Metallacycle

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A Stable Aluminacyclopropene LAl(η^2-C_2H_2) and Its End-On Azide Insertion to an Aluminaazacyclobutene[**]

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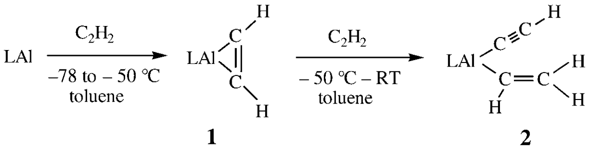
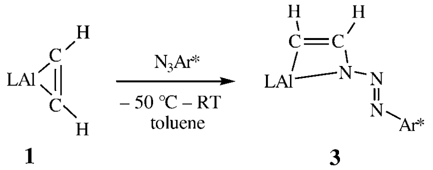
Dedicated to Kit Cummins

The MC_2 rings of cyclopropene derivatives substituted with heavier main-group elements have a highly strained structure and indicate a remarkable reactivity. They are often involved in such reactions as ring opening, insertion, substitution, dimerization, and hydrogen [1,2] sigmatropic shifts.[1] Therefore, they are of great interest in syntheses, especially in the preparation of larger heterocycles that contain main-group elements and C–C unsaturated bonds.

Such three-membered heterocyclic compounds with organic substituents at the two olefinic carbon atoms have been reported previously.[1–4] However, species with the simplest M(η^2-C_2H_2) moiety are either discussed on the basis of theoretical calculations,[5] or observed in metal-vapor deposition reactions at 12 K.[6] Among the AlC_2 ring compounds, Et(solvent)Al(η^2-C_2Ph_2) (solvent = Et_2O, THF) and ClAl(η^2-C_2R_2) (R = Me, Et) were assumed to be the respective intermediates in the formation of 1,4-(dialumina)cyclohexadiene and (ClAl·RC≡CR)$_4$.[7] The bulky β-diketiminato ligand L (L = HC(C(Me)NAr)$_2$; Ar = 2,6-*i*$Pr_2C_6H_3$) was subsequently found to stabilize the ring of the Al(η^2-$C_2R^1R^2$) species (R^1, R^2: $SiMe_3$, Ph). Such compounds have been prepared by the reductive coupling of $LAlI_2$ and potassium in the presence of $R^1C{\equiv}CR^2$.[3] Species with the formula XAl(η^2-C_2H_2) (X = H, Cl) are supported in calculations, yet are considered unstable in comparison with the acyclic isomers.[5d–e] The IR and ESR spectroscopic data on matrix-isolated products from the reaction of AlCl with C_2H_2 confirm the results.[5e] Herein, we show the reaction of the aluminum(I) monomer LAl[8] directly with C_2H_2 in the temperature range from low to room temperature and the successful isolation of the first stable aluminacyclopropene LAl(η^2-C_2H_2) **1**. The subsequent reaction of **1** with C_2H_2 results in the product **2**: LAl(C≡CH)(CH=CH$_2$) (Scheme 1). The reaction of **1** with a large bulky organic azide leads to the unusual aluminaazacyclobutene insertion product **3**: LAl(CH=CHN(N=NAr*)) (Ar* = 2,6-$Ar'_2C_6H_3$, Ar' = 2,4,6-$Me_3C_6H_2$) (Scheme 2).



Scheme 1. The stepwise reaction of LAl with C_2H_2 to **1** and **2**; L = HC(C(Me)NAr)$_2$; Ar = 2,6-*i*$Pr_2C_6H_3$



Scheme 2. The end-on insertion of N_3Ar^* into **1** to form **3**; L = HC(C(Me)NAr)$_2$; Ar = 2,6-*i*$Pr_2C_6H_3$; Ar* = 2,6-$Ar'_2C_6H_3$; Ar' = 2,4,6-$Me_3C_6H_2$

The reaction of LAl with an excess of carefully dried C_2H_2 in toluene was initially carried out in the temperature range of −78 °C to room temperature. The instant color change of the solution from red to orange and then the slow change to almost colorless was easily observed, and compound **2** was formed. Clearly, the formation of **2** indicates that LAl reacted with two molecules of C_2H_2. When this reaction was controlled in the temperature range between −78 and −50 °C, the red solution only changed to orange (this color change occurred even if the reaction was performed at ≈ −100 °C). By removal of unreacted C_2H_2, the 1:1 adduct LAl(η^2-C_2H_2) **1** was isolated. Notably, when this reaction was continued without the removal of excess C_2H_2, the corresponding ^{1}H NMR spectrum showed the formation of small amounts of **2**, whereas the reaction solution remained orange in color.

Compound **1** was obtained as an orange crystalline solid in quantitative yield and is extremely air-sensitive. Upon exposure to air, the orange color of the solution of **1** immediately becomes colorless. However, **1** is stable in an inert gas atmosphere. It is readily soluble in aromatic solvents and sparingly soluble in nonbranched hydrocarbons. Compound **2** is a colorless crystalline solid and is highly soluble in hydrocarbons. Compounds **1** and **2** were characterized by MS, ^{1}H and ^{13}C NMR spectroscopy, and by X-ray crystallography.[9a–b]

The structural analyses clearly reveal that compound **1** contains the simple Al(η^2-C_2H_2) moiety (Figure 1), whereas **2** contains terminal C≡CH and CH=CH$_2$ groups at the Al cen-

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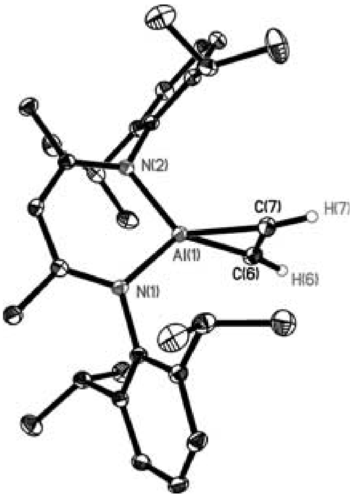

Figure 1. Molecular structure of LAl(η^2-C_2H_2) **1**. Protons in L are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.875(1), Al(1)–N(2) 1.884(1), Al(1)–C(6) 1.885(2), Al(1)–C(7) 1.878(2), C(6)–C(7) 1.358(2), C(6)–H(6) 1.000, C(7)–H(7) 1.021; N(1)-Al(1)-N(2) 97.98(5), C(6)-Al(1)-C(7) 42.30(7), Al(1)-C(6)-C(7) 68.57(10), Al(1)-C(7)-C(6) 69.13(10), H(6)-C(6)-C(7) 126.4, H(7)-C(7)-C(6) 127.1.

ter (Figure 2). The latter is the first crystallographically authenticated example of terminal C≡CH and CH=CH$_2$ groups attached to the same Al center. In **2**, the X-ray reflection data indicate that both CH=CH$_2$ and C≡CH groups are disordered in two positions (C(6)H(6)C(7)H(7)H(8), C(8)C(9)H(9), 62.2%; C(6A)H(6A)C(7A)H(7A)H(8A), C(8A)C(9A)H(9A), 37.8%). Thus, the central Al ion appears to have a disordered tetrahedral geometry with $\sphericalangle = 96.99(6)°$ for N–Al–N, and $\sphericalangle = 111.6(5)°$ for C–Al–C bond angles (av). The Al–N bond lengths in **1** (1.875(1), 1.884(1) Å) are close to those in **2** (1.895(1), 1.910(2) Å), and are similar to those observed in compounds with four-coordinate β-diketiminato aluminum(III) (1.888(2)–1.935(2) Å).[10] However, they are shorter than the Al–N bonds in LAl (1.957(2) Å) as a result of the Al^{I} center[8] having a larger radius than that of Al^{III}.

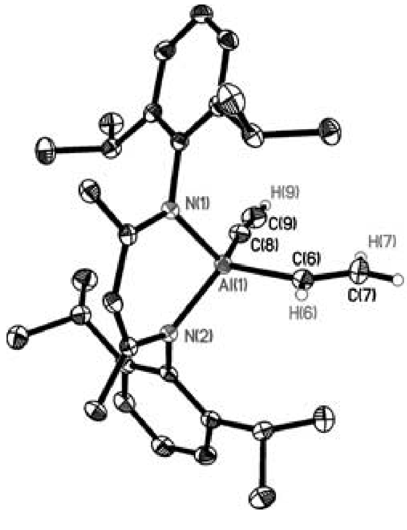

Figure 2. Molecular structure of LAl(C≡CH)(CH=CH$_2$) **2**, with both C≡CH and CH=CH$_2$ groups in 62.2% occupation. Protons in L are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.910(2), Al(1)–N(2) 1.895(1), Al(1)–C(6) 1.944(11), Al(1)–C(8) 1.962(11), C(6)–C(7) 1.325(17), C(8)–C(9) 1.173(11); N(1)-Al(1)-N(2) 96.99(6), C(6)-Al(1)-C(8) 110.8(4), Al(1)-C(6)-C(7) 124.6(12), Al(1)-C(8)-C(9) 173.9(13).

In **2**, the Al–C bond lengths (Al–$C_{C\equiv C}$ = 1.941(14) Å (av); Al–$C_{C=C}$ = 1.954(14) Å (av)) are similar to those in related compounds LAlMe$_2$ (1.955(4)–1.961(3) Å) and L′AlMe$_2$ (1.958(3)-1.970(3) Å, in which L′ = HC(C(Me)N-*p*-toluene)$_2$).[11] The C≡C (1.170(14) Å (av)) and C=C bond lengths (1.323(18) Å (av)) are indicative of characteristic C-C triple and double bonds, whereas the Al–C≡C (175.4(19)° (av)) and Al–C=C (124.6(14)° (av)) bond angles deviate from the ideal 180° and 120°, respectively.[12] The ^{1}H and ^{13}C NMR spectra of **2** confirm the functional CH=CH$_2$ and C≡CH groups at the Al center. In the Al–CH=CH$_2$ moiety, the corresponding protons resonate at $\delta = 5.70$–6.20 ppm; carbon resonances are at $\delta = 125.4$ (=*C*H$_2$) and 138.0 ppm (br, Al–*C*H=); both ^{1}H and ^{13}C NMR resonances are within the typical range for alkenyl groups. Furthermore, three groups of double doublets are observed and are indicative for these three protons in a nonequivalent steric environment. The Al–C≡CH group exhibits proton resonance at $\delta = 1.55$ ppm (s) and carbon resonances at $\delta = 94.6$ (br, ≡CH) and 137.3 ppm (br, Al–C≡). The absorptions at 1996 and 3270 cm^{-1} in the IR spectrum of **2** are tentatively assigned to the stretching frequencies of C≡C and ≡C–H bonds.

In **1**, the parameters within the Al(η^2-C_2H_2) moiety (Al–C 1.882(2) Å (av), C–C 1.358(2) Å, C–H 1.010 Å (av); $\sphericalangle$ C–Al–C 42.30(7)°, $\sphericalangle$ Al–C–C 68.85(10)° (av), $\sphericalangle$ H–C–C 126.6° (av)) fit well in comparison with those of Al(η^2-C_2) in LAl(η^2-$C_2R^1R^2$) (R^1 = SiMe$_3$, R^2 = Ph) (Al–C 1.889(2)–1.899(3) Å, C–C 1.356(5)–1.382(4) Å; C–Al–C $\sphericalangle$ 42.02(14)–42.57(11)°, Al–C–C $\sphericalangle$ 68.39(15)–68.80(19)°),[3] and are also much closer to those of the calculated HAl(η^2-C_2H_2) (Al–C 1.844–1.852 Å, C–C 1.362–1.384 Å, C–H 1.076–1.089 Å; H–C–C $\sphericalangle$ 126.8–127.3°).[5d] Notably, in the AlC$_2$ ring of **1** the average Al–C bond length is shorter than that of **2**, whereas the C–C bond length is longer (standard deviations of 0.072 and 0.036 Å, respectively). This may indicate a conjugated ring system in AlC$_2$. Furthermore, the ^{1}H and ^{13}C NMR spectra recorded in C$_6$D$_6$ show that the proton ($\delta = 8.82$ ppm (s)) and carbon resonances (177.2 ppm (br)) of the Al(η^2-C_2H_2) moiety are in the low-field region characteristic for the alkenyl system. These results indicate a certain aromatic character of the AlC$_2$ ring in **1**.

The reaction of **1** with a large bulky azide N$_3$Ar* shows an end-on azide insertion, resulting in the four-membered aluminaazacyclobutene LAl(CH=CHN(N=NAr*)) **3** (Scheme 2). A handful of reactions between monovalent Group 13 compounds and organic azides have been reported.[13] The initial N$_2$ elimination is generally accepted, and supported by experimental observations.[13e–f] The formation of a five-membered AlN$_4$ ring in LAl((NSiMe$_3$)$_2$N$_2$) was suggested to proceed through a [2+3] cycloaddition of an Al=N intermediate and N$_3$SiMe$_3$,[13d] whereas the disubstituted aluminacyclopropene LAl(η^2-C_2(SiMe$_3$)$_2$) reacted under disassociation and N$_2$ elimination with a similar bulky azide to an Al=N compound.[3] Accordingly, the end-on N_3Ar^* insertion into the Al–C bond unambiguously reveals the initial interaction between an Al center and the terminal N atom of the azide group. This type of reaction is, to the best of our knowledge, so far unknown. Compound **3** has been well-characterized by spectroscopic, analytical, and X-ray crystallographic measurements.[9c] The molecular structure of **3** is shown in Figure 3.

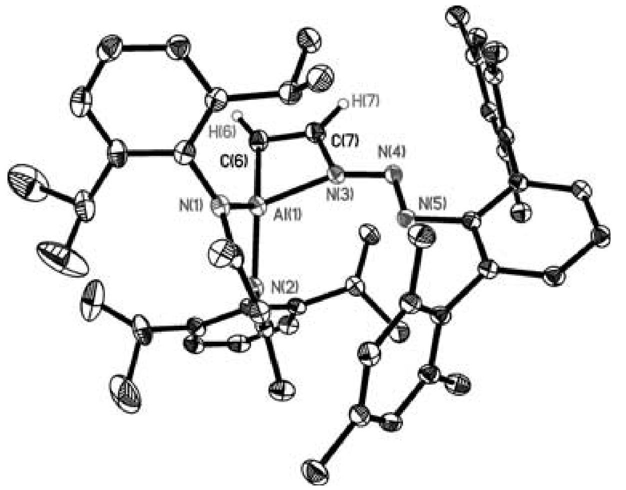

Figure 3. Molecular structure of LAl(CH=CHN(N=NAr*)) (**3**). Protons in L are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.866(2), Al(1)–N(2) 1.867(2), Al(1)–N(3) 1.892(2), Al(1)–C(6) 1.932(3), C(6)–C(7) 1.342(4), C(7)–N(3) 1.410(3), N(3)–N(4) 1.320(3), N(4)–N(5) 1.284(3); N(1)-Al(1)-N(2) 99.8(1), C(6)-Al(1)-N(3) 72.6(1), Al(1)-N(3)-C(7) 88.2(2), Al(1)-C(6)-C(7) 88.5(2), C(6)-C(7)-N(3) 110.7(2), N(3)-N(4)-N(5) 112.4(2).

In summary, we have isolated the stable aluminacyclopropene $LAl(\eta^2\text{-}C_2H_2)$ **1** from the reaction of LAl with one equivalent C_2H_2. Further reaction of **1** with another equivalent of C_2H_2 yields LAl(C≡CH)(CH=CH$_2$) **2**. This may be considered as a prebiotic reaction owing to Al^I species (AlF) and acetylene having been detected spectroscopically in dense interstellar clouds.[14] The crystallographic and NMR spectral data of **1** indicate an electron-delocalized AlC_2 heterocycle, which can be described as a Hückel 2π aromatic system. The Schmidt degradation and Curtius rearrangement of $RC(O)N_3$ to RN=C=O with the elimination of N_2 was described 105 years ago,[15] and the Staudinger reaction in which R_3P interacts with N_3R' via the R_3PNNNR' intermediate to form $R_3P{=}NR'$ with the elimination of N_2 was reported in 1919.[16] The reaction of **1** with N_3Ar^* results in an end-on azide insertion to yield an aluminaazacyclobutene LAl(CH=CHN(N=NAr*)) **3**: a novel finding in which degradation or rearrangement of the N_3 moiety is not observed. This reflects the unusual trapping ability of **1**. Current work is focused on experimental confirmation by using **1** to trap small molecules such as NO, N_2O, and CO.

Experimental Section

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a glove box filled with dry nitrogen in which the calibrated values of O_2 and H_2O were strictly controlled to below 1 ppm.

1: A toluene solution (30 mL) of LAl (0.22 g, 0.5 mmol) at decreased pressure was cooled to −78 °C and exposed to dried C_2H_2. This mixture was kept in the temperature range of −78 °C to −50 °C for 2 h. An instant color change of the solution from red to orange was observed. All volatiles were removed, and an orange crystalline solid of **1** was afforded (>95 %); m.p. 219 °C; IR (Nujol): $\tilde{\nu} = 442.7$(w), 529.1(w), 589.8(m), 613.5(w), 647.4(w), 712.7(m), 748.3(w), 758.5(w), 778.2(w), 801.0(s), 867.7(w), 893.9(w), 936.7(w), 1026.0(m), 1055.6(w), 1100.6(m), 1177.4(w), 1260.7(m), 1304.9(w), 1318.7(w), 1410.5(s), 1485.6(s), 1532.8(m), 1653.7(w) cm^{-1}; ^1H NMR (500.13 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 1.12$ (d, $^3J = 6.9$ Hz, 4 × 3 H, CH(CH_3)$_2$), 1.46 (d, $^3J = 6.9$ Hz, 4 × 3 H, CH(CH_3)$_2$), 1.53 (s, 2 × 3 H, β-CH_3), 3.33 (sept, $^3J = 6.9$ Hz, 4 × 1 H, C*H*(CH$_3$)$_2$), 4.89 (s, 1 H, γ-C*H*), 7.02–7.12 (m, 6 H, Ar-*H*), 8.82 ppm (s, 2 × 1 H, Al-η^2-C$_2H_2$); ^{13}C NMR (125.77 MHz, C_6D_6, 25 °C, TMS): $\delta = 23.4$, 24.4, 24.6, 28.9 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 96.5 (γ-*C*), 124.4, 138.8, 143.9 (Ar-*C*), 172.8 (*C*N), 177.2 ppm (broad, Al-η^2-C_2); ^{27}Al NMR (77.13 MHz, C_6D_6, 25 °C, $AlCl_3$): signal too broad to be observed. ^{27}Al NMR (77.13 MHz, [D$_8$]toluene, −70 °C, $AlCl_3$): signal too broad to be observed. MS: *m/z* (%): 469.3 (20) [M^+-1], 455.3 (30) [M^+-Me], 429.3 (100) [$M^+-\text{Me}-C_2H_2$]; elemental analysis (%) calcd for $C_{31}H_{43}AlN_2$ (470.68): C 79.10, H 9.21, N 5.95; found: C 79.43, H 9.18, N 6.03. Single crystals of **1** were obtained by keeping the *n*-hexane/toluene solution of **1** at −26 °C for one week. TMS = tetramethylsilane.

2: The initial procedure (LAl (0.22 g, 0.5 mmol), C_2H_2 (excess), and toluene (30 mL)) is the same as the synthesis of **1**. At −50 °C, the mixture was stirred and warmed to ambient temperature within 48 h, the color of the solution slowly turned to almost colorless. All volatiles were removed in vacuum and the residue was washed with *n*-hexane (2 mL) to afford a colorless crystalline solid of **2** (0.22 g, 90 %); m.p. 163 °C; IR (Nujol): $\tilde{\nu} = 1992$ (C≡C), 3277 cm^{-1} (≡CH); ^1H NMR (500.13 MHz, [D$_8$]toluene, 25 °C, TMS): $\delta = 1.08$ (d, $^3J = 6.8$ Hz, 2 × 3 H, CH(CH_3)$_2$), 1.25 (d, $^3J = 6.8$ Hz, 2 × 3 H, CH(CH_3)$_2$), 1.28 (d, $^3J = 6.8$ Hz, 2 × 3 H, CH(CH_3)$_2$), 1.44 (d, $^3J = 6.8$ Hz, 2 × 3 H, CH(CH_3)$_2$), 1.55 (s, 2 × 3 H, β-CH_3), 1.73 (s, 1 H, C≡C*H*), 3.23 (sept, $^3J = 6.8$ Hz, 2 × 1 H, C*H*(CH$_3$)$_2$), 3.81 (sept, $^3J = 6.8$ Hz, 2 × 1 H, C*H*(CH$_3$)$_2$), 4.91 (s, 1 H, γ-C*H*), 5.79 (dd, $^3J_{(trans)} = 20.9$ Hz, $^2J = 6.4$ Hz, 1 H), 6.04 (dd, $^3J_{(cis)} = 16.5$ Hz, $^2J = 6.4$ Hz, 1 H), 6.12 (dd, $^3J_{(trans)} = 20.9$ Hz, $^3J_{(cis)} = 16.5$ Hz, 1 H), (C*H*=C*H*$_2$), 6.97–7.12 ppm (m, 6 H, Ar-*H*); ^{13}C NMR (125.76 MHz, [D$_8$]toluene, 25 °C, TMS): $\delta = 23.4$, 24.5, 24.7, 24.8, 27.2, 28.2, 28.6 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 94.6 (broad, ≡*C*H), 98.4 (γ-*C*), 124.1, 124.8, 127.5, 128.8, 129.2, 137.1, 140.3, 143.7, 145.4 (Ar-*C*), 125.4, (=*C*H$_2$), 137.3 (broad, Al-*C*≡), 138.0 (broad, Al-*C*=), 170.6 ppm (*C*N); MS: *m/z* (%): 496.4 (15) [M^+], 469.4 (100) [M^+-CH=CH$_2$]; elemental analysis (%) calcd for $C_{33}H_{45}AlN_2$ (496.72): C 79.80, H 9.13, N 5.64; found: C 79.26, H 9.18, N 5.56. Single crystals of **2** were grown from the *n*-hexane solution of **2** at 4 °C within one week.

3: Toluene (25 mL) was added to a mixture of **1** (0.24 g, 0.5 mmol) and N_3Ar^* (0.18 g, 0.5 mmol) at −50 °C. The suspension was stirred and allowed to warm to room temperature. After stirring for 12 h, removal of the solvent and washing with *n*-hexane (2 mL) afforded **3** as an orange crystalline solid (0.37 g, 90 %); m.p. 215 °C; ^1H NMR (300.13 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 1.02$ (d, $^3J = 6.8$ Hz, 2 × 3 H, CH(CH_3)$_2$), 1.05 (d, $^3J = 6.8$ Hz, 2 × 3 H, CH(CH_3)$_2$), 1.16 (d, $^3J = 6.8$ Hz, 4 × 3 H, CH(CH_3)$_2$), 1.50 (s, 2 × 3 H, β-CH_3), 2.23 (s, 2 × 3 H), 2.27 (s, 4 × 3 H, *Me*(in Ar′)), 2.83 (sept, $^3J = 6.8$ Hz, 2 × 1 H, C*H*(CH$_3$)$_2$), 3.03 (sept, $^3J = 6.8$ Hz, 2 × 1 H, C*H*(CH$_3$)$_2$), 4.92 (s, 1 H, γ-C*H*), 5.03 (d, $^3J_{(cis)} = 7.6$ Hz, 1 H), 7.51 (d, $^3J_{(cis)} = 7.6$ Hz, 1 H), (*H*C=C*H*), 6.83, 6.97–7.12 (m), 7.15 ppm (14 H, Ar-*H*, Ar*-*H*, Ar′-*H*); ^{13}C NMR (75.47 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = 21.3$, 22.3, 23.0, 23.2, 24.4, 24.7, 25.0, 25.8, 26.7, 29.1, 31.9 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$, *Me*(Ar′)), 100.5 (γ-*C*), 114.8 (broad, Al-*C*=), 123.5, 123.8, 125.1, 130.9, 134.2, 136.0, 138.5, 141.6, 146.2, 147.3 (Ar-*C*, Ar*-*C*, Ar′-*C*), 162.4 (N-*C*(H)=), 171.9 ppm (*C*N); MS: *m/z* (%): 825 (5) [M^+-1], 417 (100) [$M^+-N_3Ar^*-C_2H_2-\text{Al}$]; elemental analysis (%) calcd for $C_{55}H_{68}AlN_5$ (826.17): C 79.96, H 8.30, N 8.48; found: C 79.28, H 8.38, N 8.42. Single crystals of **3**·0.5 *n*-hexane were grown from the *n*-hexane/toluene solution of **3** at 4 °C within 5 days.

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[1] E. Roskamp, C. Roskamp in *Comprehensive Heterocyclic Chemistry II*, *Vol. 2* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 305 – 332.

[2] a) A. Krebs, J. Berndt, *Tetrahedron Lett.* **1983**, *24*, 4083 – 4086; b) M. P. Egorov, S. P. Kolesnikov, Y. T. Struchkov, Y. M. Antipin, S. V. Sereda, O. M. Nefedov, *J. Organomet. Chem.* **1985**, *290*, C27-C30; c) L. R. Sita, R. D. Bicherstaff, *J. Am. Chem. Soc.* **1988**, *110*, 5208 – 5209; d) W. Ando, H. Ohgaki, Y. Kabe, *Angew. Chem.* **1994**, *106*, 723 – 725; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 659 – 661.

[3] C. Cui, S. Köpke, R. Herbst-Irmer, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, B. Wrackmeyer, *J. Am. Chem. Soc.* **2001**, *123*, 9091 – 9098.

[4] W. Uhl, T. Spies, R. Koch, W. Saak, *Organometallics* **1999**, *18*, 4598 – 4602.

[5] a) M. H. Lien, A. C. Hopkinson, *Chem. Phys. Lett.* **1981**, *80*, 114 – 118; b) M. S. Gordan, R. D. Koob, *J. Am. Chem. Soc.* **1981**, *103*, 2939 – 2944; c) J. A. Boatz, M. S. Gordan, L. D. Sita, *J. Phys. Chem.* **1990**, *94*, 5488 – 5493; d) Y. Xie, H. F. Schaefer III, *J. Am. Chem. Soc.* **1990**, *112*, 5393 – 5400; e) H.-G. Himmel, *Organometallics* **2003**, *22*, 2679 – 2687.

[6] T. R. Burkholder, L. Andrews, *Inorg. Chem.* **1993**, *32*, 2491 – 2496.

[7] a) H. Hoberg, V. Gotor, A. Milchereit, C. Krüger, J. C. Sekutowski, *Angew. Chem.* **1977**, *89*, 563 – 564; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 539 – 540; b) H. Hoberg, F. Aznar, *J. Organomet. Chem.* **1979**, *164*, C13-C15; c) H. Schnöckel, M. Leimkühler, R. Lotz, R. Mattes, *Angew. Chem.* **1986**, *98*, 929 – 930; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 921 – 922; d) C. Üffing, A. Ecker, R. Köppe, K. Merzweiler, H. Schnöckel, *Chem. Eur. J.* **1998**, *4*, 2142 – 2147.

[8] C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem.* **2000**, *112*, 4444 – 4446; *Angew. Chem. Int. Ed.* **2000**, *39*, 4274 – 4276.

[9] a) Crystal data for **1**: $C_{31}H_{43}AlN_2$, $M_r = 470.65$, monoclinic, space group $P2_1/n$, $a = 12.199(1)$, $b = 16.932(1)$, $c = 13.974(1)$ Å, $\beta = 103.87(1)°$, $V = 2802(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.116$ Mg m^{-3}, $F(000) = 1024$, $\lambda = 0.71073$ Å, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.093$ mm^{-1}; 29105 measured reflections, 4818 independent ($R_{int} = 0.0486$). The final refinements converged at $R1 = 0.0349$ and $wR2 = 0.0867$ for $I > 2\sigma(I)$ and $R1 = 0.0502$ and $wR2 = 0.0916$ for all data. Fourier synthesis gave a min/max residual electron density $-0.255/+0.263$ e Å^3; b) crystal data for **2**: $C_{33}H_{45}AlN_2$, $M_r = 496.69$, monoclinic, space group $P2_1/n$, $a = 18.844(4)$, $b = 8.732(2)$, $c = 20.080(4)$ Å, $\beta = 112.61(1)°$, $V = 3050(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.082$ Mg m^{-3}, $F(000) = 1080$, $\lambda = 0.71073$ Å, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.089$ mm^{-1}; 14544 measured reflections, 5145 independent ($R_{int} = 0.0394$). The final refinements converged at $R1 = 0.0364$ and $wR2 = 0.0820$ for $I > 2\sigma(I)$ and $R1 = 0.0582$ and $wR2 = 0.0877$ for all data. Fourier synthesis gave a min/max residual electron density $-0.208/+0.163$ e Å^3; c) crystal data for **3**: $C_{58}H_{75}AlN_5$, $M_r = 869.21$, monoclinic, space group $P2_1/c$, $a = 22.289(5)$, $b = 13.057(3)$, $c = 18.765(4)$ Å, $\beta = 109.71(3)°$, $V = 5141(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.123$ Mg m^{-3}, $F(000) = 1884$, $\lambda = 0.71073$ Å, $T = 133(2)$ K, $\mu(Mo_{K\alpha}) = 0.081$ mm^{-1}; 53490 measured reflections, 8850 independent ($R_{int} = 0.0825$). The final refinements converged at $R1 = 0.0560$ and $wR2 = 0.1371$ for $I > 2\sigma(I)$ and $R1 = 0.0933$ and $wR2 = 0.1508$ for all data. Fourier synthesis gave a min/max residual electron density $-0.437/+0.589$ e Å^3. The crystallographic data for **1**–**3** were collected on a Stoe IPDS II-array detector system using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Intensity measurements were performed on a rapidly cooled crystal with dimensions $0.40 \times 0.40 \times 0.30$ mm^3 in the range $1.92 \leq \theta \leq 24.83°$ for **1**, with $0.30 \times 0.30 \times 0.30$ mm^3 in $1.89 \leq \theta \leq 24.82°$ for **2**, and with $0.20 \times 0.10 \times 0.10$ mm^3 in $1.84 \leq \theta \leq 24.87°$ for **3**. The structures were solved by direct methods (SHELXS-97)[17] and refined with all data by full-least-squares against F^2.[18] The non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, in which the C≡CH and CH=CH$_2$ groups in **2** are both disordered and located in two positions with the same occupation ratio of 0.622/0.378. The hydrogen atoms except for H(6) and H(7) in **1** and **3** were included in geometrically idealized positions with the *U*iso tied to that of the parent atoms and were refined with the riding model. H(6) and H(7) in **1** and **3** were located by difference Fourier synthesis and refined isotropically. CCDC-265784 (**1**), 265785 (**2**), and 265786 (**3**) 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.

[10] a) C. Cui, H. W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2000**, *112*, 1885 – 1887; *Angew. Chem. Int. Ed.* **2000**, *39*, 1815 – 1817; b) V. Jancik, Y. Peng, H. W. Roesky, J. Li, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *J. Am. Chem. Soc.* **2003**, *125*, 1452 – 1453; c) G. Bai, H. W. Roesky, J. Li, M. Noltemeyer, H.-G. Schmidt, *Angew. Chem.* **2003**, *115*, 5660 – 5664; *Angew. Chem. Int. Ed.* **2003**, *42*, 5502 – 5506; d) V. Jancik, L. W. Pineda, J. Pinkas, H. W. Roesky, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *Angew. Chem.* **2004**, *116*, 2194 – 2197; *Angew. Chem. Int. Ed.* **2004**, *43*, 2142 – 2145.

[11] B. Qian, D. L. Ward, M. R. Smith III, *Organometallics* **1998**, *17*, 3070 – 3076.

[12] Structural parameters for C_2H_4 in gas phase: C–C 1.330 Å, C–H, 1.076 Å, C–C–H 121.7°, H–C–H 116.6°; for C_2H_2: C–C 1.203 Å, C–H 1.061 Å, C–C–H 180°: K. P. C. Vollhardt, N. E. Schore in *Organic Chemistry (3rd ed.)*, W. H. Freeman and Company (New York), **1998**, p. 438, 543.

[13] a) S. Schulz, L. Häming, R. Herbst-Irmer, H. W. Roesky, G. M. Sheldrick, *Angew. Chem.* **1994**, *106*, 1052 – 1054; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 969 – 971; b) S. Schulz, A. Voigt, H. W. Roesky, L. Häming, R. Herbst-Irmer, *Organometallics* **1996**, *15*, 5252 – 5253; c) P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1999**, *18*, 2037 – 2040; d) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2000**, *112*, 4705 – 4707; *Angew. Chem. Int. Ed.* **2000**, *39*, 4531 – 4533; e) N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink, P. P. Power, *Angew. Chem.* **2001**, *113*, 2230 – 2232; *Angew. Chem. Int. Ed.* **2001**, *40*, 2172 – 2174; f) R. J Wright, A. D. Phillips, T. L. Allen, W. H. Fink, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 1694 – 1695; g) H. Zhu, J. Chai, V. Chandrasekhar, H. W. Roesky, J. Magull, D. Vidovic, H.-G. Schmidt, M. Noltemeyer, P. P. Power, W. A. Merrill, *J. Am. Chem. Soc.* **2004**, *126*, 9472 – 9473.

[14] a) I. W. M. Smith, *Chem. Soc. Rev.* **2002**, *31*, 137 – 146; b) H.-P. Gail, E. Sedlmayr, *Faraday Discuss.* **1998**, *109*, 303 – 319.

[15] J. D. Roberts, M. C. Caserio in *Basic Principles of Organic Chemistry*, W. A. Benjamin, New York, **1964**, p. 656.

[16] D. E. C. Corbridge in *Phosphorus (An Outline of Its Chemistry, Biochemistry and Technology)*, 3rd ed., Elsevier Science Publishers, Dordrecht, **1985**, p. 335.

[17] SHELXS-90, *Program for Structure Solution* G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467 – 473.

[18] SHELXL-97, *Program for Crystal Structure Refinement* G. M. Sheldrick, University of Göttingen, Germany, **1997**.