

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

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Abstract: Aluminium based ligands have garnered tremendous interest in the past decades due to the fundamental significance of the structural and electronic properties as well as their applications in synthetic chemistry. 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 and is stable under an inert atmosphere. The coordination behavior of **2b** towards transition metal centers (Mn, W, Cr) is shown to afford a series of novel aluminylene complexes 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. 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. Further investigations of **2b** with IDippCuCl (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) showcase an unprecedented one-step aluminylene-alumanyl transformation leading to the facile synthesis of a rare terminal Cu-alumanyl complex. The electronic structures of such complexes and the mechanism of the unusual aluminylene-alumanyl transformation are investigated through density functional theory (DFT) calculations.

Introduction

The advances in transition metal catalysis have been of paramount interest in the past decades.¹ For these applications ancillary ligands play essential roles in tuning the reactivity, selectivity, and stability of transition metal catalysts.² It is well-known that L-type ligands can not only donate electron density to transition metal centers but also accept filled d-electrons from the metal centers via π -backdonation.^{2a, 2b, 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**. Whereas the former three types of ligations, exemplified by carbene (type **I**),⁴ carbyne (type **II**)⁵ and carbodicarbene (type **III**)⁶ complexes, are well-established, examples of the last case **IV** are seldom encountered.⁷ There are only a handful of reports describing stable mono-base-stabilized borylene/gallylene transition metal complexes featuring a typical coordination mode of **IV**⁷ as well as some transition metal complexes with an E–M (E = Al, Ga; M = transition metals) dative bonding resulting from the species HC[(CMe)(NDipp)]₂E (Dipp = 2,6-diisopropylphenyl), in which one of the extreme bonding situations can arguably belong to the type **IV**.⁸

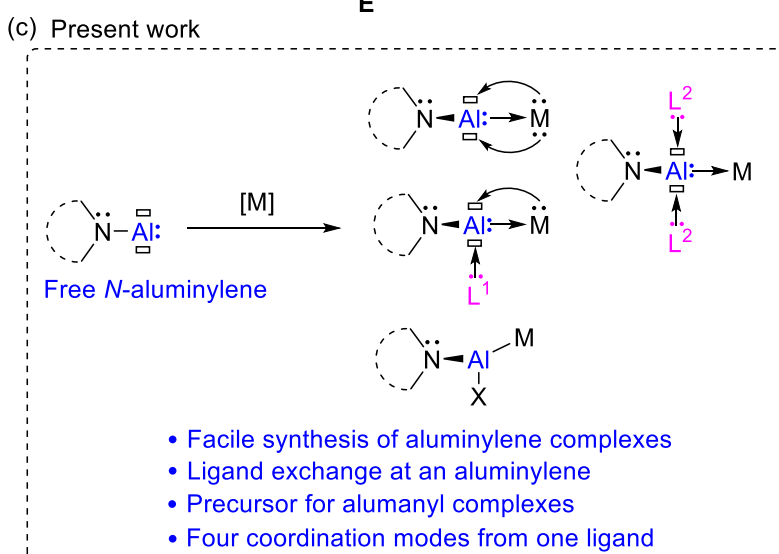
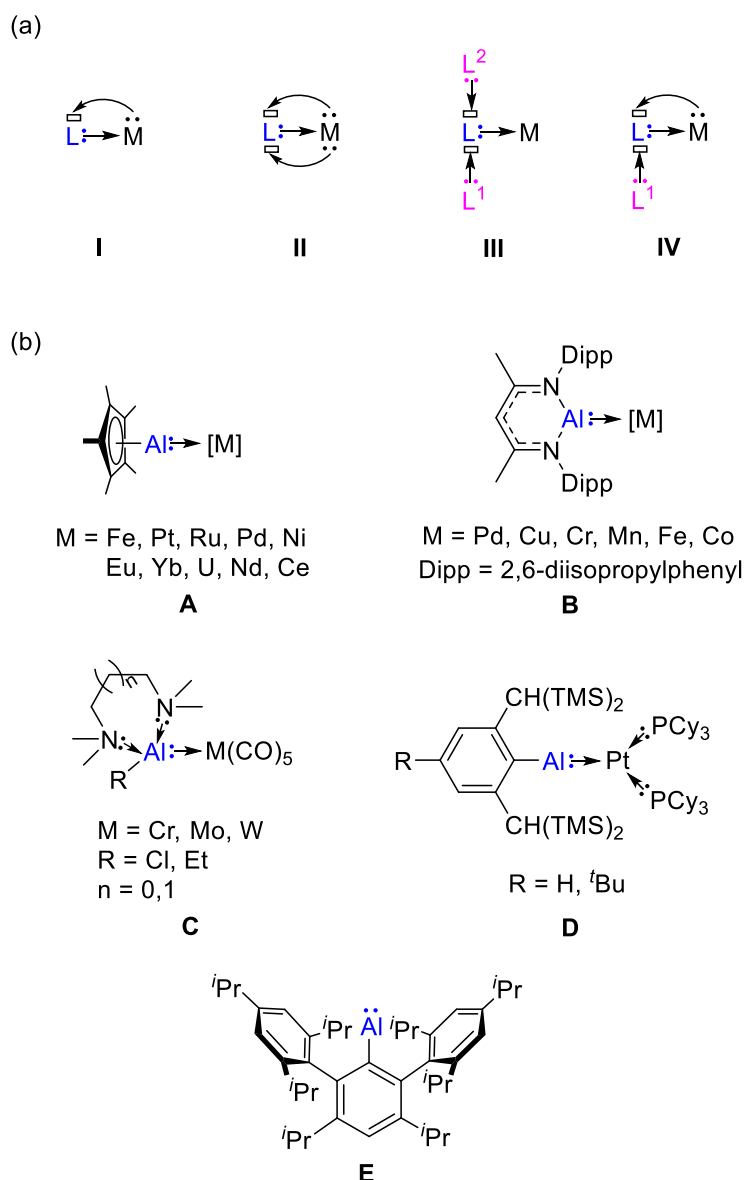


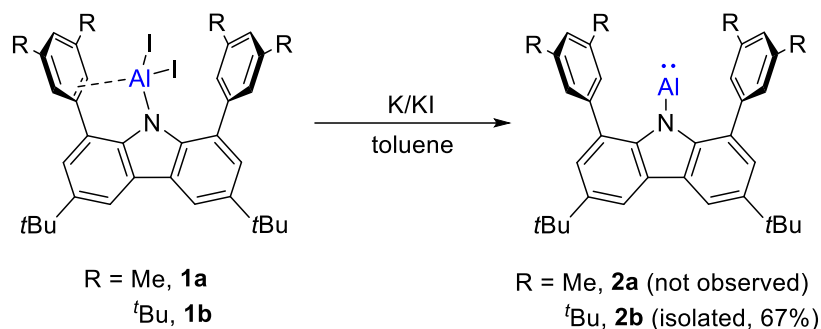
Figure 1. (a) Coordination modes of terminal L-type ligands for transition metals. (b) Representative Al(I) transition metal complexes. (c) Present work.

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.⁹ The electropositive nature of aluminium ($\chi = 1.61$) makes such ligands highly electron-releasing, thereby exhibiting unusual bonding and reactivities.¹⁰ In the case of the terminal L-type Al ligands, representative examples include transition metal complexes **A**¹¹ and **B**^{8a-d} derived from Schnöckel's (Cp*Al)₄¹² and Roesky's HC[(CMe)(NDipp)]₂Al,¹³ respectively (Figure 1b). It was independently demonstrated by the Power group^{8a} and Crimmin group^{8b} that unprecedented low-valent molecular complexes HC[(CMe)(NDipp)]₂AlCu[(NMes)(CR)]₂CH (R= Me, CF₃) feature an unsupported dispersion-enhanced Al–Cu bond. Furthermore, in the late 1990s, the aluminylene complexes **C** of type **III** were disclosed by Fischer, Frenking et al.¹⁴ 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(PCy₃)₂.¹⁵ The Al ligand in **D** reveals donor-acceptor interactions with Pt akin to the bonding mode of type **II**. 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 ^tBu₃PAuAl(NON) (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) containing an unprecedented nucleophilic Au center,¹⁶ 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} = (CH₂SiMe₂NDipp)₂) with ambiphilic Cu–Al bonding.¹⁷

Taking advantage of sterically demanding terphenyl ligands,¹⁸ Power, Tuononen et al. very recently disclosed the first and sole example of a room-temperature-stable monomeric aluminylene (alanediy) :AlAr^{*i*Pr₈} (Ar^{*i*Pr₈} = C₆H-2,6-(C₆H₂-2,4,6-*i*Pr₃)₂-3,5-*i*Pr₂) (**E**) (Figure 1b) via a reduction reaction of AlI₂Ar^{*i*Pr₈} with 5% w/w Na/NaCl.¹⁹ This breakthrough allowed further explorations into unusual/unprecedented patterns of reactivity of :AlAr^{*i*Pr₈} toward hydrogen¹⁹ and organic azides,²⁰ 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 substitutes, such as amino,²¹ phosphino²² or carbazolyl,²³ should enhance the stabilization of the inherent electron deficiency of free aluminylenes due to the possible π -donation of a N 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 carbazolidate with AlI₃, and their structures were confirmed by single crystal X-ray diffraction analysis (Figure S32). 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**.

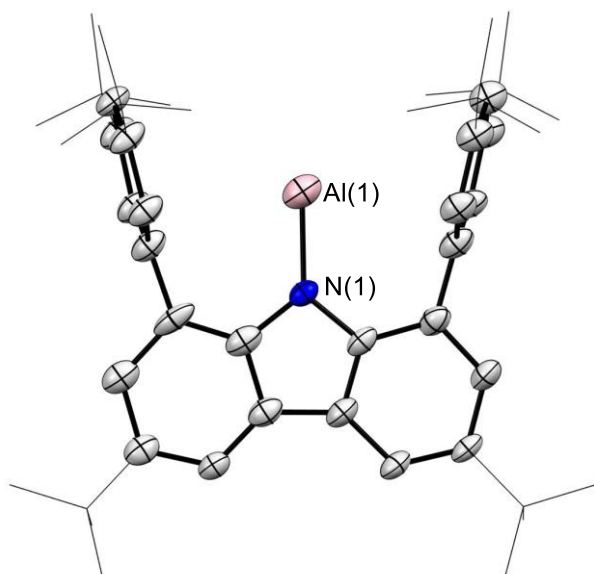


Figure 2. Solid-state structure of **2b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Single crystals of **2b** suitable for X-ray diffraction were obtained from slow evaporation of a concentrated *n*-hexane solution at room temperature within 12h. The X-ray diffraction study revealed the N(1) atom adopts a planar environment (sum of angles: 359.5°) (Figure 2). The Al(1)–N(1) bond length (1.903(4) Å) is slightly shorter than the Pyykkö standard value for an Al–N single bond (1.970 Å)²⁴ whereas much longer than those of typical Al=N double bonds ((1.705–1.725 Å) in terminal aluminum imides,²⁵ 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: 3.023 Å), which is similar to that observed for Power’s :AlAr^{*i*Pr}.¹⁹ Infrared spectroscopic studies of **2b** show no evidences for Al–H stretching frequencies (Figure S1).

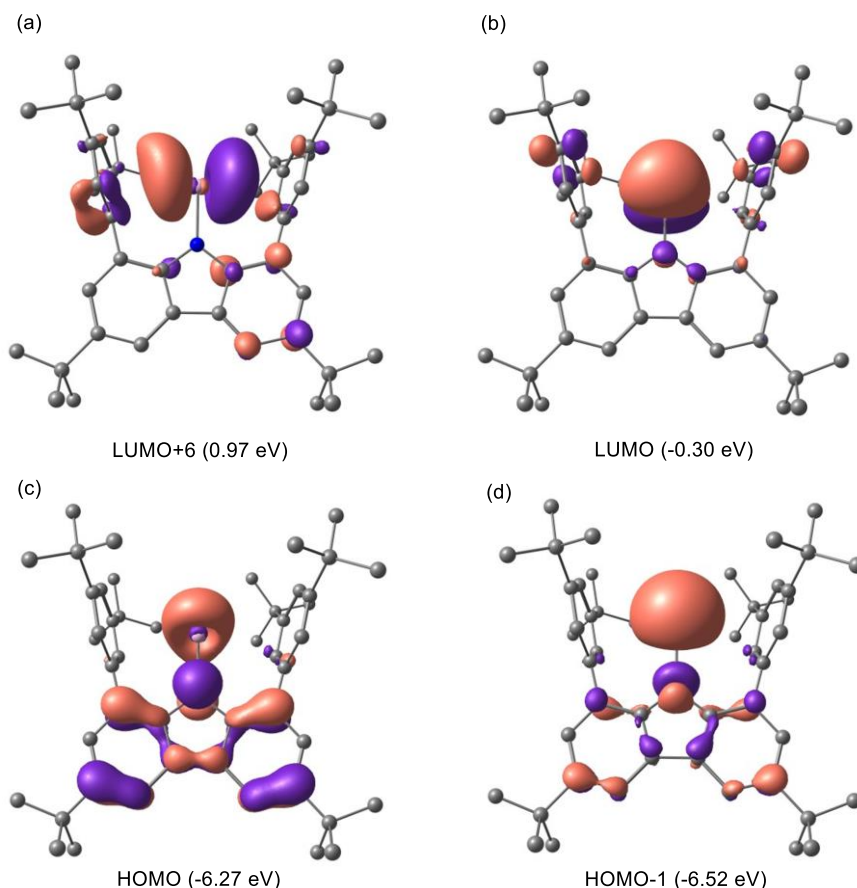
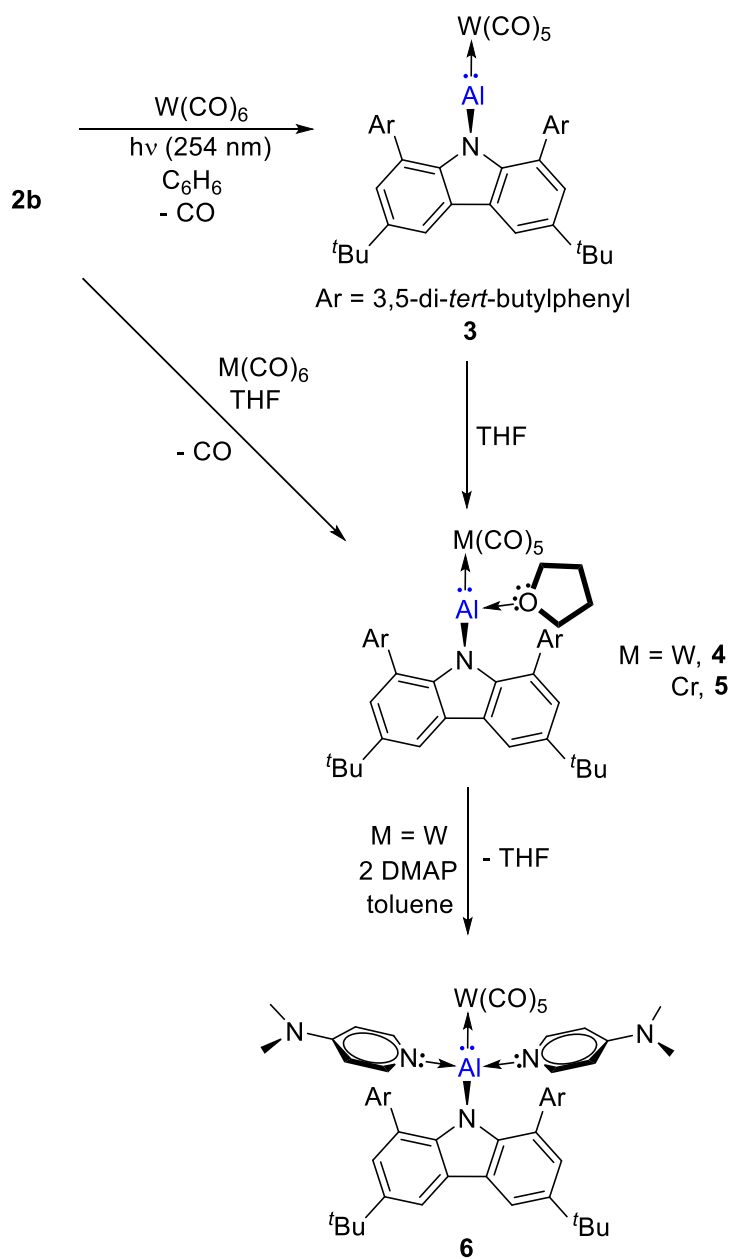


Figure 3. (a) LUMO+6 of **2b**. (b) LUMO of **2b**. (c) HOMO of **2b**. (d) HOMO-1 of **2b**. Isovalue = 0.04.

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 80°C for 10h 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 S31).

The amphiphilic nature of **2b** is unambiguously demonstrated by its frontier molecular orbitals (M06-2X/def2-SVP) (Figure 3). The LUMO+6 and LUMO are 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 mainly involves the Al nonbonding lone pair (Figures 3c and 3d). These observations are different from those calculated for $:\text{AlAr}^{\text{Pr}8}$,¹⁹ 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 due to the electropositive nature of Al ($\chi = 1.61$) (Figure S34).

Isolation of Mononuclear 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 12h. However, UV lamp (254 nm) exposure is known to facilitate the removal of CO in metal carbonyls,²⁶ so the solution was irradiated for 24h which cleanly furnished new species **3** (Scheme 2). After workup, **3** was isolated as a yellow solid in 85%. The 1H NMR spectrum of **3** shows two singlets for the tBu groups of 3,5-di-*tert*-butylphenyl substitutes at 1.35 and 1.43 ppm, indicating the asymmetric nature with respect to the carbazoyl plane. Two singlet carbonyl resonances at 197.5 and 198.8 ppm are observed via a ^{13}C NMR spectroscopic study.



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

Slow evaporation of a concentrated hexane solution of **3** at room temperature resulted in X-ray quality yellow crystals after 5 hours. 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),^{14b} 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)°),¹⁵ the bond angle of N(1)–Al(1)–W(1) (147.31(10)°) 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.¹⁵

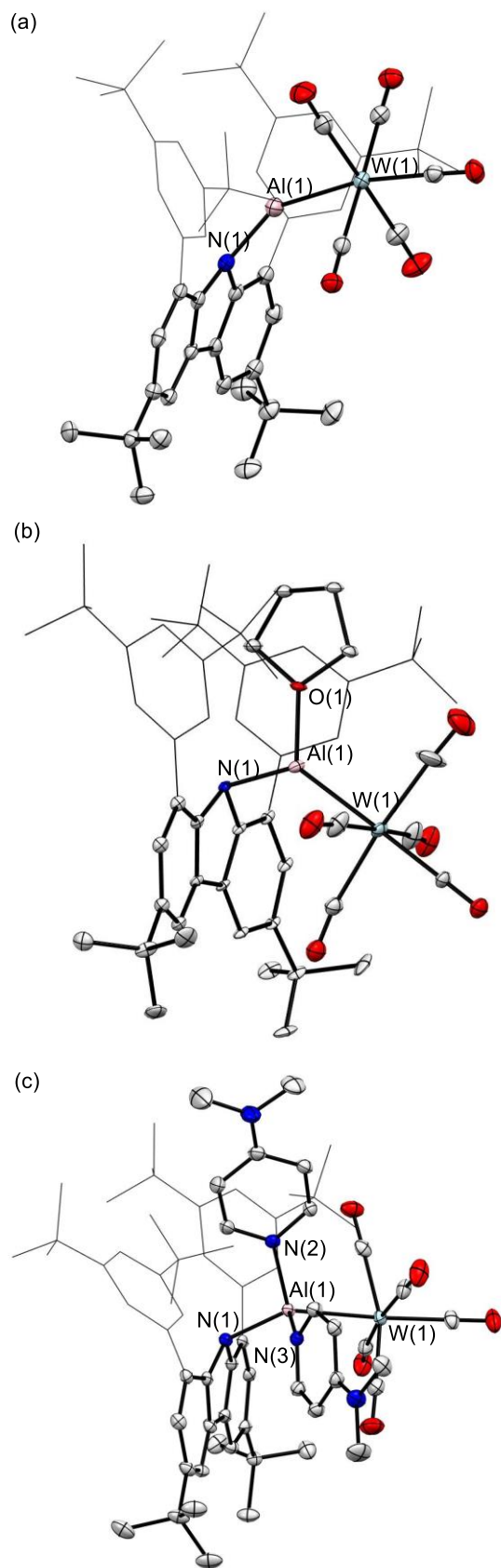


Figure 4. Solid-state structures of **3** (a) and **4** (b) and **6** (c). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

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 62% 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 1H NMR spectra of 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 S35). 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: 311.7° (**4**), 317.0° (**5**)), and the Al(1)–N(1) bonds (1.876(11) (**4**), 1.884(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 1.836(10) (**4**) or 1.852(3) Å (**5**), thereby compensating the electron deficiency of Al. The bond lengths of Al(1)–W(1) (2.603(4) Å) and Al(1)–Cr(1) (2.409(1) 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.^{14b} These imply the presence of the π -backdonation from W/Cr to Al. The angles of N(1)–Al(1)–W(1) ($131.8(4)^\circ$) and N(1)–Al(1)–Cr(1) ($132.3(1)^\circ$) 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 ($121.4(1)^\circ$) and (TMPDA)Al(Cl)Cr(CO)₅ ($123.63(5)^\circ$).^{14b} 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, 7a, 7b} In addition, the coordination behavior of free one-coordinate aluminylenes toward transition metals is hitherto unknown.^{8a-d, 9-10, 10d, 19-20} 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 4.5 kcal/mol, 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 1H 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** (2.603(4) Å), and slightly longer than that in (TMEDA)Al(Et)W(CO)₅ (2.670(1) Å).^{14b} 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).^{8b, 14b, 31}

The electronic properties of the aluminylene ligands in **3**, **4** and **6** were next established from the carbonyl stretching frequencies (ν_{CO}).³² With respect to the number of ligands at Al in the series N-Al(L)_nW(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} 2060.2, 1973.5 and 1922.1 cm⁻¹) indicative of reduced electron releasing ability of **3** compared to **4** (ν_{CO} 2045.7, 1957.9 and 1897.3 cm⁻¹) and **6** (ν_{CO} 2014.7, 1915.9 and 1854.2 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)³³ calculations and intrinsic bond orbital (IBO)³⁴ investigations were carried out. The IBO method is proven to give an exact representation of any Kohn–Sham DFT wave function.³⁴ Examinations 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, 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 are dominant between Al and W with -68.1, -71.1 and -92.3 kcal/mol for **3**, **4** and **6**, respectively (Figure S36). The Al-to-W σ -donation (**3**: -49.5 kcal/mol; **4**: -54.5 kcal/mol) coupled with the W-to-Al π -backdonation (**3**: -12.8 kcal/mol; **4**: -6.0 kcal/mol) play major roles in the Al–W bonding in **3** and **4**, whereas the Al–W bonding in **6** is mainly attributed to the Al-to-W σ -donation (-75.2 kcal/mol).

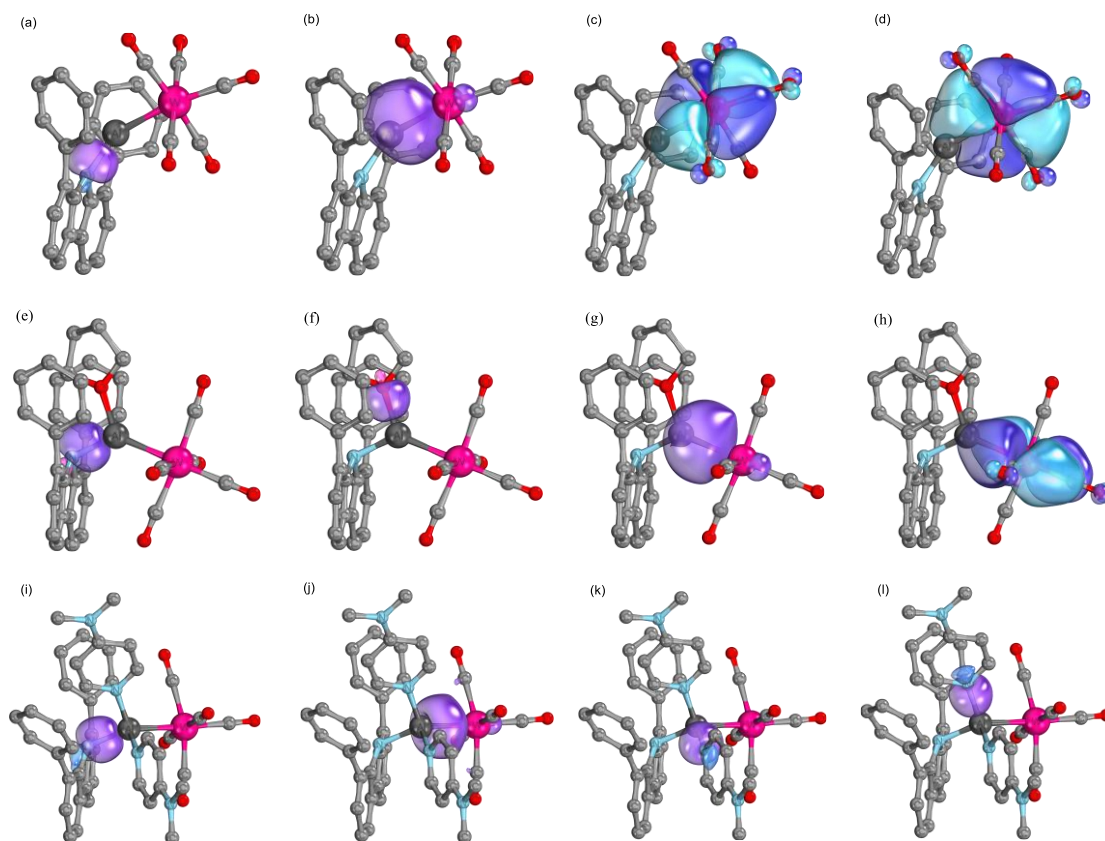
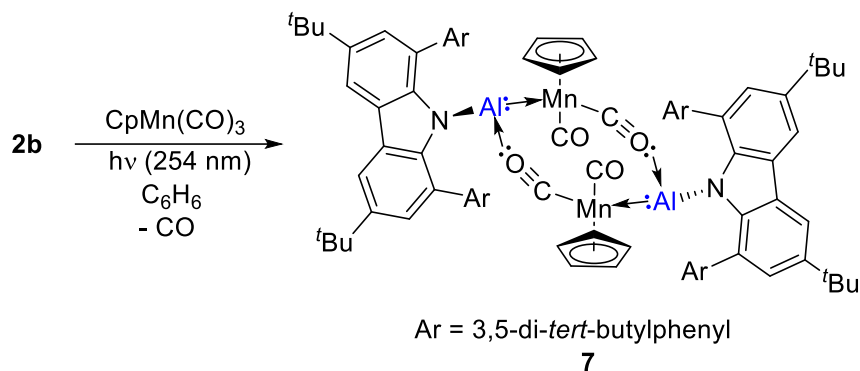


Figure 5. Selected IBOs of **3** (a-d), **4** (e-h) and **6** (i-l). Hydrogen atoms and ^tBu groups are omitted for clarity.

Isolation of a Dinuclear Aluminylene Complex. While an unidentified complicated mixture was generated if a THF solution of **2b** with an equal molar portion of $\text{CpMn}(\text{CO})_3$ was irradiated, the analogous irradiation of the benzene solution for 8h at room temperature cleanly furnished a new species **7** (Scheme 3). After workup, **7** was isolated as a yellowish powder in 71%. The solid-state structure of **7** is elucidated by crystallographic investigations to be a centrosymmetric dimer with a distorted eight-membered $\text{Mn}_2\text{Al}_2\text{C}_2\text{O}_2$ ring, featuring two Mn-aluminylene complexes held together via two bridging CO molecules (Figure 6). The Al(1) is in a planar environment with the sum of angles at 360.0° . The bond lengths of Al(1)–Mn(1) and Al(1)–O(2A) are 2.271(1) and 1.862(2) Å, respectively. The terminal C(1)–O(1) bond length (1.168(5) Å) is considerably shorter than that of the bridging C(2)–O(2) (1.226(4) Å). Analogous to **4** and **5**, the aluminylene ligand in **7** serves as σ -donor, σ -acceptor and π -acceptor. Species **7** represents a rare example of dinuclear transition metal-aluminylene complexes,^{8b} as well as the first example of such dinuclear complexes with a tricoordinate aluminylene.



Scheme 3. Synthesis of **7**.

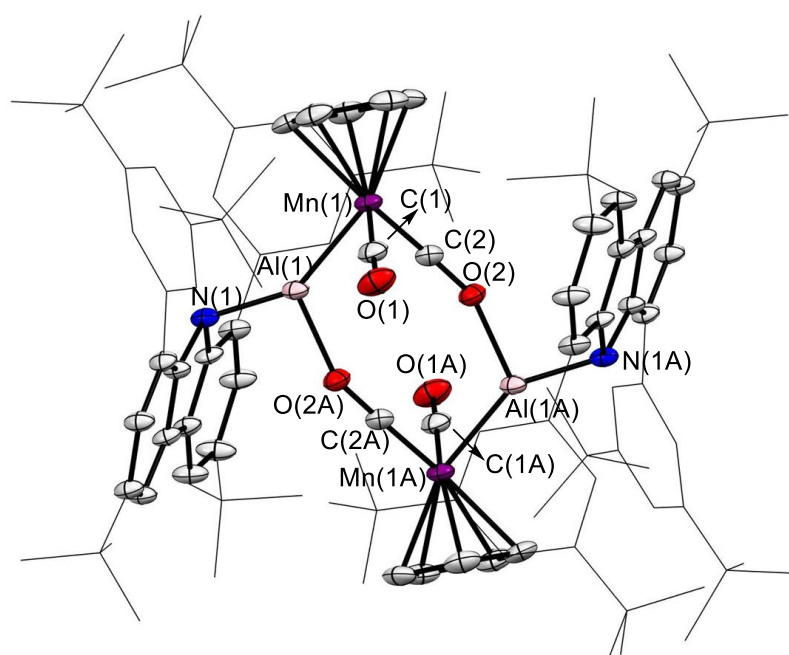
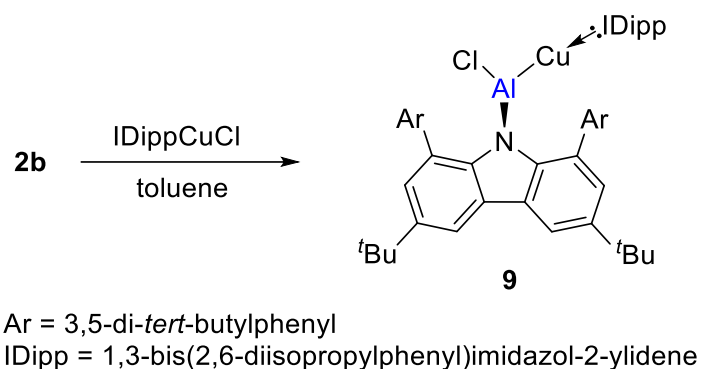


Figure 6. Solid-state structure of **7**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Isolation of an Alumannyl Complex. Further reactivity explorations reveal that **2b** is highly reducing and can readily react with (THF)AuCl (THT = tetrahydrothiophene) to afford the carbazolyl-substituted aluminium dichloride **8** as well as Au mirror. Repeated crystallization attempts of **8** yielded crystals of poor quality, nonetheless preliminary X-ray studies confirmed its formulation (Figure S33). In a similar vein, upon mixing **2b** with IDippCuCl (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in THF at ambient temperature, a white solid of the Cu-umannyl complex **9** was isolated in 71% (Scheme 4).

The solid-state structure of **9** exhibits a planar Al(1) center with the sum of angles at 359.9° (Figure 7). The Al(1)–Cu(1) bond length is 2.346(1) Å, which is comparable to that seen for LCuAl(SiN^{Dipp}) (L = N,N'-diisopropyl-4,5-dimethyl-2-ylidene, 2.3450(6) Å)¹⁷ whereas slightly longer with respect to that of HC[(CMe)(NDipp)]₂AlCu[(NMe)(CMe)]₂CH (2.3011(7) Å).^{8a} To date, the structural

authentication of terminal Cu-alumanyl complexes is limited to $\text{LCuAl}(\text{SiN}^{\text{Dipp}})$ ($\text{L} = \text{N,N}'$ -diisopropyl-4,5-dimethyl-2-ylidene and (1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene) that were very recently isolated by Hill, McMullin, and co-workers.¹⁷ These species were formed by a salt metathesis reaction of $\text{K}_2[\text{Al}(\text{SiN}^{\text{Dipp}})]_2$ with LCuCl . 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.^{9c, 9d, 16-17, 35}



Scheme 4. Synthesis of **9**.

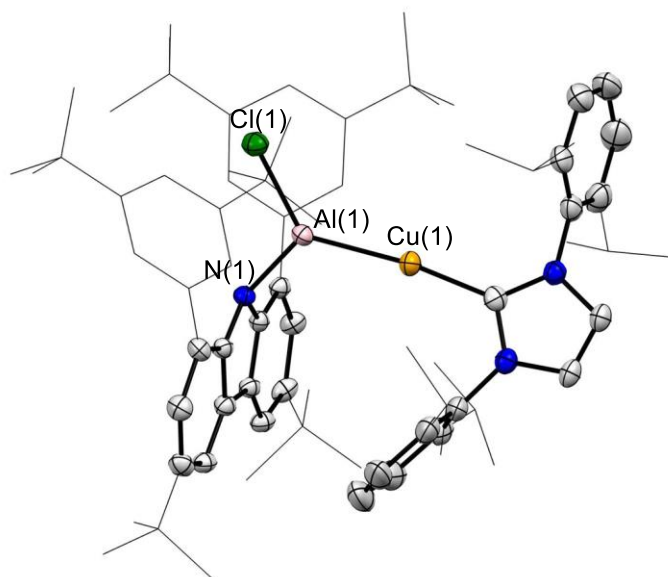


Figure 7. Solid-state structure of **9**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Mechanistic Investigations. The mechanism of the formation of **9** was probed via DFT calculations (SMD-M06-2X/def2-TZVP//M06-2X/def2-SVP) (Figure 8). The reaction begins with the approach of the alumynylene **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** (11.3 kcal/mol) in a barrier-less process (Figure S37). Subsequent oxidative addition of the Cu–Cl bond to Al proceeds via **TS1**, with the energy barrier of 13.4 kcal/mol ($\text{2b} \rightarrow \text{TS1}$), to yield the stable product **9** (-4.8 kcal/mol). Concurrent with this is the increase of the formal oxidation state of Al from +1 to +3.

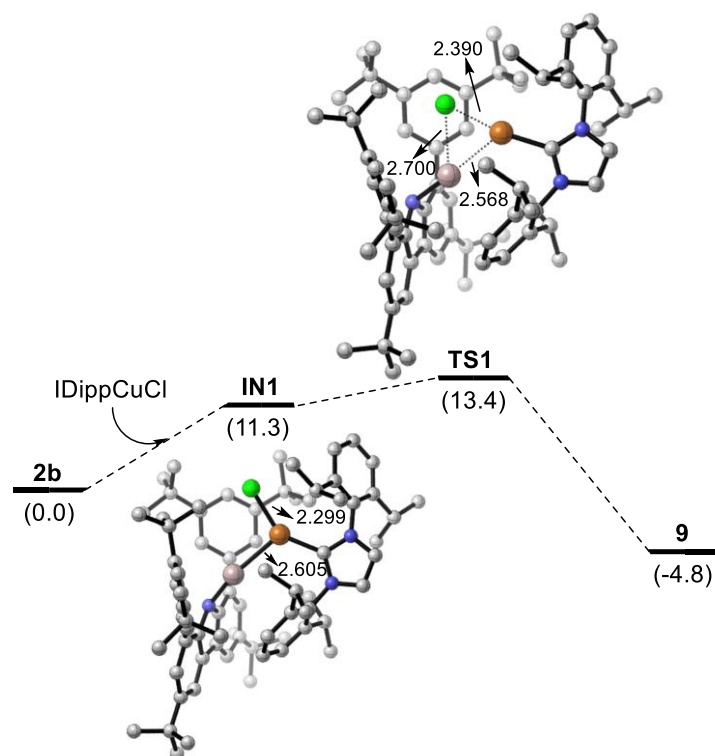


Figure 8. Free energy profile for the formation of **9**. Energies are given in kcal/mol.

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, Mn). This allows the isolation of a series of unprecedented aluminylene complexes **3-7**. 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**, **5** and **7**, 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 **9**. Considering DFT calculations, the mechanism leading to **9** 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.

ASSOCIATED CONTENT

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Notes

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