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Synthesis and Reactivity of a Dialane-Bridged Diradical

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Abstract: Radicals of the lightest group 13 element, boron, are well established and observed in numerous forms. In contrast to boron, radical chemistry involving the heavier group 13 elements (aluminum, gallium, indium, and thallium) remains largely underexplored, primarily attributed to the formidable synthetic challenges associated with these elements. Herein, we report the synthesis and isolation of planar and twisted conformers of a doubly CAAC (cyclic alkyl(amino)carbene)-radical-substituted dialane. Extensive characterization through spectroscopic analyses and X-ray crystallography confirms their identity, while quantum chemical calculations support their open-shell nature and provide further insights into their electronic structures. The dialane-connected diradicals exhibit high susceptibility to oxidation, as evidenced by electrochemical measurements and reactions with *o*-chloranil and a variety of organic azides. This study opens a previously uncharted class of dialuminum systems to study, broadening the scope of diradical chemistry and its potential applications.

Introduction

In 1904, Thiele made a groundbreaking discovery in diradical chemistry by the synthesis of a stable organic diradicaloid (later referred to as 'Thiele's hydrocarbon') from *p*-quinodimethane, marking a significant milestone in radical chemistry.[1] Subsequently, by harnessing similar strategies, a plethora of radicals, diradicals and radicaloids has been reported.[2,3] The physical and chemical properties of these compounds have been rigorously investigated from various perspectives, including chemical bond formation in organic chemistry, biological chemistry, and materials chemistry.[4–6] Although radical chemistry has been extensively explored within the realm of organic compounds, recent advances have opened up an exciting avenue in radical chemistry involving main-group elements as central components.[7–11] Traditionally, group 13 elements have primarily been perceived as electron acceptor centers for lone pairs and have been less frequently employed as spin carriers.[10,12] However, in recent years, engineering of the steric and electronic factors around the radical center has resulted in the identification of numerous boron-based radicals, diradicals and diradicaloids.[10,12–24] These compounds have proven useful in various applications such as chemical sensing, reagents for organic synthesis, polymerization initiators, and as essential elements in extended magnetic systems and beyond.[12,25] However, in contrast to the relatively well-explored boron-based diradicals, knowledge regarding the existence and properties of analogous radicals and diradicals involving the heavier group 13 elements remains scarce.[9,26]

In 1993, Pörschke and colleagues reported dialane radical anions, $[\text{Li(tmeda)}_2]^+[\{(\text{Me}_3\text{Si})_2\text{CH}\}_4\text{Al}_2]^{\bullet-[27]}$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine), utilizing the steric protection of bulky substituents. Employing a similar approach, Power and Uhl independently reported analogous

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dialane radical anions, [Li(12-crown4)$_2$]$^+$[Tip$_4$Al$_2$]$^{•-}$ and K-(DME)$_3$]$^+$[{(Me$_3$Si)$_2$CH}$_4$-Al$_2$]$^{•-}$, respectively (Tip = 2,4,6-iPr$_3$C$_6$H$_2$, DME = 1,2-dimethoxyethane).[28,29] Similar digallane radical anions[30] were also authenticated by Power and co-workers using kinetic stabilization. In 2005, Sekiguchi et al.[31] revealed that by introducing sufficiently bulky peripheral groups around the central atom, it becomes possible to isolate mononuclear tricoordinate aluminum- and gallium-centered radical anions, where both the unpaired electron and negative charge are centered on aluminum and gallium atoms. In 2014, Aldridge and co-workers were the first to obtain neutral monoradicals based on Ga, In, and Tl, using bulky boryl substituents, however, the aluminum version remained elusive, likely due to the high propensity for disproportionation in aluminum species.[32] Monomeric examples of neutral aluminum radicals were first reported by Roesky and co-workers utilizing the π-accepting ability of CAACs where the spin density is mostly borne by the carbene carbon atom.[33,34]

In general, diradicals are even less stable than monoradicals due to their bifunctional nature, enabling the pairing of their electrons through both intermolecular and intramolecular operations.[35,36] In 2009, Schnöckel and co-workers synthesized a cyclic aluminum-centered Al$_2$P$_2$ triplet diradical **I** (Figure 1) that proved too unstable for full characterization, as it readily isomerized to the singlet closed-shell compound **II** (Figure 1), a thermodynamically stable product.[36] The radical character is quenched through the formation of an element-element bond. Nevertheless, a similar diradical based on a B$_2$P$_2$ core is notably stable.[35] In 2011, our group reported that twisted diborene congeners (**III**), stabilized by CAAC donors,[21] exhibited diradical character, while their planar analogues (**IV**) were conventional diborenes with distinct B=B double bonds.[37,38] These observations are similar to those seen in twisted open-shell alkenes compared to planar closed-shell alkenes.[39,40] Quantum-chemical calculations suggested that a balance between steric and electronic factors is necessary to stabilize the twisted diradicals over the closed-shell diborenes.[41] To our knowledge, there are no known examples of group 13 diradicals with direct element-element bonds other than **III**. Although theoretical calculations have predicted a substantial amount of open-shell singlet diradical character in group 13 dimetallenes [RE=ER↔RE$^•$–$^•$ER, E = Al, Ga, In, Tl; R = H, Me, tBu, Ph),[42] experimental evidence for this phenomenon is yet to be reported.

Herein, we report the isolation of a neutral, acyclic dialane with two adjacent CAAC radical units. In the solid state, this diradical exists as two conformers: a *trans*-planar and a twisted conformation (Figure 1C), depending upon the solvent of crystallization. In contrast to the boron analogues (**III** & **IV**, Figure 1) both conformations of the diradical dialane system show diradical character, which is confirmed experimentally and theoretically. Both forms of the diradical have strong reducing properties, as exemplified in reactions with *o*-chloranil and organic azides.
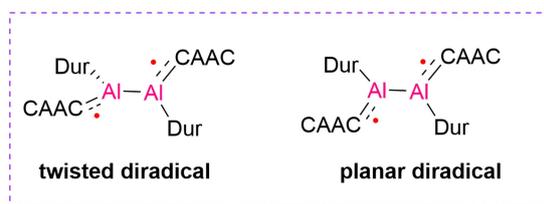
A) Example of aluminum-based diradical
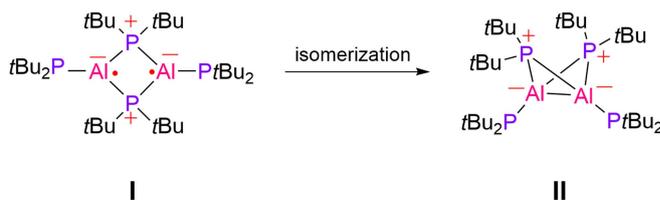

B) Twisted diradical and planar diborene analogue

R = SBu, SPh, SePh
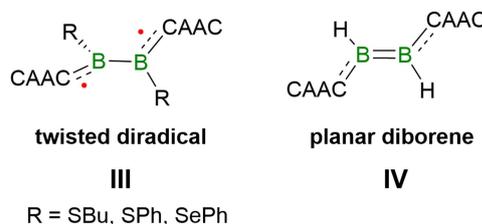
C) This work

Figure 1. Selected examples of aluminum-based diradicals (**A**), boron-based diradicals and diborene (**B**), and the twisted and planar diradicals based on aluminum, prepared in this work (**C**) (CAAC = 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene, Dur = 2,3,5,6-Me$_4$C$_6$H).
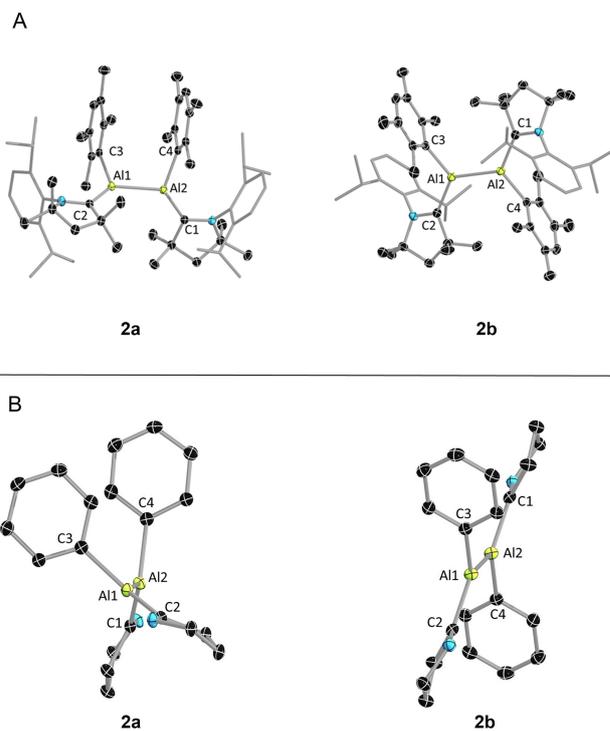
Results and Discussion

The CAAC-stabilized durylaluminum dibromide **1** was synthesized using a modified literature procedure.[43] The reaction of DurLi[44] (Dur = 2,3,5,6-Me$_4$C$_6$H) with an equivalent amount of AlBr$_3$ in a diethyl ether and hexane (1:3) mixture led to the ether-coordinated durylaluminum dibromide [(Et$_2$O)AlBr$_2$Dur], which was then treated with CAAC (1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene) to form **1** (see the Supporting Information, SI). The formation of both [(Et$_2$O)AlBr$_2$Dur] and **1** was confirmed by solid-state structural determination as well as solution and solid-state NMR spectroscopy. In the solid-state ^{13}C{^{1}H} NMR spectrum of **1** a broad resonance at 236 ppm was assigned to the carbene carbon nucleus, which remained undetected in solution due to the large quadrupolar interaction with the ^{27}Al nucleus. The diradicals **2a** and **2b** were synthesized by a Wurtz-type coupling reaction (Scheme 1).[45] Toluene was added to a solid mixture of **1** and three equivalents of KC$_8$ at −80 °C, the mixture was allowed to warm to room temperature over 6 h, followed by stirring for another 18 h at room temperature, upon which it turned from colorless to brown-red to dark violet. An aliquot of the reaction mixture proved NMR-silent, suggesting the formation of radical species. Evaporation of the
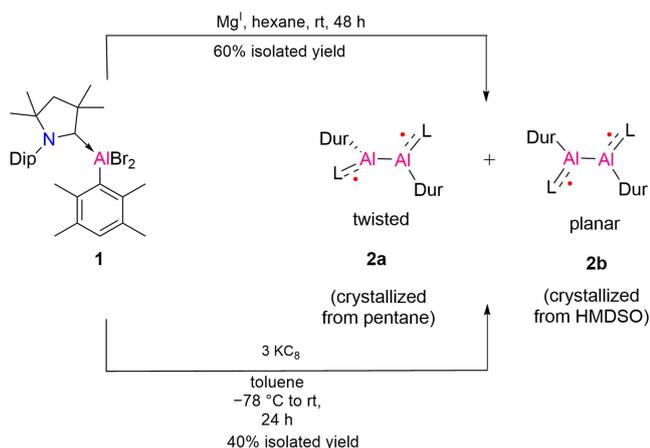
Scheme 1. Synthesis of **2a** and **2b** from **1** (Mg$^{\text{I}}$ = {($^{\text{Mes}}$Nacnac)Mg}$_2$], $^{\text{Mes}}$Nacnac = HC(MeCNMes)$_2$]$^-$, Mes = 2,4,6-Me$_3$C$_6$H$_2$).

Figure 2. A) Molecular solid-state structures of **2a** and **2b**. The structures have been represented with thermal ellipsoids (−100 °C) at the 50% probability level. All hydrogen atoms and a pentane molecule cocrystallized in **2a** are omitted for clarity. B) Sawhorse projection view of **2a** and **2b** (all methyl and aryl groups attached to the CAAC and duryl backbones are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: for **2a**: Al–Al2 2.573(1), Al2–C1=Al1–C2, 1.935(1), Al1–C3 =Al2–C4 1.986(1), C2–Al1–Al2–C1 80.50(8), C3–Al1–Al2–C4 51.27(6), C1–Al2–Al1–C3 114.11(7). Al1–Al2–C1 129.86(4), C1–Al2–C4 123.04(5), Al1–Al2–C4 105.44(4). For **2b**: Al–Al2 2.595(1), Al2–C1=Al1–C2, 1.956(1), Al1–C3=Al2–C4 1.990(1), C2–Al1–Al2–C1 180.00(7), C3–AL1–Al2–C4 180.00(7), C1–Al2–Al1–C3 10.56 (7), Al1–Al2–C1 124.17(5), C1–Al2–C4 117.09(6), Al1–AL2–C4 117.94(4).

solvent and extraction of the crude product with pentane yielded a black colloidal solution, which upon slow evaporation inside the glovebox freezer yielded dark-violet crystals of **2a** in 40% yield. The reduction of **1** in hexane with Jones' Mg(I) dimer,[46] which took 48 h to reach completion, improved the yield to about 60% overall yield (Scheme 1). Recrystallization of **2a** from HMDSO (hexamethyldisiloxane) exclusively gave rise to the dark-violet *trans*-planar conformer **2b**, from which **2a** can be regenerated by recrystallization from pentane. This phenomenon is likely due to the effect of crystal packing arising from intramolecular steric effects and differences in the polarity of the crystallization solvents.[47] The formation of the conformers **2a/b** was confirmed by single-crystal X-ray diffraction measurements (Figure 2), which showed that the twisted conformer **2a** cocrystallizes with one pentane molecule in the solid state, while the planar conformer **2b** has no cocrystallized solvent. The Al–Al bond lengths in **2a** (2.573(1) Å) and **2b** (2.595(1) Å) are significantly longer than in the NHC-stabilized dialumene [Tip(NHC)Al=Al(NHC)Tip] (2.403(1) Å, NHC=1,3-di*iso*propyl-4,5-dimethylimidazol-2-ylidene),[48] but within the range of distances reported for other Al–Al single bonds.[49,50] The Al–C$_{\text{CAAC}}$ distances in **2a** (Al1–C2=Al2–C1=1.935(1) Å) and **2b** (Al1–C2=Al2–C1=1.956(1) Å) are shorter than in the NHC-stabilized dialumenes (ca. 2.059–2.062 Å)[48,51] but closer to typical Al–C$_{\text{CAAC}}$ bond lengths (ca. 1.925 Å) of a doubly CAAC-stabilized parent Al(I) hydride[52] and CAAC-stabilized aluminum radical (ca 1.951 Å).[33,34,26] This implies that the Al–C$_{\text{CAAC}}$ bond lengths fall in the range between the distances typically associated with Al–C single and double bonds, indicating the presence of some degree of multiple bonding here.[53] The Al–C$_{\text{Dur}}$ bond lengths in **2a** (1.986(1) Å) and **2b** (1.990(1) Å) are closer to Al–C single bond lengths observed in the dialumene [Tip(NHC)Al=Al(NHC)Tip] (Al–C$_{\text{Tip}}$ (2.029(1) Å).[48] The dihedral angle C1–Al2–Al1–C2 is 80.5° in **2a** and 180.0° in **2b**, highlighting a significant difference in their geometric conformations. Similarly, the C3–Al1–Al2–C4 angle is 51.3° in **2a** but 180.0° in **2b**. These observations show that **2b** adopts a fully planar structure, akin to the reported dialumenes[48] and most diborenes,[54] whereas **2a** is a twisted

conformer, reminiscent of the structure seen in CAAC-stabilized diborane diradicals, **III**.[21]

The dark-violet solutions of **2a/b** were both found to be NMR silent. Solid-state IR spectra did not show any vibrational bands attributable to Al–H bonding (ca. 1593–1835 cm^{-1}),[51,52] ruling out the presence of a hydride attached to the aluminum center. The UV-vis absorbance maximum (489 nm) is identical for both conformers and consistent with the violet color of the compound.

It is worth mentioning here that analogous reductions of NHC-stabilized arylaluminum dihalides with potassium graphite led to a planar dialumene compound with a distinct Al=Al bond,[48,51] a self-stabilized dialumene[55] or a C–H-activated dialane,[50] in contrast to our present results. In the case of analogues with heavier group 13 elements, the reduction of an NHC-stabilized digallane also led to an NHC-stabilized digallane, which upon oxidation transformed into a digallene-based radical cation and dication.[56] The absence of an Al–Al multiple bond evidenced by the structural data and the NMR-silent nature of **2a/b** suggested that they may be triplet or

singlet diradicals, captodatively[57] stabilized by the strong σ donation and π acceptance of the CAAC ligands.[53]

To probe their diradical nature, a toluene solution of **2a/b** was subjected to continuous-wave (cw) X-band EPR-spectroscopic measurements. The room-temperature X-band EPR spectrum displayed an intense single, broad resonance at $g_{iso} = 2.0029$ without any resolved hyperfine splitting. The EPR spectrum in frozen toluene at 70 K showed a relatively strong half-field transition and partially resolved zero-field splittings in the g = 2 region (Figure 3A), characteristic of a triplet state. The simulated spectrum provides zero-field splitting parameters of D = 468 MHz (0.01561 cm^{-1}) and E = 23 MHz (0.00078 cm^{-1}). Using the relative intensity of the half-field to the allowed transition the distance r between the unpaired spins was estimated to be ca. 5.33 Å, while the point-dipole approximation yielded a value of ca. 5.50 Å.[58] From the crystal structure it is evident that this does not match the Al–Al distance (**2a**: 2.573(1) Å; **2b**: 2.595(1) Å) but matches the $C_{CAAC}\cdots C_{CAAC}$ distance far better (**2a**: ca. 5.41 Å; **2b**: ca. 5.85 Å). This suggests that the two unpaired electrons are delocalized over the Al–C_{CAAC}–N π bonding system and are mostly concentrated at the CAAC carbene centers. Thus, the system can be described as a dialane connecting two CAAC radicals. The solid-state EPR data for **2a** at 70 K revealed a zero-field splitting parameter of D = 445 MHz (0.0155 cm^{-1}) and an E value of 13 MHz (0.00045 cm^{-1}), while for **2b**, the

corresponding values were D = 468 MHz (0.01561 cm^{-1}) and E = 23 MHz (0.00078 cm^{-1}), indicating that they exhibit only marginal differences (Figure 3A). It should be noted that, unlike the planar diborene **IV**, the planar dialane **2b** exhibits diradical character. While an analysis of the EPR signal intensity was not reliable to determine the electronic ground states of the diradicals, magnetic studies of crystalline **2a** and **2b** using a superconducting quantum interference device (SQUID) magnetometer suggest (see SI) that both conformers have a singlet ground state with a thermally accessible triplet state (**2a**: 2J = −213 cm^{-1} (−0.61 kcal mol^{-1}) vs. **2b**: 2J = −483 cm^{-1} (−1.38 kcal mol^{-1}).

To provide further insights into the electronic structures of the isolated diradicals and the unusual experimental findings, quantum chemical calculations were also performed. Compounds **2a/b** could potentially possess three distinct electronic ground states: a closed-shell singlet with Al=Al bonding, an open-shell singlet, or a triplet state. To investigate these possibilities, geometry optimizations were performed using the unrestricted formalism of density functional theory (UDFT), as detailed in the SI. The application of broken-symmetry UDFT calculations for open-shell singlet biradicals is contingent upon several critical considerations. Notably, when the overlap between open-shell orbitals is minimal—indicative of the single electrons being localized on distinct atomic centers—the inherent inaccura-
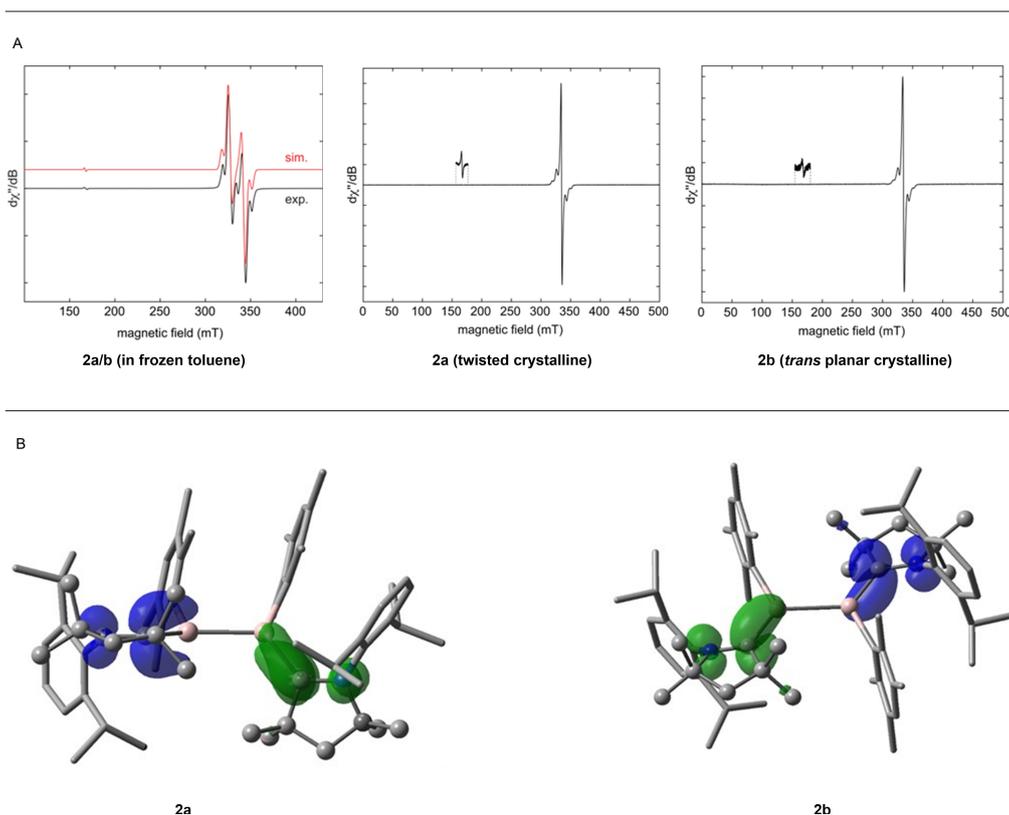
Figure 3. A) Frozen-solution and solid-state X-band EPR spectrum of **2a/b** (red line in spectrum of frozen solution indicates simulated spectra, for simulated spectra of solid samples of **2a** and **2b**, see SI). B) Alpha (green) and beta (blue) Mulliken spin densities of **2a** and **2b** in their open-shell singlet ground states, depicting spin polarization. Level of theory: UωB97X-D[69]/Def2-TZVP[70]/PCM(toluene)[71]//UωB97X-D/Def2-SVP.[70] Isovalues: 0.003 au. Hydrogen atoms are omitted for clarity.

cies of UDFT become negligible.[59a] This minimal overlap scenario often obscures UDFT's fundamental limitations in modeling open-shell singlet biradicals due to its enhanced capacity for depicting spin polarization, a feature where restricted DFT methods typically fall short. Nevertheless, it is essential to corroborate these results through further multireference calculations whenever feasible, a step we have also undertaken.

The frontier molecular orbitals of the closed-shell singlet, open-shell singlet, and triplet states of **2a** and **2b** at the (U)DFT level are represented in Figure S44 (SI). For both systems, Mayer bond order (MBO)[59b] calculations on the lowest singlet states indicate the presence of an Al–Al single bond with a partial Al–C double bond character. The latter is more pronounced in the planar structure **2b** (Al–Al: 0.90; Al–C: 1.17) than in the twisted **2a** (Al–Al: 0.99; Al–C: 1.07). Further analysis of the adiabatic energies reveals that the closed-shell singlet state is considerably higher in energy than the open-shell singlet, differing by 28.3 and 23.2 kcal mol^{-1} for **2a** and **2b**, respectively. The open-shell singlet states are slightly lower in energy than the triplet states (by 0.1 kcal mol^{-1} for **2a** and 0.3 kcal mol^{-1} for **2b**). Furthermore, the computed expectation values of the total spin, $<S^2>$, for the open-shell singlet states of **2a** and **2b**, calculated at the UDFT level prior to the annihilation of the primary spin contaminant, stand at 1.004 and 0.997, respectively. These values, hovering around 1, suggest a biradical nature of the systems. This is due to the fact that in single-determinant approaches, an open-shell singlet biradical wave function is effectively a complete mixture of the correct singlet ($<S^2>=0$) and triplet ($<S^2>=2$) wave functions.[59c]

These findings are confirmed by high-level, state-specific multireference calculations based on the second-order N-electron valence state perturbation theory (NEVPT2) with domain-based local pair natural orbitals (DLPNOs) using reference complete active space self-consistent field (CASSCF) wave functions, a method collectively known as DLPNO-NEVPT2/CASSCF (see SI).[60–65] These calculations demonstrate that both conformers exhibit an open-shell singlet ground state, with a significant biradical character of $y_0 = 0.82$ (twisted **2a**) and $y_0 = 0.87$ (planar **2b**).[66–68] The singlet-triplet energy gap for both conformers is exceptionally small (**2a**: 0.6 kcal mol^{-1}; **2b**: 0.3 kcal mol^{-1}), making them nearly isoenergetic states. These results align well with the experimental SQUID measurements. Spin density calculations on the open-shell singlet ground states of both conformers reveal electron delocalization spanning from the aluminum center to the CAAC nitrogen (Al–C–N) (Figure 3B).

The spin density is mainly localized on the carbene carbon atoms for both systems (57%), whereas the aluminum and nitrogen atoms contribute only 16% and 20%, respectively (Figure 3B). A similar result was also observed in the case of CAAC-stabilized boron-based diradical systems **III**, wherein the unpaired electrons reside predominantly on the CAAC carbon π orbitals (50% for R = SBu and 45% for R = SPh).[21] The calculated distances between the two spin centers located at the carbene carbon atoms are 5.38 Å and 5.78 Å for **2a** and **2b**, respectively (Figure 3B). These results align with the experimental determination of

the distance between the two radical centers (~5.33 Å) obtained from EPR measurements

Given the ease of oxidation suggested by CV measurements of **2a/b** (see SI), their twofold chemical oxidation was attempted. The reaction of **2a/b** with the mild oxidant, *o*-chloranil resulted in the breaking of the Al–Al bond and the oxidation of both aluminum centers, yielding compound **3** (Scheme 2). The solid-state molecular structure of **3** (Scheme 2) shows an aluminum catecholate stabilized by a CAAC unit. Compound **3** was found to be insoluble in benzene and toluene, and unstable in CH_2Cl_2, CH_3CN and THF. It was marginally stable in $CHCl_3$, therefore its identity was confirmed by ^1H NMR spectroscopy in $CDCl_3$ in addition to solid-state NMR spectra. The solid-state $^{13}C\{^1H\}$ NMR spectrum showed a C_{CAAC} resonance at 233.1 ppm, slightly upfield compared to that of **1** (236.1 ppm).

A wide range of low-valent aluminum and boron compounds have been shown to react with organic azides, yielding iminoalane and iminoborane products, respectively, often depending upon the steric profiles of the reactants.[72–77] The reaction of two equivalents of $^{Mes}TerN_3$ ($^{Mes}Ter = 2,6\text{-}Mes_2C_6H_3$, $Mes = 2,4,6\text{-}Me_3C_6H_2$) with **2a/b** yielded the aluminum imide **4** (Scheme 3). The solid-state structure of **4** (Figure 4) showed an Al–N bond length of 1.668(3) Å, which is intermediate between the reported Al–N triple bond (1.625(4)Å)[76] and double bond (1.705-(2)Å).[75] The Al1–C1 bond length (2.105(4) Å) is similar to Al–C_{CAAC} bond lengths reported for other carbene-stabilized aluminum(III) compounds and slightly longer than the Al–C_{Dur} distance. Since **4** is unstable in most common organic solvents other than hexane and pentane, its identity was confirmed by solid-state NMR spectroscopy, which showed a $^{13}C\{^1H\}$ carbene (CAAC) resonance at 235.9 ppm. The same reaction with an excess amount (four equivalents) of $^{Mes}TerN_3$ led to only a few crystals of the planar, cyclic Al_2N_2 species **5** and linear triazene derivative **6** (Scheme 3). It should be noted that addition of further $^{Mes}TerN_3$ to iminoalane **4** led to no further reaction or detection of **5** or **6**.
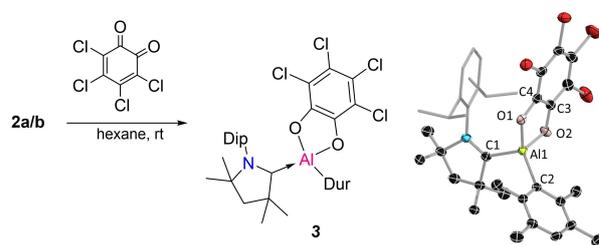
Scheme 2. Reaction of the diradical **2a/b** with *o*-chloranil and molecular structure of **3**. The solid-state structure has been represented with thermal ellipsoids ($-100\,^\circ C$) at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: C1–C2 1.415(5), C2–O1 1.351(4), C1–O2 1.333(4), Al1–C1 2.075(4); Al1–C2 1.985(3), O1–Al1 1.817(3), Al1–O2 1.794(3), O1–Al1–O2 91.41(12), C1–Al1–O1 112.20(14), C1–Al1–C2 112.64(14), O2–Al1–C2 116.23(14).
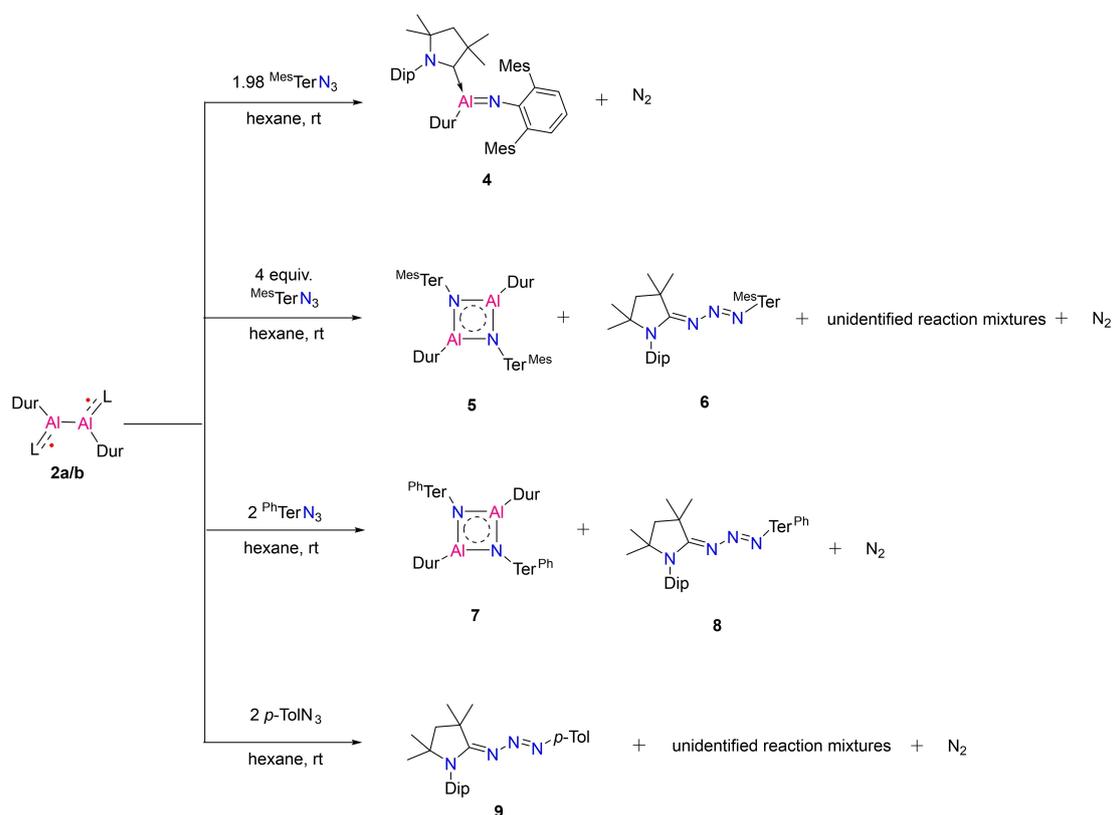
Scheme 3. Reactions of the diradical **2a/b** with azides (^{Mes}Ter = 2,6-Mes$_2$C$_6$H$_3$, ^{Ph}Ter = 2,6-Ph$_2$C$_6$H$_3$, p-Tol = 4-MeC$_6$H$_4$).
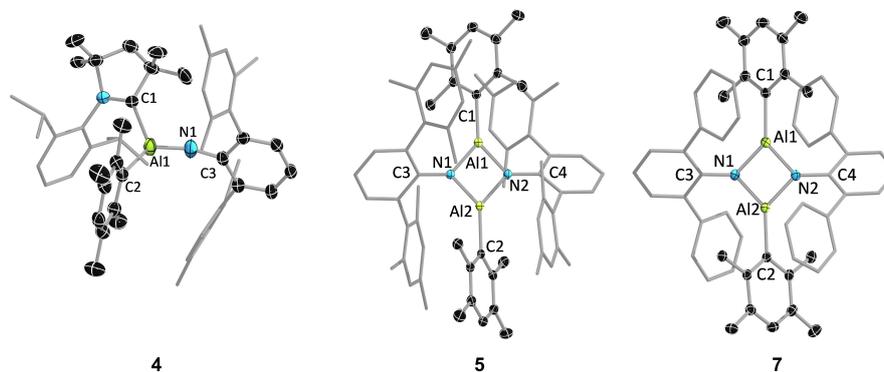
Figure 4. A) Molecular structures of **4**, **5** and **7** with thermal (−100 °C) ellipsoids at the 50 % probability level. All hydrogen atoms along with a pentane molecule (solvent of crystallization of **5**) are omitted for clarity. Selected bond lengths [Å] and bond angles [°] for **4**: Al–N1 1.668(3), Al1–C1 2.105(4), Al1–C2 1.973(3), N1–C3 1.366(5); Al1–N1–C3 166.7(3), C1–Al1–N1 112.68(15), C2–Al1–N1 124.01(14), C1–Al1–C2 120.28(14). For **5**: Al1–Al2 2.6007(9), Al1–C1 1.9645(16), N1–C3 1.403(3), Al2–N1 1.828(1), Al1–N2 1.826(1); N1–Al1–N2 89.48(6), Al1–N1–Al2 90.38(8), C1–Al1–Al2–C2 160(5). For **7**: Al1–Al2 2.588(1), Al1–C1 1.944(1), Al2–C2 1.942(1), N1–C3 1.391(3), N2–C4 1.389(1), Al2–N1 1.813(1), Al2–N2 1.814(1); N1–Al1–N2 89.00(6), Al1–N1–Al2 91.09(6), C1–Al1–Al2–C2 169.0(5) Al1–N1–Al2–N2 0.41(6).

In order to gain more insight into the reactivity of **2a/b**, it was reacted with less bulky organic azides. Reaction with ^{Ph}TerN$_3$ (Scheme 3, ^{Ph}Ter = 2,6-Ph$_2$C$_6$H$_3$) yielded a mixture of the dimeric iminoalane **7** and the triazene derivative **8** (60:40, as determined by NMR spectroscopy), while the reaction with the much smaller 1-azido-4-methylbenzene led to the formation of the triazene derivative **9** along with an unidentified mixture of products (Scheme 3). Varying the reaction conditions (temperature and reactant ratio) did not

lead to the formation of a monomeric iminoalane analogous to **4** in either case. Like other dimeric iminoalanes, **5** and **7** display planar geometries that are nearly perfect squares (Figure 4; for **5**: N1–Al1–N2 89.48(6), Al1–N1–Al2 90.38-(8)°; for **7**: N1–Al1–N2 89.00(6)°, Al1–N1–Al2 91.09(6)°). The Al–N bond lengths (**5**: ca. 1.827 Å, **7**: ca. 1.814 Å) are comparable to those reported for other dimeric iminoalanes (ca. 1.810 Å).[72,73,75,77]

Conclusion

We have successfully synthesized, isolated, and characterized a hitherto unknown diradical system based on two CAAC centers connected by an Al–Al unit that exists as two different conformers in the solid state: twisted and *trans*-planar. Quantum chemical calculations in combination with experimental findings establish that both conformers are open-shell singlets in their ground states, with exceedingly small singlet-triplet energy gaps. This highly electron-rich diradical shows facile oxidation reactivity with an orthoquinone and a range of azides.

Crystallographic data: Deposition numbers https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/anie.202401052, 2290330 (for [(Et₂O)AlBr₂(Dur)]), 2290337 (for **1**), 2290397 (for **2a**), 2290344 (for **2b**), 2290355 (for **3**), 2290373 (for **4**), 2290371 (for **5**), 2290353 (for **6**), 2290598 (for **7**), 2290364 (for **8**), 2290367 (for **9**), 2290368 (for **10**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe http://www.ccdc.cam.ac.uk/structures Access Structures service.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

[1] J. Thiele, H. Balhorn, *Dtsch. Chem. Ges.* **1904**, *37*, 1463–1470.

[2] M. Abe, *Chem. Rev.* **2013**, *113*, 7011–7088.

[3] a) T. Stuyver, B. Chen, T. Zeng, P. Geerlings, F. D. Proft, R. Hoffmann, *Chem. Rev.* **2019**, *119*, 11291–1135; b) A. Hinz, J. Bresien, F. Breher, A. Schulz, *Chem. Rev.* **2023**, *123*, 10468–10526.

[4] Z. X. Chen, Y. Li, F. Huang, *Chem* **2021**, *7*, 288–332.

[5] L. A. Pham-Huy, H. He, C. Pham-Huy, *Int. J. Biomed. Sci.* **2008**, *4*, 89–96.

[6] A. Rajca, *Chem. Rev.* **1994**, *94*, 871–893.

[7] K. C. Mondal, S. Roy, H. W. Roesky, *Chem. Soc. Rev.* **2016**, *45*, 1080–1111.

[8] Z. Feng, S. Tang, Y. Su, X. Wang, *Chem. Soc. Rev.* **2022**, *51*, 5930–5973.

[9] T. Chivers, J. Konu, *Stable and Persistent Radicals of Group 13–17 Elements. Comprehensive Inorganic Chemistry II.* Elsevier Ltd, 2013, 349–373; doi: 10.1016/b978-0-08-097774-4.00116-9.

[10] Y. Su, R. Kinjo, *Coord. Chem. Rev.* **2017**, *352*, 346–378.

[11] D. Dhara, P. K. Pal, R. Dolai, N. Chrysochos, H. Rawat, B. J. Elvers, I. Krummenacher, H. Braunschweig, C. Schulzke, V. Chandrasekhar, U. D. Priyakumar, A. Jana, *Chem. Commun.* **2021**, *57*, 9546–9549.

[12] W. Kaim, N. S. Hosmane, S. Záliš, J. A. Maguire, W. N. Lipscomb, *Angew. Chem. Int. Ed.* **2009**, *48*, 5082–5091; *Angew. Chem.* **2009**, *121*, 5184–5193.

[13] W. Kaim, A. Schulz, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 615–616; *Angew. Chem.* **1984**, *96*, 611–612.

[14] J. Fiedler, S. Zališ, A. Klein, A. Hornung, W. Kaim, *Inorg. Chem.* **1996**, *35*, 3039–3043.

[15] J. D. Hoefelmeyer, F. P. Gabbaï, *J. Am. Chem. Soc.* **2000**, *122*, 9054–9055.

[16] C.-W. Chiu, F. P. Gabbaï, *Angew. Chem. Int. Ed.* **2007**, *46*, 1723–1725; *Angew. Chem.* **2007**, *119*, 1753–1755.

[17] H. Klusik, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 870–871; *Angew. Chem.* **1981**, *93*, 903–904.

[18] M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1986**, *108*, 4235–4236.

[19] H. Braunschweig, V. Dyakonov, J. Oscar, C. Jimenez-Halla, K. Kraft, I. Krummenacher, K. Radacki, A. Sperlich, J. Wahler, *Angew. Chem. Int. Ed.* **2012**, *51*, 2977–2980; *Angew. Chem.* **2012**, *124*, 3031–3034.

[20] A. Maiti, F. Zhang, I. Krummenacher, M. Bhattacharyya, S. Mehta, M. Moos, K. Lambert, B. Engels, A. Mondal, H. Braunschweig, P. A. Ravat, A. Jana, *J. Am. Chem. Soc.* **2021**, *143*, 3687–3692.

[21] J. Böhnke, T. Dellermann, M. A. Celik, I. Krummenacher, R. D. Dewhurst, S. Demeshko, W. C. Ewing, K. Hammond, M. Heß, E. Bill, E. Welz, M. I. S. Röhr, R. Mitrić, B. Engels, F. Meyer, H. Braunschweig, *Nat. Commun.* **2018**, *9*, 1197; https://doi.org/10.1038/s41467-018-02998-3.

[22] A. Gärtner, M. Arrowsmith, M. Dietz, I. Krummenacher, R. Bertermann, F. Fantuzzi, H. Braunschweig, *J. Am. Chem. Soc.* **2022**, *144*, 21363–21370.

[23] M. Dietz, M. Arrowsmith, K. Drepper, A. Gärtner, I. Krummenacher, R. Bertermann, M. Finze, H. Braunschweig, *J. Am. Chem. Soc.* **2023**, *145*, 15001–15015.

[24] N. Kumar, R. R. Reddy, N. Eghbarieh, A. Masarwa, *Chem. Commun.* **2020**, *56*, 13–25.

[25] P. Renaud, Boron, in *radical chemistry, in Encyclopedia of Radicals in Chemistry, Biology and Materials*, John Wiley & Sons, Ltd, **2012**. DOI: 10.1002/9780470971253.rad020.

[26] M. M. Siddiqui, S. Banerjee, S. Bose, S. K. Sarkar, S. K. Gupta, J. Kretsch, N. Graw, R. Herbst-Irmer, D. Stalke, S. Dutta, D. Koley, H. W. Roesky, *Inorg. Chem.* **2020**, *59*, 11253–11258.

[27] C. Luta, K. R. Pörschke, C. Krüger, K. Hildenbrand, *Angew. Chem. Int. Ed.* **1993**, *32*, 388–390; *Angew. Chem.* **1993**, *105*, 451–453.

[28] R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon, P. P. Power, *Inorg. Chem.* **1993**, *32*, 2983–2984.

[29] W. Uhl, A. Vester, W. Kaim, J. Poppe, *J. Organomet. Chem.* **1993**, *454*, 9–13.

[30] X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon, P. P. Power, *Angew. Chem. Int. Ed.* **1993**, *32*, 717–719; *Angew. Chem.* **1993**, *105*, 761–762.

[31] M. Nakamoto, T. Yamasaki, A. Sekiguchi, *J. Am. Chem. Soc.* **2005**, *127*, 6954–6955.

[32] A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birjkumar, C. Jones, M. Kaltsoyannis, P. Mountford, S. Aldridge, *Nat. Chem.* **2014**, *6*, 315–319.

[33] B. Li, S. Kundu, A. C. Stückl, H. Zhu, H. Keil, R. Herbst-Irmer, D. Stalke, B. Schwederski, W. Kaim, D. M. Andrada, G. Frenking, H. W. Roesky, *Angew. Chem. Int. Ed.* **2017**, *56*, 397–400; *Angew. Chem.* **2017**,*129*, 407–411.

[34] S. Kundu, S. Sinhababu, S. Dutta, T. Mondal, D. Koley, B. Dittrich, B. Schwederski, W. Kaim, A. C. Stückla, H. W. Roesky, *Chem. Commun.* **2017**, *53*, 10516–10519.

[35] D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880–1881.

[36] P. Henke, T. Pankewitz, W. Klopper, F. Breher, F. H. Schnöckel, *Angew. Chem. Int. Ed.* **2009**, *48*, 8141–8145; *Angew. Chem.* **2009**,*121*, 8285–8290.

[37] M. Arrowsmith, J. Böhnke, H. Braunschweig, M. L. Celik, *Angew. Chem. Int. Ed.* **2017**, *56*, 14287–14292; *Angew. Chem.* **2017**,*129*, 14475–14480.

[38] M. Arrowsmith, J. D. Mattock, J. Böhnke, I. Krummenacher, A. Vargas, H. Braunschweig, *Chem. Commun.* **2018**, *54*, 4669–4672.

[39] V. Franzen, H.-I. Joschek, *Liebigs Ann.* **1961**, *648*, 63–68.

[40] B. Kanawati, A. Genest, P. Schmitt-Kopplin, D. Lenoir, *J. Mol. Model.* **2012**, *18*, 5089–5095.

[41] E. Welz, J. Böhnke, R. D. Dewhurst, H. Braunschweig, B. Engels, *J. Am. Chem. Soc.* **2018**, *140*, 12580–12591.

[42] J. Moilanen, P. P. Power, H. M. Tuononen, *Inorg. Chem.* **2010**, *49*, 10992–11000.

[43] M. A. Petrie, P. P. Power, V. R. Dias, K. Ruhlandt-Senge, K. M. Waggoner, R. J. Wehmschulte, *Organometallics* **1993**, *12*, 1086–1093.

[44] E. Zysman-Colman, K. Arias, J. S. Siegel, *Can. J. Chem.* **2009**, *87*, 440–446.

[45] V. Y. Lee, A. Sekiguchi, *Comprehensive Inorganic Chemistry II Elsevier Ltd.* (Second Edition), **2013**, https://doi.org/10.1016/B978-0-08-097774-4.00113-3.

[46] A. Stasch, C. Jones, *Dalton Trans.* **2011**, *40*, 5659–5672.

[47] Y. Wang, Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 3298–3299.

[48] P. Bag, A. Porzelt, P. J. Altmann, S. Inoue, *J. Am. Chem. Soc.* **2017**, *139*, 14384–14387.

[49] C. Weetman. H. Xu, S. Inoue, *Recent Developments in Low-valent Aluminum Chemistry. Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Ltd. **2020**, DOI: 10.1002/9781119951438.eibc2753.

[50] D. Dhara, F. Fantuzzi, M. Härterich, R. D. Dewhurst, I. Krummenacher, M. Arrowsmith, C. Pranckevicius, H. Braunschweig, *Chem. Sci.* **2022**, *13*, 9693–9700.

[51] C. Weetman, A. Porzelt, P. Bag, F. Hanusch, S. Inoue, *Chem. Sci.* **2020**, *11*, 4817–4827.

[52] S. K. Mellerup, Y. Cui, F. Fantuzzi, P. Schmid, J. T. Goettel, G. Bélanger-Chabot, M. Arrowsmith, I. Krummenacher, Q. Ye, V. Engel, B. Engels, H. Braunschweig, *J. Am. Chem. Soc.* **2019**. *141*, 16954–16960.

[53] M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2017**, *56*, 10046–10068; *Angew. Chem.* **2017**, *129*, 10180–10203.

[54] H. Braunschweig, R. D. Dewhurst, *Organometallics* **2014**, *33*, 6271–6277.

[55] D. Dhara, A. Jayaraman, M. Härterich, R. D. Dewhurst, H. Braunschweig, *Chem. Sci.* **2022**, *13*, 5631–5638.

[56] Z. Feng, Y. Fang, H. Ruan, Y. Zhao, G. Tan, X. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 6769–6774; *Angew. Chem.* **2020**,*132*, 6835–6840.

[57] H. G. Viehe, Z. Janousek, R. Merenyi, L. Stella, *Acc. Chem. Res.* **1985**, *18*, 148–154.

[58] S. S. Eaton, K. M. More, B. M. Sawant, G. R. Eaton, *J. Am. Chem. Soc.* **1983**, *105*, 6560–6567.

[59] a) J. Grafenstein, E. Kraka, M. Filatov, D. Cremer, *Int. J. Mol. Sci.* **2002**, *3*, 360–394; b) I. Mayer, *J. Comput. Chem.* **2007**, *28*, 204–221; c) P. Schmid, F. Fantuzzi, J. Klopf, N. B. Schröder, R. D. Dewhurst, H. Braunschweig, V. Engel, B. Engels, *Chem. Eur. J.* **2021**, *27*, 5160–5170.

[60] V. Bonačić-Koutecký, J. Koutecký, J. Michl, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 170–189; *Angew. Chem.* **1987**, *99*, 216–236.

[61] B. O. Roos, *Ab Initio Methods Quantum Chem.* Part 2, Vol. 69 (Ed.: K. P. Lawley), John Wiley & Sons, **1987**, pp. 399–445.

[62] Y. Guo, K. Sivalingam, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2016**, *144*, 094111.

[63] C. Angeli, R. Cimiraglia, J.-P. Malrieu, *Chem. Phys. Lett.* **2001**, *350*, 297–305.

[64] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J. P. Malrieu, *J. Chem. Phys.* **2001**, *114*, 10252–10264.

[65] C. Angeli, R. Cimiraglia, J. P. Malrieu, *J. Chem. Phys.* **2002**, *117*, 9138–9153.

[66] K. Yamaguchi, *Chem. Phys. Lett.* **1975**, *33*, 330–335.

[67] S. Yamanaka, M. Okumura, M. Nakano, K. Yamaguchi, *J. Mol. Struct.* **1994**, *310*, 205–218.

[68] M. Nakano, *Top. Curr. Chem.* **2017**, *375*, 47.

[69] J. D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

[70] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, 7, 3297–3305.

[71] M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002**, *117*, 43–54.

[72] A. Y. Timoshkin, *Coord. Chem. Rev.* **2005**, *249*, 2094–2131.

[73] D. Dhara, A. Jayaraman, M. Härterich, M. Arrowsmith, M. Jürgensen, M. Michel, H. Braunschweig, *Chem. Eur. J.* **2023**, *29*, e202300483.

[74] Y. Fan, J. Cui, L. Kong, *Eur. J. Org. Chem.* **2022**, e202201086.

[75] J. Li, X. Li, W. Huang, H. Hu, J. Zhang, C. Cui, *Chem. Eur. J.* **2012**, *18*, 15263–15266.

[76] J. D. Queen, S. Irvankoski, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2021**, *143*, 6351–6356.

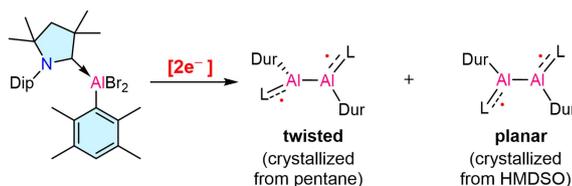[77] S. Schulz, A. Voigt, H. W. Roesky, L. Häming, R. Herbst-Irmer, *Organometallics* **1996**, *15*, 5252–5253.

Research Articles

Aluminum Chemistry

D. Dhara, L. Endres, I. Krummenacher,
M. Arrowsmith, R. D. Dewhurst, B. Engels,
R. Bertermann, M. Finze, S. Demeshko,
F. Meyer, F. Fantuzzi,*
H. Braunschweig* ————— e202401052

Synthesis and Reactivity of a Dialane-
Bridged Diradical

➤ First isolated neutral CAAC-radical-substituted dialane
➤ Exists as twisted and *trans*-planar conformers
➤ Exceptionally low singlet-triplet energy gap
➤ Highly electron-rich system

A stable, dialane-bridged diradical species has been synthesized that exists in two conformers—twisted and planar—depending on the solvent of crystallization. Both conformers have been isolated and thoroughly characterized using various analytical techniques. Their reactivity has been examined with oxidizing agents to demonstrate the reduction capability of diradicals.