain point a red solid precipitates and the reaction shows complete conversion. The solvent was removed and the residue was washed with n-pentane to give [Cp³Al−PDip]₂ (1b) (21.8 mg, 24.5 µmol, 47 %) and suitable single crystals for x-ray-diffraction.

A solution of Cp³Al (20.0 mg, 76.8 µmol) in C₆D₆ (0.6 mL) was added to P₂Dip₂ (14.7 mg, 38.4 µmol) in a J-Young-NMR tube resulting immediately in a red solution. The reaction shows a fast conversion. After a few minutes red crystals suitable for X-ray-diffraction precipitate to give [Cp³Al−PDip]₂ (1b) (16.3 mg, 18.0 µmol, 46 %).

Single crystals for X-ray diffraction were obtained by slow evaporation of a saturated n-pentane solution at −30°C.

¹H NMR (401 MHz, C₆D₆) δ [ppm] = broad signals observed due to fluctuating system.

³¹P NMR (C₆D₆): δ [ppm] = −115.3, bis −117.8 ppm. HRMS (LIFDI): (m/z) Calculated for [C₆₄H₁₀₆Al₂P]⁺ 904.6293; Found 904.6300 [M]⁺.
**Figure S14:** $^1$H NMR spectrum of $[\text{Cp}^{35}\text{Al–PDip}]_2$ (1b) in $\text{C}_6\text{D}_6$ at room temperature.

![Figure S14: $^1$H NMR spectrum of $[\text{Cp}^{35}\text{Al–PDip}]_2$ (1b) in $\text{C}_6\text{D}_6$ at room temperature.](image)

**Figure S15:** $^{31}\text{P}[^1\text{H}]$ NMR spectrum of $[\text{Cp}^{35}\text{Al–PDip}]_2$ (1b) in $\text{C}_6\text{D}_6$ at room temperature.

![Figure S15: $^{31}\text{P}[^1\text{H}]$ NMR spectrum of $[\text{Cp}^{35}\text{Al–PDip}]_2$ (1b) in $\text{C}_6\text{D}_6$ at room temperature.](image)
3.3 [Cp$^3$Al–PTip]$_2$ (1c)

A solution of Cp$^3$Al (22.2 mg, 85.4 µmol) in C$_6$D$_6$ (0.6 mL) was added to P$_3$Tip$_3$ (20.0 mg, 28.5 µmol) in a J-Young-NMR tube resulting in an orange solution. The reaction showed a very slow conversion and a continuous colour change to red was observed. Afterwards the reaction mixture was transferred into a vial inside a glove box and was filtered. The solvent was evaporated, and the residue was washed with n-pentane to give [Cp$^3$Al–PTip]$_2$ (1c) (19.1 mg, 19.6 µmol, 46%). Single crystals for X-ray diffraction were obtained by slow evaporation of a saturated C$_7$H$_8$ solution at −30°C.

$^1$H NMR (401 MHz, C$_6$D$_6$) δ [ppm] = broad signals observed due to fluctuating system.

$^{31}$P NMR (C$_6$D$_6$): δ –116.4 –118.0 ppm. HRMS (LIFDI): (m/z) Calculated for [C$_{58}$H$_{92}$Al$_2$P$_2$]$^+$ 988.7227; Found 988.7239 [M]$^+$

Figure S16: $^1$H NMR spectrum of [Cp$^3$Al–PTip]$_2$ (1c) in C$_6$D$_6$ at room temperature.
Figure S17: $^{31}$P($^1$H) NMR spectrum of $[\text{Cp}^{3}\text{Al}−\text{PTip}]_2$ (1c) in C$_6$D$_6$ at room temperature.

3.4 $[\text{Cp}^{3}\text{Al}(\mu-\text{PPh})]_2$ (1d)

A solution of $\text{Cp}^{3}\text{Al}$ (36.1 mg, 138 µmol) in C$_6$D$_6$ (0.6 mL) was added to P$_5$Ph$_5$ (15.0 mg, 27.8 µmol) in a J-Young-NMR tube resulting in a clear yellow solution. After 1 h yellow crystals precipitated. Afterwards the reaction mixture was transferred into a vial inside a glove box and was filtered. The solvent was evaporated, and the residue was washed with n-pentane to give $[\text{Cp}^{3}\text{Al}(\mu-\text{PPh})]_2$ (1d) (38.6 mg, 53.4 µmol, 77 %). Single crystals for X-ray diffraction were obtained by slow evaporated of a saturated C$_6$H$_6$ solution.
$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ [ppm] = 7.83 (m, 4H, aryl-CH), 7.23-7.19 (t, $J = 7.4$ Hz, 4H, aryl-CH), 7.09-7.05 (t, $J = 7.5$ Hz, 2H, aryl-CH), 6.35 (s, 4H, Cp-CH), 1.51 (s, 18H, Cp-C(CH$_3$)$_3$), 1.44 (s, 36H, Cp-C(CH$_3$)$_3$). $^{27}$Al NMR (104 MHz, C$_6$D$_6$): No signal could be observed, probably due to its broadness. $^{31}$P NMR (162 MHz, C$_6$D$_6$): $\delta$ [ppm] = −130.6 (s). HRMS (LIFDI): (m/z) Calculated for [C$_{46}$H$_{68}$Al$_2$P$_2$]$^+$ 736.4422; Found 736.4400 [M]$^+$.

**Figure S18:** $^1$H NMR spectrum of [Cp$^{35}$Al($\mu$-PPh)$_2$]$_2$ (1d) in C$_6$D$_6$ at room temperature.
Figure S19: $^{31}P{^1}H$ NMR spectrum of $[\text{Cp}^3\text{Al}(\mu-\text{PPh})]_2$ (1d) in $C_6D_6$ at room temperature.

3.5 $[\text{Cp}^3\text{Al}(\text{PtBu})_3]$ (2)

A solution of $\text{Cp}^3\text{Al}$ (30.0 mg, 115 µmol) in $C_6D_6$ (0.6 mL) was added to $\text{P}_3\text{Bu}_3$ (30.5 mg, 115 µmol) in a J-Young-NMR tube resulting in a clear yellow solution. After heating for 24 h at 60°C a yellow solid precipitated. The solvent was evaporated and the residue was washed with cold $n$-hexane to give $[\text{Cp}^3\text{Al}(\text{PtBu})_3]$ (2) (40.7 mg, 77.6 µmol, 67%). Single crystals for X-ray diffraction were obtained by slow evaporated of a saturated $C_6H_6$ solution.
$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ [ppm] = 6.32 (s, 2H, H$_{Cp}$), 1.63 (s, 18H, C(CH$_3$)$_3$), 1.51-1.46 (m, 27H, C(CH$_3$)$_3$), 1.29 (s, 9H, C(CH$_3$)$_3$). $^{13}$C($^1$H) NMR (101 MHz, C$_6$D$_6$): $\delta$ [ppm] = 132.6 (C$_{Cp}$), 127.4(C$_{Cp}$), 111.8 (C$_{Cp}$), 34.5-33.8 (m, C(CH$_3$)$_3$), 34.3 (s, C(CH$_3$)$_3$), 32.6 (s, C(CH$_3$)$_3$), 32.3 (s, 30.5-30.4 (m, C(CH$_3$)$_3$). $^{27}$Al NMR (104 MHz, C$_6$D$_6$): No signal could be observed, probably due to its broadness. $^{31}$P NMR (162 MHz, C$_6$D$_6$): $\delta$ [ppm] = 76.1 (d, $J = 210.6$ Hz), −60.6 (t, $J = 210.6$ Hz) HRMS (LIFDI): (m/z) Calculated for [C$_{29}$H$_{56}$AlP$_3$]$^+$ 524.3405; Found 524.3403 [M]$^+$

Figure S20: $^1$H NMR spectrum of [Cp$^{31}$Al(PtBu)$_3$] (2) in C$_6$D$_6$ at room temperature.
Figure S21: $^{13}\text{C}(1\text{H})$ NMR spectrum of [Cp$^{31}$Al(PtBu)$_3$] (2) in C$_6$D$_6$ at room temperature.

Figure S22: $^{31}\text{P}(1\text{H})$ NMR spectrum of [Cp$^{31}$Al(PtBu)$_3$](1d) in C$_6$D$_6$ at room temperature.
3.6  [Cp*Al(μ-PMes)]₂ (3a)

[AlCp*]₄ (20.0 mg, 30.8 µmol) and P₃Mes₃ (18.5 mg, 41.1 µmol) were combined in a J-Young-NMR tube and C₆D₆ (0.6 mL) was added. The mixture was heated to 80°C over a period of 16 h, resulting in an intense yellow solution. The reaction mixture was transferred into a vial inside a glove box and was filtered. Evaporation of the solvent afforded [Cp*Al(μ-PMes)]₂ (3a) as analytically pure light yellow solid (18.1 mg, 51.1 µmol, 82%). Single crystals for X-ray diffraction were obtained from a saturated n-pentane solution at −30°C.

¹H NMR (400 MHz, C₆D₆): δ [ppm] = 6.91 (s, 4H, aryl-CH), 2.88 (s, 12H, CH₃), 2.17 (s, 6H, CH₃), 1.72 (s, 30H, Cp-CH₃). ¹³C(¹H) NMR (101 MHz, C₆D₆): δ [ppm] = 143.2 (t, o-C(CH₃)), 135.2 (C₆r, p-C(CH₃)), 128.7 (C₆q), 115.95 (C₅(CH₃)₃), 27.2 (p-(CH₃)), 21.2 (o-(CH₃)), 10.1(Cp-CH₃). ²⁷Al NMR (104 MHz, C₆D₆): No signal was detected, probably due to its broadness. ³¹P NMR (162 MHz, C₆D₆): δ [ppm] = −208.2 (s). HRMS (LIFDI): (m/z) Calculated for [C₃₈H₅₂Al₂P₂]⁺ 624.3170; Found 624.3168 [M]⁺.
Figure S23: $^1$H NMR spectrum of [Cp*Al(μ-PMes)]$_2$ (3a) in C$_6$D$_6$ at room temperature.

Figure S24: $^{13}$C($^1$H) NMR spectrum of [Cp*Al(μ-PMes)]$_2$ (3a) in C$_6$D$_6$ at room temperature.
Figure S25: $^{31}\text{P}^{[1\text{H}]}$ NMR spectrum of $[\text{Cp}^*\text{Al}(\mu-\text{PMes})]_2$ (3a) in $\text{C}_6\text{D}_6$ at room temperature.

3.7 $[\text{Cp}^*\text{Al}(\mu-\text{PDip})]_2$ (3b)

$[\text{AlCp}^*]_4$ (20.0 mg, 30.8 µmol) and $\text{P}_3\text{Dip}_3$ (23.7 mg, 41.1 µmol) were combined in a J-Young-NMR tube and $\text{C}_6\text{D}_6$ (0.6 mL) was added. The mixture was heated to 80°C over a period of 16 h, resulting in an intense yellow solution. The reaction mixture was transferred into a vial inside a glove box and was filtered. Evaporation of the solvent afforded $[\text{DipP-AlCp}^*]_2$ (3b) as analytically pure off-white powder (37.8 mg, 61.7 µmol, 86%). Single crystals for X-ray diffraction were obtained from a saturated $n$-pentane solution at −30°C.
$^1$H NMR (400 MHz, C$_6$D$_6$): δ [ppm] = 7.20-7.11 (m, 6H, aryl-CH), 4.82 (m, 4H, CH(CH$_3$)$_2$), 1.72 (s, 30H, Cp-CH$_3$), 1.56-1.54 (d, J = 6.8 Hz, 24H, CH(CH$_3$)$_2$). $^{13}$C($^1$H) NMR (101 MHz, C$_6$D$_6$): δ [ppm] = 153.8 (t, C$_{quat}$), 137.5 (t, C$_{Ar}$), 127.2 (t, C$_{Ar}$), 122.9 (t, C$_{Ar}$), 115.9 (C$_{Cp}$), 34.2 (t, CH(CH$_3$)$_2$)), 25.2 (CH(CH$_3$)$_2$)), 10.6 (Cp-CH$_3$). $^{27}$Al NMR (104 MHz, C$_6$D$_6$): No signal could be observed, probably due to its broadness. $^{31}$P NMR (162 MHz, C$_6$D$_6$): δ [ppm] = –230.6 (s). HRMS (LIFDI): (m/z) Calculated for [C$_{44}$H$_{64}$Al$_2$P$_2$]$^+$ 708.4109; Found 708.4105 [M]$^+$

**Figure S26:** $^1$H NMR spectrum of [Cp*Al(μ-PDip)$_2$]$_2$ (3b) in C$_6$D$_6$ at room temperature.
**Figure S27:** $^{13}$C{H} NMR spectrum of $[\text{Cp}^*\text{Al}(\mu-\text{PDip})]_2$ (3b) in C$_6$D$_6$ at room temperature.

**Figure S28:** $^{31}$P{H} NMR spectrum of $[\text{Cp}^*\text{Al}(\mu-\text{PDip})]_2$ (3b) in C$_6$D$_6$ at room temperature.
3.8  [Cp*Al(μ-PTip)]$_2$ (3c)

[AlCp*]$_4$ (0.018 g, 0.027 mmol) and P$_3$Tip$_3$ (0.025 g, 0.035 mmol) were combined in an NMR tube fitted with a J-Young valve and C$_6$D$_6$ (0.6 mL) was added. The mixture was heated to 80°C over a period of 16 h, resulting in a clear yellow solution. Afterwards the reaction mixture was transferred into a vial inside a glove box and was filtered. Evaporation of the solvent afforded [Cp*Al(μ-PTip)]$_2$ (3c) as an analytically pure off-white powder. X-ray quality crystals were grown from a saturated n-hexane solution at −30°C for 24 h. NMR spectra were obtained from the same sample that was used for single crystal XRD, thus a minimal amount of the hydrolysis product TipPH$_2$ is detected.

**Yield:** 0.035 g, 0.044 mmol (92 %)

**CHN calc.** (found) for C$_{50}$H$_{76}$Al$_2$P$_2$ in %: C 75.72 (75.32), H 9.66 (9.82).

**$^1$H NMR** (300.13 MHz, C$_6$D$_6$): δ [ppm] = 7.12 (s, 4H, aryl-$CH$), 4.89–4.75 (m, 4H, o-$CH(\text{CH}_3)_2$), 2.84 (sept, $^3$J$_{H,H} = 6.8$ Hz, 2H, p-$CH(\text{CH}_3)_2$), 1.73 (s, 30H, Cp-$CH_3$), 1.61 (d, $^3$J$_{H,H} = 6.8$ Hz, 24H, o-$CH(\text{CH}_3)_2$), 1.26 (d, $^3$J$_{H,H} = 6.8$ Hz, 12H, p-$CH(\text{CH}_3)_2$).

**$^{13}$C NMR** (75.48 MHz, C$_6$D$_6$): δ [ppm] = 153.78 (C$_{\text{quat}}$), 147.23 (C$_{\text{quat}}$), 134.68 (C$_{\text{quat}}$), 120.96 (Aryl-$CH$), 115.95 (C$_5(\text{CH}_3)_5$), 34.73 (C, p-$CH(\text{CH}_3)_2$), 34.31 (t, 2C, o-$CH(\text{CH}_3)_2$), 25.46 (4C, o-$CH(\text{CH}_3)_2$), 24.44 (2C, p-$CH(\text{CH}_3)_2$), 10.67 (5C, Cp-$CH_3$).

**$^{31}$P NMR** (122 MHz, C$_6$D$_6$) δ [ppm] = −231.60.
Figure S29: $^1$H NMR spectrum of $[\text{Cp}^*\text{Al(μ-PTip)}]_2$ (3c) in $\text{C}_6\text{D}_6$ at room temperature.

Figure S30: $^{13}$C($^1$H) NMR spectrum of $[\text{Cp}^*\text{Al(μ-PTip)}]_2$ (3c) in $\text{C}_6\text{D}_6$ at room temperature.
**Figure S31**: $^{31}$P-$^1$H NMR spectrum of [Cp*Al(μ-PTip)]$_2$ (3c) in C$_6$D$_6$ at room temperature.

3.9 [Cp*Al(μ-AsDip)]$_2$ (4a)

[Cp*$_4$Al$_4$] (0.020 g, 0.031 mmol) and Dip$_3$As$_3$ (0.029 g, 0.041 mmol) were suspended in 0.6 mL of C$_6$D$_6$. The suspension was heated to 80 °C for 16 h to give a yellow suspension. The suspension was filtered through a microfiber filter and the remaining solid was washed with 0.6 mL of n-pentane. All volatile components were removed from the combined solutions under reduced pressure to give [Cp*Al(μ-AsDip)]$_2$ (4a) as a yellow solid.

Crystals suitable for single crystal X-ray diffraction were obtained from a saturated solution of 4a in n-pentane at −30 °C.
Yield: 0.039 g (0.049 mmol; 79%).

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): $d = 1.51$ (d, $^3$J$_{H,H}$ = 6.8 Hz, 24H, CH(CH$_3$)$_2$), 1.71 (s, 30H, C$_5$(CH$_3$)$_5$), 4.64 (hept, $^3$J$_{H,H}$ = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 7.11-7.13 (m, 1H, CH$_{Aryl}$), 7.11-7.16 (m, 5H, CH$_{Aryl}$)* ppm (* = overlap with C$_6$D$_5$H signal). $^{13}$C($^1$H) NMR (75 MHz, C$_6$D$_6$, 298 K): $d = 10.6$ (C$_5$(CH$_3$)$_5$), 25.2 (CH(CH$_3$)$_2$), 36.0 (CH(CH$_3$)$_2$), 116.3 (C$_5$(CH$_3$)$_5$), 123.0 (CH$_{Aryl}$), 127.4 (CH$_{Aryl}$), 142.6 (C$_{q,Aryl}$), 152.9 (C$_{q,Aryl}$) ppm.

To obtain a sufficient CHN analysis different strategies were tried, but the C content was invariably too low, even though isolated single crystals were used.

Figure S32: $^1$H NMR spectrum of [Cp*Al(μ-AsDip)]$_2$ (4a) in C$_6$D$_6$ at room temperature.
**Figure S33**: $^{13}$C($^1$H) NMR spectrum of [Cp*Al(μ-AsDip)]$_2$ (4a) in C$_6$D$_6$ at room temperature.

3.10  [Cp*Al(μ-AsTip)]$_2$ (4b)

[Cp*$_4$Al$_4$] (0.015 g, 0.023 mmol) and Tip$_3$As$_3$ (0.026 g, 0.031 mmol) were suspended in 0.6 mL of C$_6$D$_6$. The suspension was heated to 80 °C for 16 h to give a yellow suspension. The suspension was filtered through a microfiber filter and the remaining solid was washed with 0.6 mL of n-pentane. All volatile components were removed from the combined solutions under reduced pressure to give [Cp*Al(μ-AsTip)]$_2$ (4b) as a yellow solid.

Crystals suitable for single crystal X-ray diffraction were obtained from a saturated solution of 4b in n-pentane at −30 °C.
**Yield:** 0.027 g (0.031 mmol; 66%).

**$^1$H NMR** (300 MHz, C$_6$D$_6$, 298 K): $d = 1.27$ (d, $^3$$J_{H,H} = 6.9$ Hz, 12H, CH(CH$_3$)$_2$), $1.58$ (d, $^3$$J_{H,H} = 6.8$ Hz, 24H, CH(CH$_3$)$_2$), $1.72$ (s, 30H, C$_5$(CH$_3$)$_5$), $2.83$ (hept, $^3$$J_{H,H} = 6.6$ Hz, 2H, CH(CH$_3$)$_2$), $4.66$ (hept, $^3$$J_{H,H} = 6.8$ Hz, 4H, CH(CH$_3$)$_2$), 7.14-7.15 (m, 4H, CH$_Aryl$) ppm.

**$^{13}$C($^1$H) NMR** (75 MHz, C$_6$D$_6$, 298 K): $d = 10.6$ (C$_5$(CH$_3$)$_5$), $24.4$ (CH(CH$_3$)$_2$), $25.3$ (CH(CH$_3$)$_2$), $34.6$ (CH(CH$_3$)$_2$), $36.0$ (CH(CH$_3$)$_2$), $116.2$ (C$_5$(CH$_3$)$_5$), $121.0$ (CH$_Aryl$), $139.6$ (C$_q$Aryl), $147.1$ (C$_q$Aryl), $152.9$ (C$_q$Aryl) ppm.

To obtain a sufficient CHN analysis different strategies were tried, but the C content was invariably too low, even though isolated single crystals were used.

**Figure S34:** $^1$H NMR spectrum of [Cp*Al(μ-AsTip)]$_2$ (4b) in C$_6$D$_6$ at room temperature.
**Figure S35:** $^{13}$C($^1$H) NMR spectrum of [Cp$^*$Al($\mu$-AsTip)]$_2$ (4b) in C$_6$D$_6$ at room temperature.

3.11 [Cp$^{3t}$Al(l$i$Pr$_2$)(µ-PPh)]$_2$ (5)

A solution of l$i$Pr$_2$ (8.37 mg, 54.3 µmol) in C$_6$D$_6$ (0.6 mL) was added to [Cp$^{3t}$Al(µ-PPh)]$_2$ (1d) (20.0 mg, 27.2 µmol) in a J-Young-NMR tube resulting in a clear yellow solution. After 1 h yellow crystals precipitated. The solvent was evaporated, and the residue was washed with n-pentane to give [Cp$^{3t}$Al(l$i$Pr$_2$)(µ-PPh)]$_2$ (38.6 mg, 53.4 µmol, 77 %). Single crystals for X-ray diffraction were obtained by slow evaporated of a saturated C$_6$H$_6$ solution.

$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ [ppm] = 7.85 (d, $J$=7.1, 4H), 7.17 (t, $J$=7.5, 4H), 7.00 (t, $J$=7.1, 2H), 6.52 (s, 4H), 6.20 (s, 4H), 5.71 (m, 4H), 1.56 (s, 36H), 1.23 (d, $J$=6.7, 12H), 1.12 (s,
18H), 1.01 (d, J=6.1, 12H). $^{13}\text{C} (\text{^1H}) \text{ NMR}$ (101 MHz, $\text{C}_6\text{D}_6$): $\delta$ [ppm] = 149.8 (C$_{\text{quat}}$), 139.4 (CH$_\text{Cp}$), 136.0 (CH-aryl), 128.5 (C$_{\text{quat}}$), 126.7 (CH-aryl), 122.6 (C$_{\text{quat}}$), 116.9 (CH$_{\text{iPr}}$), 51.7 (CH(CH$_3$), 37.3 (C$_{\text{quat}}$), 34.1 (C$_{\text{quat}}$), 33.7 (C(CH$_3$)$_3$), 30.2 (C(CH$_3$)$_3$), 24.3 (CH(CH$_3$)$_2$), 23.6 (CH(CH$_3$)$_2$). $^{27}\text{Al NMR}$ (104 MHz, $\text{C}_6\text{D}_6$): No signal could be observed, probably due to its broadness. $^{31}\text{P NMR}$ (162 MHz, $\text{C}_6\text{D}_6$, r.t.): $\delta$ [ppm] = −123.3. (162 MHz, $\text{C}_7\text{D}_8$, −80 °C): −122.4-122.8 (d, $J$ = 67.1 Hz) 129.5-129.9 (d, $J$ = 67.1 Hz) $\text{HRMS (LIFDI)}$: (m/z) Calculated for $\text{C}_{64}\text{H}_{100}\text{Al}_2\text{N}_4\text{P}_2$ 1041.4181; Found 1041.4113 [M]$^+$. 

Figure S36: $^1\text{H NMR}$ spectrum of [Cp$^{3}\text{Al}(\text{iPr}_2)(\mu-\text{PPh})]_2$ (5) in $\text{C}_6\text{D}_6$ at room temperature.
**Figure S37**: $^{13}$C($^1$H) NMR spectrum of [Cp$^{35}$Al(iPr$_2$)(μ-PPh)$_2$ (5) in C$_6$D$_6$ at room temperature.

**Figure S38**: $^{31}$P($^1$H) NMR spectrum of [Cp$^{35}$Al(iPr$_2$)(μ-PPh)$_2$ (5) in C$_6$D$_6$ at room temperature.
Figure S39: $^{31}$P{$^1$H} NMR spectrum of [Cp$^{30}$Al(iPr$_2$)(μ-PPh)]$_2$ (5) in toluene-$d_8$ at −80 °C.
4 Additional spectroscopic details

4.1 UV-vis spectra and extinction coefficients of 1b and 1c.

UV-vis spectra of substances 1b and 1c were recorded in benzene. The UV-vis cuvettes were filled in the Glovebox and sealed with Teflon tape and Teflon grease.

*Figure S40*: UV-vis spectra of 1b (c = 0.08 mg/mL, top) and 1c (c = 0.08 mg/mL, blue, bottom) in benzene at room temperature (absorption maxima see Table S5).
Table S5. Absorption maxima $\lambda_{\text{max}}$ and experimental extinction coefficients $\varepsilon$ for 1b and 1c.

| Comp | $\lambda_{\text{max}}$ [nm] | $\varepsilon$ [l·mol$^{-1}$·cm$^{-1}$] |
|------|----------------------------|---------------------------------|
| 1b   | 339                        | 4347                            |
| 1c   | 340                        | 3954                            |
5 Computational details

5.1 General remarks

Computations were carried out using Gaussian16, revision C.01[11] and the standalone versions of NBO 7.0,[12] IBOView,[13] and Multiwfn 3.8.[14]

Structure optimizations employed the hybrid DFT functional PBE0[15] in conjunction with Grimme’s dispersion correction D3(BJ)[16] and the def2-SVP basis set[17] (notation PBE0-D3(BJ)/def2-SVP). All structures were fully optimized and confirmed as minima by frequency analyses. Partial charges were determined by the atomic dipole moment corrected Hirshfeld (ADCH)[18] population method. The bonding situation of selected systems was analysed using the Mayer bond order,[19] natural bond orbital (NBO),[12] and intrinsic bond orbital (IBO)[13] methods. Chemical shifts and coupling constants were derived by the GIAO method.[20] The calculated absolute shifts ($\sigma_{\text{calc},X}$) were referenced to the experimental absolute shift of 85% H$_3$PO$_4$ in the gas phase ($\sigma_{\text{ref},1} = 328.35$ ppm),[21] using PH$_3$ ($\sigma_{\text{ref},2} = 594.45$ ppm) as a secondary standard:[22]

$$\delta_{\text{calc},X} = (\sigma_{\text{ref},1} - \sigma_{\text{ref},2}) - (\sigma_{\text{calc},X} - \sigma_{\text{calc},PH_3})$$

$$= \sigma_{\text{calc},PH_3} - \sigma_{\text{calc},X} - 266.1 \text{ ppm}$$

At the PBE0-D3/def2-SVP level of theory, $\sigma_{\text{calc},PH_3}$ amounts to +629.17 ppm.

Free energy calculations were computed by single-point calculations at the PBE0-D3(BJ)/def2-TZVP level.[16,17] Solvation effects were taken into account using the SMD[23] model (solvent=benzene, $\varepsilon=2.2706$). A concentration correction of $\Delta G_{0\rightarrow*} = RT \ln(24.46) = 1.89 \text{ kcal mol}^{-1}$ ($T = 298.15 \text{ K}$) was added to the free energies of all calculated species to change the 1.00 atm gas phase values to the condensed phase standard state concentration of 1.00 mol/L, which leads to a proper description of associative/dissociative steps.[24]
### 5.2 Summary of calculated data

**Table S3.** Summary of calculated data, including electronic energies and thermal corrections.

| Compd.                  | $E_{\text{tot}}$ | $G_{\text{tot}}$ | ADCH charge | $\sigma_{\text{calc},X}$ (ppm) | $\delta_{\text{calc},X}$ (ppm) |
|-------------------------|------------------|------------------|--------------|-------------------------------|-------------------------------|
| Cp$^{3}$Al              | -907.085508      | -906.707931      | -            | -                             | -                             |
| (Cp*Al)$_4$             | -2528.644576     | -2527.839057     | -            | -                             | -                             |
| (PMes)$_3$              | -2071.713331     | -2071.250071     | -            | -                             | -                             |
| (PtBu)$_3$              | -1496.911913     | -1496.586521     | -            | -                             | -                             |
| (PDip)$_3$              | -2425.229849     | -2424.515115     | -            | -                             | -                             |
| (PTip)$_3$              | -2778.774572     | -2777.826381     | -            | -                             | -                             |
| (PPh)$_5$               | -2863.624691     | -2863.218533     | -            | -                             | -                             |

**Alternating Al$_2$P$_2$ Heterocycles**

| [Cp$^{3}$Al($\mu$-PMes)$_2$]$_2$ (1a) | -3195.413338 | -3194.311661 | P: -0.186 | Al: +0.162 | 559.91 | -196.84 |
| [Cp$^{3}$Al]$_2$(PPh)$_3$ (1d)       | -2959.715682 | -2958.767090 | P: -0.184 | Al: +0.156 | 511.66 | -148.59 |
| [Cp$^{3}$Al($\mu$-PDip)$_2$]$_2$     | -3431.024735 | -3429.744721 | -           | -           | -     | -     |
| [Cp$^{3}$Al($\mu$-PtBu)$_2$]$_2$     | -2812.195224 | -2811.185656 | -           | -           | -     | -     |

**Head-to-head Al$_2$P$_2$ Heterocycles**

| [(Cp$^{3}$Al)$_2$(PDip)$_3$] (1b)     | -3431.063993 | -3429.788879 | P: -0.065 | Al: +0.061 | 510.06 | -146.99 |
| [(Cp$^{3}$Al)$_2$(PTip)$_3$] (1c)     | -3666.763177 | -3665.333337 | P: -0.069 | Al: +0.060 | 509.90 | -146.83 |
| [(Cp$^{3}$Al)$_2$(PPh)$_3$]          | -3195.384040 | -3194.281993 | -           | -           | -     | -     |

**AlP$_3$ Heterocycles**

| [Cp$^{3}$Al(PtBu)$_3$] (2)          | -2404.060592 | -2403.334154 | P(1): -0.098 | P(2): -0.017 | P(3): -0.107 | Al: +0.194 | 313.17 | 444.64 | 49.90 | -81.57 |
| [Cp$^{3}$Al(PMes)$_3$]              | -2978.855877 | -2977.995979 | -           | -           | -     | -     |

**Systems with AlCp***

| [Cp*Al($\mu$-PMes)$_2$] (3a)        | -2645.522001 | -2644.812999 | P: -0.257 | Al: +0.157 | 560.18 | -197.11 |
| [Cp*Al($\mu$-PDip)$_2$] (3b)        | -2881.195254 | -2880.309422 | P: -0.211 | -           | 604.64 | -241.57 |
| Compd. | $E_{\text{tot}}$[a] | $G_{\text{tot}}$[b] | ADCH charge | $\sigma_{\text{calc,x}}$ (ppm) | $\delta_{\text{calc,x}}$ (ppm) |
|--------|-----------------|-----------------|-------------|-----------------|-----------------|
|        |                 |                 | Al: +0.157  |                 |                 |
| [Cp*Al(\(\mu\)-PTip)]_2 (3c) | -3116.893938    | -3115.852709   | P: -0.211    | 604.96          | -241.89         |
|        |                 |                 | Al: +0.157  |                 |                 |
| [(Cp*Al)_2(PDip)_2] | -2881.170828    | -2880.288611   | -           | -               | -               |

**Lewis Base Stabilised Al\(_2\)P\(_2\) Heterocycles**

| Compd. | $E_{\text{tot}}$[a] | $G_{\text{tot}}$[b] | ADCH charge | $\sigma_{\text{calc,x}}$ (ppm) | $\delta_{\text{calc,x}}$ (ppm) |
|--------|-----------------|-----------------|-------------|-----------------|-----------------|
|        |                 |                 | Al(1): +0.162 | 513.86          | -150.79         |
|        |                 |                 | P(2): -0.237 |                 |                 |
|        |                 |                 | Al(3): +0.158 |                 |                 |
|        |                 |                 | P(4): -0.142 |                 |                 |

[a] Total SCF energy in a.u. at the SMD(solvent=benzene)/PBE0-D3(BJ)/def2-TZVP level from optimized structures at PBE0-D3(BJ)/def2-SVP. [b] Total Gibbs free energy in a.u. (298.15 K, including concentration correction) at the SMD(solvent=benzene)/PBE0-D3(BJ)/def2-TZVP level.

5.3 Bonding analysis of 1a

*Figure S41:* The P–Al bonding in 1a as depicted by the NBO (left) and IBO (right) approaches.
5.4 Optimized structures (.xyz-files)

5.4.1 Cp³Al

| Atom  | Coordinates |
|-------|-------------|
| Al    | 0.413939000 | -0.002509000 | -1.885596000 |
| C     | 1.596750000 | -0.005747000 | 0.121042000  |
| C     | 3.111761000 | -0.011092000 | 0.231702000  |
| C     | 0.744519000 | -1.132020000 | 0.116356000  |
| H     | 1.085259000 | -2.162951000 | 0.117579000  |
| C     | 0.750566000 | 1.121011000 | 0.100606000  |
| H     | 1.092508000 | 2.151806000 | 0.082527000  |
| C     | 3.702754000 | -1.236682000 | -0.469686000 |
| H     | 3.342655000 | -2.175377000 | -0.022516000 |
| H     | 4.800569000 | -1.232214000 | -0.385118000 |
| C     | 3.441756000 | -1.247164000 | -1.539666000 |
| C     | -0.624236000 | -0.723920000 | 0.105568000  |
| C     | -0.621716000 | 0.719419000  | 0.078477000  |
| H     | 3.704270000 | 1.255337000 | -0.390353000 |
| H     | 3.434494000 | 1.339831000 | -1.454926000 |
| C     | 4.802634000 | 1.238540000 | -0.316456000 |
| H     | 3.354633000 | 2.163459000 | 0.123361000  |
| C     | -1.721781000 | 1.786822000 | 0.151771000  |
| C     | -2.972589000 | 1.469723000 | -0.671353000 |
| C     | -2.717134000 | 1.307158000 | -1.730304000 |
| H     | -3.670007000 | 2.320083000 | -0.620731000 |
| H     | -3.513840000 | 0.588556000 | -0.310077000 |
| C     | -2.098032000 | 1.997651000 | 1.627883000  |
| H     | -2.511255000 | 1.088111000 | 2.083179000  |
| H     | -2.848659000 | 2.799085000 | 1.722224000  |
| H     | -1.211865000 | 2.288654000 | 2.212002000  |
| C     | -1.191969000 | 3.127619000 | -0.382711000 |
| H     | -0.387585000 | 3.541052000 | 0.241751000  |
| H     | -2.006764000 | 3.867167000 | -0.386974000 |
| H     | -0.816276000 | 3.031045000 | -1.413500000 |
| C     | 3.470713000 | -0.058638000 | 1.724960000  |
| H     | 3.059462000 | 0.813696000 | 2.255304000  |
| H     | 4.564085000 | -0.062356000 | 1.863390000  |
| H     | 3.061919000 | -0.963522000 | 2.199009000  |
| C     | -1.748881000 | -1.774444000 | 0.147076000  |
| C     | -2.506671000 | -1.875845000 | -1.185315000 |
| C     | -2.960725000 | -0.927300000 | -1.490827000 |
| C     | -3.399222000 | -2.627362000 | -1.108830000 |
| C     | -1.825784000 | -2.191047000 | -1.991211000 |
| C     | -1.156503000 | -3.166471000 | 0.414490900  |
| H     | -0.489872000 | -3.493913000 | -0.396800000 |
| H     | -1.972684000 | -3.901531000 | 0.481621000  |
| H     | -0.596290000 | -3.197918000 | 1.360987000  |
| C     | -2.719799000 | -1.493172000 | 1.301210000  |
| H     | -2.178099000 | -1.416940000 | 2.256357000  |
| H     | -3.446477000 | -2.316146000 | 1.388670000  |
| H     | -3.298352000 | -0.567907000 | 1.162304000  |
5.4.2  (Cp*Al)$_4$

(Cp*Al)$_4$ @ PBE0-D3(BJ)/def2-SVP

Al  0.868087000  0.958241000  1.035285000
C  1.260677000  3.041696000  1.948119000
C  2.476909200  2.634610000  1.325145000
C  2.944571000  1.476292000  2.003686000
C  2.024241000  1.170613000  3.049687000
C  0.985071000  2.145135000  3.022916000
C  0.498131000  4.279749000  1.613085000
C  3.119453000  4.279749000  0.174573000
C  4.215264000  0.729056000  1.772657000
C  2.217662000 -0.051377000  4.018435000
C  0.98513000  2.245996000  3.944439000
H  0.392135000  4.413501000  0.527601000
H  1.012415000  5.174404000  2.005178000
H  4.154088000  3.000422000  0.023834000
H  3.147877000  4.425855000  0.340291000
H  2.577132000  3.166662000 -0.771950000
H  4.819724000  1.190444000  0.981859000
H  4.033478000 -0.317482000  1.485560000
H  4.826794000 -0.837352000  3.121857000
H  1.464008000  0.065746000  4.815647000
H  3.288720000  0.118610000  4.497508000
H  2.161562000 -0.934082000  3.527488000
H  -1.135210000  1.997156000 -0.887991000
H  -0.289201000  3.264355000  4.350264000
H  -0.085075000  1.563046000  4.798780000
Al  -1.062938000  0.941109000 -0.887991000
C  -3.262682000  1.670818000 -1.240225000
C  -2.455976000  2.816233000 -0.972967000
C  -1.491499000  2.930582000 -2.014345000
C  -1.696335000  1.843366000 -2.914854000
C  -2.797202000  1.070583000 -2.442811000
C  -4.444277000  1.278656000 -0.417914000
C  -2.683736000  3.735427000  0.181054000
C  -4.493240000  3.989856000 -2.174577000
C  -0.984896000  1.630269000 -4.208499000
C  -3.341454000 -0.144351000 -3.121857000
H  -4.165136000  1.036258000  0.618688000
H  -4.958996000  0.496519000 -0.837352000
H  -5.174842000  2.103381000 -0.372300000
H  -3.727536000  4.089117000  0.197372000
H  -2.035654000  4.619432000  0.133480000
H  -2.494300000  3.238403000  1.147684000
H  -0.632400000  4.837259000 -1.499786000
H  -0.439358000  4.385624000 -3.201693000
H  0.564951000  3.610796000 -1.959112000
H  -0.859273000  0.561324000 -4.431508000
H  0.012518000  2.087936000 -4.284527000
H  -1.550272000  2.075210000 -5.045826000
H  -2.623884000 -0.982701000 -3.187160000
H  -3.575581000  0.061288000 -4.178242000
H  -4.266582000 -0.493822000 -2.643163000
Al  1.046259000 -0.781323000 -1.041855000
C  2.273258000 -0.810532000 -3.020840000
C  3.213167000 -0.890671000 -1.952282000
5.4.3 (PMes)$_3$
### 5.4.4 \((\text{PtBu})_3\)

| Atoms | Cartesian Coordinates |
|-------|-----------------------|
| P     | 0.192730000 1.132103000 0.841082000 |
| P     | -0.986216000 0.037940000 -0.661204000 |
| P     | 0.098658000 -1.097754000 0.871500000 |
| C     | 1.594217000 2.032007000 -0.096330000 |
| C     | -2.781179000 0.129887000 -0.661204000 |
| C     | 1.345933000 -2.169813000 -0.092850000 |
| C     | 0.549642000 -3.458914000 -0.329930000 |
| H     | 0.136277000 -4.226916000 0.606823000 |
| C     | 1.863892000 -1.649897000 -1.423628000 |
| H     | 2.520779000 -0.780080000 0.129678000 |
| H     | 1.040261000 -2.834209000 1.835286000 |
| H     | 2.455837000 -3.197400000 1.739560000 |
| H     | 1.671550000 -1.474947000 -0.998882000 |
| C     | -2.937199000 0.150328000 -1.991749000 |
| C     | 1.435345000 -0.535408000 1.936345000 |
| H     | 1.381715000 3.489616000 -0.371570000 |
| C     | 2.938562000 1.543159000 0.438097000 |
| C     | 1.021363000 2.359275000 1.739560000 |
| C     | 3.353270000 1.499754000 -0.409350000 |
| H     | 2.344079000 2.555126000 1.430970000 |
| C     | 0.402848000 3.870913000 0.005891000 |
| H     | 2.161637000 4.127571000 -0.112140000 |
| C     | 3.352020900 1.421168000 -1.745923000 |
| H     | -2.842891000 2.300145000 -0.248511000 |
| C     | -3.468726000 -1.103231000 -0.626170000 |
| C     | -3.502090000 -1.143397000 -1.722812000 |
| H     | 2.938562000 1.543159000 0.438097000 |
| C     | 3.155200000 0.513941000 0.121323000 |
| H     | 2.602918000 3.870913000 0.005891000 |
| C     | 3.750789000 2.190356000 0.065022000 |
| P     | 0.113591000 -1.180438000 -0.424711000 |
| P     | -1.340022000 0.091032000 0.651021000 |
| C     | -3.820187000 -0.034566000 -0.804407000 |
| C     | -2.860713000 -0.738441000 -0.033583000 |
| C     | -3.736641000 1.465907000 -1.003198000 |
| H     | -2.672215000 1.717807000 -1.128581000 |
| C     | 1.764438000 -1.361865000 0.395512000 |

### 5.4.5 \((\text{PDip})_3\)

| Atoms | Cartesian Coordinates |
|-------|-----------------------|
| P     | -1.804380000 -0.424711000 |
| P     | -0.910320000 0.651021000 |
| C     | -0.034566000 -0.804407000 |
| C     | -0.738441000 -0.033583000 |
| C     | 1.465907000 -1.003198000 |
| H     | 1.717807000 -1.128581000 |
| C     | -1.361865000 0.395512000 |
|   | X          | Y          | Z          |
|---|------------|------------|------------|
| H | 4.367614000 | 0.142841000 | -0.738045000 |
| C | -0.906275000 | 3.509133000 | 0.176588000  |
| H | -1.529135000 | 2.697071000 | 0.176588000  |
| C | 2.717029000  | 0.906275000 | -1.956959000 |
| H | 2.087912000  | -0.010310000 | -1.783526000 |
| C | -1.379036000 | 4.798698000 | -0.100292000 |
| H | -0.819442000 | 5.675872000 | 0.260817000  |
| H | -2.445167000 | 4.975691000 | 0.111459000  |
| C | 1.585159000  | 4.133315000 | 0.590688000  |
| H | 1.284672000  | 0.006530000 | 1.183780000  |
| C | 2.834957000  | 3.982677000 | 0.226854000  |
| H | 3.579942000  | 1.346452000 | 2.517540000  |
| H | 2.715154000  | 0.560294000 | 4.113518000  |
| H | 3.046403000  | 2.242675000 | 4.113518000  |

5.4.6 (PTip)_3

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(PTip)_3 @ PBE0-D3(BJ)/def2-SVP

|   | X          | Y          | Z          |
|---|------------|------------|------------|
| P | -1.380679000 | 0.388955000 | -0.410790000 |
| P | -0.376511000 | -1.423695000 | -0.321902000 |
| C | 1.280314000  | -1.726063000 | 0.453919000  |
| C | 1.995170000  | -0.936536000 | -1.389536000 |
| C | -3.207060000 | 0.118295000  | 0.231044000  |
| C | 1.853000000  | -2.950390000 | 0.003750000  |
| C | -3.898049000 | -0.593379000 | -0.782729000 |
| C | -3.958284000 | 0.717671000  | 1.279378000  |
| C | 3.104337000  | -3.337819000 | 0.486757000  |
| H | 3.544698000  | -4.273738000 | 0.137043000  |
| C | 3.828545000  | -2.559329000 | 1.384620000  |
| C | 1.421494000  | 0.314905000  | 2.016530000  |
| H | 0.788714000  | 0.795674000  | 1.259988000  |
| C | 3.251653000  | -1.368127000 | 1.819421000  |
| H | 3.799827000  | -0.744141000 | 2.527706000  |
| C | -5.348004000 | 0.569706000  | 1.303040000  |
| H | -5.916935000 | 1.023252000  | 2.116570000  |
| C | -3.329388000 | 1.494596000  | 2.427523000  |
| H | -2.282062000 | 1.698017000  | 2.160171000  |
| C | -6.037407000 | -0.136245000 | 0.320763000  |
| C | -3.239268000 | -1.260391000 | -1.975438000 |
| H | -2.156952000 | -1.098687000 | -1.912954000 |
| C | -5.287869000 | -0.700179000 | -0.710278000 |
| H | -5.804814000 | -1.253182000 | -1.493570000 |
| C | 1.132901000  | -3.883129000 | -0.963890000 |
| C | 0.522827000  | -3.257080000 | -1.635906000 |
| C | 5.209465000  | -2.974403000 | 1.841910000  |
| C | 5.399535000  | -3.974914000 | 1.416602000  |
| C | 0.527933000  | -0.059685000 | 3.198504000  |
| H | -0.254641000 | -0.772099000 | 2.898748000  |

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### 5.4.7 (PPh)$_5$

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| (PPh)$_5$ @ PBE0-D3(BJ)/def2-SVP |
|-----------------------------------|
| P | -1.23538000 | -1.29285800 | 1.17511500 |
| P | 0.24053100 | 0.22543000 | 1.76389200 |
| P | 0.15689300 | 1.46014400 | -0.18068600 |
| P | 0.35296600 | 0.01475700 | -1.80622400 |
| P | -1.22263000 | -1.36728900 | -1.14379000 |
| C | -2.75409000 | -0.45288800 | -1.56325600 |
| C | -2.80842500 | 0.84597400 | -2.08345200 |
| C | -3.95745700 | -1.13527200 | -1.32550700 |
| C | -4.03617700 | 1.45112500 | -2.34246500 |
| C | -1.88663600 | 1.39712600 | -2.28182700 |
| C | -5.18238100 | -0.51948200 | -1.56052900 |
| H | -3.93298500 | -2.15712000 | -0.93696800 |
| C | -5.22540000 | 0.77780400 | -2.06980300 |
| H | -4.06017500 | 2.46493100 | -2.74950100 |
| H | -6.10830500 | -1.05849400 | -1.34753200 |
| H | -6.18500000 | 1.26177200 | -2.25883800 |
| C | 1.84160500 | -1.05629000 | -1.65986600 |
| C | 1.78933800 | -2.36746300 | -2.15333300 |
| C | 3.07126600 | -0.54256200 | -1.22788700 |
| C | 2.94098000 | -3.15049300 | -2.19867000 |
| H | 0.83823600 | -2.78321000 | -2.49647000 |
| H | 4.21920000 | -1.32697100 | -1.28357300 |
| H | 3.13518400 | 0.46886800 | -0.82629300 |
| C | 4.16070500 | -2.63259600 | -1.76854700 |
| H | 2.88087400 | -4.17357800 | -2.57825400 |
| H | 5.16593800 | -0.93167800 | -0.92893800 |
5.4.8 \([\text{Cp}^{3\text{Al}(\mu-\text{PMes})}_2]\) (1a)

\[
\begin{array}{ccc}
\text{H} & 5.063558000 & -3.246661000 & -1.806394000 \\
\text{C} & 1.624325000 & 2.499156000 & -0.115425000 \\
\text{C} & 2.281140000 & 2.829509000 & -1.310721000 \\
\text{C} & 2.019255000 & 3.141585000 & 1.068174000 \\
\text{C} & 3.323432000 & 3.753136000 & -1.313975000 \\
\text{H} & 1.979688000 & 2.353160000 & -2.248176000 \\
\text{C} & 3.064156000 & 4.062378000 & 1.060166000 \\
\text{C} & 2.281114000 & 2.829509000 & -1.310721000 \\
\text{C} & 2.019255000 & 3.141585000 & 1.068174000 \\
\text{C} & 3.323432000 & 3.753136000 & -1.313975000 \\
\text{H} & 1.979688000 & 2.353160000 & -2.248176000 \\
\end{array}
\]
|   | X       | Y       | Z       |
|---|---------|---------|---------|
| H | -1.61899000 | -5.79851800 | 2.35289900 |
| H | -0.08270300 | -6.63807000 | 2.02679200 |
| Al | -0.45787000 | -1.06673100 | 1.15246200 |
| P | 0.49920000 | -1.26959500 | -0.95217500 |
| C | -0.76684600 | -1.44373900 | 3.36562700 |
| C | 0.04713900 | -2.47069900 | 2.81643400 |
| H | 1.06484500 | -2.68552600 | 3.13094400 |
| C | -0.69349600 | -3.25150700 | 1.87628500 |
| C | -1.99344300 | -2.62842800 | 1.76658300 |
| C | -2.00338700 | -1.53449300 | 2.69748200 |
| H | -2.83216500 | -0.84734400 | 2.83873000 |
| C | -3.26878700 | -2.99120800 | 0.96859800 |
| C | -4.39960700 | -2.02819700 | 1.33763000 |
| H | -4.66356200 | -2.09535700 | 2.48347800 |
| H | -4.15383200 | -0.98129800 | 1.18929000 |
| H | -5.29597100 | -2.28953000 | 0.75530000 |
| C | -3.73878200 | -4.39823200 | 1.35265100 |
| H | -3.85589800 | -4.48797600 | 2.44353500 |
| H | -4.71599000 | -4.60170900 | 0.88698300 |
| C | -3.04882000 | -5.18234900 | 1.02806000 |
| C | -3.07430500 | -2.89125500 | -0.55121900 |
| H | -2.26940100 | -3.52708400 | -0.92746000 |
| H | -4.00786000 | -3.17911600 | -1.06057800 |
| H | -2.83263700 | -1.86341600 | -0.85292600 |
| C | -0.39334500 | -0.54227700 | 4.52426600 |
| C | -1.48420900 | 0.50307000 | 4.74596900 |
| H | -1.19302700 | 1.19611400 | 5.54981700 |
| H | -1.66784300 | 1.08943500 | 3.83626600 |
| H | -2.43297800 | 0.02939300 | 5.04063800 |
| C | 0.95491100 | 0.14256600 | 4.27478500 |
| H | 1.75894000 | -0.59699100 | 4.13417100 |
| H | 0.91253700 | 0.77655900 | 3.37571100 |
| H | 1.23053000 | 0.77113700 | 5.13618900 |
| C | -0.28689400 | -1.42540100 | 5.77753900 |
| H | -0.52531800 | -0.81039300 | 6.66129000 |
| H | -1.23336200 | -1.95433100 | 5.96795500 |
| H | 0.50657900 | -2.18070100 | 5.66902900 |
| C | 2.08178500 | -2.16696400 | -1.23047300 |
| C | 3.23126600 | -1.91817900 | -0.43254300 |
| C | 4.42187200 | -2.59863600 | -0.70532400 |
| H | 5.29704100 | -2.38298600 | -0.88167800 |
| C | 4.52831200 | -3.52788500 | -1.73723100 |
| C | 3.38637900 | -3.79041200 | -2.48763600 |
| H | 3.43544700 | -4.53542900 | -3.28835700 |
| C | 2.16875800 | -3.13768900 | -2.25632000 |
| C | 0.99831200 | -3.54372200 | -3.10996900 |
| H | 0.12854800 | -2.89533200 | -2.93945700 |
| H | 1.25835000 | -3.51127200 | -4.17861900 |
| H | 0.69988800 | -4.57931100 | -2.88140100 |
| C | 5.83196100 | -4.21346300 | -2.02302300 |
| H | 5.69612200 | -5.07920700 | -2.68664300 |
| H | 6.54094200 | -3.52632700 | -2.51435500 |
| H | 6.31354900 | -4.56416800 | -1.09731300 |
| C | 3.18839600 | -0.99633100 | 0.74687000 |
| H | 4.19584400 | -0.80178800 | 1.14235900 |
| H | 2.70841700 | -0.04160300 | 0.49790700 |
| H | 2.58042000 | -1.42777400 | 1.56018700 |
### 5.4.9 \[
\text{[(Cp}^3\text{Al)}_2\text{(PPh)}_2\text{]}(1d)\]

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| P    | 0.142828   | -1.338823  | 1.012746   |
| Al   | 1.585132   | 0.251022   | 0.119218   |
| C    | 3.574114   | -0.086434  | -0.869616  |
| C    | 3.659409   | -0.570095  | 0.498750   |
| C    | 3.485466   | 0.556263   | 1.338148   |
| H    | 3.378765   | 0.522425   | 2.423847   |
| C    | 3.206800   | 1.729711   | 0.556756   |
| C    | 3.333890   | 1.323580   | -0.788326  |
| H    | 3.165682   | 1.966962   | -1.646478  |
| C    | 3.679756   | -0.791019  | -2.231840  |
| C    | 3.669926   | 0.248748   | -3.361793  |
| H    | 3.767855   | -0.267951  | -4.328204  |
| H    | 4.508696   | 0.955609   | -3.272393  |
| H    | 2.730994   | 0.818236   | -3.395040  |
| C    | 4.993959   | -1.568654  | -2.367454  |
| H    | 5.085723   | -1.970478  | -3.388560  |
| H    | 5.065153   | -2.415603  | -1.675890  |
| C    | 2.469793   | -1.707999  | -2.468370  |
| C    | 2.556571   | -2.214860  | -3.443264  |
| H    | 1.544702   | -1.110355  | -2.489734  |
| H    | 2.356181   | -2.473627  | -1.693440  |
| C    | 4.075184   | -1.906862  | 1.123104   |
| C    | 3.480894   | -3.151806  | 0.454772   |
| H    | 3.790968   | -4.045944  | 1.017175   |
| H    | 3.819885   | -3.288749  | -0.577937  |
| H    | 2.380693   | -3.110221  | 0.462256   |
| C    | 5.612101   | -1.973320  | 1.096691   |
| C    | 5.960718   | -2.897576  | 1.585206   |
| C    | 6.042858   | -1.117500  | 1.638533   |
| C    | 6.012045   | -1.956118  | 0.075156   |
| C    | 3.641971   | -1.966620  | 2.596041   |
| H    | 3.914196   | -2.947028  | 3.014331   |
| C    | 2.555281   | -1.846357  | 2.708954   |
| C    | 4.144721   | -1.206262  | 3.210902   |
| C    | 2.966322   | 3.127746   | 1.094628   |
| C    | 2.531577   | 4.069309   | -0.028233  |
| C    | 2.360418   | 5.080710   | 0.371100   |
| H    | 1.593723   | 3.717821   | -0.485738  |
| H    | 3.300437   | 4.145952   | -0.812184  |
| C    | 4.279139   | 3.632694   | 1.709552   |
| C    | 4.153687   | 4.651980   | 2.108859   |
| H    | 5.081062   | 3.654985   | 0.955984   |
| H    | 4.690443   | 2.981236   | 2.533169   |
| C    | 1.872527   | 3.108487   | 2.169216   |
| H    | 1.765896   | 4.110845   | 2.575084   |
| H    | 2.147708   | 2.447565   | 3.011889   |
| H    | 0.917821   | 2.744616   | 1.747726   |
| C    | -0.068414   | -1.455711  | 2.825628   |
| C    | 0.395353   | -0.424034   | 3.784294   |
| H    | 0.753686   | 0.485667   | 3.297888   |
| C    | 0.098143   | -0.538654   | 5.076431   |
| H    | 0.394659   | 0.279998   | 5.737432   |
| C    | -0.495683   | -1.684635   | 5.606176   |
| H    | -0.665872   | -1.770467   | 6.681881   |
|   |    |    |    |
|---|----|----|----|
| C | -0.864490000 | -2.721401000 | 4.750032000 |
| H | -1.322784000 | -3.627972000 | 5.153675000 |
| C | -0.643795000 | -2.612760000 | 3.378039000 |
| H | -0.921831000 | -3.438002000 | 2.717557000 |
| P | -0.142828000 | 1.338823000 | -1.012746000 |
| Al | -1.585132000 | -0.251022000 | -0.119218000 |
| C | -3.574140000 | 0.886834000 | 0.869616400 |
| C | -3.659409000 | 0.570095000 | 0.788326000 |
| C | -3.405466000 | -0.556263000 | 0.788326000 |
| H | -3.378765000 | -0.522425000 | 0.788326000 |
| C | -3.574114000 | -2.612760000 | 3.378039000 |
| H | -3.659409000 | -3.438002000 | 2.717557000 |
| C | -0.864490000 | 2.721401000 | -4.750032000 |
| C | -0.305353000 | 0.424034000 | -3.704294000 |
| C | -0.753686000 | -0.856670000 | -3.297880000 |
| C | -0.981433000 | 0.538654000 | -5.076431000 |
| C | -0.394650000 | -0.279998000 | -5.737432000 |
| C | 0.495683000 | 1.684635000 | -5.601760000 |
| C | 0.665872000 | 1.770467000 | -6.681881000 |
| C | 0.864490000 | 2.721401000 | -4.750032000 |
5.4.10 \([\text{Cp}^{3}\text{Al}(\mu-\text{PDip})]_2\)

\[
\begin{array}{cccc}
\text{C} & 4.531317000 & 1.809358000 & -0.233623000 \\
\text{C} & 3.767470000 & 2.792263000 & -1.133244000 \\
\text{H} & 3.767470000 & 2.792263000 & -1.133244000 \\
\text{H} & 3.767470000 & 2.792263000 & -1.133244000 \\
\text{H} & 3.767470000 & 2.792263000 & -1.133244000 \\
\text{H} & 3.767470000 & 2.792263000 & -1.133244000 \\
\text{C} & 4.645529000 & 2.452655000 & 1.143528000 \\
\end{array}
\]
5.4.11  \([\text{Cp}^3\text{Al(μ-PtBu)}]_2\)

|  |  |  |  |
|---|---|---|---|
| P  | 0.124265000 | -1.734063000 | -0.850470000 |
| P  | -0.012327000 | 0.488779000 | 1.651540000 |
| Al | 1.641470000 | -0.308698000 | 0.144356000 |
| C  | 3.552923000 | -0.415904000 | -0.937030000 |
| H  | 3.624855000 | -1.073120000 | -1.797223000 |
| C  | 3.197716000 | 0.969884000 | -0.994189000 |
| C  | 3.241020000 | 1.462288000 | 0.370113000 |
| C  | 3.793779000 | -0.817555000 | 0.405181000 |
| C  | 4.374753000 | -2.139701000 | 0.856580000 |
|     |   |   |   |
|-----|---|---|---|
| C   | 3.605445000 | 0.360239000 | 1.185631000 |
| H   | 3.694679000 | 0.399906000 | 2.266155000 |
| C   | 2.928878000 | 1.651216000 | -2.347454000 |
| C   | 3.061622000 | 2.855790000 | 0.986854000 |
| C   | 0.194057000 | -2.866018000 | -2.382853000 |
| C   | -0.002912000 | -0.689482000 | 3.178492000 |
| C   | 1.429332000 | 1.902372000 | -2.550831000 |
| H   | 1.812134000 | 2.547311000 | -1.768515000 |
| H   | 0.875824000 | 0.951376000 | -2.524453000 |
| C   | 1.241657000 | 2.383235000 | -3.524343000 |
| C   | -1.308166000 | -0.439591000 | 3.946544000 |
| H   | -2.178502000 | -0.745557000 | 3.363513000 |
| H   | -1.412507000 | 0.625716000 | 4.200001000 |
| H   | -1.303051000 | -1.016720000 | 4.888157000 |
| C   | 3.398426000 | 0.740936000 | -3.491408000 |
| H   | 3.232371000 | 1.250399000 | -4.452587000 |
| H   | 2.843372000 | -0.204808000 | -3.524755000 |
| H   | 4.471955000 | 0.512255000 | -3.411156000 |
| C   | 0.119545000 | -2.167455000 | 2.834403000 |
| H   | 1.060724000 | -2.387878000 | 2.308733000 |
| H   | -0.684268000 | -2.505656000 | 2.164636000 |
| H   | 0.089410000 | -2.779712000 | 3.753723000 |
| C   | 3.675813000 | -3.306186000 | 0.154937000 |
| H   | 2.600492000 | -3.325031000 | 0.390901000 |
| H   | 4.118917000 | -4.264365000 | 0.468038000 |
| H   | 3.774363000 | -3.238730000 | -0.939221000 |
| C   | 1.170073000 | -0.273905000 | 4.066835000 |
| H   | 1.180605000 | -0.884923000 | 4.986677000 |
| H   | 1.095351000 | 0.782656000 | 4.364664000 |
| H   | 2.135128000 | -0.416861000 | 3.561212000 |
| H   | 0.459031000 | -4.289140000 | -1.885400000 |
| H   | 0.499635000 | -4.990436000 | -2.738191000 |
| H   | -0.335522000 | -4.627005000 | -1.203113000 |
| H   | 1.413912000 | -4.355689000 | -1.344329000 |
| C   | 4.239028000 | -2.311097000 | 2.369468000 |
| H   | 4.764877000 | -1.515751000 | 2.918575000 |
| H   | 4.675085000 | -3.272354000 | 2.681482000 |
| H   | 3.184944000 | -2.303855000 | 2.683150000 |
| C   | 1.861467000 | 3.630995000 | 0.433216000 |
| H   | 1.960502000 | 3.883825000 | -0.628017000 |
| H   | 1.751759000 | 4.579064000 | 0.981985000 |
| H   | 0.935186000 | 3.054919000 | 0.575852000 |
| C   | 3.715929000 | 2.956917000 | -2.506966000 |
| H   | 4.790699000 | 2.792832000 | -2.336500000 |
| H   | 3.380166000 | 3.747977000 | -1.828552000 |
| H   | 3.591491000 | 3.334229000 | -3.533922000 |
| C   | -1.134212000 | -2.834312000 | -3.132414000 |
| H   | -1.345976000 | -1.834348000 | -3.532688000 |
| C   | -1.968735000 | -3.132984000 | -2.483598000 |
| H   | -1.182574000 | -3.539766000 | -3.981602000 |
| C   | 2.827347000 | 2.743872000 | 2.500356000 |
| H   | 2.674341000 | 3.751086000 | 2.916407000 |
| H   | 3.687186000 | 2.305144000 | 3.027253000 |
| H   | 1.928729000 | 2.147727000 | 2.713257000 |
| C   | 4.365018000 | 3.650881000 | 0.798534000 |
| H   | 4.621117000 | 3.806164000 | -0.255514000 |
| H   | 5.205654000 | 3.120002000 | 1.270938000 |
| H   | 4.275978000 | 4.639662000 | 1.277011000 |
| C   | 5.865751000 | -2.137288000 | 0.485647000 |
| H   | 6.002141000 | -2.035709000 | -0.601621000 |

S67
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 6.34688 | -3.07562| 0.885664|
| H       | 6.38908 | -1.29983| 0.970576|
| C       | 1.31188 | -2.43237| -3.324374|
| H       | 2.28996 | -2.44704| -2.823228|
| H       | 1.13298 | -1.41756| -3.708822|
| H       | 1.37016 | -3.11758| -4.188696|
| C       | -3.67194 | 0.09516 | 1.124220 |
| Al      | -1.51918 | -0.41783 | -1.007725 |
| C       | -3.51839 | -0.58709 | -1.007725 |
| H       | -3.84696 | 0.074803 | 2.194577 |
| C       | -3.40194 | 1.26463 | 0.379822 |
| H       | -1.13298 | -1.41756 | -3.708822 |
| C       | -3.15568 | 0.837513 | -0.983682 |
| C       | -3.45034 | 2.647796 | 1.046247 |
| C       | -3.01263 | 1.585254 | -2.317068 |
| C       | -4.14056 | -2.44897 | 0.671493 |
| C       | -3.86204 | -2.759469 | 2.145676 |
| C       | -3.48439 | -3.52352 | -0.191530 |
| C       | -5.65923 | -2.462988 | 0.438541 |
| H       | -3.29389 | -1.20621 | -1.894270 |
| C       | -2.10522 | 3.387697 | 1.049132 |
| C       | -3.84886 | 2.497633 | 2.521946 |
| C       | -4.54010 | 3.507580 | 0.388258 |
| H       | -2.20668 | 2.881263 | -2.253396 |
| C       | -3.30880 | 0.694292 | -3.350320 |
| C       | -4.42727 | 1.883546 | -2.842313 |
| H       | -1.70625 | 3.560090 | 0.045596 |
| H       | -1.35393 | 2.810970 | 1.697650 |
| H       | -2.22647 | 4.369776 | 1.534111 |
| H       | -3.90182 | 3.494145 | 2.985590 |
| H       | -3.10665 | 1.911120 | 3.082211 |
| H       | -4.83505 | 2.023360 | 2.638679 |
| H       | -2.78263 | -2.777658 | 2.354229 |
| H       | -4.27201 | -3.747021 | 2.407910 |
| H       | -4.32729 | -2.029630 | 2.816680 |
| H       | -3.73700 | -3.393508 | -1.254493 |
| H       | -3.83732 | -4.522345 | 0.107999 |
| H       | -2.38740 | -3.498955 | -0.094492 |
| H       | -2.68786 | 3.657596 | -1.651484 |
| H       | -2.08638 | 3.286051 | -3.270596 |
| H       | -1.19980 | 2.702409 | -1.846630 |
| H       | -5.56833 | 2.983187 | 0.392460 |
| H       | -4.30518 | 3.770346 | -0.650252 |
| H       | -4.66853 | 4.450304 | 0.945254 |
| H       | -2.14279 | 1.263835 | -4.276953 |
| H       | -2.90647 | -0.187442 | -3.619340 |
| H       | -1.33178 | 0.348201 | -2.979188 |
| H       | -4.98946 | 2.533061 | -2.158633 |
| H       | -4.99932 | 0.951066 | -2.962551 |
| H       | -4.37473 | 2.382348 | -3.823745 |
| H       | -6.16023 | -1.705583 | 1.060235 |
| H       | -6.08241 | -3.449503 | 0.688123 |
| H       | -5.89476 | -2.243942 | -0.614010 |
5.4.12 \([(\text{Cp}^3\text{Al})_2(\text{PDip})_2]\) (1b)

\[
\begin{array}{cccc}
\text{P} & 1.058297000 & 1.226074000 & 0.262653000 \\
\text{P} & -1.056510000 & 1.228438000 & -0.263827000 \\
\text{Al} & 1.333673000 & -1.136817000 & -0.104418000 \\
\text{Al} & -1.336238000 & -1.133685000 & 0.105113000 \\
\text{C} & 2.353947000 & -3.206136000 & 0.329977000 \\
\text{H} & 1.801631000 & -4.029213000 & 0.769110000 \\
\text{C} & 2.447147000 & -2.949851000 & 2.328141000 \\
\text{C} & -1.777143000 & 2.368936000 & 0.905387000 \\
\end{array}
\]

\[
\begin{array}{cccc}
P & 1.056510000 & 1.228438000 & -0.263827000 \\
\text{P} & -1.056510000 & 1.228438000 & -0.263827000 \\
\text{Al} & 1.333673000 & -1.136817000 & -0.104418000 \\
\text{Al} & -1.336238000 & -1.133685000 & 0.105113000 \\
\text{C} & 2.353947000 & -3.206136000 & 0.329977000 \\
\text{H} & 1.801631000 & -4.029213000 & 0.769110000 \\
\text{C} & 2.447147000 & -2.949851000 & 2.328141000 \\
\text{C} & -1.777143000 & 2.368936000 & 0.905387000 \\
\end{array}
\]
5.4.13 [(Cp^3Al)_2(PTip)_2] (1c)

\[
\begin{array}{ccc}
\text{H} & -1.098023000 & 4.827300000 & -2.684815000 \\
\text{H} & -0.205133000 & 4.156491000 & -1.302090000 \\
\text{C} & -0.107198000 & 1.634150000 & -3.795665000 \\
\text{H} & -0.856771000 & 1.963544000 & -3.063274000 \\
\text{H} & -0.530932000 & 0.799390000 & -4.374217000 \\
\text{C} & 0.088339000 & 2.462592000 & -4.495020000 \\
\text{C} & -0.601878000 & -0.928485000 & -0.332832000 \\
\text{H} & -0.613597000 & -1.535970000 & -1.242376000 \\
\text{H} & -0.880448000 & -0.190250000 & -0.346476000 \\
\text{H} & -0.218851000 & -1.595085000 & 0.528898000 \\
\text{C} & -4.764704000 & 0.621991000 & 1.079489000 \\
\text{H} & -5.068245000 & 0.016846000 & 1.946028000 \\
\text{H} & -5.514552000 & 1.418220000 & 0.967269000 \\
\text{H} & -3.805879000 & 1.106704000 & 1.301739000 \\
\text{C} & -3.643525000 & 4.491887000 & -1.733807000 \\
\text{H} & -4.538309000 & 3.946054000 & -1.398706000 \\
\text{H} & -3.635140000 & 4.487816000 & -2.834840000 \\
\text{H} & -3.752501000 & 5.542353000 & -1.420010000 \\
\text{C} & -3.239622000 & -4.589384000 & 2.703673000 \\
\text{H} & -4.002432000 & -3.887511000 & 3.073264000 \\
\text{H} & -2.964192000 & -5.263080000 & 3.531196000 \\
\text{H} & -3.695508000 & -5.193085000 & 1.904404000 \\
\text{C} & -3.087205000 & -2.243193000 & -2.617157000 \\
\text{C} & 3.648870000 & 4.485032000 & 1.736187000 \\
\text{H} & 4.542690000 & 3.937861000 & 1.400716000 \\
\text{H} & 3.638752000 & 4.480870000 & 2.837218000 \\
\text{H} & 3.759779000 & 5.535490000 & 1.423236000 \\
\text{C} & -2.320355000 & -1.065650000 & -3.230533000 \\
\text{H} & -2.693602000 & -0.091764000 & -2.896354000 \\
\text{H} & -2.373988000 & -1.098952000 & -4.330529000 \\
\text{H} & -1.257896000 & -1.112959000 & -2.944306000 \\
\text{C} & -2.412762000 & -3.527511000 & -3.117816000 \\
\text{H} & -1.357729000 & -3.582840000 & -2.822802000 \\
\text{H} & -2.445078000 & -3.549328000 & -4.217518000 \\
\text{H} & -2.924876000 & -4.428916000 & -2.748862000 \\
\text{C} & -4.525449000 & -2.289972000 & -3.149116000 \\
\text{H} & -5.084151000 & -3.121481000 & -2.692917000 \\
\text{H} & -4.509649000 & -2.451429000 & -4.238304000 \\
\text{H} & -5.082572000 & -1.365085000 & -2.966287000 \\
\end{array}
\]

\[5.4.13 \quad [(\text{Cp}^3\text{Al})_2(\text{PTip})_2] (1c)\]
|   | C        | 1.071219000 | 1.119123000 | 3.638723000 |
|   | H        | 1.380373000 | 0.162972000 | 3.194878000 |
|   | H        | 0.221783000 | 0.930502000 | 4.312676000 |
|   | H        | 1.902635000 | 1.508606000 | 4.247733000 |
|   | C        | 1.071101000 | -1.120030000 | -3.638813000 |
|   | H        | 1.381041000 | -0.164077000 | -3.195066000 |
|   | H        | 0.222040000 | -0.930730000 | -4.313041000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|   | C        | 0.112701000 | -3.390572000 | -3.155404000 |
|   | H        | 0.836369000 | -3.873609000 | -3.830342000 |
|   | H        | 0.221783000 | -0.930502000 | -4.312676000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|   | C        | 0.112701000 | -3.390572000 | -3.155404000 |
|   | H        | 0.836369000 | -3.873609000 | -3.830342000 |
|   | H        | 0.221783000 | -0.930502000 | -4.312676000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|   | C        | 0.112701000 | -3.390572000 | -3.155404000 |
|   | H        | 0.836369000 | -3.873609000 | -3.830342000 |
|   | H        | 0.221783000 | -0.930502000 | -4.312676000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|   | C        | 0.112701000 | -3.390572000 | -3.155404000 |
|   | H        | 0.836369000 | -3.873609000 | -3.830342000 |
|   | H        | 0.221783000 | -0.930502000 | -4.312676000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|   | C        | 0.112701000 | -3.390572000 | -3.155404000 |
|   | H        | 0.836369000 | -3.873609000 | -3.830342000 |
|   | H        | 0.221783000 | -0.930502000 | -4.312676000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|   | C        | 0.112701000 | -3.390572000 | -3.155404000 |
|   | H        | 0.836369000 | -3.873609000 | -3.830342000 |
|   | H        | 0.221783000 | -0.930502000 | -4.312676000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|   | C        | 0.112701000 | -3.390572000 | -3.155404000 |
|   | H        | 0.836369000 | -3.873609000 | -3.830342000 |
|   | H        | 0.221783000 | -0.930502000 | -4.312676000 |
|   | H        | 1.902288000 | -1.510357000 | -4.247733000 |
|      |          |          |          |
|------|----------|----------|----------|
| C    | 4.177728000 | 0.542760000 | -1.903319000 |
| H    | 5.171698000 | 0.720574000 | -1.461070000 |
| H    | 4.321662000 | 0.175816000 | -2.932219000 |
| H    | 3.690618000 | -0.255950000 | -1.327027000 |
| C    | 5.235830000 | -4.147776000 | -2.127124000 |
| H    | 5.993167000 | -3.106850000 | -1.340932000 |
| C    | -3.510742000 | -2.394132000 | -2.706831000 |
| H    | -2.984526000 | -1.478146000 | -2.639471000 |
| H    | -4.151337000 | -2.315078000 | -3.598846000 |
| C    | 5.881547000 | 3.289013000 | 3.220789000 |
| H    | 5.172072000 | 3.099349000 | 4.042283000 |
| H    | 6.763079000 | 3.791825000 | 3.649422000 |
| C    | 6.195960000 | 2.312303000 | 2.825385000 |
| H    | 6.944766000 | 2.890683000 | 1.340932000 |
| H    | 5.371250000 | 3.831916000 | -2.748585000 |
| H    | 6.224956000 | 2.544865000 | -3.843340000 |
| C    | 6.491267000 | 3.115560000 | -2.537033000 |
| C    | 6.166373000 | -0.546337000 | 1.903817000 |
| H    | 6.220544000 | -0.724802000 | 1.461634000 |
| H    | 6.390130000 | 0.252703000 | 1.327027000 |
| C    | 4.823547000 | 5.513834000 | 2.659866000 |
| H    | 4.320153000 | 0.179459000 | 2.932718000 |
| H    | 3.690103000 | 0.252703000 | 1.327027000 |
| C    | 4.819256000 | 5.517652000 | 2.659909000 |
| H    | 4.376993000 | 6.132539000 | 1.864269000 |
| H    | 5.689258000 | 6.053544000 | 3.075214000 |
| C    | 4.075297000 | 5.420100000 | 3.463170000 |
| C    | -5.109836000 | -3.928481000 | -1.555944000 |
| H    | -4.409358000 | -4.770455000 | -1.663364000 |
| H    | -5.779345000 | -3.925849000 | -2.431318000 |
| C    | -5.718201000 | -4.108276000 | -0.656677000 |
| C    | -4.819256000 | -5.517652000 | -2.659909000 |
| C    | 4.376993000 | -6.136254000 | -1.864605000 |
| H    | 5.684618000 | -6.057954000 | -3.075283000 |
| H    | 4.071256000 | -5.423050000 | -3.463312000 |
| C    | 5.789352000 | -3.293570000 | -3.219852000 |
| H    | 5.170291000 | -3.103182000 | -4.041527000 |
| H    | 6.760632000 | -3.796953000 | -3.648332000 |
| H    | 6.197025000 | -2.317210000 | -2.824087000 |

5.4.14 [(Cp^3Al)_2(PMes)_2]
5.4.15 $[\text{Cp}^{3\text{t}}\text{Al(PtBu)}_{3}]$ (2)

| $[\text{Cp}^{3\text{t}}\text{Al(PtBu)}_{3}]$ (2) @ PBE0-D3(BJ)/def2-SVP |
|---------------------------------|-----------------|-----------------|
| P                               | 1.426375000     | -1.573756000    |
| P                               | 2.744883000     | 0.185754000     |
| P                               | 1.175717000     | 1.673192000     |
| Al                              | -0.330814000    | 0.018479000     |
| C                               | -2.164265000    | -1.130580000    |
| H                               | -2.080672000    | -2.043256000    |
| C                               | -2.164440000    | -1.012683000    |
| C                               | -2.279698000    | 0.485515000     |
| C                               | -2.271350000    | 0.174229000     |
| C                               | -2.557347000    | 0.470821000     |
| C                               | -2.346215000    | 1.086682000     |
| H                               | -2.420705000    | 2.163611000     |
| C                               | -2.160911000    | -2.277217000    |
| C                               | -2.502859000    | 1.198870000     |
| C                               | 1.943483000     | -2.296648000    |
| C                               | 3.537794000     | -0.137460000    |
| C                               | 1.437604000     | 2.988767000     |
| C                               | -0.924519000    | -2.411190000    |
| H                               | -0.760698000    | -1.538662000    |
| H                               | -0.819985000    | -2.555671000    |
| H                               | -1.839955000    | -3.289996000    |
| C                               | 2.773666000     | 3.672585000     |
| H                               | 3.685517000     | 2.954251000     |
| H                               | 2.785388000     | 4.120164000     |
| H                               | 2.957871000     | 4.473868000     |
| C                               | -2.170764000    | -3.525330000    |
| H                               | -2.170104000    | -4.423470000    |
| H                               | -1.274139000    | -3.573548000    |
| H                               | -3.064116000    | -3.570215000    |
| C                               | 1.457853000     | 2.408078000     |
| H                               | 0.511305000     | 1.897425000     |
| H                               | 2.272142000     | 1.677975000     |
| H                               | 1.606179000     | 3.206300000     |
| C                               | -1.567904000    | -0.242604000    |
| H                               | -0.548282000    | 0.145114000     |
| H                               | -1.843548000    | -0.090354000    |
| H                               | -1.545135000    | -1.326783000    |
| C                               | 0.299318000     | 3.999331000     |
| H                               | 0.434329000     | 4.823422000     |
| H                               | 0.269198000     | 4.435371000     |
| H                               | -0.680399000    | 3.539653000     |
| C                               | 2.150870000     | -1.253331000    |
| H                               | 2.462844000     | -1.739171000    |
| H                               | 2.933196000     | -0.535639000    |
| H                               | 1.229889000     | -0.689323000    |
| C                               | -2.510187000    | 1.974481000     |
| H                               | -3.271258000    | 2.515406000     |
| H                               | -2.707236000    | 2.170065000     |
| H                               | -1.526557000    | 2.402789000     |
| C                               | -1.735351000    | 0.680220000     |
| H                               | -2.078823000    | -0.318480000    |
| H                               | -1.891740000    | 1.367120000     |
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | -0.653865000 | -3.303820000 | 0.640447000 |
| C    | 2.523455000 | -2.855287000 | -0.449417000 |
| H    | 3.039642000 | -3.815287000 | -0.624890000 |
| H    | 1.944770000 | -2.610550000 | -1.352931000 |
| H    | 1.823911000 | -2.995812000 | 0.389801000  |
| C    | -3.442482000 | -2.400731000 | -2.322586000 |
| H    | -4.336269000 | -1.770877000 | -2.193620000 |
| H    | -3.459900000 | -3.178160000 | -1.549169000 |
| H    | -3.519749000 | -2.906550000 | -3.297560000 |
| C    | 3.252215000 | 1.663676000  | -3.054150000 |
| H    | 3.139862000 | 0.890948000  | -3.829080000 |
| H    | 4.054027000 | 1.345339000  | -2.369713000 |
| C    | 3.577955000 | 2.599594000  | -3.541260000 |
| H    | 2.070769000 | -2.103001000 | 2.662259000  |
| H    | -2.215879000 | -3.050757000 | 3.201951000  |
| H    | -2.666388000 | -1.343410000 | 3.188279000  |
| C    | -1.006165000 | -1.833525000 | 2.732297000  |
| C    | 4.488932000 | -1.578595000 | -1.318407000 |
| H    | 5.233269000 | -0.790549000 | -1.120932000 |
| H    | 3.935159000 | -1.392130000 | -2.231723000 |
| C    | 4.057410000 | -2.517991000 | -1.516636000 |
| C    | 4.319333000 | -2.113439000 | 1.127558000  |
| H    | 4.854498000 | -3.068488000 | 0.989280000  |
| H    | 3.643289000 | -2.225572000 | 1.990136000  |
| C    | 5.063835000 | -1.339179000 | 1.372426000  |
| C    | -4.012936000 | -2.578137000 | 1.197973000  |
| C    | 5.032789000 | -2.517991000 | -1.516636000 |
| C    | 4.319333000 | -2.113439000 | 1.127558000  |
| H    | 4.854498000 | -3.068488000 | 0.989280000  |
| H    | 3.643289000 | -2.225572000 | 1.990136000  |
| C    | 5.063835000 | -1.339179000 | 1.372426000  |
| C    | 4.057410000 | -2.517991000 | -1.516636000 |
| C    | 4.319333000 | -2.113439000 | 1.127558000  |
| H    | 4.854498000 | -3.068488000 | 0.989280000  |
| H    | 3.643289000 | -2.225572000 | 1.990136000  |
| C    | 5.063835000 | -1.339179000 | 1.372426000  |
| C    | 5.032789000 | -2.517991000 | -1.516636000 |
| C    | 4.319333000 | -2.113439000 | 1.127558000  |
| H    | 4.854498000 | -3.068488000 | 0.989280000  |
| H    | 3.643289000 | -2.225572000 | 1.990136000  |
| C    | 5.063835000 | -1.339179000 | 1.372426000  |

5.4.16  [Cp\textsuperscript{3}Al(PMes)\textsubscript{3}]

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| P    | 1.074749000 | 1.294643000 | 0.509328000 |
| P    | -0.880877000 | 1.666924000 | -0.483247000 |
| P    | -1.659209000 | -0.250260000 | 0.342273000 |
| Al   | 0.593661000 | -0.987637000 | 0.219014000 |
| C    | 2.473577000 | -1.981680000 | 0.960040000 |
| H    | 3.280582000 | -1.393405000 | 1.383907000 |
| C    | 1.363822000 | -2.502775000 | 1.703568000 |
| C    | 0.510407000 | -3.179548000 | 0.746695000 |
| C    | 2.340046000 | -2.272572000 | -0.411320000 |
| C    | 3.358562000 | -2.041592000 | -1.510740000 |
| C    | 1.113990000 | -2.983354000 | -0.536847000 |
| H    | 0.723265000 | -3.391618000 | -1.467181000 |
| C    | 1.278841000 | -2.306082000 | 3.226055000 |
| C    | -0.721147000 | -4.084714000 | 0.878930000 |
| C    | -1.745867000 | 2.993277000 | 0.484711000 |
| C    | 0.143825000 | -3.346084000 | 3.688854000 |
|   |   |   |   |
|---|---|---|---|
| H | -0.836375000 | -1.672852000 | 3.245859000 |
| H | 0.332836000 | -0.346876000 | 3.187423000 |
| H | 0.087365000 | -1.241177000 | 4.703896000 |
| C | 2.577496000 | -1.669669000 | 3.741375000 |
| H | 2.515637000 | -1.556902000 | 4.833960000 |
| H | 2.735037000 | -0.668788000 | 3.321166000 |
| H | 3.458636000 | -2.289140000 | 3.516164000 |
| C | 4.435204000 | -1.057652000 | -1.059319000 |
| H | 4.986140000 | -1.436820000 | -0.186640000 |
| C | 2.681824000 | -1.508201000 | -2.774516000 |
| H | 1.903464000 | -2.193340000 | -3.144083000 |
| H | 3.421157000 | -1.380073000 | -3.579981000 |
| H | 2.219758000 | -0.529246000 | -2.586113000 |
| C | -1.767640000 | -3.688161000 | 1.888152000 |
| H | -1.403055000 | -3.613355000 | 2.921105000 |
| H | -2.642211000 | -4.274829000 | 1.847440000 |
| C | 1.137513000 | -3.647547000 | 3.955260000 |
| H | 1.948732000 | -4.335298000 | 3.670915000 |
| H | 0.183767000 | -4.146874000 | 3.751969000 |
| C | -1.444319000 | -4.204020000 | -0.472349000 |
| H | -2.346299000 | -4.820609000 | -0.345835000 |
| H | -0.826310000 | -4.696686000 | -1.236588000 |
| H | -1.767959000 | -3.225385000 | -0.854693000 |
| C | -0.222271000 | -5.490737000 | 1.254335000 |
| H | 0.293452000 | -5.504789000 | 2.222521000 |
| H | 0.480585000 | -5.866521000 | 0.495212000 |
| H | -1.071779000 | -6.190256000 | 1.308792000 |
| C | 4.011026000 | -3.399245000 | -1.815654000 |
| C | 4.493411000 | -3.813692000 | -0.917367000 |
| H | 4.778837000 | -3.283440000 | -2.597843000 |
| H | 3.267723000 | -4.130711000 | -2.168042000 |
| C | 2.520187000 | 2.002240000 | -0.383407000 |
| C | -1.860857000 | 3.095632000 | 1.892781000 |
| C | -2.569813000 | 4.167340000 | 2.443174000 |
| C | -3.174333000 | 5.149178000 | 1.655979000 |
| C | -3.061089000 | 5.829514000 | 0.272686000 |
| C | -2.363417000 | 3.976350000 | -0.326984000 |
| C | -1.259841000 | 2.097819000 | 2.833816000 |
| H | -2.652539000 | 4.231325000 | 3.530921000 |
| C | -3.900905000 | 6.302160000 | 2.284100000 |
| H | -3.534741000 | 5.778558000 | -0.369147000 |
| C | -2.312669000 | 3.936470000 | -1.832632000 |
| H | -1.597486000 | 1.077893000 | 2.590526000 |
| H | -1.538853000 | 2.322365000 | 3.872613000 |
| H | -0.161847000 | 2.091099000 | 2.754302000 |
| H | -2.877635000 | 4.779883000 | -2.255467000 |
| H | -2.736601000 | 3.003174000 | -2.233161000 |
| H | -1.280061000 | 3.996406000 | -2.210117000 |
| H | -4.485988000 | 5.980870000 | 3.158969000 |
| C | -4.585126000 | 6.785090000 | 1.571845000 |
| C | -3.191509000 | 7.070910000 | 2.633834000 |
| C | 3.648533000 | 2.246734000 | 0.442989000 |
| C | 4.837715000 | 2.706234000 | -0.126729000 |
| C | 4.959739000 | 2.954337000 | -1.493397000 |
| C | 3.836999000 | 2.730429000 | -2.288821000 |
| C | 2.624900000 | 2.265425000 | -1.769868000 |
### 5.4.17 \([\text{Cp}^*\text{Al}(\mu-\text{PMes})_2] (3a)\)

|          |          |          |
|----------|----------|----------|
| Al       | -0.050580000 | -1.131240000 | 1.057133000 |
| P        | 0.213350000  | 1.188090000  | 1.274647000  |
| C        | -1.191752000 | 2.078415000  | 2.064919000  |
| C        | -2.549217000 | 1.819033000  | 1.761532000  |
| C        | -3.552222000 | 2.561412000  | 2.395690000  |
| H        | -4.597278000 | 2.352230000  | 2.146792000  |
| C        | -3.265772000 | 3.555614000  | 3.330884000  |
| C        | -1.922397000 | 3.794338000  | 3.628388000  |
| H        | -1.667752000 | 4.565685000  | 4.362238000  |
| C        | -0.888261000 | 3.078706000  | 3.022389000  |
| C        | 0.530962000  | 3.381699000  | 3.407538000  |
| H        | 0.573791000  | 4.185618000  | 4.156345000  |
| H        | 1.129842000  | 3.680571000  | 2.533769000  |
| C        | 1.029839000  | 2.490861000  | 3.821497000  |
| C        | -2.962901000 | 0.762689000  | 0.782980000  |
| H        | -4.056359000 | 0.718304000  | 0.683043000  |
| H        | -2.613067000 | -0.235890000 | 1.089560000  |
| C        | -2.538816000 | 0.931575000  | -0.220222000 |
| C        | -4.356205000 | 4.332923000  | 4.888138000  |
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | -4.18056  | 5.41774   | 3.93620   |
| H    | -4.41247  | 4.08736   | 5.08146   |
| H    | -5.33944  | 4.11878   | 3.56572   |
| C    | 0.80308   | -1.91475  | 2.98911   |
| C    | 1.02718   | -2.88527  | 1.95341   |
| C    | -0.24377  | -3.33316  | 1.49072   |
| C    | -1.25450  | -2.61335  | 2.19896   |
| C    | -0.60110  | -1.75014  | 3.14227   |
| C    | -1.25095  | -0.81521  | 4.10812   |
| H    | -1.36215  | -1.26083  | 5.11575   |
| H    | -2.27467  | -0.55462  | 3.80643   |
| H    | -0.69229  | 0.12861   | 4.18802   |
| C    | 1.83722   | -1.16490  | 3.76230   |
| H    | 1.75401   | -1.37178  | 4.84100   |
| H    | 1.72794   | -0.07682  | 3.61628   |
| C    | 2.85360   | -1.43865  | 3.44822   |
| C    | 2.34388   | -3.43064  | 1.50082   |
| H    | 2.54541   | -4.40373  | 1.97855   |
| H    | 3.17527   | -2.76079  | 1.75963   |
| H    | 2.36878   | -3.58517  | 0.41204   |
| C    | -0.47292  | -4.35169  | 0.42602   |
| H    | -0.45463  | -5.37289  | 0.84293   |
| H    | 0.30864   | -4.29652  | -0.35492  |
| C    | -1.44569  | -4.20781  | -0.06260  |
| H    | -2.72793  | -2.81965  | 2.04618   |
| H    | -3.04037  | -3.77063  | 2.50815   |
| H    | -3.02786  | -2.85375  | 0.98778   |
| H    | -3.39126  | -2.01766  | 2.53070   |
| Al   | 0.05058   | 1.13124   | -1.05713  |
| P    | -0.21335  | -1.18809  | -1.27464  |
| C    | 1.19175   | -2.07841  | -2.06491  |
| C    | 2.54921   | -1.81903  | -1.76153  |
| C    | 3.55222   | -2.56141  | -2.39569  |
| H    | 4.59727   | -2.35230  | -2.14679  |
| C    | 3.26577   | -3.55561  | -3.33088  |
| C    | 1.92239   | -3.79433  | -3.62838  |
| H    | 1.66775   | -4.56568  | -4.36233  |
| C    | 0.88826   | -3.07870  | -3.02239  |
| C    | -0.53096  | -3.38169  | -3.40758  |
| H    | -0.57391  | -4.18561  | -4.15634  |
| H    | -1.12984  | -3.68057  | -2.53376  |
| H    | -1.02983  | -2.49086  | -3.82149  |
| C    | 2.96298   | -0.76269  | -0.78298  |
| H    | 4.05635   | -0.71830  | -0.68343  |
| H    | 2.61307   | 0.23589   | -1.09056  |
| H    | 2.53881   | -0.93157  | 0.22022   |
| C    | 4.35620   | -4.33292  | -4.00813  |
| H    | 4.18805   | -5.41777  | -3.93620  |
| H    | 4.41247   | -4.08736  | -5.08146  |
| H    | 5.33944   | -4.11878  | -3.56572  |
| C    | -0.80308  | 1.91475   | -2.98911  |
| C    | -1.02718  | 2.88527   | -1.95341  |
| C    | 0.24377   | 3.33316   | -1.49072  |
| C    | 1.25450   | 2.61335   | -2.19896  |
| C    | 0.60110   | 1.75014   | -3.14227  |
| C    | 1.25095   | 0.81521   | -4.10812  |
| H    | 1.30215   | 1.26083   | -5.11575  |
| H    | 2.27467   | 0.55462   | -3.80643  |
| H    | 0.69229   | -0.12861  | -4.18802  |
| C    | -1.83722  | 1.16490   | -3.76230  |
5.4.18  [Cp²Al(μ-PDip)]₂ (3b)

[[Cp²Al(μ-PDip)]₂ (3b) @ PBE0-D3(BJ)/def2-SVP]

|        |        |        |
|--------|--------|--------|
| 112    | 112    | 112    |
| Al     | 0.351239000  | 1.186336000  | 1.122833000  |
| C      | -0.505646000  | 2.197277000  | 2.877710000  |
| C      | -0.066521000  | 3.155278000  | 1.916082000  |
| C      | 1.347692000   | 2.995479000  | 1.749060000  |
| C      | 1.780466000   | 1.967858000  | 2.644082000  |
| C      | 0.644848000   | 1.471000000  | 3.338499000  |
| C      | -1.925063000  | 2.018083000  | 3.309020000  |
| H      | -2.565474000  | 1.724986000  | 2.469920000  |
| H      | -2.332826000  | 2.952756000  | 3.727267000  |
| H      | -2.017657000  | 1.240471000  | 4.078940000  |
| C      | -0.961762000  | 4.103457000  | 1.190193000  |
| H      | -1.620974000  | 3.580661000  | 0.476940000  |
| H      | -0.387937000  | 4.846164000  | 0.619875000  |
| H      | -1.608471000  | 4.648862000  | 1.894902000  |
| C      | 2.266188000   | 3.832631000  | 0.918559000  |
| H      | 2.895360000   | 3.223502000  | 0.250771000  |
| H      | 2.944878000   | 4.419421000  | 1.562646000  |
| H      | 1.711376000   | 4.543055000  | 0.294264000  |
| C      | 3.188703000   | 1.527272000  | 2.850648000  |
| H      | 3.234154000   | 0.477899000  | 3.172177000  |
| H      | 3.682892000   | 2.137339000  | 3.626207000  |
| H      | 3.783027000   | 1.620847000  | 1.930911000  |
| C      | 0.703828000   | 0.446685000  | 4.425372000  |
| H      | 1.215839000   | -0.472606000 | 4.183200000  |
| H      | -0.297257000  | 0.164536000  | 4.774020000  |
| H      | 1.255455000   | 0.845730000  | 5.292066000  |
| P      | 1.411310000   | -0.816704000 | 0.389986000  |
| C      | 1.919448000   | -1.977935000 | 1.739225000  |
| C      | 3.302346000   | -2.029701000 | 2.068922000  |
| C      | 3.711204000   | -2.740352000 | 3.200663000  |
| H      | 4.768929000   | -2.766812000 | 3.468090000  |
| C      | 2.793965000   | -3.420374000 | 3.991825000  |
| H      | 3.125260000   | -3.958761000 | 4.882853000  |
| C      | 1.454757000   | -3.438829000 | 3.622388000  |
| H      | 0.747017000   | -4.009979000 | 4.226056000  |
| C      | 0.996180000   | -2.745375000 | 2.496189000  |
| C      | 4.347317000   | -1.387021000 | 1.725780000  |
| H      | 3.893262000   | -0.467753000 | 0.767898000  |
|   | C         | H         | H         | C         | H         | H         |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| C | 5.645167000 | -1.007995000 | 1.875714000 |
| H | 6.225778000 | -1.893320000 | 2.181175000 |
| H | 5.466311000 | -0.397016000 | 2.773178000 |
| H | 6.285197000 | -0.427335000 | 1.193713000 |
| C | 4.628341000 | -2.301861000 | -0.021184000 |
| H | 3.703881000 | -2.508932000 | -0.579381000 |
| H | 5.048685000 | -3.263916000 | 0.313316000 |
| H | 5.345841000 | -1.835360000 | -0.715045000 |
| C | -0.473441000 | -2.858916000 | 2.126428000 |
| H | -0.525433000 | -2.679638000 | 1.039177000 |
| C | -1.848026000 | -4.246851000 | 2.397249000 |
| H | -2.870038000 | -4.319842000 | 1.997634000 |
| H | -1.115625000 | -4.462133000 | 3.474877000 |
| H | -0.437259000 | -5.038321000 | 1.936564000 |
| C | -1.337256000 | -1.792996000 | 2.792997000 |
| H | -0.978614000 | -0.782564000 | 2.553705000 |
| H | -1.329957000 | -1.910058000 | 3.888073000 |
| H | -2.379563000 | -1.859106000 | 2.443792000 |
| Al | -0.351239000 | -1.106336000 | -1.122833000 |
| C | 0.505646000 | -2.197277000 | -2.877710000 |
| C | 0.066521000 | -3.155278000 | -1.916082000 |
| C | -1.347692000 | -2.995479000 | -1.749060000 |
| C | -1.780466000 | -1.967858000 | -2.644802000 |
| C | -0.644848000 | -1.471000000 | -3.338499000 |
| C | 1.925063000 | -2.018083000 | -3.309020000 |
| H | 2.565474000 | -1.724986000 | -2.460992000 |
| H | 2.332026000 | -2.952756000 | -3.727267000 |
| H | 2.017657000 | -1.240471000 | -4.078940000 |
| C | 0.961762000 | -4.103457000 | -1.190193000 |
| H | 1.628974000 | -3.580661000 | -0.476949000 |
| H | 0.387937000 | -4.846164000 | -0.619875000 |
| H | 1.608471000 | -4.648862000 | -1.894902000 |
| C | -2.266188000 | -3.832631000 | -0.918559000 |
| H | -2.895369000 | -3.223502000 | -0.250771000 |
| H | -2.944878000 | -4.414921000 | -1.562646000 |
| H | -1.711376000 | -4.543955000 | -0.294264000 |
| C | -3.188703000 | -1.527272000 | -2.850648000 |
| H | -3.234154000 | -0.477889000 | -3.172177000 |
| H | -3.682982000 | -2.137339000 | -3.626207000 |
| H | -3.783027000 | -1.628847000 | -1.930911000 |
| C | -0.703828000 | -0.446685000 | -4.425372000 |
| H | -1.215893000 | 0.4726060000 | -4.103280000 |
| H | 0.297257000 | -0.164536000 | -4.774020000 |
| H | -1.255455000 | -0.845730000 | -5.292860000 |
| P | -1.411310000 | 0.816704000 | -0.389986000 |
| C | -1.919448000 | 1.977935000 | -1.739225000 |
| C | -3.302346000 | 2.029701000 | -2.068922000 |
| C | -3.711284000 | 2.740352000 | -3.200663000 |
| H | -4.768929000 | 2.766012000 | -3.468590000 |
| C | -2.793065000 | 3.420374000 | -3.991825000 |
| H | -3.125260000 | 3.958761000 | -4.882853000 |
| C | -1.454757000 | 3.438829000 | -3.622388000 |
| H | -0.747017000 | 4.009979000 | -4.226056000 |
| C | -0.996180000 | 2.745375000 | -2.496189000 |
| C | -4.347317000 | 1.387021000 | -1.172578000 |
| H | -3.893026000 | 0.467753000 | -0.767898000 |
| C | -5.645167000 | 1.087995000 | -1.875714000 |
| H | -6.225778000 | 1.893820000 | -2.181175000 |
| H | -5.466311000 | 0.397016000 | -2.773178000 |
| H | -6.285197000 | 0.427335000 | -1.193713000 |
5.4.19  \([\text{Cp}^*\text{Al}(\mu-\text{PTip})]_2\) (3c)

\[
\begin{array}{ccc}
\text{C} & -4.628341000 & 2.301861000 & 0.021184000 \\
\text{H} & -3.703881000 & 2.508932000 & 0.579381000 \\
\text{H} & -5.345841000 & 1.835360000 & 0.715045000 \\
\text{C} & 0.473441000 & 2.858916000 & -2.126428000 \\
\text{H} & 0.525433000 & 2.679638000 & -1.839177000 \\
\text{C} & 1.048026000 & 4.246851000 & -2.397249000 \\
\text{H} & 1.115625000 & 4.462133000 & -3.474877000 \\
\text{H} & 1.337256000 & 1.792996000 & -2.792997000 \\
\text{H} & 0.978614000 & 0.782564000 & -2.553705000 \\
\text{H} & 1.329957000 & 1.910058000 & -3.888730000 \\
\text{H} & 2.379563000 & 1.859106000 & -2.443792000 \\
\end{array}
\]
| Atom | X Position | Y Position | Z Position |
|------|------------|------------|------------|
| C    | 0.28396500 | 1.24007700 | 3.47727000 |
| C    | -1.10843800 | 0.95983100 | 3.44742800 |
| C    | -1.75067700 | 1.95049400 | 2.64079000 |
| C    | -0.74733300 | 2.87104400 | 2.19531000 |
| C    | 1.81966600  | 3.08988200 | 2.41610200 |
| H    | 2.03623200  | 3.11765700 | 1.33559900 |
| H    | 2.65141600  | 2.56799500 | 2.98790000 |
| H    | 1.81417700  | 4.12907400 | 2.78277000 |
| C    | 1.28110100  | 0.47533000 | 4.28689100 |
| H    | 1.07942600  | 0.60905700 | 5.36220100 |
| H    | 2.30625900  | 0.81792600 | 4.09989000 |
| C    | 1.24767000  | -0.60411800 | 4.07555100 |
| C    | -1.79278600 | -1.14472000 | 4.17518000 |
| H    | -1.11441800 | -0.99223000 | 4.34419300 |
| H    | -2.66449600 | -0.51940700 | 3.62152100 |
| C    | -2.15252700 | 0.19766000 | 5.16212600 |
| C    | -3.22993200 | 2.05668100 | 2.45474500 |
| H    | -3.72660100 | 2.25126200 | 3.41920700 |
| C    | -3.66562600 | 1.31327500 | 2.04654000 |
| C    | -3.49388500 | 2.87547800 | 1.77484300 |
| C    | -0.94122200 | 4.06399000 | 1.31933900 |
| H    | -0.40691700 | 4.93758600 | 1.72343100 |
| H    | -2.00260300 | 4.33255400 | 1.23152000 |
| H    | -0.56088300 | 3.89014800 | 0.29352000 |
| Al   | -0.32710600 | 0.85044500 | 1.32996900 |
| P    | 0.39597700  | 1.40739700 | -0.82545600 |
| C    | 0.48204100  | -2.47824600 | 2.05130200 |
| C    | 1.89353800  | -2.51369200 | 2.19120100 |
| C    | 2.45111900  | -3.16953200 | 3.40882700 |
| C    | 1.67445500  | -3.83477000 | 4.24026000 |
| C    | 0.29690500  | -3.87493300 | 4.03444200 |
| H    | -0.31837700 | -4.43317000 | 4.74534800 |
| C    | -0.31499200 | -3.22889800 | 2.95677000 |
| C    | 2.83350900  | -1.86687400 | 1.18767100 |
| H    | 2.27504000  | -1.81776000 | 0.23768500 |
| C    | 3.20028100  | -0.43379400 | 1.55935100 |
| H    | 3.75471400  | -0.40439500 | 2.51062500 |
| H    | 3.82666800  | 0.02592000  | 0.77892500 |
| H    | 2.30318500  | 0.19165300  | 1.66535700 |
| C    | 4.09553100  | -2.69018500 | 0.94368800 |
| H    | 3.85693300  | -3.73277800 | 0.68344000 |
| H    | 4.68321800  | -2.25272600 | 0.12338300 |
| H    | 4.75322900  | -2.79020300 | 1.82651400 |
| C    | 2.30379100  | -4.49545700 | 5.44733600 |
| H    | 1.48416600  | -4.97142300 | 6.01294500 |
| C    | 3.28951600  | -5.59326400 | 5.04987500 |
| H    | 4.14463200  | -5.17934000 | 4.49197700 |
| H    | 3.69034900  | -6.10291700 | 5.94028400 |
| H    | 2.80815000  | -6.34753700 | 4.49626000 |
| C    | 2.95901800  | -3.46213200 | 6.36398600 |
| H    | 2.23815200  | -2.68934000 | 6.67017300 |
| H    | 3.36094300  | -3.93750100 | 7.27281500 |
| H    | 3.79431300  | -2.95483900 | 5.85503000 |
| C    | -1.80750800 | -3.39648100 | 2.73319800 |
| H    | -2.17291800 | -2.44118700 | 2.32175900 |
| C    | -2.04594700 | -4.45853600 | 1.65775900 |
| C    | -1.66225400 | -5.43633300 | 1.98392000 |
| H    | -3.12078500 | -4.56477700 | 1.44012500 |
| H    | -1.53641700 | -4.18665700 | 0.72203900 |
### 5.4.20 \([(\text{Cp}^*\text{Al})_2(\text{PDip})_2]\)

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| P       | 0.96238500 | -1.08247700 | -0.50339900 |
| P       | -0.96232500 | -1.08241100 | 0.50360500  |
| Al      | 1.23241200  | 1.46762000  | -0.45353400 |
| Al      | -1.23288600 | 1.46773800  | 0.45307800  |
| C       | 3.43443300  | 1.89286300  | -0.41776600 |
| C       | -2.21150900 | -1.69805000 | -0.68457600 |
| C       | -2.37232100 | -1.30482000 | -2.03443500 |
| C       | 2.21213300  | -1.69721900 | 0.68469400  |
| C       | -2.73564300 | 3.12497500  | 0.15841800  |
| C       | -3.43522500 | 1.89201900  | 0.41757000  |
| C       | -3.19972500 | -2.65494500 | -0.13234400 |
| C       | 2.37297400  | -1.29949800 | 2.03449500  |
| C       | 3.11083400  | -2.65358400 | 0.13239100  |
| C       | 3.08889400  | 1.46251800  | -1.72805400 |
| C       | 1.95713100  | 3.43579900  | -1.30279700 |
| C       | -2.89007200 | 3.95529000  | -1.07527800 |
| C       | -3.08957600 | 1.46147400  | 1.72775100  |
| C       | -1.95840300 | 3.43519300  | 1.30299200  |
| C       | 2.73446700  | 3.12554200  | -0.15831900 |
| C       | -4.16015100 | -3.14300100 | -0.91437500 |
| H       | -4.85636500 | -3.86807200 | -0.48947400 |
| C       | 3.62976200  | 0.25849200  | -2.42132500 |

\[(\text{Cp}^*\text{Al})_2(\text{PDip})_2\]
5.4.21  [Cp^3t(IiPr_2)Al(μ-PPh)]_2 (5)

| Atom | x-value | y-value | z-value |
|------|---------|---------|---------|
| Al   | 1.880539000 | 0.411889000 | 0.870214000 |
| P    | 0.402295000 | -0.707275000 | -0.542084000 |
| Al   | -1.362302000 | 0.638696000 | 0.179105000 |
| P    | 0.267675000 | 2.189225000 | 1.069338000 |
| C    | 0.342168000 | -2.489757000 | -0.882758000 |
| C    | 1.534143000 | -3.232774000 | -0.976530000 |
| H    | 2.486822000 | -2.708334000 | -0.857038000 |
| C    | 1.513220000 | -4.604196000 | -1.214860000 |
| C    | 2.455184000 | -5.158026000 | -1.262929000 |
| C    | 0.302707000 | -5.272445000 | -1.405442000 |
| C    | 0.285586000 | -6.347352000 | -1.599230000 |
| C    | -0.885215000 | -4.543012000 | -1.354312000 |
| C    | -1.841349000 | -5.051245000 | -1.504222000 |
| C    | -0.868676000 | -3.174868000 | -1.089656000 |
| C    | -1.811866000 | -2.628217000 | -1.002071000 |
| C    | 0.721645000 | 3.366388000 | -0.327966000 |
| C    | 0.707728000 | 2.938859000 | -1.683843000 |
| H    | 0.437817000 | 1.912118000 | -1.947780000 |
| C    | 1.068849000 | 3.844305000 | -2.680958000 |
| H    | 1.048228000 | 3.530546000 | -3.727837000 |
| C    | 1.475820000 | 5.137165000 | -2.348917000 |
| H    | 1.768312000 | 5.842021000 | -3.130884000 |
| C    | 1.508381000 | 5.516831000 | -1.006847000 |

172  [Cp^3t(IiPr_2)Al(μ-PPh)]_2 (5) @ PBE0-D3(BJ)/def2-SVP
| C | 1.827970000 | 6.525217000 | -0.730469000 |
| C | 1.124630000 | 4.616670000 | -0.014855000 |
| H | 1.138681000 | 4.923535000 | 1.034643000 |
| C | 3.826686000 | 0.671668000 | 0.179740000 |
| C | 3.583691000 | 0.918977000 | -1.246371000 |
| H | 3.162995000 | 1.850175000 | -1.621371000 |
| C | 3.926556000 | -0.162753000 | -2.028906000 |
| C | 4.484980800 | -1.192676000 | -1.111503000 |
| H | 4.376341000 | -0.693146000 | 0.166845000 |
| H | 4.753842000 | -1.184430000 | 1.062062000 |
| C | 4.707378000 | 1.726953000 | 0.914864000 |
| C | 3.638152000 | -0.200558000 | -3.523150000 |
| H | 5.325643000 | -2.454549000 | -1.378802000 |
| H | 5.092616000 | 1.231541000 | 2.309433000 |
| C | 4.215396000 | 0.880893000 | 2.869100000 |
| H | 5.574173000 | 2.036595000 | 2.887445000 |
| C | 5.803472000 | 0.394070000 | 2.254674000 |
| C | 3.989699000 | 3.070581000 | 1.016169000 |
| H | 3.058081000 | 3.000599000 | 1.598751000 |
| C | 3.799834000 | 3.449835000 | 0.023425000 |
| H | 4.637555000 | 3.823932000 | 1.493428000 |
| H | 6.002677000 | 1.934905000 | 0.115567000 |
| H | 6.700533000 | 2.584694000 | 0.668810000 |
| H | 5.795880000 | 2.402828000 | -0.857618000 |
| H | 6.502439000 | 0.973162000 | -0.075142000 |
| C | 3.010896000 | 1.124816000 | -3.970476000 |
| H | 2.058867000 | 1.299497000 | -3.453222000 |
| H | 2.811438000 | 1.091609000 | -5.053208000 |
| H | 3.669027000 | 1.984501000 | -3.774167000 |
| C | 4.911335000 | -0.374381000 | -4.362446000 |
| H | 5.439165000 | -1.314134000 | -4.165973000 |
| H | 5.614995000 | 0.448869000 | -4.162532000 |
| C | 4.663201000 | -0.355466000 | -5.436285000 |
| C | 2.595866000 | -1.285661000 | -3.836808000 |
| H | 2.942761000 | -2.296079000 | -3.601151000 |
| H | 2.325361000 | -1.261139000 | -4.905186000 |
| C | 1.688871000 | -1.104083000 | -3.239390900 |
| C | 6.757894000 | -1.982967000 | -1.693865000 |
| H | 7.170533000 | -1.420372000 | -0.842962000 |
| H | 6.784974000 | -1.321277000 | -2.569982000 |
| H | 7.416953000 | -2.844524000 | -1.893289000 |
| C | 4.855619000 | -3.383234000 | -2.584416000 |
| H | 5.519363000 | -4.260901000 | -2.546875000 |
| H | 4.883214000 | -2.912818000 | -3.492211000 |
| H | 3.833612000 | -3.747947000 | -2.336841000 |
| C | 5.396187000 | -3.328808000 | -0.118479000 |
| C | 5.875341000 | -2.811659000 | 0.724514000 |
| H | 5.991713000 | -4.231395000 | -0.325348000 |
| H | 4.394036000 | -3.649672000 | 0.281013000 |
| C | -2.985708000 | -0.015563000 | 1.346174000 |
| C | -3.098796000 | -1.471480000 | 1.151344000 |
| H | -2.386615000 | -2.178554000 | 1.569124000 |
| C | -4.243293000 | -1.826301000 | 0.481780000 |
| C | -4.944921000 | -0.559131000 | 0.131387000 |
| C | -4.198847000 | 0.459025000 | 0.665887000 |
| H | -4.484341000 | 1.504442000 | 0.627783000 |
| C | -4.663101000 | -3.294734000 | 0.337204000 |
| C | -6.293659000 | -0.239011000 | -0.538201000 |
| C | -2.866537000 | 0.403414000 | 2.850688000 |
| C | -6.054140000 | -3.516020000 | 0.949671000 |
|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| H   | -0.154439 | 2.322378  | 3.912527  |
| H   |  0.761405 | 3.557493  | 4.792906  |
| C   | -2.241087 | 1.602919  | -1.447820 |
| N   | -2.755567 | 2.856382  | -1.523803 |
| C   | -3.280196 | 3.093628  | -2.772672 |
| H   | -3.737288 | 4.038949  | -3.047234 |
| C   | -3.082532 | 1.966051  | -3.502970 |
| H   | -3.340482 | 1.735498  | -4.531408 |
| N   | -2.440522 | 1.073171  | -2.676455 |
| C   | -2.691615 | 3.893032  | -0.482060 |
| H   | -2.831782 | 3.475059  |  0.294309 |
| C   | -2.822394 | -0.267758 | -3.100462 |
| H   | -1.406215 | -0.639088 | -2.269120 |
| C   | -4.061733 | 4.194379  |  0.185430 |
| H   | -4.511928 | 3.320862  |  0.589722 |
| H   | -4.756025 | 4.555833  | -0.669352 |
| H   | -3.964226 | 4.984094  |  0.863859 |
| C   | -2.055947 | 5.158344  | -1.040671 |
| H   | -1.804066 | 5.836207  | -0.213751 |
| H   | -2.750565 | 5.693262  | -1.708350 |
| C   | -1.133313 | 4.937992  | -1.590059 |
| C   | -1.125573 | -0.190740 | -4.323283 |
| H   | -0.274195 | 0.480614  | -4.142544 |
| H   | -1.667701 | 0.153623  | -5.218508 |
| H   | -0.720703 | -1.189589 | -4.537902 |
| C   | -3.227727 | -1.169920 | -3.276248 |
| H   | -2.897530 | -2.186012 | -3.533957 |
| H   | -3.892778 | -0.812634 | -4.079354 |
| H   | -3.800341 | -1.221840 | -2.340318 |
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