Al–Al σ Bonds

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Snapshots of the Al–Al σ-Bond Formation Starting from {AlR$_2$} Units: Experimental and Computational Observations**

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Dedicated to Professor Wilhelm Preetz on the occasion of his 75th birthday.

Radicals are key intermediates in fundamental chemical processes such as bond formation and cleavage. The simplest model systems for these processes involve species such as Na atoms, [MgX]$^•$ units, and [AlX$_2$]$^•$ units, each of which has one unpaired electron occupying an s orbital. However, we could show in a recent study on [MgCl]$^•$ radicals in low-temperature matrices that the latter spontaneously dimerize in an exothermic process under Mg–Mg bond formation.[1] To our knowledge, s^1-type radicals have never been isolated as intermediates in chemical reactions, which can mainly be attributed to their high tendency to dimerize.[2] To achieve this goal, we intended to trap conceivable intermediates during a very slow Al–Al σ-bond-formation process using particularly mild conditions.[7] In addition to these extensive experimental investigations, detailed quantum chemical calculations have been performed, which were published recently in a separate contribution.[9] The main computational results are summarized in Figure 1. Highly energetic [AlR$_2$]$^•$ species (R = P*t*Bu$_2$) should dimerize under formation of a to date unknown biradical intermediate [RAl$^↑$(μ-R$_2$)Al$^↑$R] (**1**; C_i symmetry)[9,10] with a long Al–Al separation of approximately 350 pm and with each unpaired electron residing in a p-type singly occupied molecular orbital localized on one of the Al atoms. These triplet molecules **1** can formally undergo a spin-flip procedure and a subsequent disrotatorial ring closure leading to closed-shell bicyclic molecules [RAlR$_2$AlR] (**2**, C_2 symmetry) as thermodynamically stable species (σ-bond formation). This process is reminiscent of the ring inversion of bicyclo[1.1.0]butanes. The planar singlet transition state (TS) **4** ([RAl$^↑$(μ-R$_2$)Al$^↓$R], C_i symmetry) with an imaginary frequency of 11*i* cm^{-1} has the two electrons in π orbitals. This TS lies 24 kJ mol^{-1} above the corresponding butterfly-shaped bicycle **2**.[9]

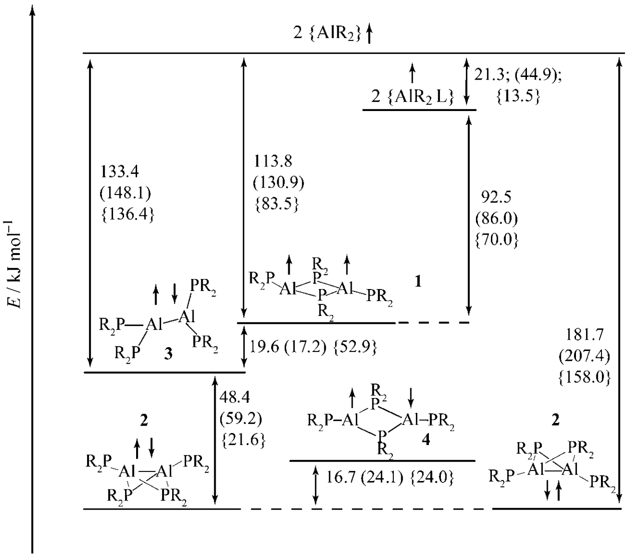

Figure 1. Relative energies (kJ mol^{-1}) for the [Al$_2$(P*t*Bu$_2$)$_4$] isomers **1**, **2**, **3**, and the transition state **4** with respect to the radical [Al(P*t*Bu$_2$)$_2$]$^•$ ("AlR$_2$$^↑$") and the Et$_2$O-stabilized radical {AlR$_2$$^↑$L} at the DFT/def2-TZVP//DFT/def2-TZVP† level of theory with DFT = BP86, (TPSS), and {B3LYP}.

Herein we demonstrate that, despite the aforementioned difficulties, the species **1** and **2** can be trapped and investigated by single crystal X-ray diffraction starting from molecules bearing {AlX$_2$} entities (see below), which in turn are formed as intermediates during the disproportionation reaction in AlX solutions.

The concomitant deposition of AlCl molecules (generated at about about 900 °C) and a mixture of toluene and diethyl ether (3:1) at −196 °C[11] and subsequent warming to −78 °C yielded a solution of AlCl that was metastable with respect to the disproportionation to Al(s) and AlCl$_3$. LiP*t*Bu$_2$ was added to this solution at −78 °C, and the mixture was then heated to 55 °C for a short time. LiCl was filtered off and the solvent was removed in vacuo. The residue was dissolved in pentane yielding a green solution, from which green crystals of [Al$_2$(P*t*Bu)$_4$] (**1**) were obtained.[12] The molecular structure of **1** and the main structural parameters (experimental and computational) are presented in Figure 2.[10]

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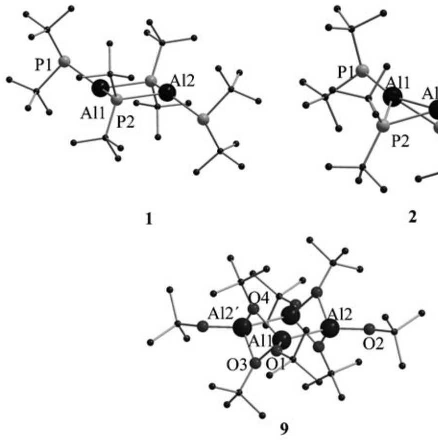
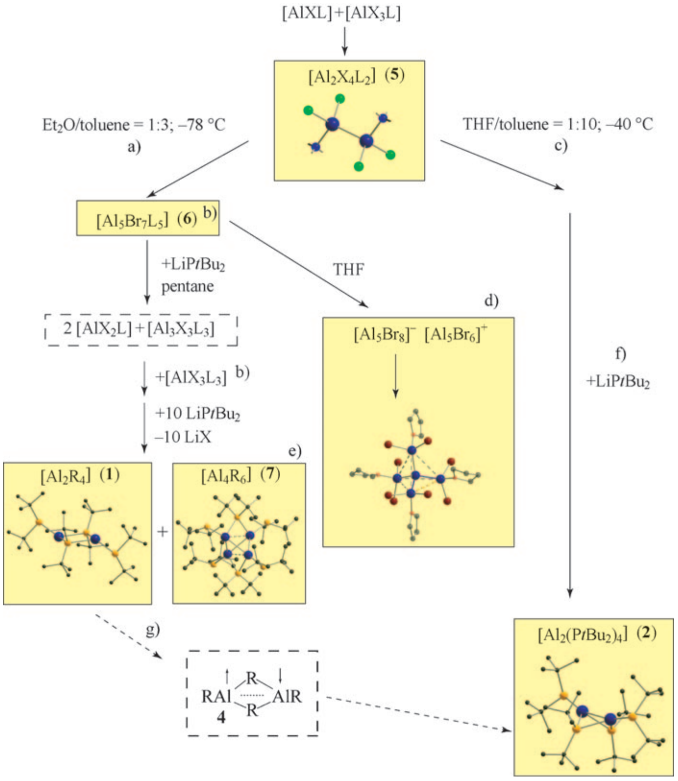


Figure 2. Crystal structures of **1**, **2**, and [{Al$_2$(O*t*Bu$_2$)$_4$}$_2$] **9**. The experimental and calculated (in parentheses; BP86/def2-TZVP†) distances [pm] and angles [°]: **1**: Al1-Al2 350.8 (346.2), Al1-P1 239.9 (239.1), Al1-P2 247.8 (245.0), Al2-P2 245.8 (243.9); Al1-P2-Al2 90.5 (90.2). **2**: Al1-Al2 258.7 (261.8), Al1-P1 237.0 (240.6), Al1-P2 242.2 (245.2), Al2-P2 236.2 (239.8); Al1-P2-Al2 65.4 (65.3). **9**: Al1-Al2 261.7 (262.1), Al1-Al2′ 273.8 (277.5), Al1-O1 170.8 (173.2), Al2-O2 170.4 (173.2), Al2′-O3 186.5 (190.1), Al1-O3 186.4 (190.6), Al1-O4 188.5 (190.6); Al1-O3-Al2′ 94.5 (93.6).



Scheme 1. Reactions in a metastable AlX solution (containing small amounts of AlX$_3$, X = Cl, Br; L = donor molecule) and stabilization of intermediates by fast substitution reactions (replacing X$^-$ by R = P*t*Bu$_2^-$). Intermediates characterized by crystal structure analysis are highlighted in yellow; Al blue, Br dark red, C black/gray, O light red, P orange, X green. a) Fast insertion reaction of AlX at −78 °C.[17] b) Even at low temperatures, small amounts of solid Al metal are formed: [Al$_5$Br$_7$]→[Al$_2$Br$_6$] + AlBr + 2 Al. c) Further insertion reactions of AlX at −40 °C are very slow. d) The salt formed by a halogen transfer reaction can be isolated from a THF solution. e) Alternatively, from [Al$_3$X$_3$L$_3$] and [AlXD], the primary structurally known product [Al$_4$Br$_4$L$_4$] can be formed (along with others).[16] f) The fast substitution reaction with LiP*t*Bu$_2$ forms compound **2** exclusively (the unbridged dialane **3** is thermodynamically less stable; cf. Figure 1). g) The symmetry-broken singlet state in the DFT approach and the singlet state from multireference calculations of **1** are energetically more stable than the triplet solution. Consequently, compound **2** can be formed by a spin flip and subsequent σ-bond formation.[9]

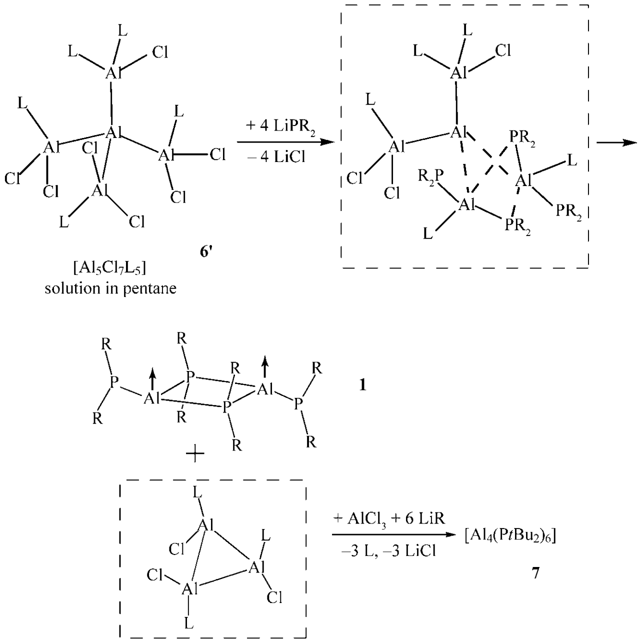
In contrast, yellow crystals of [Al$_2$(P*t*Bu$_2$)$_4$] (**2**) were formed from a yellow pentane solution when the cocondensation (described above) was carried out with AlBr in the gas phase using a low donor concentration (toluene/THF = 10:1).[13] In this case, the cold AlBr solution (−78 °C) was slowly warmed to −40 °C. After addition of LiP*t*Bu$_2$ and further warming to −20 °C, the formed solid LiBr was filtered off and the solvent mixture was removed. The butterfly structure of **2** and the main structural parameters (experimental and computational) are given in Figure 2. The most notable structural feature is the large variation in the observed Al−Al distances between **1** (350.8 pm; calcd 346.2 pm) and **2** (258.7 pm, calcd 261.8 pm). We find good agreement between the experimental and computed structural parameters.[14] The general feasibility of the formation of dimeric units of [Al$_2$R$_4$] molecules was further supported by employing the bridging ligand [O*t*Bu]$^-$ (see the Experimental Section for details). Synthesis and structural characterization of [Al$_4$(O*t*Bu)$_8$] (**9**, Figure 2) revealed it to be isostructural to the corresponding gallium compound [Ga$_4$(O*t*Bu)$_8$].[15] Further aspects of the formation of [Al$_4$R$_8$] units will be discussed below. In the following, we will demonstrate why

a) differences in the reaction conditions lead in one case to the high-energy triplet molecule **1** and in the other to the stable butterfly molecule **2**;
b) the observed molecular structure of **1** should be assigned to this triplet molecule;
c) the overall orientation of the triplet molecules **1** in the crystal supports the assignment in (b).

Regarding (a): The initial formulation of the formation of **1** and **2** from the radical intermediates [AlX$_2$]$^\bullet$ and [AlR$_2$]$^\bullet$ shown above (Figure 1) is only a formal description. Thus, we propose herein a plausible reaction pathway (Scheme 1), considering known intermediates that have been structurally characterized by XRD. As a result of its generation process, the AlCl solution generally contains a small percentage of AlCl$_3$.[8] Compound **1** is formed from AlCl and AlCl$_3$ in donor-rich solutions via [Al$_2$Cl$_4$L$_2$] (**5**)[16] and [Al$_5$Br$_7$L$_5$] (**6**)[13,17] even at −78 °C.

In compound **6** and in the known [Al$_5$Br$_8$L$_4$]$^-$ ion,[18] the AlBr$_2$ entities are separated by 410 pm (Al center to Al center). Consequently, the AlX$_2$ groups in these molecular units are arranged in an ideal topological fashion that allows for the stepwise substitution of halide units X by PR$_2$ groups. The latter can partially act as bridging ligands, thus mediating a successive approach of the Al atoms. These predefined subunits are ideally suited to finally produce **1** (Scheme 2).

At the same time, the compound [Al$_4$R$_6$] (**7**) is formed from the remaining [Al$_3$Cl$_3$L$_3$] units and AlCl$_3$[20] and LiR.[21]



Scheme 2. Intermediates in the formation of **1** and **7** by substitution reactions (Cl→P*t*Bu$_2$) and Al–Al bond formation via the hypothetical subhalide [Al$_5$Cl$_7$L$_5$] **6'** (cf. [Ga$_5$Cl$_7$(Et$_2$O)$_5$][19]).

The formation of this cluster compound, which consists of a distorted tetrahedral {Al$_4$} framework with four terminal and two bridging ligands, is indeed observed under these reaction conditions, nicely supporting the proposed reaction scheme for the formation of **1**.[22] The overall process [Eq. (1)] was also investigated by computational methods using the following model reaction (see the Supporting Information):

$$\begin{aligned}&[\mathrm{Al_5Cl_7(OMe_2)_5}]\ (\mathbf{6'}) + {}^{10}\!/_3\,\mathrm{Al(P}t\mathrm{Bu_2)_3} \rightarrow [\mathrm{Al_4(P}t\mathrm{Bu_2)_6}]\ (\mathbf{7}) + \\ &\quad [\mathrm{Al_2(P}t\mathrm{Bu_2)_4}]\ (\mathbf{1}) + {}^{7}\!/_3[\mathrm{AlCl_3(OMe_2)}] + {}^{8}\!/_3\,\mathrm{OMe_2}\end{aligned} \tag{1}$$

The calculations revealed the formation of **1** and **7** to be slightly endothermic. However, the Gibbs free energy $\Delta_R G$ was found to be exergonic ($-28\ \mathrm{kJ\,mol^{-1}}$, see the Supporting Information), which leads to the assumption that the formation of **1** should be feasible under the experimental conditions described above. The alternative formation of **2** in solutions with low donor (THF) concentration arises from the different reaction conditions. In solutions with low donor concentration, the insertion reaction to form [Al$_5$Cl$_7$L$_5$] (**6'**) proceeds very slowly. In this type of solution at temperatures between −40 and −20 °C, [Al$_2$Cl$_4$L$_2$] is the predominant species,[6] which in turn can be trapped by the reactive P*t*Bu$_2$ groups to finally yield the thermodynamically stable product **2**.[23]

Regarding (b): The intermediate formation of compound **1** and the reactive triplet state of this molecule are consistent with both the reaction conditions discussed above and with the determined crystal structure. Furthermore, the observed green color of crystals of **1** is supported by the calculated UV/Vis spectrum, which shows absorptions in the red frequency area at 650 and 710 nm.[9] The hypothetical normal-valent molecule [Al$_2$H$_2$(P*t*Bu$_2$)$_4$] (**8**), in which both unpaired electrons in **1** are saturated by AlH bonds, should be colorless according to these calculations. As evidenced by these results, the alternative interpretation of the crystal structure of **1** to be the normal-valent molecule **8** can be excluded.[24]

Regarding (c): The arrangement of the triplet molecules **1** in the crystal (Figure 3) puts further emphasis on the extraordinary bonding situation present in this species. It appears that the molecules' assembly in the crystal shows a distinct directional preference. We have recently described a similar, though as yet not understood, stabilization of a radical species [Al$_7$R$_6$] in the crystal.[27,28] The sterically demanding P*t*Bu substituents in **1** obviously prevent the intermolecular interaction between [Al$_2$(PR$_2$)$_4$] molecules and only permit a weakly interacting column structure (Figure 3) and not the formation of dimers, as observed for the sterically less demanding O*t*Bu ligand in compound **9** (Figure 2).[29] Smaller substituents (R = H, Me) also result in energetically favored dimers, as predicted by calculations.[9]

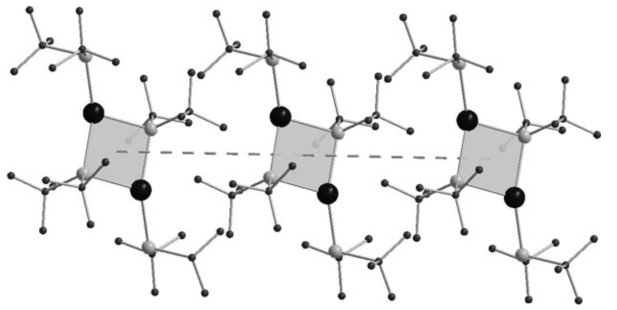
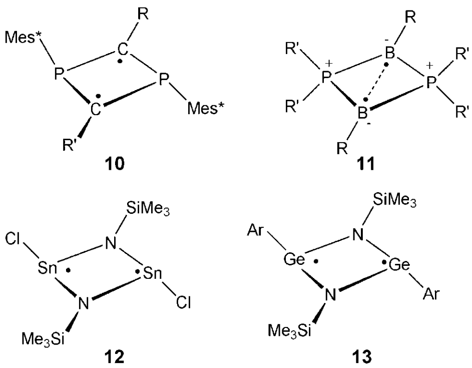


Figure 3. Layer assembly of the biradical molecules in the crystal structure of [Al$_2$(P*t*Bu$_2$)$_4$] **1**. Al black, P light gray, C dark gray. The plane-to-plane distance of 8.915 Å corresponds to the length of the *a* axis in the unit cell.

In contrast to very short-lived radical intermediates of organic reactions, numerous biradicaloids of heavy main-group elements could be isolated in crystalline form in recent years, some of which formally represent intermediates in the σ-bond-formation process.[30,31] Pioneering work in this field was performed by Niecke and co-workers for P$_2$C$_2$R$_4$ ring compounds **10** (R = H, R' = SiMe$_3$, Mes* = 2,4,6-tri-*tert*-butylphenyl)[32] as well as by Bertrand and co-workers with systematic investigations on B$_2$P$_2$R$_6$ species **11** (R = *t*Bu, R' = *i*Pr).[33] These structures are exemplified in Scheme 3, together with the biradicaloid molecules [Sn$_2$N$_2$Cl$_2$(SiMe$_3$)$_2$] (**12**)[34] and [Ge$_2$N$_2$(SiMe$_3$)$_2$Ar$_2$] (**13**, Ar = 2,6-bis(2,6-diisopropylphenyl)phenyl).[35]

The presented results for the [Al$_2$(PR$_2$)$_4$] compounds extend the area of intermediates of σ-bond-formation processes by contributing additional structurally characterized snapshots. For the first time, a particularly large distance between two metal centers was investigated in a biradical species, which, after several further steps, finally leads to a σ bond. This unprecedented discovery was only possible owing to the particularly mild reaction conditions present in metastable AlX/AlR solutions. These mixtures show a complex disproportionation behavior, which is marked by several other intermediates that have already been characterized,



Scheme 3. Biradicaloid four-membered-ring compounds reported in the literature (see text for details).

finally forming the metal and AlX$_3$. Apparently, the $\{Al_2P_4\}$ ring system under study is particularly suited for such investigations because its Al–Al σ bond is weak, yet still strong enough to compete with the bridging Al–P bonds. Ongoing investigations in this area are aimed at optimizing the crystallization process to yield larger crystals that are suitable for further physical and chemical investigations. Apart from the direct detection of the triplet character of **1**,[36] the reactivity of such species, for example in the formation of Al–Al bonds on the way to bulk material and in the formation of crystalline AlP, is of particular interest.

Experimental Section

1: A suspension of LiP*t*Bu$_2$ (320 mg, 2.1 mmol) in toluene (10 mL) at −78 °C is stratified with an aluminum monochloride solution (0.28 M, 6.5 mL, toluene/diethyl ether = 3:1). The two phases are unified after half an hour and then heated quickly to 55 °C. The solvent is removed under reduced pressure, and the residue is suspended in pentane. The insoluble fraction (LiCl) is filtered off the intensely green solution. After about 15 min a large amount of an amorphous, colorless solid precipitates from this green solution. From this amorphous solid, green crystals of **1** can be isolated. Yield: a few green crystals

2: An aluminum monobromide solution in toluene/THF (10:1, 5 mL, 0.39 M, 1.9 mmol) is added to a suspension of LiP*t*Bu$_2$ (710 mg, 4.7 mmol) in toluene (20 mL) at −40 °C. Within one week the temperature is increased to −20 °C. Then the solvent is removed under reduced pressure. The residue is soluble in cold pentane, with the exception of the formed LiBr (salt of the metathesis). The solution is filtered off the insoluble solid with a cannula under nitrogen pressure. Yellow crystals of **2** form overnight at −28°. Yield: 330 mg (0.25 mmol). Crystals of **2** were dissolved in [D$_8$]toluene, and ^{1}H and ^{31}P NMR spectra were measured. They show broadened signals at $\delta = 1.8$–1.2 ppm and 41.8–39.9 ppm, respectively, indicating dynamic behavior.[21] These investigations will be published in a separate paper.

9: A cold solution (−78 °C) of aluminum monochloride (25 mL, 0.34 M, 8.5 mmol) in toluene/diethyl ether (3:1) is added at −30 °C to solid KO*t*Bu (1 g, 8.9 mmol). The reaction solution is stirred overnight at −30 °C. The temperature then is elevated in steps of 5 °C each day to −10 °C and in one last step to room temperature. The solvent is removed under reduced pressure, and the residue is suspended in pentane. The dark brown solution is filtered off the insoluble solid with a cannula under nitrogen pressure. Within a few days, light yellow to colorless crystals of **9** are obtained. Yield: 560 mg (0.81 mmol) ^{1}H NMR (400 MHz, [D$_8$]toluene): 1.04 ppm.

All DFT calculations were carried out with the program package TURBOMOLE.[37] The structures of **1**–**4** and **8** were optimized using the GGA functional BP86,[38] the *meta*-GGA functional TPSS,[39] and the hybrid functional B3LYP.[40] A def2-TZVP basis set ("triple zeta valence" plus polarization functions) was used for the Al and P atoms. The smaller def2-SV(P) basis set ("split valence" plus polarization functions on non-hydrogen atoms) was used for the H and C atoms.[41] This mixed basis set is referred to as def2-TZVP† in the text. Final energies were evaluated using the full def2-TZVP basis set for all atoms. Optimizations and energy calculations of compound **9** were performed analogously, employing the functionals BP86 and B3LYP. Thermochemistry data of the reaction in Equation (1) were obtained at the DFT/def2-TZVP//BP86/def2-SVP (DFT: BP86, TPSS, and B3LYP) level of theory and within the ideal gas approximation, using the module FREEH. Harmonic vibrational frequencies were calculated analytically to correct energies for the zero-point vibrations.[42]

The RI approximation ("resolution of the identity"), employing appropriate auxiliary basis sets, was used throughout all energy calculations and geometry optimizations to reduce the computational costs.[41,43,44] More detailed technical information concerning the quantum chemical calculations can be found in Ref. [9] and the Supporting Information.

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[7] Intermediates in the disproportionation of metastable AlX solutions[8] ($3\,AlX \rightarrow 2\,Al + AlCl_3$) after the substitution with bridging ligands PR$_2$ (AlPR$_2$Al-bridged bonding) were to be trapped.

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[10] Crystal data for **1**, **2**, and **9**. Compound **1**: $C_{32}H_{72}Al_2P_4$, $M_r = 634.74$, crystal size $0.42 \times 0.20 \times 0.18$ mm^3, $T = 200(2)$ K, triclinic space group $P\bar{1}$, $a = 8.9147(18)$, $b = 10.392(2)$, $c = 11.741(2)$ Å, $\alpha = 79.02(3)$, $\beta = 68.54(3)$, $\gamma = 78.29(3)°$, $V = 983.2(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.059$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.252$ mm^{-1}, $\theta_{max} = 25.91$, 7033 reflections collected, 3595 unique reflections, 3595 refined parameters, GooF = 1.044, $R_1(I>2\sigma(I)) = 0.0511$, $wR_2 = 0.1364$, ρ(min/max): −0.289/0.527 e Å^{-3}. **2**: $C_{32}H_{72}Al_2P_4$, $M_r = 634.74$, crystal size $0.22 \times 0.20 \times 0.21$ mm^3, $T = 150(2)$ K, monoclinic space group Cc, $a = 11.7439(6)$, $b = 20.6423(15)$, $c = 17.1151(9)$ Å, $\beta = 108.459(4)°$, $V = 3935.6(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.071$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.255$ mm^{-1}, $\theta_{max} = 25.93°$, 27523 reflections collected, 7612 unique reflections, 7612 refined parameters, GooF = 1.109, $R_1(I>2\sigma(I)) = 0.0286$, $wR_2 = 0.0650$, ρ(min/max): −0.146/0.297 e Å^{-3}. **9**: $C_{32}H_{72}Al_4O_8$, $M_r = 692.84$, crystal size $0.42 \times 0.20 \times 0.18$ mm^3, $T = 200(2)$ K, monoclinic space group $P2_1/n$, $a = 9.807(2)$, $b = 17.775(4)$, $c = 12.632(3)$ Å, $\beta = 101.36(3)°$, $V = 2158.8(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.066$ g cm^{-3}, μ-

$(\mathrm{Mo}_{K\alpha}) = 0.252\ \mathrm{mm}^{-1}$, $\Theta_{\max} = 25.93°$, 16755 reflections collected, 4174 unique reflections, 343 refined parameters, GooF: 1.013, $R_1(I>2\sigma(I)) = 0.0326$, $wR_2 = 0.0911$, ρ(min/max): $-0.206/0.632\ \mathrm{e\,Å}^{-3}$. Diffractometer: $\lambda = 0.7103$ Å, Stoe IPDS II area detector, two-circle goniometer; computer programs: SHELXS-97, SHELXL-97, Stoe IPDS software; structures are refined with direct methods, H atoms are calculated; CCDC 725584 (**1**), 725585 (**2**), and 725586 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] At the same time, an amorphous colorless solid is formed that makes the separation of the green crystals challenging.

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[22] Under different conditions, **7** is the primary product formed.[21]

[23] The elongation of an existing Al−Al σ bond (e.g. in **5**) and subsequent formation of compound **1** is not possible from a thermodynamic point of view.

[24] There are further arguments that exclude the formation of **8**: In various ESI mass spectrometry measurements the AlH fragment was never observed. Also in characterized intermediates and products such as $[\mathrm{Al_4R_6}]$ **7**,[21] the butterfly molecule **2**, and $[\mathrm{Al_4R_5X}]$ compounds, no {AlH} fragments are present. These facts justify ruling out the formation of **8**. Furthermore, no absorptions around 1800 cm^{-1} are observed in the IR spectra of the products or mixtures of products.[25] Under the present mild reaction conditions apparently no AlH bonds are formed, that is, these conditions are different from those reported for a gallium compound $[((\mathrm{SiMe_3})_3\mathrm{C})\mathrm{Ga(H)}(\mathrm{P(C_6H_5)_2})_2\mathrm{Ga(H)}(\mathrm{C(SiMe_3)_3})]$ by Uhl and El-Hamdan.[26] These authors attribute the Ga−H bond formation to hydrogen abstraction from the solvent by radical intermediates under their drastic reaction conditions.

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[29] Though the butterfly conformation of the monomeric $[\mathrm{Al_2}(\mathrm{O}t\mathrm{Bu})_4]$ unit is not a local minimum in the DFT calculations, the butterfly motif is present in the dimeric species **9**. Formally, new Al−Al bonds (e.g., Al1−Al2) are formed between two "butterfly monomers" (Figure 2). A dimerization enthalpy of about 200 kJ mol^{-1} is calculated (e.g., −213.7 kJ mol^{-1} for BP86/def2-TZVP).[9]

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[36] The above-mentioned difficulties in the synthesis and isolation of **1** and its low stability at room temperature even in crystalline form did not allow for a definite experimental determination of the triplet state by ESR and SQUID measurements. Analyses of **1** in solution are less promising, as dissolving the crystals does not restore the green color of the solution the crystals were originally obtained from. Apparently, compound **1** is only formed in stationary low concentrations within the reaction solution according to Equation (1) and is immediately stabilized by the crystallization process. This process seems to circumvent a spin flip and the thermodynamically favored formation of compound **2**.

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