# Synthesis and Structure of a Monomeric Aluminum(I) Compound [{HC(CMeNAr)$_2$}Al] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$): A Stable Aluminum Analogue of a Carbene**

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*Dedicated to Professor Francois Mathey*

There is a widespread interest in the chemistry of monovalent Group 13 species from several perspectives including synthetic methodology, structure, and theoretical implications.[1, 2] Generally these unique species can be obtained by using bulky protecting groups and form various aggregates in the solid state. Compared to the chemistry of Al$^{III}$, that of low-valent aluminum compounds is much less developed. To the best of our knowledge, there are only a handful of stable neutral Al$^{I}$ organometallic compounds, namely [(Cp*Al)$_4$] (Cp* = C$_5$Me$_5$),[3a, 3b] [{(CMe$_3$)$_3$SiAl}$_4$],[3c] [{(SiMe$_3$)$_3$CAl}$_4$],[4a] [Cp$^*_3$Al$_3$AlN(SiMe$_3$)$_2$],[4b] and [{(SiMe$_3$)$_3$SiAl}$_4$],[4c] that have been structurally characterized. These compounds have tetrahedral arrangements in the solid state. The compound [(Cp*Al)$_4$] has been reported to dissociate in solution at high temperature and in the gas phase to give monomeric Cp*Al.[5] At present, however, there are no structures known of monomeric Al$^{I}$ species in the condensed phase. Herein, we report on the use of the very crowded bidentate *β*-diketoiminate ligand HC(CMeNAr)$_2^-$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) for the preparation of the monomeric Al$^{I}$ compound [{HC(CMeNAr)$_2$}Al], a stable aluminum analogue of a carbene.

We have been particularly interested in using bulky bi- and tridentate ligands in aluminum chemistry[6] in the hope of generating unusual species. For example, we recently isolated the first stable Group 13 compound containing the SeH ligand (that is, [{HC(CMeNAr)$_2$}Al(SeH)$_2$]) and its condensation product by using the bulky protecting group HC(CMeNAr)$_2$.[6c] As a continuation of our studies we have focussed on exploring aluminum chemistry further with this ligand, especially with regard to the preparation of low-aggregated Al$^{I}$ compounds by reduction of the corresponding dihalides. Recent work in our laboratory has shown that organometallic aluminum diiodides can be more easily reduced than the related dibromides and dichlorides.[7] Aluminum diiodide compounds can be easily obtained by reaction of the corresponding dimethyl derivatives with I$_2$.[6a] Thus, the reaction of the dimethyl compound [{HC(CMeNAr)$_2$}AlMe$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)[8] with two equivalents of I$_2$ proceeds under mild conditions to afford the diiodide [{HC(CMeNAr)$_2$}AlI$_2$] (**1**) in high yield [Eq. (1)].

$$[\{HC(CMeNAr)_2\}AlMe_2] + 2\,I_2 \longrightarrow \underset{\mathbf{1}}{[\{HC(CMeNAr)_2\}AlI_2]} + 2\,MeI \qquad (1)$$

Compound **1** forms essentially colorless crystals. It has been characterized by NMR spectroscopy, EI mass spectrometry, and elemental analysis. The EI mass spectrum shows the highest peak at [$M^+ - I$]. The formation of **1** was finally confirmed by an X-ray single-crystal analysis.[6e]

Reduction of **1** with potassium for three days afforded the first example of a room-temperature stable monomeric Al$^{I}$ species [{HC(CMeNAr)$_2$}Al] (**2**) in about 21% yield [Eq. (2)].

$$\underset{\mathbf{1}}{[\{HC(CMeNAr)_2\}AlI_2]} + 2\,K \longrightarrow \underset{\mathbf{2}}{[\{HC(CMeNAr)_2\}Al]} + 2\,KI \qquad (2)$$

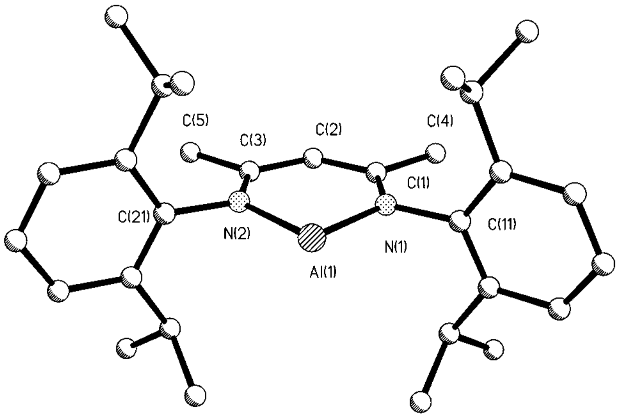

Figure 1. Molecular structure of **2** in the crystal. The hydrogen atoms have been omitted for clarity. Selected bond lengths [pm] and angles [°]: Al(1)-N(1) 195.7(2), Al(1)-N(2) 195.7(2), N(1)-C(1) 134.0(3), N(2)-C(3) 134.2(3), C(1)-C(2) 139.1(3), C(2)-C(3) 139.1(3); N(1)-Al(1)-N(2) 89.86(8), C(1)-N(1)-Al(1) 128.87(15), C(1)-C(2)-C(3) 126.8(2), N(1)-C(1)-C(2) 122.8 (2).

Compound **2**, crystallized as red crystals from toluene, is soluble in benzene and toluene but only sparingly soluble in *n*-hexane and *n*-heptane. It is stable at room temperature under an inert atmosphere, however, significant decomposition can be observed above 150 °C. Compound **2** has been characterized by $^1$H and $^{13}$C NMR spectroscopy, EI-mass spectrometry, elemental analysis, and X-ray single-crystal analysis. The NMR spectra of **2** give the expected patterns, which are different from those of the reported colorless dihydride [{HC(CMeNAr)$_2$}AlH$_2$].[6c] Single crystals of **2** suitable for X-ray analysis were obtained from toluene at −30 °C. Compound **2** crystallizes in the monoclinic space group *P*2$_1$/*n*,[10] and its structure is shown in Figure 1. It consists of well-separated [{HC(CMeNAr)$_2$}Al] monomers. There are no close contacts between Al and other atoms as indicated by the closest distance of Al···H (*i*Pr, 314.2 pm). As expected, the Al–N bond lengths (195.7(2) pm) are longer than those of the Al$^{III}$ compounds [{HC(CMeNAr)$_2$}AlMe$_2$] (av 192.2 pm) and [{HC(CMeNAr)$_2$}Al(SeH)$_2$] (av 189.9 pm). A similar lengthening has been noted in [In(2,6-Trip$_2$C$_6$H$_3$)] (Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$) whose In–C distance is about 10 pm longer than that of the corresponding In$^{III}$ derivative.[11] Similarly, the In–N distance in monomeric In$^{I}$ tripyrazolylborates may be as much as 20 pm longer than those in related In$^{III}$ derivatives.[12] Furthermore the N-Al-N angle (89.86(8)°) in **2** is more

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acute than those of [{HC(CMeNAr)$_2$}AlMe$_2$] (96.18(9)°) and [{HC(CMeNAr)$_2$}Al(SeH)$_2$] (97.1(4)°). The lengthening of the N–Al bonds and the nearly perpendicular N-Al-N angle indicate that two 3p orbitals on the aluminum center are essentially involved in the bonding to the two nitrogen atoms. It has been argued that Al–N bonds in aluminum(III) amide derivatives are largely ionic, which usually leads to a relatively short Al–N distance due to the Lewis acidic Al$^{III}$ centers.[9] The lengthening of the Al–N bonds in **2** also indicates that these bonds are more covalent than those of the Al$^{III}$ derivatives and the Al$^{I}$ center is much less acidic. It is noteworthy that in **2** the Al atom and the ligand backbone (N-C-C-C-N) form an essentially planar six-membered ring, which is in contrast to the Al$^{III}$ compounds [{HC(CMeNAr)$_2$}-AlMe$_2$] and [{HC(CMeNAr)$_2$}Al(SeH)$_2$], in which the Al atoms are positioned out of the planar ligand backbone.

A further notable aspect of the structure of **2** is the coordination number of two at the Al center. Compounds with three- and four-coordinate aluminum centers are well known,[13] however, there are no compounds reported with two-coordinate aluminum atoms. The unique two-coordinate nature of the Al atom in **2** is undoubtedly due to the protection afforded by the Ar groups and the presence of a nonbonded lone pair of electrons at the Al atom.

A preliminary insight into the peculiarities of the aluminum cycle is gained from ab initio calculations,[14] by analyzing the Laplacian of electronic density[15] within the plane (see Figure 2). First of all, it is noteworthy that there exists a lone pair of electrons[16] accommodated on the metal atom and arranged outside of the cycle in a quasi-trigonal-planar manner with the two Al–N bonds around the Al atom. This allows one to argue that the electrons originating from an s$^2$ configuration of the Al$^{I}$ center are stereochemically active, leading to an sp-like hybrid. In this conjecture, the "off-cycle" side of the aluminum(I) atom can be considered as a Lewis base. At the same time, the charge depletion close to the Al atom in the semiplane of the cycle can be described as Lewis acid type behavior.

In summary, we have prepared and fully characterized the first example of a monomeric Al$^{I}$ compound. The existence of a nonbonded lone pair of electrons at the aluminum center indicates a singlet carbene character of the aluminum atom. The other reported Group 13 carbene is anionic ([CHN(*t*Bu)]$_2$Ga$^-$,[17]), while **2** is neutral. Compound **2** could be used in carbene-type reactions and as a Lewis base as well as a reducing reagent, which may have broad and interesting chemistry. Presently we are involved in the reactions to study the electronic equivalence of **2** for CO in metal carbonyl complexes.

## *Experimetal Section*

All operations were performed under an argon atmosphere using Schlenk line techniques.

**1**: Toluene (60 mL) was added to a mixture of [{HC(CMeNAr)$_2$}AlMe$_2$] (4.74 g, 10 mmol) and I$_2$ (5.08 g, 20 mmol) at room temperature. The deep red solution was stirred for three days after which it developed into a slightly brown-yellow solution. The solution was concentrated (ca. 20 mL) and stored at $-30$°C in a freezer overnight to afford slightly yellow crystals of **1** (5.8 g, 83%). M.p. 251–252°C; $^1$H NMR (C$_6$D$_6$): $\delta = 7.11$ (m, 6H; Ph), 5.05 (s, 1H; $\gamma$-CH), 3.58 (sept, 4H, $J = 6.75$ Hz; C*H*Me$_2$), 1.49(s, 6H; Me), 1.43 (d, 12H, $J = 6.80$ Hz; CH*Me*$_2$), 1.08 (d, 12H, $J = 6.80$ Hz; CH*Me*$_2$); $^{13}$C NMR (C$_6$D$_6$): $\delta = 172.5$ (CN), 144.9, 138.9, 125.1 (Ph), 100.4 ($\gamma$-C), 29.2 (*C*HMe$_2$), 26.6 (CH*Me*$_2$), 24.5(CH*Me*$_2$), 24.3 (Me); $^{27}$Al NMR (C$_6$D$_6$): $\delta = 83.2$ ($\nu_{1/2} = 620$ Hz); EI-MS: *m/z* (%): 571 (100%, [*M* − I]$^+$).

**2**: A solution of **1** (2.08 g, 3.0 mmol) in toluene (30 mL) was added to a suspension of finely divided potassium (0.25 g, 6.4 mmol) in toluene (10 mL) at room temperature. The mixture was vigorously stirred at room temperature for three days. The solution developed an orange-red color and all the potassium was consumed. The solution was filtered, and the orange-red filtrate was concentrated to about 5 mL. On standing overnight at $-30$°C the solution afforded X-ray quality red crystals of **2** (0.28 g, 21%). Further products in the solution could not be characterized. M.p. >150°C (decomp); $^1$H NMR (C$_6$D$_6$): $\delta = 7.16$ (m, 6H; Ph), 5.18 (s, 1H; $\gamma$-CH), 3.16 (sept, 4H, $J = 6.80$ Hz; C*H*Me$_2$), 1.65 (s, 6H; Me), 1.38 (d, 12H, $J = 6.80$ Hz; CH*Me*$_2$), 1.13 (d, 12H, $J = 6.80$ Hz; CH*Me*$_2$); $^{13}$C NMR (C$_6$D$_6$): $\delta = 165.3$ (CN), 143.7, 142.3, 124.2 (Ph), 100.9 ($\gamma$-C), 29.0 (*C*HMe$_2$), 25.1 (CH*Me*$_2$), 23.9 (CH*Me*$_2$), 23.8(Me); $^{27}$Al NMR (C$_6$D$_6$): could not be observed; EI-MS: *m/z* (%): 444 (12, [*M*$^+$]), 429 (100, [*M* − Me]$^+$); elemental analysis (%) calcd for C$_{29}$H$_{41}$AlN$_2$ (444.62): C 78.3, H 9.3, N 6.3; found: C 77.9, H 9,7, N 6.3.

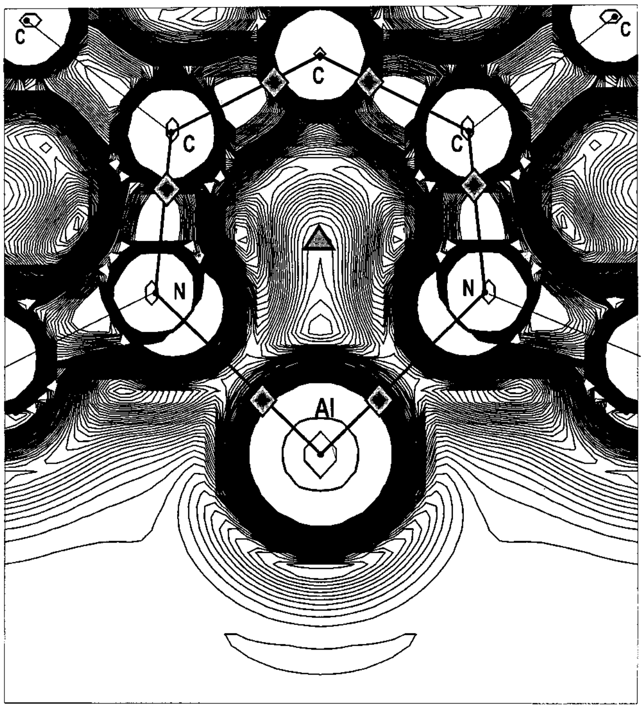

Figure 2. Contours from values of the Laplacian of electronic density ($\nabla^2\rho$) in the plane of the heterocycle of the title compound. The dark contours (areas with $\nabla^2\rho < 0$), which denote the sites of electron density accumulation, indicate the locations of the lone pair of electrons at the Al$^{I}$ center and the deformed valence shells of the C and N atoms in the molecule. The light contours (areas with $\nabla^2\rho > 0$) denote the electron deficiency effects; those around the Al$^{I}$ center in the direction of the cycle are remarkable. The diamonds (◆) posted on the interatomic axes show the $(3,-1)$ type of critical points, which verifies the chemical bonding, while the triangle in the center (△) denotes the $(3,+1)$ type of critical points, a quantum measure of the cyclic structural pattern. The $\pi$ density, perpendicular to the plane, does not contribute to the depicted $\nabla^2\rho$.

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# Alumoxane Hydride and Aluminum Chalcogenide Hydride Compounds with Pyrazolato Ligands**

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*Dedicated to Professor Marianne Baudler*
*on the occasion of her 80th birthday*

Since 1980 intense interest in alkylalumoxanes has been generated primarily from the work of Sinn and Kaminsky,[1] who found methylalumoxane (MAO) to be a good cocatalyst for the transition metal catalyzed polymerization of alkenes.[1–3] Although the role of MAO seems to be understood,[4] the structure of the catalytically active species of methylalumoxane remains unknown. Especially the coordination number of the aluminum center is still a question of debate. Recently, several alumoxanes $(t\mathrm{BuAlO})_n$ ($n = 6-9$) and aluminum hydroxides (aluminum oxide hydroxides) displaying a lower degree of aggregation were prepared by the reaction of $R_3Al$ (R = $t$Bu, Me, 2,4,6-$Me_3C_6H_2$ (Mes), Ph) with water or anhydrous lithium hydroxide.[5, 6] On the other hand, it has been shown that aluminum hydride compounds can be used as precursors for the synthesis of organoaluminum chalcogenides with the formula $(\mathrm{RAlE})_n$ (R = organic group; E = O, S, Se, Te) upon reaction with species such as $(Me_2SiO)_3$,[7] $S(SiMe_3)_2$,[8] Se(Te),[9a, 10] or $(RE)_2$ (E = Se, Te).[9b] The recent results in the chemistry of 3,5-*tert*-butylpyrazolatoaluminum dihydride ($[\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz}(\mu\text{-Al})\mathrm{H_2}]_2$ (**1**))[11] prompted us to synthesize compounds of the formula $[(\eta^1\text{-}3,5\text{-}t\mathrm{Bu_2pz}(\mu\text{-Al})\mathrm{H})_2\mathrm{E}]_n$ (E = O (**2**) ($n = 2$); S (**3**), Se (**4**), Te (**5**) ($n = 1$)). Herein we present the molecular structures of **2**–**5**. To the best of our knowledge, **2** represents the first example of a structurally characterized alumoxane hydride in which two of the Al atoms are five-coordinate. Product **3** is the first compound prepared by the reaction involving aluminum hydride and elemental sulfur.

A solution of compound **1** in dry dioxane was stirred at room temperature for five days to yield **2** (Scheme 1). The X-ray crystal structure of **2** confirms the tetrameric arrangement (Figure 1),[12] as also indicated for the gas phase by the MS(EI) spectrum ($m/z$ 860). The $Al_2O_2$ core of the molecule consists of a quite regular parallelogram, and interestingly all the Al and O atoms are coplanar (the sum of angles at O is $359.98(22)^\circ$). Each oxygen atom is connected to three AlH groups to form a $\mu_3$-O bridge. The Al atoms located outside

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