A Free Aluminylene with Diverse σ-Donating and Doubly σ/π-Accepting Ligand Features for Transition Metals

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Dedicated to Professor Guy Bertrand

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Abstract: We report herein the synthesis, characterization, and coordination chemistry of a free N-aluminylene, namely a carbazolylaluminylene **2b**. This species is prepared via a reduction reaction of the corresponding carbazolyl aluminium diiodide. The coordination behavior of **2b** towards transition metal centers (W, Cr) is shown to afford a series of novel aluminylene complexes **3**-**6** with diverse coordination modes. We demonstrate that the Al center in **2b** can behave as: 1. a σ-donating and doubly π-accepting ligand; 2. a σ-donating, σ-accepting and π-accepting ligand; and 3. a σ-donating and doubly σ-accepting ligand. Additionally, we show ligand exchange at the aluminylene center providing access to the modulation of electronic properties of transition metals without changing the coordinated atoms. Investigations of **2b** with IDippCuCl (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) show an unprecedented aluminylene-alumanyl transformation leading to a rare terminal Cu-alumanyl complex **8**. The electronic structures of such complexes and the mechanism of the aluminylene-alumanyl transformation are investigated through density functional theory (DFT) calculations.

Introduction

Ancillary ligands play essential roles in modern synthetic chemistry and materials science.[1] It is well-known that L-type ligands can not only donate electron density to transition metal centers (σ-donating) but also accept d-electrons from the metal centers via π-backdonation (π-accepting).[1-2] Such ligands in the coordination sphere of transition metals can also exhibit the σ-accepting ability to act as a Lewis acid for external ligands.[3] According to the coordination modes of terminal L-type ligands (Figure 1a), they can be classified into four broadly defined categories, namely σ-donating/π-accepting type **I**, σ-donating and doubly π-accepting type **II**, σ-donating and doubly σ-accepting type **III**, and σ-donating, σ- and π-accepting type **IV**.

Ligands based on Al have attracted considerable attention due to the fundamental significance of the structural and electronic properties as well as their applications in synthetic chemistry.[4] The electropositive nature of aluminium (χ = 1.61) makes such ligands highly electron-releasing, thereby exhibiting unusual bonding and reactivities.[5] In the case of the terminal L-type Al ligands, representative examples include transition metal complexes **A**[6] and **B**[3g-j] derived from Schnöckel's $(Cp^*Al)_4$[7] and Roesky's $HC[(CMe)(NDipp)]_2Al$,[8] respectively (Figure 1b). It was independently demonstrated by the Power group[3g] and Crimmin group[3h] that unprecedented low-valent molecular complexes $HC[(CMe)(NDipp)]_2AlCu[(NMes)(CR)]_2CH$ (R= Me, CF_3) feature an unsupported dispersion-enhanced Al−Cu bond. Furthermore, in the late 1990s, the aluminylene complexes **C** of type **III** were

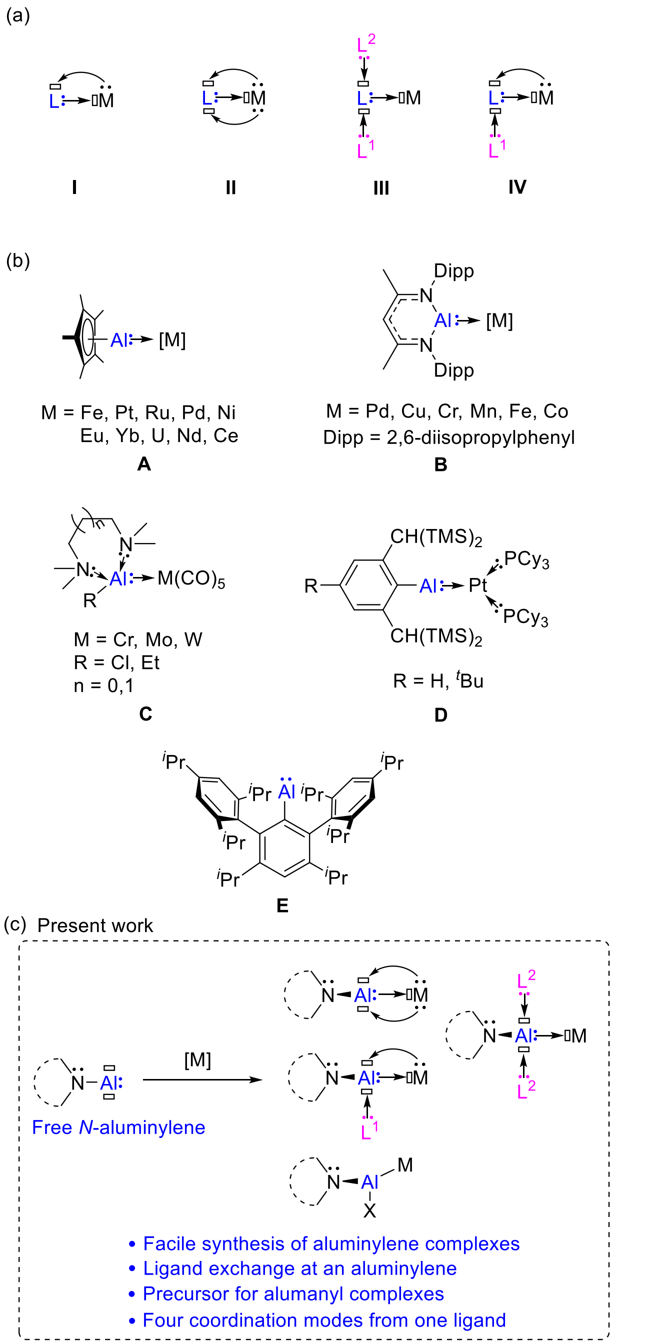


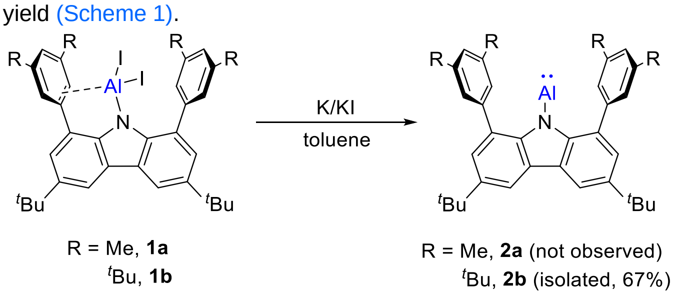
Figure 1. (a) Coordination modes of terminal L-type ligands for transition metals. (b) Representative Al(I) transition metal complexes and a crystalline free aluminylene. (c) Present work.

disclosed by Fischer, Frenking et al.[9] In 2014, Tokitoh and co-workers described the synthesis of terminal Pt-aluminylene complexes **D** bearing a di-coordinate Al atom via the reaction of a dialumene-benzene adduct with $Pt(PCy_3)_2$.[10] The Al ligand in **D** reveals donor-acceptor interactions with Pt akin to the bonding mode of type **II**. Additionally, a few of aluminium-transtion metal hydride complexes have been shown to feature aluminylene character.[4k, 11] For transition metal-alumanyl complexes with a terminal X-type Al ligand, in two recent examples, Aldridge, Goicoechea et al. isolated an Au-alumanyl complex $^{t}Bu_3$PAuAl(NON) (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) containing an unprecedented nucleophilic Au center,[12] while Hill, McMullin et al. reported the syntheses of two Cu-alumanyl complexes LCuAl(SiN^{Dipp}) (L = N,N'-diisopropyl-4,5-dimethyl-2-ylidene and (1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene, SiN^{Dipp} = $(CH_2SiMe_2NDipp)_2$) with ambiphilic Cu−Al bonding.[13]

Taking advantage of sterically demanding terphenyl ligands,[14] Power, Tuononen et al. very recently disclosed the first and sole example of a room-temperature-stable monomeric aluminylene (alanediyl) :$AlAr^{iPr8}$ (Ar^{iPr8} = C_6H-2,6-$(C_6H_2$-2,4,6-$^{i}Pr_3)_2$-3,5-$^{i}Pr_2$) (**E**) (Figure 1b) via a reduction reaction of AlI_2Ar^{iPr8} with 5% w/w Na/NaCl.[15] This breakthrough allowed further explorations into unusual/unprecedented patterns of reactivity of **E** toward hydrogen[15] and organic azides,[16] in which the latter led to the first stable iminoalane with an Al≡N triple bond. In the present work, we report the synthesis, characterization and coordination chemistry of a free one-coordinate N-aluminylene (Figure 1c). Of note, this aluminylene functions as a σ-donating and doubly σ/π-accepting ligand for transition metals, leading to a series of unprecedented aluminylene and alumanyl complexes with diverse coordination modes via a simple one-step process.

Results and Discussion

Synthesis, Characterization and Bonding Analysis of *N*-Aluminylene. The installation of Al with bulky π-donor substituents, such as amino,[17] phosphino[18] or carbazolyl,[19] should enhance the stabilization of the inherent electron deficiency of free aluminylenes due to the possible π-donation of a N/P lone pair into an accessible vacant p orbital at Al. We thus chose the carbazolyl-substituted aluminium diiodides **1** as the precursors (Scheme 1). These species were readily accessible from a salt metathesis reaction of the respective potassium carbazolide with AlI_3, and their structures were confirmed by single crystal X-ray diffraction analysis (Figure S30).[20] While all attempts of reducing **1a** afforded an unidentified mixture, stirring a toluene solution of the more sterically encumbering **1b** with excess 5% w/w K/KI (4 equivalents) from −15 to 13 °C for 2 days gave rise to the free aluminylene **2b** as a white powder in 67% yield (Scheme 1).



Scheme 1. Synthesis of **2b**.

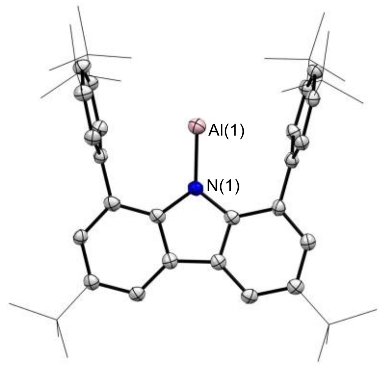


Figure 2. Solid-state structure of **2b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

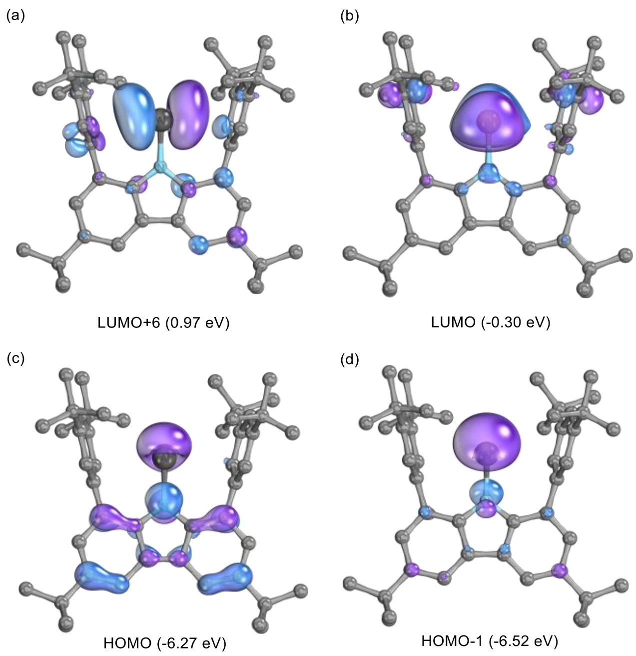


Figure 3. (a) LUMO+6 of **2b**. (b) LUMO of **2b**. (c) HOMO of **2b**. (d) HOMO-1 of **2b**. Isovalue = 0.04.

Single crystals of **2b** suitable for X-ray diffraction were obtained from slow evaporation of a concentrated *n*-hexane solution at room temperature within 12 h. The X-ray diffraction study revealed the N(1) atom adopts a planar environment (sum of angles: 359.3º) (Figure 2). The Al(1)−N(1) bond length (1.913(9) Å) is slightly shorter than the Pyykkö standard value for an Al−N single bond (1.970 Å)[21] whereas much longer than those of typical Al=N double bonds (1.705(2)−1.725(1) Å) in terminal aluminum imides,[22] indicative of the presence of a weak N-to-Al π-donation. The Al(1) atom is located nearly symmetrically between the two flanking 3,5-di-*tert*-butylphenyl rings of the carbazolyl substituent. There is no strong secondary bonding interaction between Al and the two arenes in the solid state (the shortest Al−C distance: 3.015(3) Å), which is similar to that observed for Power's :$AlAr^{iPr8}$.[15] Infrared spectroscopic studies of **2b** show no evidences for Al−H stretching frequencies (Figure S1).

Crystalline **2b** can be stored at room temperature under an inert atmosphere for over a month. A benzene solution of **2b** was heated up to 80ºC for 10 h without noticeable decomposition. However, it is extremely sensitive to moisture and oxygen, leading to the complete scission of the Al−N bond affording the corresponding carbazole and unidentified Al-containing species (Figure S29).

The ambiphilic nature of **2b** is unambiguously demonstrated by its frontier molecular orbitals (M06-2X/def2-SVP) (Figure 3). The

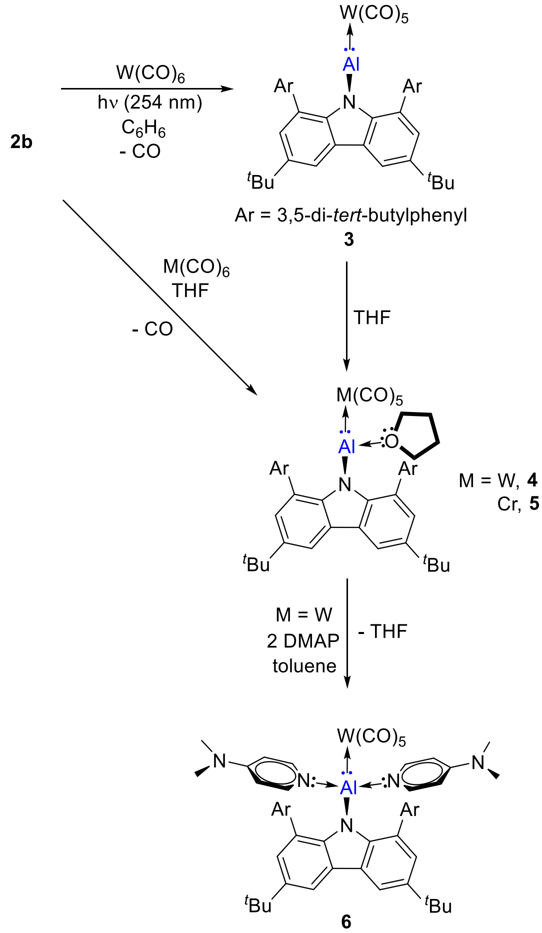
LUMO+6 and LUMO are mainly the in-plane and out-of-plane Al 3p orbitals, respectively (Figures 3a and 3b). The HOMO is composed of the lone pairs at both Al and N atoms as well as some π-bonding orbitals over the carbazolyl substituent, while the HOMO-1 predominantly involves the Al nonbonding lone pair (Figures 3c and 3d). These observations are different from those calculated for :AlAr^{iPr8},[15] illustrating that the *N*-substitution at Al dramatically affects the electronic structure of aluminylenes. Moreover, the natural population analysis (NPA) shows that the Al atom is positively charged (0.79 a.u.) and the N atom carries a negative charge (-0.96 a.u.). The Wiberg bond index (WBI) of the Al-N bond is 0.28 which can be explained by its substantial ionic nature. 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 a small stabilization energy of 16.5 kcal mol^{-1} due to the electropositive nature of Al (χ = 1.61) (Figure S32). For comparison, the calculated stabilization energies arising from a N-to-Al π-donation in ^{t}Bu$_2$AlNMes$_2$[23] (Mes = mesityl) and (Mes*AlNPh)$_2$[24] (Mes* = 2,4,6-(^{t}Bu)$_3$C$_6$H$_2$) are 4.4 and 21.3 kcal mol^{-1}, respectively (Figure S33).

Compound **2b** shows two absorption maxima in the UV/Vis spectrum in toluene at 346 and 356 nm (Figure S2), which are blue-shifted relative to those of :AlAr^{iPr8} (351 and 467 nm).[15] These absorptions are attributed to the HOMO–LUMO and HOMO-1–LUMO transitions according to TD-DFT calculations (Figure S35).

Isolation of Aluminylene Complexes. We thus speculated that **2b** should be an interesting ligand featuring σ-donor and σ/π-acceptor properties for transition metals if the Al atom is kinetically accessible. **2b** is completely inert upon stirring its benzene solution with an equal molar portion of W(CO)$_6$ at room temperature for 12 h. However, UV lamp (254 nm) exposure is known to facilitate the removal of CO in metal carbonyls,[25] so the solution was irradiated for 24 h which cleanly furnished a new species **3** (Scheme 2). After workup, **3** was isolated as a yellow solid in 85%. The ^{1}H NMR spectrum of **3** shows two singlets for the ^{t}Bu groups of 3,5-di-*tert*-butylphenyl substituents at 1.35 and 1.43 ppm, indicating the asymmetric nature with respect to the carbazolyl plane. Two singlet carbonyl resonances at 197.5 and 198.8 ppm are observed via a ^{13}C NMR spectroscopic study.

Slow evaporation of a concentrated hexane solution of **3** at room temperature resulted in X-ray quality yellow crystals after 5 h. The solid-state structure of **3** was determined by X-ray diffraction (Figure 4a). In contrast to **2b**, the N(1) atom in **3** is slightly pyramidalized (sum of angles: 351.8°), and the Al(1)−N(1) bond (1.841(3) Å) is bent out of the carbazolyl plane, which consequently reduces the effective steric bulk of the substituent drastically. It is observed that the Al(1)−W(1) bond length (2.5363(11) Å) in **3** is much shorter compared to those of (TMEDA)Al(Et)W(CO)$_5$ (2.670(1) Å) (TMEDA = N,N,N',N'-tetramethylethylenediamine) and (TMPDA)Al(Cl)W(CO)$_5$ (2.645(2) Å) (TMPDA = N,N,N',N'-tetramethylpropanediamine),[9b] indicating the stronger π-backdonation from W to Al in our case. Although the only known examples of terminal base-free aluminylene complexes **D** (Figure 1b) reveal an almost linear geometry at Al (R = H, 179.2(2)°; R = ^{t}Bu, 174.0(1)°),[10] the bond angle of N(1)−Al(1)−W(1) (147.31(10)°) in **3** appears to be bent, likely due to the steric hindrance arising from two 3,5-di-*tert*-butylphenyl substituents. The aluminylene ligand in **3** acts as σ-donor and double π-acceptor (vide infra). Species **3** represents the first example of an early transition metal-aluminylene complex with a di-coordinated Al atom.[10]

As the aluminylene ligand in **3** formally contains two vacant p orbitals, **3** should be susceptible to Lewis base coordination. Indeed, **3** rapidly converted to a new product **4** quantitatively in THF (Scheme 2). Alternatively, treatment of **2b** with W(CO)$_6$ in THF at room temperature yielded **4** as well in 60% yield. In an analogous fashion, the reaction of **2b** with Cr(CO)$_6$ in THF led to a species **5** as a white solid in 62% yield. The NMR spectroscopic features of **4** and **5** are very comparable. The ^{1}H NMR spectra of



Scheme 2. Synthesis of **3**-**6**.

both cases display two diagnostic broad singlets (**4**: 0.96 and 3.30 ppm; **5**: 0.96 and 3.32 ppm), integrating to four protons each. This suggests the presence of a coordinated THF molecule.

Colorless single crystals of **4** and **5** were obtained via slow evaporation of their concentrated benzene solutions. In the solid state, species **4** and **5** appear to be a W-aluminylene and a Cr-aluminylene complexes, respectively (Figures 4b and S34). The structural parameters of the carbazolyl aluminylene parts in **4** and **5** are similar. The N(1) atoms in both cases are clearly pyramidalized (sum of angles: 311.9° (**4**), 316.9° (**5**)), and the Al(1)−N(1) bonds (1.898(7) (**4**), 1.883(3) Å (**5**)) are bent out of the carbazolyl plane. This allow the coordination of a THF molecule to Al with a Al(1)−O(1) bond length of 1.862(5) (**4**) or 1.853(3) Å (**5**), thereby compensating the electron deficiency of Al. The bond lengths of Al(1)−W(1) (2.601(2) Å) and Al(1)−Cr(1) (2.4087(12) Å) are shorter than those seen for (TMEDA)Al(Et)W(CO)$_5$ (2.670(1) Å) and (TMPDA)Al(Cl)Cr(CO)$_5$ (2.482(1) Å), respectively.[9b] These imply the presence of the π-backdonation from W/Cr to Al. The angles of N(1)−Al(1)−W(1) (131.8(4)°) and N(1)−Al(1)−Cr(1) (132.3(1)°) are wider in comparison to those of the respective R−Al−M (R = Cl, M = Cr; R = Et, M = W) in (TMEDA)Al(Et)W(CO)$_5$ (121.4(1)°) and (TMPDA)Al(Cl)Cr(CO)$_5$ (123.63(5)°).[9b] Of note, the aluminylene ligand in **4** and **5** behaves as σ-donor, σ-acceptor and π-acceptor (vide infra), and such bonding modes are extremely rare for coordination chemistry.[3c, 7] The σ-acceptor property of ligands has been invoked in mechanistic studies using aluminylene ligands[4k, 5n] and related gallylene systems.[26] Importantly, Crimmin et al. disclosed that such property of aluminylenes is crucial to catalytic processes.[4k, 5n-p]

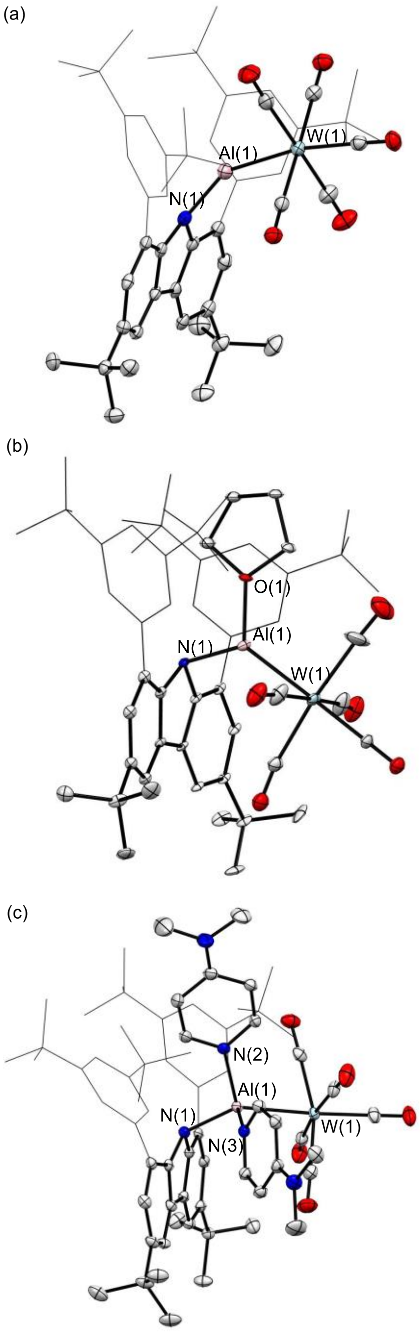


Figure 4. Solid-state structures of **3** (a) and **4** (b) and **6** (c). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

In addition, the coordination behavior of free one-coordinate aluminylenes toward transition metals is hitherto unknown.[3g-j, 4a-j, 5a, 5d, 15-16] The formation of **3**-**5** demonstrates the facile access to metal-aluminylene complexes through this straightforward process.

DFT modelling reveals that dissociation of the THF from **4** to produce **3** is only unfavorable by the free energy of 4.5 kcal mol^{-1}, indicative of the labile nature of the THF. We thus envisioned the possibility for ligand exchange reactions at Al. To this end, 4-dimethylaminopyridine (DMAP) was employed (Scheme 2). Addition of 2 equivalents of DMAP to a toluene solution of **4** at room temperature immediately yielded a sole product **6**, which was isolated as a yellow powder in 90%. A C_6D_6 solution of **6** displays a characteristic singlet at 2.13 ppm integrating for twelve protons corresponding to the methyl groups of DMAP in the ^{1}H NMR spectrum, and there is no evidence for the presence of THF. This suggests that the coordinated THF in **4** is completely replaced by two DMAP molecules.

Indeed, in the solid state, **6** bears a tetracoordinate Al(1) center with the tetrahedron geometry (Figure 4c). The bond length of Al(1)−N(1) (1.9549(17) Å) is slightly shorter than those observed for Al(1)−N(2) (2.0281(19) Å) and Al(1)−N(3) (1.9892(18) Å). As expected, the Al(1)−W(1) bond length (2.7143(6) Å) appears much longer in comparison to those of **3** (2.5363(11) Å) and **4** (2.601(2) Å), and slightly longer than that in (TMEDA)Al(Et)W(CO)$_5$ (2.670(1) Å).[9b] The formation of **6** undergoes a formal ligand exchange reaction at an aluminylene, reminiscent of scarce examples of ligand exchanges at low-valent main group centers, such as borylene,[27] phosphinidene,[28] carbene,[29] and vinylidene.[30] Moreover, **6** is a rare example of complexes containing a group 13 ligand with the coordination type **III** (Figure 1a).[3h, 9b, 31]

It is interesting to note that the presence of weak semi-bridging carbonyl interactions is observed with the asymmetry parameter (α)[32] taking values of 0.50, 0.55, 0.56 and 0.55 for these complexes **3**-**6**, respectively. Such values are slightly larger than those of HC[(CMe)(NDipp)]$_2$AlFe(CO)$_3$L (L = CO, 0.47; L = Cy$_3$P, 0.49) reported by Crimmin and Kong.[3h]

The electronic properties of the aluminylene ligands in **3**, **4** and **6** were next established from the carbonyl stretching frequencies (ν_{CO}).[33] With respect to the number of ligands at Al in the series N-Al(L)$_n$W(CO)$_5$ (n = 0-2), which can consecutively suppress W-to-Al π-backdonation while enhance Al-to-W σ-donation, there is significant decrease of the frequencies. **3** exhibits distinctly high frequencies (ν_{CO} 2060, 1974 and 1922 cm^{-1}) indicative of reduced electron releasing ability of the Al ligand in **3** compared to those in **4** (ν_{CO} 2046, 1958 and 1897 cm^{-1}) and **6** (ν_{CO} 2015, 1916 and 1854 cm^{-1}). These modifications at the ligand site (i.e. coordination of THF or DMAP) drastically influence the electronic properties of the transition metal without changing the coordinated Al ligand.

Bonding Analyses. For a better understanding bonding scenarios of **3**, **4** and **6**, density functional theory (DFT) calculations, coupled with energy decomposition analyses with natural orbitals for chemical valence (EDA-NOCV)[34] calculations and intrinsic bond orbital (IBO)[35] investigations were carried out. The IBO method is proven to give an exact representation of any Kohn−Sham DFT wave function.[35] Inspections of IBOs of **3** demonstrate that the Al center forms two σ-bonds (Al−N and Al−W σ-bonds) (Figures 5a and 5b). It is observed that two formally vacant 3p orbitals of Al accept electron density from symmetrically accessible filled 5d orbitals of W, forming two apparent π-back-bonding (Figures 5c and 5d). This accounts for the relatively short Al(1)−W(1) bond length (vide supra). In contrast, the Al center of **4** is coordinated with a THF molecule and thus three σ-bonds (Al−N, Al−O and Al−W σ-bonds) at Al are observed (Figures 5e-5g), along with a W-to-Al π-back-bonding (Figure 5h). For **6**, the coordination of two DMAP molecules prevents forming π-back-bonding (Figure S36), thereby giving four σ-bonds at Al (Al−W and three Al−N σ-bonds) (Figures 5i-5l). Additionally, EDA-NOCV calculations demonstrate that, in all cases, the orbital interactions ΔE_{orb} are dominant between Al and W with the magnitude of -68.1, -71.1 and -92.3 kcal mol^{-1} for **3**, **4** and **6**, respectively (Figures S37-S39). Examinations of the deformation density plots allow visualization of this donor-acceptor interaction (Figure S40). In all cases, the Al-to-W σ-donation (**3**: -49.5 kcal mol^{-1}; **4**: -54.5 kcal mol^{-1}; **6**: -75.2 kcal mol^{-1}) comprises the most significant contribution to ΔE_{orb}, whereas the W-to-Al π-backdonation of **3** and **4** plays a minor role in contributions to ΔE_{orb} (**3**: -12.8 kcal mol^{-1}; **4**: -6.0 kcal mol^{-1}).

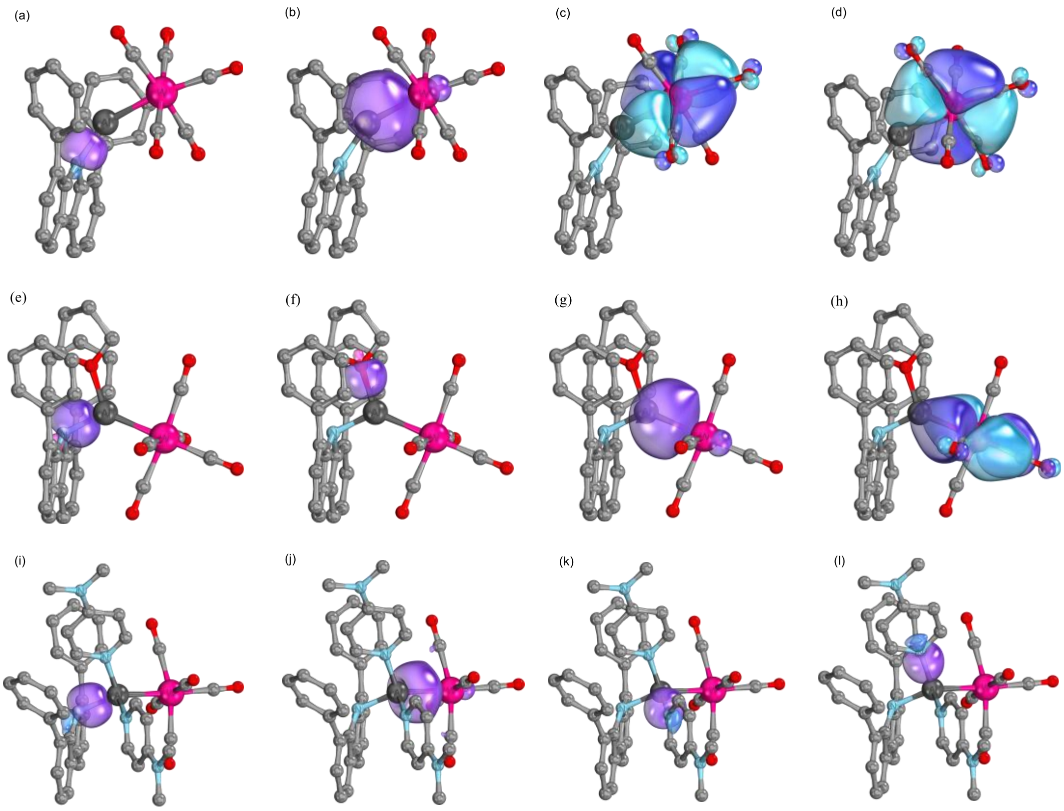
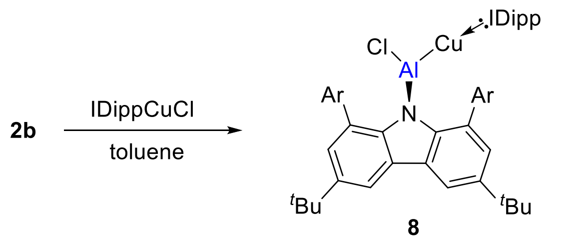


Figure 5. Selected IBOs of **3** (a-d), **4** (e-h) and **6** (i-l). Hydrogen atoms and ^{t}Bu groups are omitted for clarity.

Isolation of an Alumanyl Complex. Further reactivity explorations reveal that **2b** is highly reducing and can readily react with (THT)AuCl (THT = tetrahydrothiophene) to afford the carbazolyl-substituted aluminium dichloride **7** as well as Au mirror (Figure S31). Repeated crystallization attempts of **7** yielded crystals of poor quality, nonetheless preliminary X-ray studies confirmed its formulation (Figure S31). In a similar vein, upon mixing **2b** with IDippCuCl (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in toluene at ambient temperature, a white solid of the Cu-alumanyl complex **8** was isolated in 71% (Scheme 3).

The solid-state structure of **8** exhibits a planar Al(1) center with the sum of angles at 359.9° (Figure 6). The Al(1)−Cu(1) bond length is 2.3448(13) Å, which is comparable to that seen for LCuAl(SiN^{Dipp}) (L = N,N'-diisopropyl-4,5-dimethyl-2-ylidene, 2.3450(6) Å)[13] whereas slightly longer with respect to that of HC[(CMe)(NDipp)]$_2$AlCu[(NMes)(CMe)]$_2$CH (2.3011(7) Å).[3g] To date, the solid-state structural authentication of terminal Cu-alumanyl complexes is limited to LCuAl(SiN^{Dipp}) (L = N,N'-diisopropyl-4,5-dimethyl-2-ylidene and (1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene)[13] and K[Cu[Al(NON)]$_2$].[36] These species were formed by a salt metathesis reaction of the corresponding potassium aluminyl compound with a ligand-stabilized copper halide. It is important to note that the facile synthesis of **8** showcases a new avenue to terminal alumanyl complexes that are extremely rare and otherwise difficult to prepare.[4c, 4d, 12-13, 36-37]



Ar = 3,5-di-*tert*-butylphenyl
IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene

Scheme 3. Synthesis of **8**.

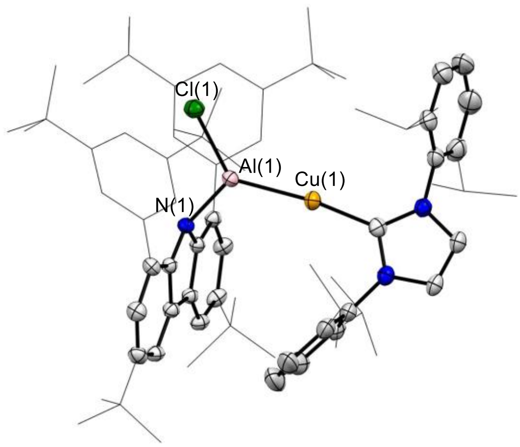


Figure 6. Solid-state structure of **8**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Mechanistic Investigations. The mechanism of the formation of **8** was probed via DFT calculations (SMD-M06-2X/def2-

TZVP//M06-2X/def2-SVP) (Figure 7). The reaction begins with the approach of the aluminylene **2b** toward the Cu atom of IDippCuCl. This prompts the slight pyramidalization of N and the formation of an Al−Cu dative bond to generate an intermediate **IN1** (free energy of 11.3 kcal mol^{-1}) in a barrier-less process (Figure S41). Subsequent oxidative addition of the Cu−Cl bond to Al proceeds via **TS1**, with the energy barrier of 13.4 kcal mol^{-1} (**2b**→**TS1**), to yield the stable product **8** (-4.8 kcal mol^{-1}). Concurrent with this is the increase of the formal oxidation state of Al from +1 to +3.

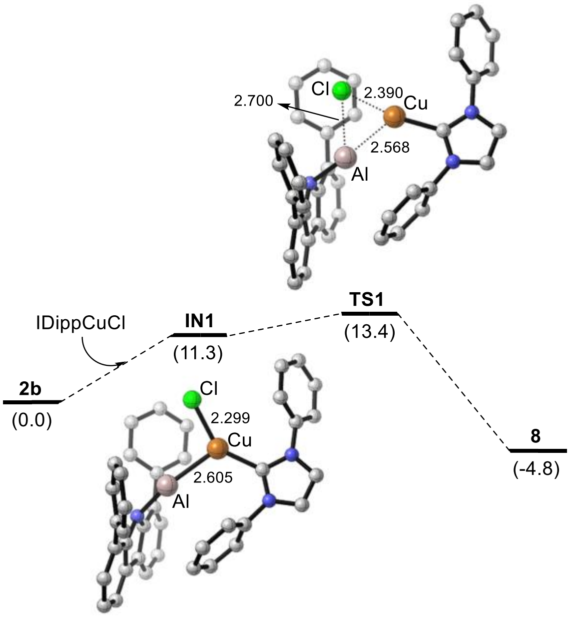


Figure 7. Free energy profile for the formation of **8**. Hydrogen atoms, ^{i}Pr and ^{t}Bu groups are omitted for clarity. Energies are given in kcal mol^{-1}. Bond lengths are given in Å.

Conclusion

In summary, a room-temperature-stable N-substituted free aluminylene **2b** has been isolated and characterized by spectroscopic, crystallographic and computational techniques. While the planarization of the N atom coupled with two flanking 3,5-di-*tert*-butylphenyl rings of the carbazolyl substituent in **2b** results in the thermodynamic and kinetic stabilization at Al, the facile pyramidalization of the same N atom making the Al kinetically accessible can occur upon treating **2b** with a variety of transition metal complexes (i.e. W, Cr). This allows the isolation of a series of unprecedented aluminylene complexes **3**-**6**. Interestingly, this Al ligand showcases σ-donor and σ/π-acceptor properties in diverse manners for transition metals. For **3**, the Al is a σ-donating and doubly π-accepting ligand. For **4** and **5**, the Al serves as a σ-donating, σ-accepting and π-accepting ligand. Significant to note is that **6** is prepared via an intriguing Al-centered ligand exchange reaction of **4** with DMAP and the Al functions as a σ-donating and doubly σ-accepting ligand. Infrared spectroscopic investigations show that such modifications of ligands at the Al (i.e. coordination of THF or DMAP) significantly affect the electronic properties of transition metals without changing the coordinated atoms. Finally, the first example of aluminylene-alumanyl conversion has been demonstrated, generating a Cu-alumanyl complex **8**. Considering DFT calculations, the mechanism leading to **8** involves an initial Al−Cu coordination followed by an oxidative addition of a Cu−Cl bond at Al. We anticipate that these discoveries can pave a way for other unknown metal-alumanyl complexes. The utility of **2b** in the production of other intriguing species, the subsequent chemistry of these new complexes and the extension of this Al ambiphilicity to catalysis are the subjects of ongoing work.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Aluminylene • Aluminium Ligand • Coordination • σ-Donating • σ/π-Accepting

[1] (a) R. Jazzar, M. Soleilhavoup, G. Bertrand, *Chem. Rev.* **2020**, *120*, 4141-4168; (b) M. Koy, P. Bellotti, M. Das, F. Glorius, *Nat. Catal.* **2021**, *4*, 352-363.

[2] (a) A. G. Orpen, N. G. Connelly, *Organometallics* **1990**, *9*, 1206-1210; (b) J. T. Goettel, H. Braunschweig, *Coord. Chem. Rev.* **2019**, *380*, 184-200; (c) H. Braunschweig, R. D. Dewhurst, V. H. Gessner, *Chem. Soc. Rev.* **2013**, *42*, 3197-3208.

[3] (a) G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Angew. Chem., Int. Ed.* **2000**, *39*, 948-950; (b) H. Braunschweig, K. Radacki, D. Rais, D. Scheschkewitz, *Angew. Chem., Int. Ed.* **2005**, *44*, 5651-5654; (c) H. Braunschweig, T. Kramer, K. Radacki, R. Shang, E. Siedler, C. Werner, *Chem. Sci.* **2014**, *5*, 2271-2276; (d) H. Braunschweig, J. O. C. Jimenez-Halla, K. Radacki, R. Shang, *Chem. Commun.* **2015**, *51*, 16569-16572; (e) H. Braunschweig, M. A. Celik, R. D. Dewhurst, K. Ferkinghoff, A. Hermann, J. O. C. Jimenez-Halla, T. Kramer, K. Radacki, R. Shang, E. Siedler, F. Weißenberger, C. Werner, *Chem. Eur. J.* **2016**, *22*, 11736-11744; (f) T. Cadenbach, C. Gemel, D. Zacher, R. A. Fischer, *Angew. Chem., Int. Ed.* **2008**, *47*, 3438-3441; (g) K. L. Mears, C. R. Stennett, E. K. Taskinen, C. E. Knapp, C. J. Carmalt, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2020**, *142*, 19874-19878; (h) R. Y. Kong, M. R. Crimmin, *Dalton Trans.* **2021**, *50*, 7810-7817; (i) A. Kempter, C. Gemel, R. A. Fischer, *Chem. Commun.* **2006**, 1551-1553; (j) A. Kempter, C. Gemel, R. A. Fischer, *Chem. Eur. J.* **2007**, *13*, 2990-3000; (k) N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667-2679.

[4] (a) R. C. Cammarota, L. J. Clouston, C. C. Lu, *Coord. Chem. Rev.* **2017**, *334*, 100-111; (b) J. Takaya, *Chem. Sci.* **2021**, *12*, 1964-1981; (c) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem., Int. Ed.* **2021**, *60*, 1702-1713; (d) K. Hobson, C. J. Carmalt, C. Bakewell, *Chem. Sci.* **2020**, *11*, 6942-6956; (e) M. Zhong, S. Sinhababu, H. W. Roesky, *Dalton Trans.* **2020**, *49*, 1351-1364; (f) P. Bag, C. Weetman, S. Inoue, *Angew. Chem., Int. Ed.* **2018**, *57*, 14394-14413; (g) R. J. Baker, C. Jones, *Coord. Chem. Rev.* **2005**, *249*,

1857-1869; (h) H. W. Roesky, S. S. Kumar, *Chem. Commun.* **2005**, 4027-4038; (i) Y. Wang, G. H. Robinson, *Organometallics* **2007**, *26*, 2-11; (j) P. J. Brothers, P. P. Power, in *Adv. Organomet. Chem., Vol. 39* (Eds.: F. Gordon, A. Stone, R. West), Academic Press, **1996**, pp. 1-69; (k) M. Batuecas, N. Gorgas, M. R. Crimmin, *Chem. Sci.* **2021**, *12*, 1993-2000.

[5] (a) S. Morisako, S. Watanabe, S. Ikemoto, S. Muratsugu, M. Tada, M. Yamashita, *Angew. Chem., Int. Ed.* **2019**, *58*, 15031-15035; (b) P. Bag, A. Porzelt, P. J. Altmann, S. Inoue, *J. Am. Chem. Soc.* **2017**, *139*, 14384-14387; (c) C. Weetman, P. Bag, T. Szilvási, C. Jandl, S. Inoue, *Angew. Chem., Int. Ed.* **2019**, *58*, 10961-10965; (d) T. Nakamura, K. Suzuki, M. Yamashita, *J. Am. Chem. Soc.* **2017**, *139*, 17763-17766; (e) R. J. Wright, M. Brynda, P. P. Power, *Angew. Chem., Int. Ed.* **2006**, *45*, 5953-5956; (f) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature* **2018**, *557*, 92-95; (g) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *J. Am. Chem. Soc.* **2019**, *141*, 11000-11003; (h) R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles, *Angew. Chem., Int. Ed.* **2019**, *58*, 1489-1493; (i) R. J. Schwamm, M. P. Coles, M. S. Hill, M. F. Mahon, C. L. McMullin, N. A. Rajabi, A. S. S. Wilson, *Angew. Chem., Int. Ed.* **2020**, *59*, 3928-3932; (j) K. Koshino, R. Kinjo, *J. Am. Chem. Soc.* **2020**, *142*, 9057-9062; (k) S. Grams, J. Eyselein, J. Langer, C. Färber, S. Harder, *Angew. Chem., Int. Ed.* **2020**, *59*, 15982-15986; (l) S. Kurumada, S. Takamori, M. Yamashita, *Nat. Chem.* **2020**, *12*, 36-39; (m) K. Nagata, T. Murosaki, T. Agou, T. Sasamori, T. Matsuo, N. Tokitoh, *Angew. Chem., Int. Ed.* **2016**, *55*, 12877-12880; (n) T. N. Hooper, M. Garçon, A. J. P. White, M. R. Crimmin, *Chem. Sci.* **2018**, *9*, 5435-5440; (o) F. Rekhroukh, W. Chen, R. K. Brown, A. J. P. White, M. R. Crimmin, *Chem. Sci.* **2020**, *11*, 7842-7849; (p) T. N. Hooper, R. K. Brown, F. Rekhroukh, M. Garçon, A. J. P. White, P. J. Costa, M. R. Crimmin, *Chem. Sci.* **2020**, *11*, 7850-7857; (q) K. Koshino, R. Kinjo, *Organometallics* **2020**, *39*, 4183-4186.

[6] (a) Y. Liu, J. Li, X. Ma, Z. Yang, H. W. Roesky, *Coord. Chem. Rev.* **2018**, *374*, 387-415; (b) B. Buchin, T. Steinke, C. Gemel, T. Cadenbach, R. A. Fischer, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2756-2762; (c) T. Steinke, C. Gemel, M. Winter, R. A. Fischer, *Chem. Eur. J.* **2005**, *11*, 1636-1646; (d) T. Steinke, M. Cokoja, C. Gemel, A. Kempter, A. Krapp, G. Frenking, U. Zenneck, R. A. Fischer, *Angew. Chem., Int. Ed.* **2005**, *44*, 2943-2946; (e) D. Weiss, T. Steinke, M. Winter, R. A. Fischer, N. Fröhlich, J. Uddin, G. Frenking, *Organometallics* **2000**, *19*, 4583-4588; (f) Q. Yu, A. Purath, A. Donchev, H. Schnöckel, *J. Organomet. Chem.* **1999**, *584*, 94-97; (g) J. Weiss, D. Stetzkamp, B. Nuber, R. A. Fischer, C. Boehme, G. Frenking, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 70-72; (h) M. T. Gamer, P. W. Roesky, S. N. Konchenko, P. Nava, R. Ahlrichs, *Angew. Chem., Int. Ed.* **2006**, *45*, 4447-4451; (i) S. G. Minasian, J. L. Krinsky, V. A. Williams, J. Arnold, *J. Am. Chem. Soc.* **2008**, *130*, 10086-10087; (j) S. G. Minasian, J. L. Krinsky, J. D. Rinehart, R. Copping, T. Tyliszczak, M. Janousch, D. K. Shuh, J. Arnold, *J. Am. Chem. Soc.* **2009**, *131*, 13767-13783.

[7] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 564-565.

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

[9] (a) M. M. Schulte, E. Herdtweck, G. Raudaschl-Sieber, R. A. Fischer, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 424-426; (b) R. A. Fischer, M. M. Schulte, J. Weiss, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S. F. Vyboishchikov, *J. Am. Chem. Soc.* **1998**, *120*, 1237-1248; (c) H. Fölsing, O. Segnitz, U. Bossek, K. Merz, M. Winter, R. A. Fischer, *J. Organomet. Chem.* **2000**, *606*, 132-140.

[10] (a) K. Nagata, T. Agou, N. Tokitoh, *Angew. Chem., Int. Ed.* **2014**, *53*, 3881-3884; (b) T. Agou, K. Nagata, N. Tokitoh, *Angew. Chem., Int. Ed.* **2013**, *52*, 10818-10821.

[11] (a) J. A. B. Abdalla, I. M. Riddlestone, J. Turner, P. A. Kaufman, R. Tirfoin, N. Phillips, S. Aldridge, *Chem. Eur. J.* **2014**, *20*, 17624-17634; (b) O. Ekkert, A. J. P. White, H. Toms, M. R. Crimmin, *Chem. Sci.* **2015**, *6*, 5617-5622.

[12] J. Hicks, A. Mansikkamäki, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nat. Chem.* **2019**, *11*, 237-241.

[13] H.-Y. Liu, R. J. Schwamm, M. S. Hill, M. F. Mahon, C. L. McMullin, N. A. Rajabi, *Angew. Chem., Int. Ed.* **2021**, *60*, 14390-14393.

[14] (a) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877-3923; (b) P. P. Power, *Organometallics* **2020**, *39*, 4127-4138; (c) D. L. Kays, *Chem. Soc. Rev.* **2016**, *45*, 1004-1018; (d) P. P. Power, *Nature* **2010**, *463*, 171-177.

[15] J. D. Queen, A. Lehmann, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* **2020**, *142*, 20554-20559.

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

[17] R. Nakano, R. Jazzar, G. Bertrand, *Nat. Chem.* **2018**, *10*, 1196-1200.

[18] (a) L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem* **2016**, *1*, 147-153; (b) F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* **2012**, *337*, 1526-1528.

[19] (a) F. Ortu, G. J. Moxey, A. J. Blake, W. Lewis, D. L. Kays, *Chem. Eur. J.* **2015**, *21*, 6949-6956; (b) A. Hinz, *Chem. Eur. J.* **2019**, *25*, 3267-3271; (c) A. Hinz, *Angew. Chem., Int. Ed.* **2020**, *59*, 19065-19069; (d) P. M. Chapple, S. Kahlal, J. Cartron, T. Roisnel, V. Dorcet, M. Cordier, J.-Y. Saillard, J.-F. Carpentier, Y. Sarazin, *Angew. Chem., Int. Ed.* **2020**, *59*, 9120-9126; (e) Q. Yu, L. Zhang, Y. He, J. Pan, H. Li, G.-q. Bian, X. Chen, G. Tan, *Chem. Commun.* **2021**, *57*, 9268-9271.

[20] Deposition Numbers 2105192 (1a), 2105193 (1b), 2105194 (2b), 2105195 (3), 2105196 (4), 2105197 (5), 2105198 (6) and 2105200 (8) contain the supplementary crystallographic data for this paper. These can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

[21] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186-197.

[22] (a) J. Li, X. Li, W. Huang, H. Hu, J. Zhang, C. Cui, *Chem. Eur. J.* **2012**, *18*, 15263-15266; (b) M. D. Anker, R. J. Schwamm, M. P. Coles, *Chem. Commun.* **2020**, *56*, 2288-2291; (c) A. Heilmann, J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem., Int. Ed.* **2020**, *59*, 4897-4901.

[23] M. A. Petrie, K. Ruhlandt-Senge, P. P. Power, *Inorg. Chem.* **1993**, *32*, 1135-1141.

[24] R. J. Wehmschulte, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 791-797.

[25] (a) P. Bissinger, H. Braunschweig, T. Kupfer, K. Radacki, *Organometallics* **2010**, *29*, 3987-3990; (b) M. Kawano, Y. Kobayashi, T. Ozeki, M. Fujita, *J. Am. Chem. Soc.* **2006**, *128*, 6558-6559.

[26] J. A. B. Abdalla, A. Caise, C. P. Sindlinger, R. Tirfoin, A. L. Thompson, A. J. Edwards, S. Aldridge, *Nat. Chem.* **2017**, *9*, 1256-1262.

[27] H. Braunschweig, I. Krummenacher, M.-A. Légaré, A. Matler, K. Radacki, Q. Ye, *J. Am. Chem. Soc.* **2017**, *139*, 1802-1805.

[28] M. M. Hansmann, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 15885-15888.

[29] E. Tomás-Mendivil, M. M. Hansmann, C. M. Weinstein, R. Jazzar, M. Melaimi, G. Bertrand, *J. Am. Chem. Soc.* **2017**, *139*, 7753-7756.

[30] P. W. Antoni, J. Reitz, M. M. Hansmann, *J. Am. Chem. Soc.* **2021**, *143*, 12878-12885.

[31] (a) L. Kong, Y. Li, R. Ganguly, D. Vidovic, R. Kinjo, *Angew. Chem., Int. Ed.* **2014**, *53*, 9280-9283; (b) L. Kong, R. Ganguly, Y. Li, R. Kinjo, *Chem. Sci.* **2015**, *6*, 2893-2902.

[32] S. R. Parmelee, N. P. Mankad, *Dalton Trans.* **2015**, *44*, 17007-17014.

[33] (a) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723-6753; (b) T. Dröge, F. Glorius, *Angew. Chem., Int. Ed.* **2010**, *49*, 6940-6952.

[34] (a) A. Michalak, M. Mitoraj, T. Ziegler, *J. Phy. Chem. A* **2008**, *112*, 1933-1939; (b) M. Mitoraj, A. Michalak, *J. Mol. Model.* **2008**, *14*, 681-687.

[35] (a) G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834-4843; (b) G. Knizia, J. E. M. N. Klein, *Angew. Chem., Int. Ed.* **2015**,

54, 5518-5522.
[36] C. McManus, J. Hicks, X. Cui, L. Zhao, G. Frenking, J. M. Goicoechea, S. Aldridge, *Chem. Sci.* **2021**, 10.1039/D1031SC04676D.
[37] K. Sugita, M. Yamashita, *Chem. Eur. J.* **2020**, *26*, 4520-4523.

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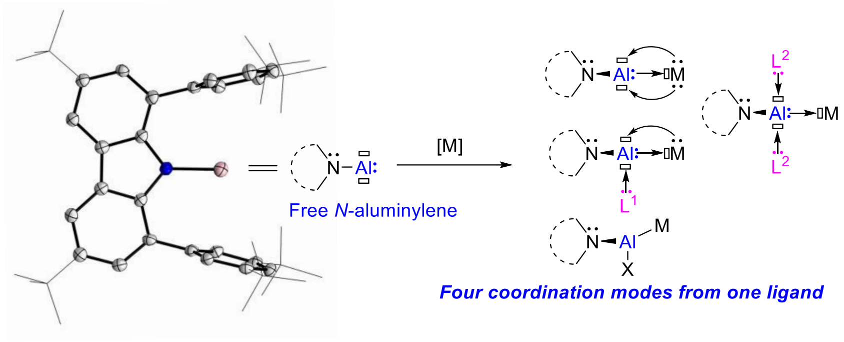

A crystalline carbazolylaluminylene with a monocoordinated aluminium atom featuring a lone pair of electrons and two vacant orbitals has been isolated at room temperature. The coordination behavior of this aluminylene towards transition metal centers is shown to afford a series of novel aluminylene and alumanyl complexes with diverse coordination modes in a one-step process.

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