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Reactions of an aluminium(I) diketiminate compound with arenes

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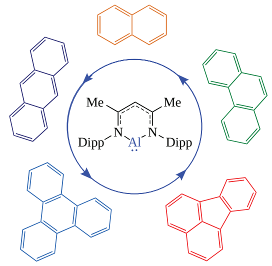
The reactivity of an aluminium(I) diketiminate compound NacNacAl (NacNac is [ArNC(Me)CHC(Me)NAr]$^-$, where Ar is 2,6-diisopropylphenyl) towards arenes has been systematically explored. Heating NacNacAl in benzene results in a fragmentation of the NacNac moiety due to cleavage of the C=N bond, while anthracene adds to the main group carbenoid in a [4+1] fashion. Reactions with phenanthrene, triphenylene and fluoranthene demonstrate a reversible [4+1] addition process.



Keywords: aluminium complexes, diketiminate, naphthalene, anthracene, phenanthrene, triphenylene, fluoranthene.

Main-group carbenoids react with aromatics in different ways, encompassing C–H bond activation, C–C bond cleavage[1–3] and cycloaddition to C=C.[4–7] In 2011, Braunschweig demonstrated [2+1] cycloaddition of naphthalene to borylene to give adduct **1** (Figure 1).[8] A year later, Cummins reported dibenzo-7λ^3-phosphanorbornadiene **2** which undergwent a retro-Diels–Alder reaction upon heating to 80 °C, affording the corresponding phosphinidene.[9] More pertinent to this current report, Power described trapping of dialumene generated *via* the reduction of 2,6-(2,6-$Pr^i_2C_6H_3)_2C_6H_3AlI_2$ with potassium graphite in toluene, in the form of a Diels–Alder-type product **3**, which was formed as the result of [4+2] cycloaddition to the solvent.[10] Furthermore, Yamashita reported a related [4+1] cyclization yielding an isolable dialkylaluminyl anion **4** (see Figure 1).[11] Herein, we report a systematic insight into the reactivity of the NacNacAl carbenoid **5** towards aromatic compounds.

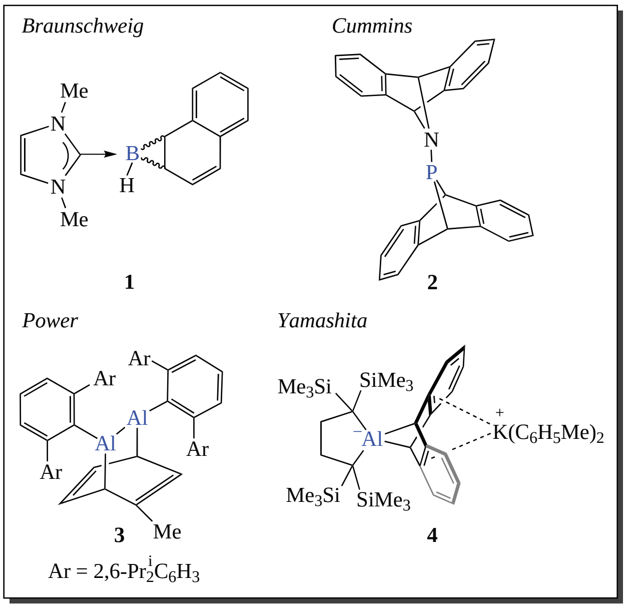
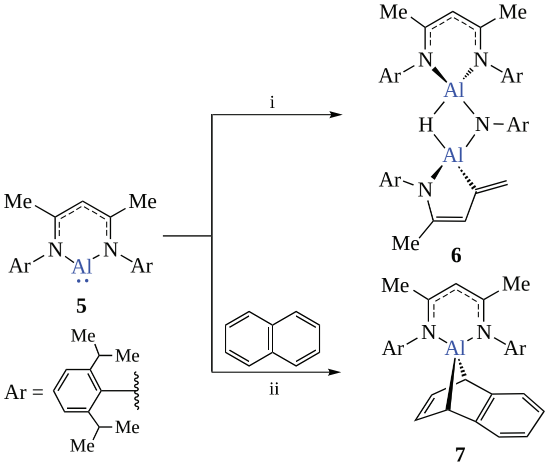


Figure 1 Products of [2+1], [4+2] and [4+1] cycloaddition for low-valent Group 13–15 element systems.

Compound **5** was prepared in benzene or toluene *via* the reduction of $NacNacAlI_2$ and stored in both solvents without decomposition for weeks (Scheme 1). However, gradually heating a toluene solution of **5** resulted in the slow formation of a new product. The progress of this reaction was particularly noticeable when the temperature reached 90 °C. The ^{1}H NMR spectrum of the resulting product contained eight methine septets and sixteen doublets for the Pr^i groups of the NacNac ligand, which suggested that the product contained two NacNac moieties, with the overall symmetry being reduced to C_1. X-ray diffraction analysis revealed this species to have structure **6** containing one fragmented NacNac moiety as a result of C=N bond cleavage. The resulting imide fragment is in the bridging position, as is a hydride ligand generated *via* deprotonation of one of the backbone methyl groups of the former NacNac ligand. An identical compound, formed in 7% yield as a by-product of a reaction between NacNacNa and



Scheme 1 *Reagents and conditions*: i, PhMe, 90 °C, 2 weeks; ii, PhMe, 40 °C, 8 h.

$(AlCp^*)_4$, has been recently described by the Kretschmer group.[12]

Apparently, the nucleophilicity of **5** is not high enough to allow for direct reaction with highly stabilized mononuclear aromatic hydrocarbons. To test whether this reactivity can be augmented by decreasing the substrate aromaticity, we turned our attention to investigate fused polycyclic aromatic compounds. In this respect, addition of 1 equiv. of naphthalene to a solution of NacNacAl in toluene leads to no immediate reaction at room temperature. However, gentle heating the reaction mixture to 40 °C resulted in a [4+1] cycloaddition reaction with clean formation of compound **7** after 8 h (see Scheme 1). The identity of the resulting product was revealed by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H spectrum is consistent with an averaged C_s symmetry. The molecular structure of **7** was further elucidated by SC-XRD (Figure 2).† One naphthalene ring is puckered at C(30) and C(33) as the result of [4+1] cycloaddition with NacNacAl, so that the overall geometry can be described as a 7-alumabenzonorbornadiene, ligated by NacNac at the aluminium vertex.

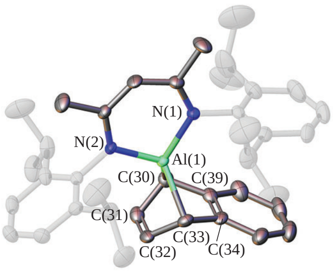
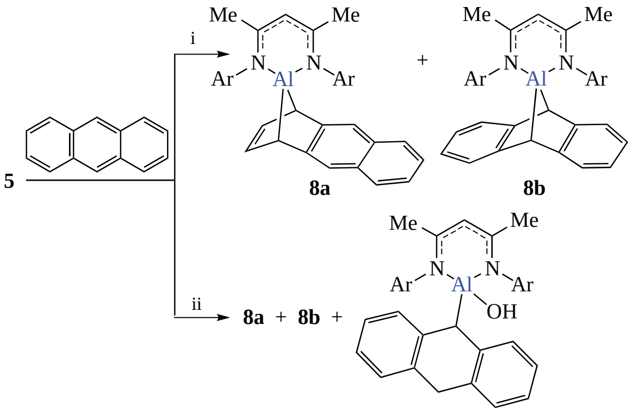
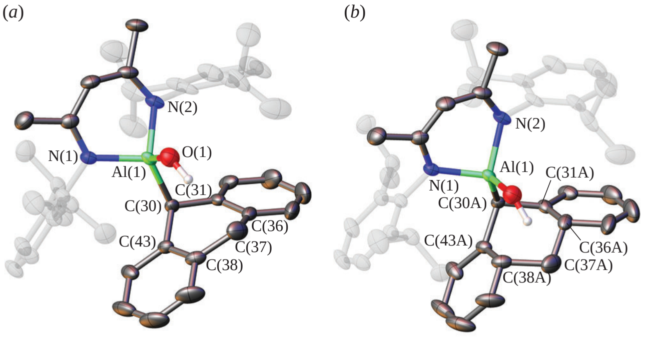


Figure 2 Molecular structure of compound **7**. H-atoms are omitted for clarity and thermal ellipsoids are plotted at 50% probability.



Scheme 2 *Reagents and conditions*: i, PhMe, room temperature, 12 h; ii, Et_2O (with H_2O traces), room temperature, 12 h.

Anthracene presents a dilemma in that it can react with **5** either at the central ring or at one of the two lateral rings. In fact, it reacted at both (Scheme 2). In this respect, when 1 equiv. of anthracene was added to a solution of NacNacAl in diethyl ether, the colour of the reaction mixture changed from dark red to bright yellow. The progress of the reaction was monitored by ^{1}H NMR, with 100% consumption of NacNacAl reached overnight. The products were identified by NMR spectroscopy and X-ray diffraction analysis to be the isomeric species **8a** and **8b**, differing in the mode of attachment of the NacNacAl moiety. This study was still in progress when Crimmin published the syntheses and characterization of these two compounds,[13] and therefore their spectroscopic and structural details will not be discussed herein. In that report,[13] the equilibrium between **8a** and **8b** was discussed. We also observed an exchange process within the lateral compound **8a**. That is, analysis of the ^{1}H–^{1}H NOESY NMR spectrum of **8a** in C_6D_6 revealed an exchange between the protons on the left and right sides of the NacNac ligand, namely the backbone methyl groups CH_3 (1.50 and 1.35 ppm), isopropyl methines $CH(CH_3)_2$ (3.21 and 3.08 ppm) and methyls $CH(CH_3)_2$ (1.48 and 1.46 ppm; 1.05 and 0.88 ppm), and the aromatic protons of the Ar substituent. This exchange process was attributed to the formal rotation of the anthracene scaffold around the aluminium centre. The energy barrier for such a rotation was determined by EXSY kinetic studies. The activation parameters were determined to be $\Delta H^\ddagger = 80(1)$ kJ mol^{-1} and $\Delta S^\ddagger = 38(4)$ J mol^{-1} K^{-1}, suggesting facile rotation of the ring *via* a dissociatively activated pathway. Repeating the reaction of anthracene with NacNacAl in ether containing adventitious water resulted in the formation of **8a**, **8b** and a new C_s symmetric species **8c**, identified by ^{1}H NMR spectroscopy. X-ray diffraction studies confirmed that **8c** was the product of the partial hydrolysis of the symmetric adduct **8b** (see Scheme 2, Figure 3).† The atoms C(30) and C(37) of the



boat　　*chair*

Figure 3 Molecular structures of the (*a*) *boat* and (*b*) *chair* conformations of compound **8c** obtained by SC-XRD. The *boat*/*chair* ratio is 0.87 : 0.13. H atoms are omitted for clarity and thermal ellipsoids are plotted at 50%.

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† Crystals of compounds **7** and **8c** were grown by slow evaporation of diethyl ether at –30 °C under inert atmosphere of dry nitrogen in the MBraun glovebox.

Crystal data for **7**. $C_{39}H_{49}AlN_2$, $M = 572.78$, monoclinic, space group $P2_1/c$, 150.0(1) K, $a = 15.4217(15)$, $b = 13.4391(13)$ and $c = 18.0681(18)$ Å, $\alpha = \gamma = 90°$, $\beta = 91.384(3)°$, $Z = 4$, $V = 3743.6(6)$ Å^3, $d_{calc} = 1.016$ g cm^{-3}, $F(000) = 1240$. Yellow irregularly shaped single crystal with dimensions $0.135 \times 0.115 \times 0.105$ mm was selected and intensities of 48380 reflections were measured using a Bruker APEX-II CCD diffractometer (ω and φ scans, sealed tube, $\lambda[\mathrm{MoK}\alpha] = 0.71073$ Å, $\mu = 0.080$ mm^{-1}, $2\theta_{max} = 54.206°$). After merging of equivalents and absorption correction, 8244 independent reflections ($R_{int} = 0.0725$) were used for structure solution and refinement. Final R factors: $R_1 = 0.0824$, $wR_2 = 0.1691$ [$I \geqslant 2\sigma(I)$]; $R_1 = 0.1079$, $wR_2 = 0.1829$ (all reflections), GOF = 1.064.

Crystal data for **8c**. $C_{43}H_{53}AlN_2O$, $M = 640.85$, monoclinic, space group $P2_1/n$, 150.0(1) K, $a = 10.6800(12)$, $b = 15.4361(16)$ and $c = 22.0580(20)$ Å, $\alpha = \gamma = 90°$, $\beta = 93.826(3)°$, $Z = 4$, $V = 3628.3(7)$ Å^3, $d_{calc} = 1.173$ g cm^{-3}, $F(000) = 1384$. Yellow plate with dimensions $0.176 \times 0.155 \times 0.153$ mm was selected and intensities of 36244 reflections were measured using a Bruker APEX-II CCD diffractometer (ω and φ scans, sealed tube, $\lambda[\mathrm{MoK}\alpha] = 0.71073$ Å, $\mu = 0.091$ mm^{-1}, $2\theta_{max} = 51.362°$). After merging of equivalents and absorption correction, 6841 independent reflections ($R_{int} = 0.0368$) were used for structure solution and refinement. Final R factors: $R_1 = 0.0885$, $wR_2 = 0.1876$ [$I \geqslant 2\sigma(I)$]; $R_1 = 0.1020$, $wR_2 = 0.1953$ (all reflections), GOF = 1.120.

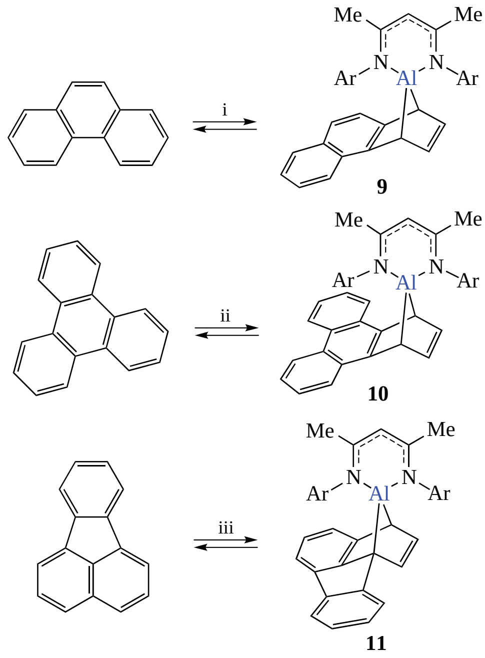
The structures were solved by intrinsic phasing algorithm and refined with full-matrix technique against F^2 in anisotropic approximation. The positions of the hydrogen atoms were calculated geometrically and refined using the riding model. All calculations were carried out with SHELXT (structure solution)[14] and SHELXL program (structure refinement).[15] Molecular graphics were drawn using OLEX2 program.[16]

CCDC 2116013–2116017 contain the supplementary crystallographic data for this paper. These datasets can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

central ring are sp^3-hybridised, with the corresponding C(31)–C(30)–C(43) and C(36)–C(37)–C(38) angles being close to tetrahedral, while two lateral rings are planar. Careful refinement of the disorder in the crystal structure and analysis of the residual electron density reveal that it contains a primary compound with a *boat* conformation (87%), together with a secondary compound with a *chair* conformation (13%).

Phenanthrene was chosen as the closest analogue of anthracene. There was no immediate reactivity upon mixing the polycycle and NacNacAl, however heating at 50 °C for two days afforded a C_1 symmetric species **9** with a 45% conversion determined by ^{1}H NMR spectroscopy (Scheme 3). Longer heating did improve the conversion, while exposing the sample to higher temperatures resulted in regeneration of NacNacAl and phenanthrene in the free form, consistent with the occurrence of an equilibrium. Analysis of the ^{1}H–^{1}H NOESY spectrum revealed an exchange between the protons assigned to the left and right flanking aryl groups, analogous to the previously discussed anthracene system. During thermal studies, slow formation of the dinuclear complex **6** (see Scheme 1) was noticed once the temperature of the reaction mixture reached 90 °C. The decomposition was complete within 14 days affording free phenanthrene and **6**. Because the same outcome is achieved when **5** is heated at 90 °C in the absence of the polycycle (*vide supra*), the transformation of **9** into **6** likely proceeds *via* dissociation of NacNacAl from adduct **9** followed by a thermal rearrangement.

Triphenylene reacted with NacNacAl **5** to afford trace amounts of a C_s symmetric species at room temperature. After heating to 70 °C for 24 h, the conversion reached 62%, at which point an equilibrium was attained (see Scheme 3). As in the case of phenanthrene, the reaction product **10** is in a dynamic equilibrium with the starting compounds, so that heating the reaction mixture to a higher temperature results in dissociation of the polycycle from the Al complex. The regioselectivity of the NacNacAl addition is apparently dictated by optimization of aromatic stabilization within the system, attributed to the presence of three fused aromatic rings in **10**. In contrast, the addition to the central ring would generate only one benzene ring and two other rings would be of the cyclohexadiene type.



Scheme 3 *Reagents and conditions*: i, **5**, PhH, 50 °C, 2 days; ii, **5**, PhH, 70 °C, 24 h; iii, **5**, PhH, room temperature, 1 h.

Fluoranthene reacted with **5** exclusively at its naphthalene part. However, in contrast to the very naphthalene, the addition occurred rapidly at room temperature, so that the equilibrium was established within 1 h. At this time, according to ^{1}H NMR spectroscopy, adduct **11** accounted for 68% of the mixture.

Considering the results of reactions with three fused polyarenes, we concluded that the stronger aromatic character of the product of NacNacAl coordination to the aromatic polycycle resulted in a greater amount of this product at a given temperature. The addition process of NacNacAl to fluoranthene was therefore studied in more detail. The composition of the reaction mixture was determined by ^{1}H NMR spectroscopy at eight temperatures and a van’t Hoff plot was used to determine the thermodynamic parameters. As expected, both the enthalpy and entropy of the addition process were found to be negative ($\Delta_r H^\circ = -52.4(8)$ kJ mol^{-1}; $\Delta_r S^\circ = -115(2)$ J mol^{-1} K^{-1}, $\Delta_r G^\circ(298\ \mathrm{K}) = -18$ kJ mol^{-1}), consistent with a favourable [4+1] cycloaddition that decreases the number of free moving particles.

In conclusion, the carbenoid aluminium compound NacNacAl reacts with aromatic compounds in a [4+1] Diels–Alder cycloaddition manner whose propensity increases from naphthalene to more aromatically conjugated systems. This reactivity mode is in contrast to closely related aluminyl anions which show both C–H bond activation and cycloaddition reactions.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.022.

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