Transfer of an Aluminium Atom: An Avenue to Aluminium Heterocycles

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Abstract

Synthetic chemistry targets building up molecular complexity using simple substrates through simple processes. We disclose an unprecedented Al-atom transfer strategy for the synthesis of aluminium heterocycles with high atom economy. This strategy involves an effective cycloaddition of a free carbazolyl-aluminylene with unsaturated hydrocarbons, followed by facile cleavage of the N-Al bond. The aluminylene formally behaves as an [Al⁺] cation transfer reagent in a two-step manner, and the only byproduct is a carbazolide salt that can be utilized to regenerate the aluminylene. The carbazolyl Al-heterocycles show unique luminescent properties, one of which exhibits dual emission. Our approach not only has a significant impact on the future design of single-atom addition reactions, but also paves the way for emissive materials based on Al-heterocycles.

Keywords

Aluminium heterocycles • Atom transfer • Dual emission • Alumole • Aluminylene

Introduction

Synthetic chemistry not only aims to construct molecular complexity from simple feedstocks, but also to exert selective modifications to chemically complex molecules.¹⁻⁴ Single-atom transfer reactions that perform atomically precise additions of molecular architectures are one of the ideal approaches (Figure 1a).⁵ Indeed, precise delivery of a chalcogen atom to a low valent main group center has opened avenues to unique species.⁶ For example, oxidation of silylenes,⁷⁻¹¹ germinylenes,^{12, 13} an aluminyl anion¹⁴ or a base-stabilized [P⁺] cation¹⁵

with N₂O has proven to give access to the respective silanones, germanones, a monoalumoxane anion or a base-stabilized [PO⁺] cation. However, such single-atom addition reactions are much less encountered with elements other than chalcogens, despite possessing the huge potential to effectively access various intriguing compounds. For group 15 elements, Bertrand, Frenking et al. described a free phosphinonitrene **A** capable of transferring an N atom (Figure 1b).¹⁶ Driess et al. isolated a silylene-stabilized zero-valent P₂ complex **B** as a P-source.¹⁷ In addition, compounds of [L₂E][X]¹⁸⁻²⁰ and NaECO²¹⁻²⁵ (L = two-electron donor ligand; E = P, As; X= counter anion) are two representative examples of E-atom transfer reagents. For group 14 elements, the fascinating ability of a few zero-valent silicon species, namely silylones **C**²⁶ and a base-stabilized disilicon **D**²⁷, have been demonstrated as surrogates of elemental silicon.²⁸ Scheschkewitz et al. showed atomically precise expansion of unsaturated silicon clusters through SiCp*₂ (**E**)²⁹ and (NHC)GeCl₂ (NHC = 2,3,4,5-tetramethylimidazolylidene)³⁰, while the group of Wesemann disclosed a base-stabilized germasilenylidene **F** that delivers a Si atom.³¹ Nevertheless, the development of analogous reactions with group 13 elements remains extremely challenging due to the lack of suitable precursors. Transfer of a single Al atom to unsaturated hydrocarbons is hitherto unknown.

Aluminium heterocyclic compounds play crucial roles in numerous aspects of chemistry.^{32-37,38-53} Among them, aluminacyclopentadienes (also referred to as alumoles) have been shown to feature little antiaromaticity.^{54, 55} These species usually emerge as key intermediates⁵⁶ and potent synthons⁵⁷ in organometallic transformations. In a rare case, alumoles derived from Roesky's [HC(CMeNDipp)₂]Al (Dipp = 2,6-diisopropylphenyl)⁵⁸ have also found applications in aggregation-induced emission (AIE) in the solid state although such fluorescence emissions in benzene are almost negligible.⁵⁹ Despite such utility, synthetic routes towards alumoles are exceedingly limited and largely rely on the employment of organo-dilithium⁶⁰⁻⁶⁶ or zirconocene-based^{56, 67-69} reagents. There is only a single report describing alumole syntheses via carboboration of the aluminum dialkynyl LAI(CCR)₂ (L = N, N-chelate ligand and R = organic group) with B(C₆F₅)₃ by Roesky, Zhu, Wang et al.⁵⁹ (a)



Precise delivery of AI to simple unsaturated hydrocarbons
Facile access to diverse AI-heterocycles with luminescent properties
Figure 1. (a) Single-atom transfer reactions. (b) Examples of single-atom transfer reagents. (c) This work.

Experimental Methods

All manipulations were carried out in a nitrogen-filled glovebox or under an atmosphere of dry nitrogen using standard Schlenk techniques, unless otherwise stated. Toluene, *n*-hexane and tetrahydrofuran were purified by distillation over sodium or LiAlH₄ and stored over molecular sieves. C₆D₆ was degassed by three freeze-pump-thaw cycles and stored over molecular sieves. 2,3-dimethyl-1,3-butadiene, trans,trans-1,4-diphenyl-1,3-butadiene, diphenylacetylene, 18-Crown-6, *n*-BuLi, ^{*t*}BuOK, PhLi, KHMDS and 3-hexyne were purchased from commercial sources and used as received. Full experimental details for syntheses of compounds reported in

this work can be found in the Supporting Information.

Results and Discussion

Recently, following the first isolation of a stable free aluminylene (alanediyl) :AlAr^{*i*Pr8} (Ar^{*i*Pr8} = C₆H-2,6-(C₆H₂-2,4,6-^{*i*}Pr₃)2-3,5-^{*i*}Pr₂) by Power, Tuononen et al.,⁷⁰ we⁷¹ and Hinz⁷² group independently demonstrated an isolable free carbazoly aluminylene **1** (Figure 2). The reactivity of :AlAr^{*i*Pr8} with hydrogen⁷⁰ and organic azides⁷³ as well as the coordination chemistry of **1** with transition metals⁷¹ and Lewis bases⁷⁴ were further explored.⁷⁵ In this contribution, we present an unprecedented Al-atom delivery strategy for the preparation of alumole derivatives employing **1** and unsaturated hydrocarbons (Figure 1c). The carbazolyl substituent of these alumoles can be replaced, making **1** formally behave as a "naked" [Al⁺] cation⁷⁶ transfer reagent, which enables the formation of four new bonds at Al in a two-step manner.

Unlike the remarkable cycloaddition reactivity of base-stabilized aluminylenes^{74, 77-83} and aluminyl anions,³⁷ we showed the inertness of **1** with naphthalene and biphenylene, which is due to the large HOMO-LUMO gap of 5.97 eV.⁷⁴ Nonetheless, **1** reacted with 2,3-dimethyl-1,3-butadiene and *E*, *E*-1,4-diphenyl-1,3-butadiene in toluene at room temperature to give [4+1] cycloaddition products **2** (80%) and **3** (72%), respectively (Figure 2). In the solid state, compounds **2** and **3** feature a 2,5-dihydro-1*H*-alumole skeleton (Figures 3a and 3b).⁸⁴ The Al and N atoms in **2** adopt a trigonal planar geometry, whereas in the case of **3** the steric repulsion arising from the phenyl and 3,5-di-*tert*-butylphenyl substituents, coupled with a weak arene coordination to Al (Al(1)-C(1) distance of 2.536(2) Å), results in a distorted tetrahedral geometry at Al (sum of angles: 337.23°) and a trigonal pyramidal N (sum of angles: 351.24°) centers. The N-Al bond lengths in **2** (1.868(2) Å) and **3** (1.876(2)Å) lie in between the Pyykkö's standard values for N-Al single (1.97 Å) and double (1.73 Å) bonds.⁸⁵



Figure 2. Synthesis of 2-5. Ar = 3,5-di-tert-butylphenyl.

Density functional theory (DFT) investigations suggest a concerted [4+1] cycloaddition process with the activation barrier of 16.4 or 9.9 kcal/mol for the formation of **2** or **3**, respectively (Figures S24 and S25). Whereas this reactivity of **1** is reminiscent of cycloadditions of Roesky's $HC[(CMe)(NDipp)]_2AI^{77, 86}$ and Schnöckel's $(Cp*AI)_4^{87}$ (Cp* = pentamethylcyclopentadiene) with dienes, the syntheses of **2** and **3** represent the first examples of cycloadditions of a monocoordinate aluminylene with unsaturated hydrocarbons.



Figure 3. Solid-state structures of 2 (a), 3 (b), 4 (c) and 5 (d). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at

the 40% probability level.

Combination of **1** with an equimolar portion of 3-hexyne (EtC=CEt) at room temperature in 5 min led to complete consumption of EtC=CEt and generation of two new species, along with the unchanged **1**. High-resolution mass spectrometry of the reaction mixture revealed the formation of [N]-Al(CEt)₂^{37, 88, 89} and [N]-Al(CEt)₄ (**4**) ([N] = carbazolyl) (Figure 2). Adding an additional equivalent of EtC=CEt to the mixture or altering the reaction stoichiometry to 1:2.3 (**1**:EtC=CEt) allowed the isolation of **4** as the sole product, indicative of the intermediacy of [N]-Al(CEt)₂ that underwent the subsequent ring-expansion reaction.⁹⁰ This stepwise mechanism is also supported by DFT calculations, which is much more favorable in comparison to a concerted process (Figure S26). It is noteworthy that HC[(CMe)(NDipp)]₂Al(CR₂)₂ (R = Ph, TMs) could only be achieved via a radical process.⁸⁹

In a similar vein, species **5** was prepared via the reaction of **1** with diphenylethyne (PhC=CPh) (2.2 equiv.). The structures of **4** and **5** as 1*H*-alumole derivatives were unambiguously authenticated by single-crystal X-ray diffraction (Figures 3c and 3d). Both **4** and **5** contain a trigonal planar Al center and the geometric parameters are comparable to those observed for Mes*Al(CEt)₄ (Mes* = 2,4,6-tri-*tert*-butylphenyl).⁶⁴ The N-Al bond lengths in **4** (1.868(2) Å) and **5** (1.841(2) Å) are comparable to those of **2** and **3** (vide supra). Of note, the facile access to **4** and **5** showcases the first examples of alumole syntheses using simple alkynes with a low-valent Al species.

Note that the structure of **2**, **4** and **5** adopts a nearly perpendicular (dihedral angles 85.04, 71.87 and 63.75° respectively) arrangement of the carbazolyl and Al-heterocycle planes due to the steric repulsion (Figure 3). This indicates very weak or almost negligible N-to-Al π donation.^{91, 92} Indeed, for **4** and **5**, the second-order perturbation theory of the natural bond orbital (NBO) method reveals that the donor-acceptor interaction from a N lone pair into a vacant p orbital at Al has stabilization energies E⁽²⁾ of 2.0 and 1.8 kcal mol⁻¹, respectively (Figures S27 and S28), while no N-to-Al π donation was observed for **2**. These values are much smaller than

those calculated for ${}^{t}Bu_{2}AINMes_{2}{}^{93}$ (Mes = mesityl) (4.4 kcal mol⁻¹) and (Mes*AINPh)₂ 94 (Mes* = 2,4,6-(${}^{t}Bu$)₃C₆H₂) (21.3 kcal mol⁻¹) at the same level of theory.⁷¹

Molecular materials based on carbazole derivatives often exhibited luminescent properties.⁹⁵⁻⁹⁹ We thus probed the potential of these carbazolyl-substituted Al-heterocycles for electro-optical applications. The UV-Vis absorption and emission spectra of **1-5** in toluene indicate that they are emissive of violet light (350-475 nm) stemming from the carbazolyl substituent (Figures 4a and 4b and S23). Interestingly, **5** displays an additional emissive band in the range of cyan light (475-625 nm). Time-dependent DFT calculations of **5** show the absorption ($\lambda_{max} = 433$ nm) attributable to the HOMO \rightarrow LUMO transition, of which the orbitals mainly involve the Al-heterocycle (Figures 4 and S30). The combination of tetraphenyl-alumole with the carbazolyl gives rise to dual emissive molecules. It is worth noting that such dual emissive materials are still rare but are very attractive for their large scope of applications, such as the construction of cost-efficient white organic light-emitting diodes (WOLEDs).^{100, 101}

Remarkably, in contrast to previous reports describing cycloadditions of low-valent Al species with hydrocarbons,^{37, 74, 77-83} the Al atom in compounds **2**, **4** and **5** remains three-coordinate. This provides opportunities for further functionalizations. It is worth noting that Power reported the reaction of organogallium(I) compound Ar*Ga (Ar* = C_6H_3 -2,6-Trip₂) with 2,3-dimethyl-1,3-butadiene giving a digalla-macrocycle,^{102, 103} which was probably formed via dimerization of a five-membered Ga-heterocycle analogous to **2**.



Figure 4. (a) UV/Vis spectra of 1-7 and 11 in toluene (10^{-5} M). (b) Emission spectra of 1-7 and 11 in toluene (10^{-5} M) with the magnified low-energy emission of 5 in the inset. (c) Photographs showing the colors (left), fluorescent colors (right) of 1-7 and 11 (λ_{ex} = 365 nm).

We envisioned the likelihood for scission of the N-Al bonds in **2-5** would be more probable if they formed aluminate salts to increase the carbazolide character as well as to decrease the N-Al bond order. This may enable transfer of the Al-heterocycles.¹⁰⁴⁻¹⁰⁶ To this end, we initially treated **2** and **3** with various anionic nucleophiles including ^tBuOK, potassium bis(trimethylsilyl)amide (KHMDS), and PhLi. These reactions resulted in a complicated mixture and only potassium or lithium carbazolide could be identified. However, treatment of

2 and **3** with benzyl potassium (BnK,1.0 equiv.) yielded aluminate salts **6** (81 %) and **7** (72 %), respectively (Figures 5, 6a and 6b). Similarly, **8** was isolated in almost quantitative yield using **5** and BnK (1.0 equiv.) (Figure 5). The electronic spectral data of **6** and **7** are comparable to those for **1-4** (Figure 4).

Single crystal X-ray diffraction demonstrates that the N-Al bond lengths in **6** (1.961(3) Å) and **7** (1.973(4) Å) elongate relative to those in **2** (1.868(2) Å) and **3** (1.876(2) Å) (Figures 6a and 6b). Natural population analyses (NPA) of the aluminates in **6-8** display a more negatively charged carbazolyl group (**6**: -0.81 a.u.; **7**: -0.80 a.u.; **8**: -0.78 a.u.) as well as a smaller Wiberg bond index (WBI) of the N-Al bond (**6**: 0.30; **7**: 0.30; **8**: 0.32), in comparison to those calculated for **2** (-0.71 a.u., 0.33), **3** (-0.69 a.u., 0.35) and **5** (-0.68 a.u., 0.34). This result supports the electronic structures of **6-8** as carbazolide-ligated alumole derivatives.



Figure 5. Synthesis of **6-11**. Ar = 3,5-di-*tert*-butylphenyl.

We next attempted on the cleavage of the N-Al bonds in **6-8**. Whereas a complicated reaction mixture was obtained upon reacting **6** and **7** with BnK, **8** smoothly reacted with BnK to form a new species **9** that was isolated as a green solid in 69 % yield. Alternatively, **9** could be prepared via the reaction of **5** with 2 equivalents of BnK in a 75% yield. Green single crystals of **9** suitable for X-ray analysis were grown from a concentrated benzene

solution at room temperature within 12 h. Gratifyingly, X-ray data show that **9** forms a one-dimensional polymeric chain, in which the N-AI bond is completely split with the N(1)-AI(1) separation of 8.033(2) Å (Figure 6c). The carbazolides and alumole anions are linked by the K(1) and K(2) atom. Addition of 18-C-6 immediately broke up the polymeric chain to produce **11** in 73% yield (Figures 5 and 6e), concurrent with the formation of potassium carbazolide. Analogously, treatment of **4** with BnK (2.0 equiv.) followed by 18-C-6 furnished **10** in 76 % yield (Figures 5 and 6d). **10** is extremely sensitive to UV-light, precluding the record of its emissive data. Nevertheless, **11** exhibits an absorption maximum at 360 nm, while displays two emissive bands at 374 and 388 nm (Figure 4).



Figure 6. Solid-state structures of **6** (a), **7** (b), **9** (c), **10** (d) and **11** (e). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Strikingly, the Al center forms four new bonds during the transformation from 1 to 10 or 11 in a two-step

manner, and only simple alkynes and BnK were utilized. The sole byproduct is potassium carbazolide that can be used to regenerate **1**.⁷¹ Overall, **1** formally behaves as a "naked" [Al⁺] cation transfer reagent, enabling the atomically precise delivery of Al to the unsaturated hydrocarbons with high atom economy. Mechanistically, as the Al centers of **6-8** are sterically hindered and the LUMOs of the aluminates in **6-8** do not involve Al (Figure S29), we propose that **6-8** equilibrate with the partially dissociated complex in solution albeit the equilibrium substantially shifts to **6-8** (Figure 7). The addition of BnK to **8** facilitates the forward reaction to furnish the transfer of Al-heterocycles.



Figure 7. Proposed mechanism for the formation of **10** and **11**.

Conclusion

In summary, we have demonstrated an unprecedented Al-atom delivery strategy for the synthesis of alumole derivatives. This protocol involves two steps, which include consecutive cycloadditions of **1** with alkynes and a following nucleophile-induced cleavage of the N-Al bonds. In comparison with known reports on cycloadditions of low-valent Al species with hydrocarbons, the distinction in this work appears to be that the Al atom in the products **2**, **4** and **5** remains three-coordinate, which allows further elaboration. Overall, the carbazolyl group acts as a carrier for the delivery of the Al units, thus unveiling a new ability of these emerging substituents in main group chemistry. Importantly, the installation of tetraphenyl alumole with a bulky carbazolyl gives rise to unique luminescent materials with dual emission, showcasing huge potential of these Al-heterocycles for electro-optical applications. The utility of such transfer reactions for the construction of other unique Al species is currently under active investigation in our laboratory.

Supporting Information

Supporting Informaiton is available and includes: (1) synthesis and characterization of all compounds, (2) NMR spectra, (3) crystallographic data, (4) photophysical data and (4) details of the quantum chemical calculations.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information (required)

We gratefully acknowledge financial support from the National Natural Science Foundation of China (22271132, 22101114 and 22201122), Guangdong Basic and Applied Basic Research Foundation (2022A1515011717) and Guangdong Provincial Key Laboratory of Catalysis (2020B121201002). X.Z. thanks China Postdoctoral Science Foundation (CPSF) for financial support (2022T150289). Y.M. thanks CPSF for financial support (2021M691420 and 2022T150288).

Preprint Statement (required, if applicable)

A previous version of this work was posted in ChemRxiv 2022, DOI 10.26434/chemrxiv-2022-k2k13

Acknowledgments

The theoretical work is supported by the Center for Computational Science and Engineering and CHEM High-Performance Supercomputer Cluster at SUSTech. We acknowledge the assistance of SUSTech Core Research Facilities. Prof. Qiao Song is thanked for assistance in UV/Vis experiments. Dr. Liang Han is thanked for for helping in Fluorescence spectrum experiments.

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Table of Contents Graphic (required)



Access to Al-heterocycles with luminescent properties

A free N-aluminylene undergoes facile cycloaddition reactions with unsaturated hydrocarbons, leading to Alheterocycles with a three-coordinate Al. Further reactions with anionic nucleophiles give rise to cleavage of N-Al bond to deliver the Al moiety. This two-step process enables precise transfer of a single Al atom. One of these Al-heterocycles shows unique dual emission.